

Interactive comment on “Impact of VOCs on the formation of ozone in a central China city during severe pollution periods” by Bowei Li et al.

Bowei Li et al.

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Comment and response The authors thank for all valuable comments and suggestions to our manuscript. We have point-to-point response to each comment as below. Comment 1: The title can also be changed, since the influence of VOCs on O₃ formation forms only a small part of the paper. The main focus of the paper is on the measured VOCs. Response: Thanks for the suggestion, the title has been revised as “Characterisation of VOCs and their related atmospheric processes in a central China city during severe pollution periods” Comment 2: I am not sure about the use of this acronym for the 57 VOCs. A VOC is a species and PAMS is not Response: The term has been replaced by “VOCs”. Comment 3: A high VOC/NO_x ratio usually signifies that an area is NO_x sensitive and not VOC sensitive. Changes in VOC concentration do therefore

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not cause any changes in O₃ concentrations, while increased NO_x causes increased O₃. Response: According to the ratio of VOCs /NO_x, the ozone formation regime was prone to VOC-limited. The statement has been revised accordingly. Comment 4: Which four sites? Where you measured VOC precursor species? You mentioned that VOCs were measured in Zhengzhou City and precursor species were measured at four different sites Response: This refers to the four sites located in Zhengzhou city where we collected the samples in this study. The details of sampling location have been described in the main texts. Comment 5: A VOC-limited regime is associated with low VOCs not high VOCs. Your high VOC/NO_x ratio indicate a NO_x limited regime and therefore NO_x must be reduced and not VOCs to reduce O₃. However, I think this area is VOC-limited (very high NO_x) and reduction on VOCs will result in reduced O₃. And therefore your high VOC/NO_x ratio does not make sense Response:

Sorry for the unclear description in previous statement. Yes, it should be VOC-limited. The related statements have been revised. Comment 6: Fuel evaporation? Solvent evaporation, I agree with. Response:

Solvent (i.e., from industry and household) is a major source of VOCs definitely, while fuel evaporation is also a contributor to VOCs originated from industries or other sources powered by fossil fuels. Comment 7: Where? In the USA or in China? Response: This refers to worldwide countries, including China and USA. Comment 8: This sentence read that the nationwide deterioration of air quality contributes the measurements being scarce. Please improve. Response: We have revised the sentence as "In China, investigations involving the source apportionment of VOCs, acquirement of emission profiles and interpretation of the seasonal variations were mainly concentrated in Yangtze River Delta (YRD), Pearl River Delta (PRD) and Beijing-Tianjin region (BJT) (An et al., 2014; Wang et al., 2014; Chen et al., 2014; Liu et al., 2016a; Guo et al., 2017), while studies in less developed or developing regions, such as southwestern and northwestern China, where contributions from the burning of biomass with high abundances of toxics and reactive compounds (such as, benzene) are prominent, are

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very limited. (Li et al., 2014;Li et al., 2017a)..” Comment 9: These sites are only in the USA Response: The term of PAMS was widely used to present the most critical contributors in the production of ozone in the atmosphere. It does not mean the sampling sites. Comment 10: This sentence does not fit within the context of this paragraph that is focusing on VOC measurement in China and the gaps in knowledge. Response: The original lines 64-66 have been deleted Comment 11: why? Due to VOCs/CO or NOx? Response: The statement has been revised as " the combustion of biomass had the highest contribution to O3 formation potential (40Comment 12: The first two paragraphs are not well structure and must be improved. Response: The paragraphs have been revised, specified in newly lines 29-57. Comment 13: Why? Due to increased NOx emissions? Response: The sentence has been revised as: " The percentage of VOC-limited regime in North China Plain (NCP) has expanded from 4Comment 14: please improve Response: The sentence has been revised as: “Based upon the density of population, industrial facilities, and the prevailing winds, four sites have been selected for sample collection” Comment 15: If possible, it would be nice to show the major pollutant sources on the map in Fig. 1. This will help a lot with interpretation of results e.g. discussion in Section 1 on the influence of wind direction on the different Σ VOCs measured at each of the sites for all the months. Response: This is a good idea. Suggestion taken. The map was improved as below:

Fig 1. Map of Zhengzhou, China showing the locations of sampling sites. Comment 16: Please better explain. Why only 10 days? Were there only ten days in each month that it did not rain? Response: The sentence has been revised as: “Ten sampling days with the rainfall record (ca. 0 mm) were chosen in every month during the period of May - September, 2017 consequently, to represent a typical air quality conditions in a month” Comment 17: What was considered to be valid samples? Response: “Valid samples” means that those samples were not influenced by high humidity, wrong operation, and fault of instrument. Comment 18: I do not think that this is a good acronym for your VOC species studied Response: Suggestion taken. The term has been replaced in the whole manuscript. Comment 19: According to what? Why were only these species

considered relevant? Also, I assume from the rest of the discussion in the paper, these 57 species are only hydrocarbons. Therefore rather say that the 57 species included 28 were alkanes, 11 alkenes, acetylene and 17 aromatics. Response: The sentence has been revised as: “The standard gas named with PAMS (1 ppm; Spectra Gases Inc, NJ, USA) was used to build calibration curves, which containing 57 VOCs, including 28 alkanes, 11 alkenes, acetylene and 17 aromatics” Comment 20: This sentence and table is not necessary in the document and can be removed. Although it could be included a supplementary material, I do not think these analytical specifications contribute to the main content of this paper. Response: Thanks for the suggestion. It has been moved to supporting information, depicted as Table S1. Comment 21: Uncertain what is meant here. Response: The statement has been revised as: “No obvious disturbances due to improperly activities (such as smoking, spray perfumes, etc.) of sample collectors were present during the sampling events” Comment 22: Not sure that this is the correct term Response: The term has been was replaced by “QC/QA”. Comment 23: Unnecessary Response:

It has been deleted

Comment 24: Please improve the description of the PMF technique (line 166 - 184) Look at the paper Jaars, et al., Atmospheric Environment, 172 133–148, 2018, <http://dx.doi.org/10.1016/j.atmosenv.2017.10.047>. Response: Thanks for the reference. The description has been revised.

Comment 25: Please structure this entire Section better. Numerous examples of incoherent writing is illustrated in the paragraphs in this section.) Response: The section has been revised. Comment 26: Air mass does not originate but pass over a source region/city/sources. Response: The statement has been revised as: “In May, the largest cluster (27.2) Comment 27: It will be better here to say that the Σ VOCs different for all the months at all the sites, with the site with highest Σ VOCs not being the same each months. This can be attributed to numerous factors that will be explored later in the paper. And then you can present the influence of prevalent wind direction on

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concentrations measured. Response: The related section has been revised according to the suggestion, specified in newly lines 169-175. Comment 28: This discussion on the influence of prevailing wind direction and -speed could be significantly improved with an appropriate wind rose overlaid on a map of the city indicating the four sites and the major sources. Response: They have been presented in Fig. 6 and Fig S2. Comment 29: Can you indicate this on a topographical map of the city? Response: A reference contained the topographical map has been added. “Mu, B., Mayer, A. L., He, R., and Tian, G.: Land use dynamics and policy implications in Central China: A case study of Zhengzhou, *Cities*, 58, 39-49, 10.1016/j.cities.2016.05.012, 2016.” Comment 30: from where Response: The statement has been removed because of the adjustment of Table 2 and Fig. 10: Comment 31: A figure with meteorological data for the sampling period must be included to assist in the discussion of the data. Response: The statement has been removed because of the adjustment of Table 2 and Fig. 10, and the meteorological data was presented in Fig S1. Comment 32: The authors must consider to rather include a figure with the statistical distributions (e.g. box and whisker plots with mean, median, as well as 25th, 75th percentiles) of the VOC species presented for the entire sampling period instead of the large Table 3. This will greatly assist in the discussion of concentrations measured at different sites. Table 3 could then only include the Σ VOC for each month at each of the site if they want to elaborate on the influence of wind direction and -speed on VOC concentrations measured at each site. Response: Thanks for the suggestion, Fig.10 has been added.

Fig.10 concentration level of 57 VOCs at each site for the whole sampling period, the whisker was ranged from 5-95. Comment 33: Nowhere in the text it is indicated that these 57 VOCs were classified into alkane, alkenes, alkynes and aromatics, which are further discussed. Response: The statement has been revised as “The standard gas named with PAMS (1 ppm; Spectra Gases Inc, NJ, USA) was used to build calibration curves, which containing 57 VOCs, including 28 alkanes, 11 alkenes, acetylene and 17 aromatics.” Comment 34 why is this? Response: It was attributed to the busy traffic in urban city. The sentence was revised as

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" Among the four major organic classes, alkane was the most abundant group as a result of busy traffic in urban city and its longevity " Comment 35: Which will be nicely indicated in figure as suggested above presenting the statistical data of all VOCs measured at all the sites. Response:

Suggestion taken. It has been presented in Fig.S3.

Fig. S3 Compositions of ethane, iso-pentane and C7-C8 alkanes at JK, MEM, YH and GS. Comment 36: What compounds? Alkanes in general, or the species contributing to alkane levels at MEM only? If the latter, why not elaborate on alkanes at the other sites? Response:

They referred to ethane, isopentane and alkanes with 7-8 carbon atoms, which have been presented in Fig.S3.

Comment 37 missing an introductory sentence on the daytime and night-time concentration that is additionally presented in figure2 Response: The typo has been corrected. Comment 38 how so? Response: The statement has been revised as "the increases in alkene compositions (about 4. 3Comment 39: Please include a table where in these VOC results can be contextualized and compared to other cities. Only Beijing, Nanjing and Guangzhou included in Figure 2. Furthermore, the fact that concentrations for these three cities are included in Fig.2 are also not properly introduced in the text. Response: The information has been added in revised Table 3. Comment 40: Are you speaking generally here, i.e. all the cities in China? Response: It refers to the countries discussed here. Comment 41 Here again you mention aromatics. An examples of a sentence "coming from nowhere" within the context of a paragraph that is trying to contextualize results. Response: The statement has been revised as "With regard to the weight percentage of major groups (Table 3), the composition of alkanes was the largest in all cities because of their long-lives and widespread sources (Fig. 7), while the composition of aromatics was lower than alkenes in these cities except for Guangzhou" Comment 42: You are only comparing your results to the three cities

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included in Fig. 2 and not all the cities listed here in your discussion above Response: The results have been shown in Table 3. Comment 43: Reference of biofuel as source of acetylene Response: A reference has been added. “Zhu, Y., Yang, L., Chen, J., Wang, X., Xue, L., Sui, X., Wen, L., Xu, C., Yao, L., Zhang, J., Shao, M., Lu, S., and Wang, W.: Characteristics of ambient volatile organic compounds and the influence of biomass burning at a rural site in Northern China during summer 2013, Atmospheric Environment, 124, 156-165, 10.1016/j.atmosenv.2015.08.097, 2016.” Comment 44: The problem with the dataset is that it does not cover a full year, i.e. all seasons. Therefore rather combine local (wind direction and -speed as done in Section 3.1) and long-range transport (back trajectories as done in Section 3.7) here to explain temporal variation. Response: Suggestion taken. Comment 45: better to have meteorological parameters in separate fig as indicated in previous comment. Response: It has been presented in Fig S1 Comment 46: Are you sure it is for all pollutants? Response: It refers to air pollutants we monitored in this study, including SO₂, CO, NO₂, O₃ and VOCs. We have revised the statement as “The results showed a distinctive temporal characteristic where lower levels of SO₂, CO, NO_x, O₃ and Σ VOCs were observed in July and August (mid-summer)” Comment 47 You did not collect VOCs on rainy days as indicated in your experimental section. Response: Yes, this observation was referred to the results from other studies. Comment 48: This is very difficult to see in Fig. 3. Fig. 3 must be improved to be more legible and easier to observe observations Response: It has been changed to newly Fig 8.

Fig. 8 Temporal variations of mixing ratios of Σ VOCs, NO_x and O₃ at the four sites during the whole sampling period, in which Σ VOCs-07 stands for the concentration level of Σ VOCs observed at 07:00 LT, and Σ VOCs-14 was that observed at 14:00 LT.

Comment 49: I cannot see this in Fig. 3 Response: We have presented it in newly Fig. 9.

Fig. 9 The relationship between mixing ratio of Σ VOCs and the composition of alkane, the data points were color coded with the composition of aromatic. Comment 50: Not

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easily observed in Fig.3 Response: We have modified the figure and presented in newly Fig. 9. Comment 51: Why? Can you show this? Response: The simultaneous increases in concentration of SO₂, CO and NO_x represent the characters of potential combustion source, which could be caused by the nearby thermal power plant. Comment 52: (Reason for disturbance? Response: During the sampling period, the building where we conducted the sampling had painting activities during June, 2017. Comment 53: Wind direction will confirm this Response: The wind direction was added as: "indicating the possible impact from a gas-fueled power plants located about 1 km southwest of the site (about 18 Comment 54: Combine with next paragraph Response: We think it is not so appropriate to combine the two paragraphs. The discussion of next paragraph is on alkyne. Comment 55: Give a reference for acetylene associated with biomass burning. Response: A reference of Zhu et al, 2016 has been added. "Zhu, Y., Yang, L., Chen, J., Wang, X., Xue, L., Sui, X., Wen, L., Xu, C., Yao, L., Zhang, J., Shao, M., Lu, S., and Wang, W.: Characteristics of ambient volatile organic compounds and the influence of biomass burning at a rural site in Northern China during summer 2013, Atmospheric Environment, 124, 156-165, 10.1016/j.atmosenv.2015.08.097, 2016." Comment 56: Instead of Table 4, rather presented a figure with statistical distributions of total VOCs, SO₂, O₃ etc measured at each site. This will greatly assist in discussion. Paragraph in Section 3.1 where different monthly total VOC concentrations at each of the sites are explained with the influence of wind direction and -speed will also better fit within the discussion on spatial variations. The structure of this section must also be improved. Response: The original table has been replaced by Fig. 11.

Fig. 11 The distribution of concentration point on O₃, Σ VOCs, NO_x, SO₂ and CO at each site, the range of the box was 25 While the paragraph in Section 3.1 was more focus on meteorological factors, so it has not been moved to this section Comment 57: Not really. Differences are marginal Response: Yes, we agree that the difference is marginal. However, it is true that GS and JK had higher absolute values, so we have changed it to "slightly higher" in the text. Comment 58: This is not true. Differences are marginal Response: Yes, the difference is marginal. We have thus

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changed to "SO₂ and CO were more abundant, though marginal, in western area of Zhengzhou (GS and MEM)". Comment 59: Again, marginal differences between sites Response: The sentence has been rewritten as "With high VOCs and sufficient NO_x, the highest average mixing ratio of O₃ was observed at GS, followed by YH site even with the lowest VOCs and NO_x, indicating there are many other factors, in addition to the absolute concentrations of VOCs and NO_x, which contribute to ozone formation at YH." Comment 60: Inconsequential statement from observation Response: The point has been deleted Comment 61: This sentence does not fit within the flow of the content Response: For in June, the O₃ concentration often exceeded the national standard level of 80 ppbv, meaning severe air pollution caused by ozone during this period, in this section we focus on the period to discuss the relationship between VOCs and O₃ as a result. Comment 62: Small differences. Cannot really make this statement. Response: We do agree this. The sentence has been thus rewritten as "The higher level of O₃ at GS is accompanied with a higher Σ VOCs (39.29±25.37ppbv). The weight percentage of aromatics (15.62±12.06Comment 63: How is this substantiated? Response: Solvent usage is an important source of aromatics. Considering the renovation activity in June at GS, the higher aromatic composition should be caused by the renovation. According to aromatics with high reactivity, we thus suspect that the higher ozone level in June at GS was associated with the renovation activity Comment 64: O₃ levels were only higher at GS Response: Thank for the pointing out this. The statement has been revised as: "The higher level of O₃ at GS is accompanied with a higher Σ VOCs (39.29±25.37ppbv)" Comment 65: Bad writing Response: The statement has been revised as: " Even though both the Σ VOCs and specifically O₃ formation potential compounds (such as, alkenes and aromatics) at MEM were slightly higher than those at YH (Table 5), the O₃ concentration at MEM was not higher than YH," Comment 66: O₃ can only be formed from NO₂. Response: We certainly recognize this. However, NO₂ was formed from NO, and NO could consume O₃. Considering that ozone formation involved all the process mentioned above, we do think it is reasonable to address the NO_x impact on

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ozone formation. Comment 67: In China? Give a reference please. Where is Hebei located in relation to Beijing? Sentences 311 - 315 another example of incoherent writing. Response: The statement has been revised as: "It is well known that many O₃ episodes were attributable not only to local sources but also to regional transports. For example, Streets et al. (2007) reported that during continuous southern wind, the ozone level in Beijing was 20-30". Comment 68: From Fig. 3 this surely does not look like the day on which O₃ peaks at all the sites in this study. Response: Yes, it is only happened at YH, and the content was revised accordingly in the text. Comment 69: VOCs are the important contributors to O₃ formation within a VOC-limited regime, i.e. very high NO_x. I am sure that this is the case for the very polluted regions in China. Response: Thank you for the reminder. The evidence has been added as "On that day, the ratios of VOCs /NO_x at the four sites were all less than 6.5 (ppbC/ppbv) (Fig. S4), indicating a regional VOC-control system, and that VOCs are the critical contributors to the formation of O₃ in Zhengzhou". Comment 70: Fig. 4 is poorly introduced in the text and not sufficiently discussed. Response: The statement has rewritten as "while the reduction of ΣVOCs and active compounds (i.e., aromatic+alkene) at 14:00 relative to 07:00, determined as 35%". Comment 71: You refer to aging in air masses. Response: Yes, this can be confirmed with its high E/X ratio (0.91) at 14:00, while the ratio for fresh air usually scattered around 0.3. Comment 72: Therefore VOC-limited due to very high NO_x. Response: Yes, it is. Comment 73: The construction in this section must also be improved. The authors interchange between T/B ratios and T/B correlations, which are two totally different aspects. Both are indicative of source, but in different manner. T/B ratios can be related to source and aging. This section also links to your source apportionment section. Response: Yes, it is exactly right. The original text may be obscure. The explanation has been improved as below: "In this study, the R² value for the correlation between benzene and toluene was better in May (0.73 - 0.84) than during other months for all sites (Fig. 15), indicating the source of benzene and toluene in May was more similar, and the average ratio in May varied within the range of 1.81 - 3.36 for all four sites, suggesting that evident impacts were observed

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from vehicle emissions on the VOCs during this period.” Comment 74“ Poorly written sentence Response: The statement has been rewritten as " For each site, the T/B ratio was scattered in different ranges, suggesting spatio-temporally varied emission sources (Fig. 15 and Fig.S5)" Comment 75“ Increased regionally in view of temporal variations?? This deduction does not make sense. Response: The statement has been revised as " In addition, the atmospheric lifetimes of toluene and benzene are different, it was reported that when the OH concentration was assumed to be 106 rad cm^{-3} (Monod et al., 2001), the lifetime for toluene and benzene was 1.9 days and 9.4 days, respectively, which maybe one of factors for the lower T/B ratios at 14:00 LT than those at 07:00 LT, and higher T/B ratios in September.” Comment 76“ Please do not confuse T/B ratio and T/B correlations here. T/B correlation is indicative of similar sources, while T/B ratio indicate sources and aging. What does this mean/imply? Response: We agree with this point. The statement has been revised as “The R2 value for the correlation between benzene and toluene was better in May (0.73 - 0.84) than during other months for all sites, indicating the source of benzene and toluene in May was more similar” Comment 77“ One would start/begin the paragraph with these sentences to indicate to what sources specific ratios of these two compounds can be related to and then you discuss your observed ratios in your study and relate them to these typical ratios. Another example of incoherent writing. Response: Newly lines 402-407 have been revised accordingly. Comment 78“ Toluene is an aromatic species and NOT an alkene. Response: Yes, we truly know this. The original statement may lead confusion and it has been revised as “As to individual species, the 10 most biggest contributors included ethylene, isoprene, m,p-xylene, toluene, propylene, acetylene, n-butane, i-pentane and propane” Comment 79“ What type of combustion? This paragraph is poorly structured and must be improved. Response: Based on analysis conducted in other sections, we inferred the combustion source as vehicle emissions and biofuel burning. and the paragraph was restructured. Comment 80“ The VOC/NOx ratio is used to establish whether a region is VOC or NOx limited. Here you must indicate whether VOCs or NOx are the limiting factors. High VOC/NOx

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ratio indicative of region being NO_x limited. In such a region NO_x determine O₃ levels and not VOCs. Higher ratios only indicate high VOCs in relation to NO_x. If there is not enough NO_x, O₃ will not form, since it can only form from NO₂. Therefore to say that higher O₃ correspond to higher VOC/NO_x ratios does not make sense. More VOCs in the absence of NO_x will not form O₃. Therefore, I think at your site you have high NO_x, which is the only scenario where O₃ formation is considered VOC sensitive.

Response: We have added a new section 3.4, which is mainly discussed the variation of VOCs/NO_x ratios. "The VOCs/NO_x ratio is usually used to establish whether a region is VOCs or NO_x limited in ozone formation. In this study, the mean level of VOCs /NO_x (ppbC/ppbv) were below 5 at all four sites (Fig.12), and 75The specific data distribution of VOCs /NO_x showed some differences in the four sites (Fig. 12), with the lowest value presented at MEM (about 3.8), and the highest value observed at JK (about 4.7), demonstrating that due to the impact of thermal-power plant, the production of ozone at MEM was more sensitive to VOCs than JK. Meanwhile, about 14As to the daily variation of VOCs /NO_x ratios (Fig. 12), higher values at 14:00 relative to 07:00 were observed at the four sites, which may be correlated with less vehicle emissions or more consumption path of NO_x at noon time. The increment of VOCs /NO_x at 14:00 relative to 07:00 was more obvious at JK and GS, showing more emission sources of VOCs at these two sites at daytime, and resulting the ozone formation system at JK and GS shifting to the transition area in the afternoon. Researches have shown that ozone formation depends not only on its precursors (mainly VOCs and NO_x), but also has VOCs /NO_x ratios (Ilana B. Pollack, 2013). In our research, the mixing ratio of O₃ at 14:00 LT presented a small positive trend ($p < 0.05$) with the uplift of VOCs /NO_x at JK (Fig. 13), which was similar to the results observed at Shanghai (Gao et al, 2017), where the O₃ formation was more sensitive to NO_x concentration under high O₃ levels. This may be a result of the increased ozone production efficiency at high VOCs /NO_x. There were no discernible trends at other sites, possibly due to the counteraction imposed by other uncertain factors."

Comment 81ijž Similar to all other sections, this section can also be better written

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and structured (section 3.7). Response: This section has been re-structured in other parts. Comment 82: This section must also be improved. I also suggest to combine this with Section 3.1 where differences in VOC concentrations for different months are discussed and explained with wind direction and -speed. Therefore combine local and long-range transport. Also see general comment at Section 3.1 to include all this in Section 3.2. Response: It has been incorporated in section 3.1 and 3.2 Comment 83: Very busy figure with too much information. Response: Suggestion taken. The original figures have been decomposed as Fig.15 and Fig.S5. Comment 84: Please describe this better. All the figures are small. You mean "smaller" figures. Response: Thanks for the reminder. The vertical axis in every small figure represents the mixing ratio of toluene (ppbv), while the horizontal axis stands for benzene level (ppbv).

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2018-397/acp-2018-397-AC1-supplement.zip>

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-397, 2018>.

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