Response to the Comments of the Reviewers

Dear Editor and Reviewers,

We would like to thank you and the reviewers for the great efforts and elaborate work on this manuscript.

We revised the manuscript by responding to each of the suggestions in the reviews. In our response, the questions of the reviewers are shown in *Italic* form and the responses in standard form.

We appreciate your help and time.

Sincerely yours,

Xin Li and Co-authors.

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Manuscript Number: acp-2020-704.

Manuscript Title: Spatiotemporal Variation, Sources, and Secondary Transformation Potential of VOCs in Xi'an, China.

Response to Reviewer #2

General comments

Understanding the sources of VOCs is vital to the mitigation of O_3 pollution. Song et al. performed comprehensive field observations and VOC grid sampling in Xi'an to elucidate the concentration levels, source characteristics, and secondary conversion ability of VOCs. They found that vehicle exhaust was the dominant source of VOC emissions in Xi'an. This paper has important implications for the control of O_3 pollution in megacities, so it is well within the scope of ACP. I recommend this paper to be published after addressing the comments below.

Response:

We would like to thank reviewer #2 for carefully reading our manuscript and for the valuable and constructive comments. The manuscript was significantly revised according to the reviewer's suggestions. Listed below are our point-by-point responses to reviewer's comments. Lastly, we would like to thank you for your comments and guidance.

Comments

1. Lines 33-38: The authors only present VOC sources for some specific cities. Can the authors summarize the results of previous studies for various regions of China, e.g. Beijing-Tianjin-Hebei, Yangtze River Delta, Pearl River Delta?

Response:

We appreciate the reviewer's comments. After investigating a large amount of literature, we found that different studies have very different PMF source resolution methods, including source numbers and source definition. We categorize the sources of VOCs in these studies into 7 sources, as shown in Figure R4. From the Figure R4 we found that the concentrations of VOCs in urban areas were seriously affected by vehicle exhaust. In addition, southern China was significantly affected by paint solvent usage sources. However, it is difficult to summarize the results for different regions of China.

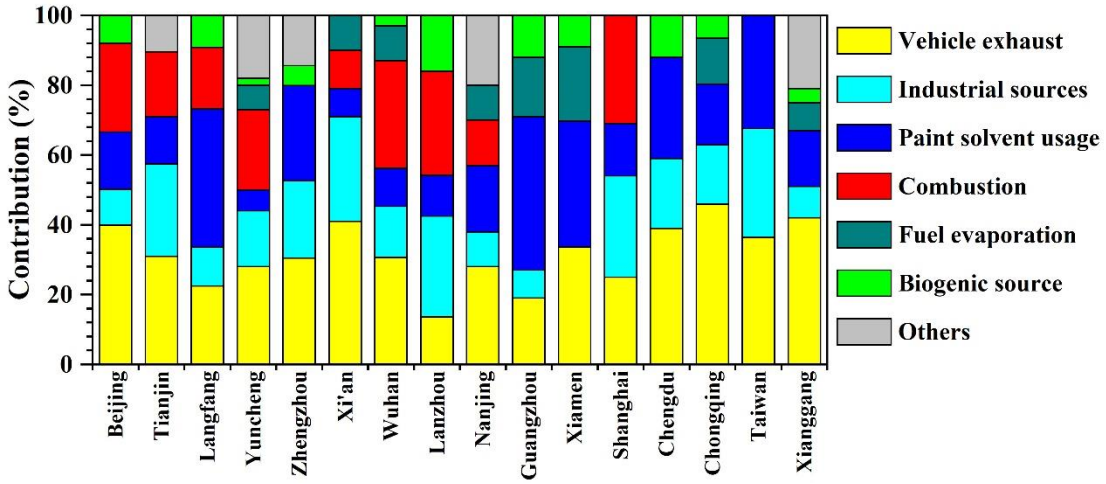

Figure R4. Newly researches about Source apportionment of VOCs at 16 sites in China

Note: The 16 sites include Beijing (Li et al., 2020), Tianjin (Yang et al., 2019), Langfang (Zhang et al., 2019a), Yuncheng (Gao et al., 2020), Zhengzhou (Zhang et al., 2019b), Xi'an (This study), Wuhan (Shen et al., 2020), Lanzhou (Zhou et al., 2019), Nanjing (An et al., 2017), Guangzhou (Ling et al., 2011), Xiamen (Zhuang et al., 2019), Shanghai (Wang et al., 2013), Chengdu (Song et al., 2018), Chongqing (Li et al., 2018), Taiwan (Chen et al., 2019), Hong Kong (Ling and Guo, 2014).

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2. Lines 78-79: How often were external standards run? Please provide more details.

Response:

We appreciate the reviewer's comments. We agree with reviewer and carefully revised the manuscript according to the reviewer's suggestion. Now it reads as follows:

External and internal standard gas produced by The Linde Group in the United States were used to calibrate the GC–MS/FID. External standard gas were used to calibrate the GC–MS/FID weekly during the campaign to ensure quantitative accuracy. In addition, the instruments were also daily calibrated by internal standard gases (Bromochloromethane, 1,4-Dichlorobenzene, Chlorobenzene, and Fluorobromobenzene) to ensure the stability of the instrument.

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3. Lines 88-89: What's the duration for sampling? Did the authors also test blank samples?

Response:

This study uses instantaneous sampling to collect air samples, and the sampling time is about 2 min. In addition, blank sample tests were performed on the VOC gridded sampling in each sampling period (July 1 7:00, July 1 15:00, July 14 7:00, and July 14 15:00). The concentration of all VOCs species in the blank sample is below the method detection limits (MDLs), indicating that the canisters were not contaminated during transportation.

We appreciate the reviewer's comments. We have added the above sampling information in the revised manuscript. Now it reads as follows:

Before VOC gridded sampling, the Silonite™ canisters were cleaned with high purity nitrogen using the Entech 3100 canister cleaning system, and then they were evacuated to a vacuum. Instantaneous sampling method was adopted for ambient air sample collection with a sampling duration of approximately 2min. VOCs in the sampled air were analyzed using a GC–MS/FID system, which was the same as that

used for online measurements, but it was running in off-line mode. In this study, blank sample tests were performed on the VOC gridded sampling in each sampling period (July 1 7:00, July 1 15:00, July 14 7:00, and July 14 15:00). The concentration of all VOCs species in the blank sample is below the MDLs, indicating that the canisters were not contaminated during transportation.

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4. Lines 158-159: It is recommended to provide the VOC list in the supporting information.

Response:

We appreciate the reviewer's comments. We agree with reviewer and added VOC list in the supporting information. Now it reads as follows:

During the field observation campaign, 99 VOCs were measured, including 29 alkanes, 11 alkenes, 1 alkyne, 16 aromatics, 28 halohydrocarbons, 13 oxygenated VOCs (OVOCs), and 1 acetonitrile (Table S1).

Table S1: Measured VOC species in CB, DHS, and QL sites.

Classification	VOC Species		
Alkanes	Ethane	3-Methylpentane	Methylcyclohexane
	Propane	n-Hexane	2,3,4-Trimethylpentane
	Iso-butane	2,4-Dimethylpentane	2-Methylheptane
	n-Butane	Methylcyclopentane	3-Methylheptane
	Cyclopentane	2-Methylhexane	n-Octane
	Iso-pentane	Cyclohexane	n-Nonane
	n-Pentane	2,3-Dimethylpentane	n-Decane
	2,2-Dimethylbutane	3-Methylhexane	n-Undecane
	2,3-Dimethylbutane	2,2,4-Trimethylpentane	n-Dodecane
	2-Methylpentane	n-Heptane	
Alkenes	Ethene	Cis-butene	Isoprene
	propene	1,3-Butadiene	cis-2-Pentene
	Trans-2-butene	1-Pentene	1-Hexene
	1-Butene	trans-2-Pentene	
Alkynes	Ethyne		
Aromatics	Benzene	iso-Propylbenzene	1,2,4-Trimethylbenzene
	Toluene	n-Propylbenzene	1,2,3-Trimethylbenzene
	Ethylbenzene	m-ethyltoluene	m-diethylbenzene
	m/p-Xylene	p-ethyltoluene	p-diethylbenzene
	o-Xylene	1,3,5-Trimethylbenzene	
	Styrene	o-Ethyltoluene	
Halohydro-carbons	Freon114	cis-1,2-Dichloroethylene	1,1,2-trichloroethane
	Chloromethane	Chloroform	Tetrachloroethene
	Vinylchloride	1,1,1-Trichloroethane	1,2-Dibromoethane
	Bromomethane	Tetrachloromethane	Chlorobenzene
	Chloroethane	1,2-Dichloroethane	1,3-Dichlorobenzene
	Freon11	Trichloroethylene	1,4-Dichlorobenzene
	1,1-Dichloroethene	1,2-Dichloropropane	Benzylchloride

	Freon113	Bromodichloromethane	1,2-Dichlorobenzene
	Dichloromethane	trans-1,3-Dichloropropene	
	1,1-Dichloroethane	cis-1,3-Dichloropropene	
OVOCs	Acetaldehyde	Methyl Vinyl Ketone	3-Pentanone
	Acrolein	Methyl Ethyl Ketone	n-Hexanal
	Propanal	n-Butanal	MTBE
	Acetone	2-Pentanone	
	Methacrolein	n-Pentanal	
Others	Acetonitrile		

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5. Lines 172-173: It is not clear to me how good the correlation between O3 and temperature is. What is R2? It seems that the correlation is moderate.

Response:

We appreciate the reviewer's comments. From figure R5 we can see, the linear correlations between O_3 and temperature on polluted days ($R_{Pearson}$=0.7, R^2=0.5) is stronger than that on clean days ($R_{Pearson}$=0.5, R^2=0.2) at CB site. The correlation between O_3 and temperature at the DHS site shows similar characteristics, and the linear correlations (R^2) between O_3 and temperature on polluted days and clean days were 0.4 ($R_{Pearson}$=0.7) and 0.3 ($R_{Pearson}$=0.5), respectively.

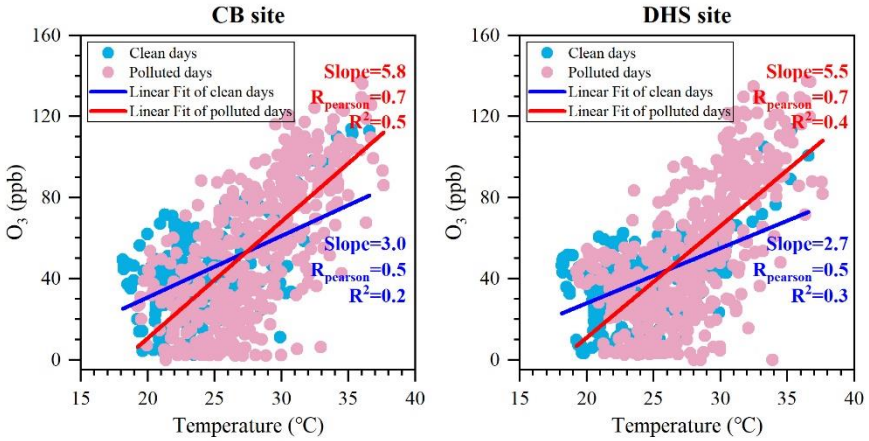

Figure R5: Linear correlations between O_3 and temperature on clean and polluted days.

We also agree with the reviewer that the statement was not very it may not be very appropriate to express a significant positive correlation between O_3 and temperature. We carefully revised the statement according to the reviewer's suggestion. Now it reads as follows:

The variation trends of O_3 and temperature display a positive correlation, and the linear correlations between O_3 and temperature on polluted days ($R_{Pearson}$=0.7) is stronger than that on clean days ($R_{Pearson}$=0.5). The value of temperature, O_3, and TVOCs all increased significantly on polluted days, indicating that the secondary transformation of VOCs to O_3 is more conducive at high temperatures.

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6. Lines 175-180: The average temperature on polluted days is much higher than that on clean days, which will increase the emission of some VOCs, e.g. isoprene as well as solvent evaporation. As the precursor of MVK and MACR, did the concentrations of isoprene increase on the polluted days?

Response:

That's a very good comments. Because of the low concentration of isoprene, it was discussed as part of the alkene when comparison was considered in the original manuscript. According to the suggestions of reviewers, we analyzed isoprene separately from other alkenes and found that the emission of isoprene increased significantly during the polluted days, along with the increase of temperature (Figure 3c, 3f). However, concentrations of most aromatics which were regarded as tracers of solvent evaporation remained unchanged (Figure 3c, 3f). Therefore, we think there is no clear evidence that the emissions of solvent evaporation increased on the polluted days.

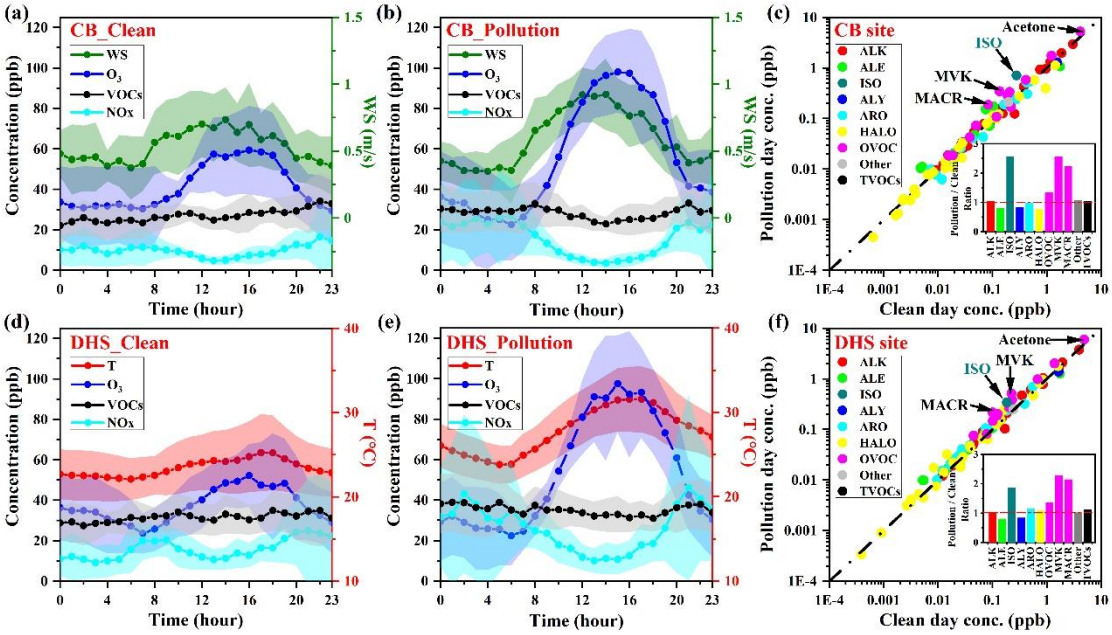

Figure 3: Diurnal variations in wind speed (WS), temperature (T), O_3, NOx, and TVOCs on clean and polluted days at the (a) and (b) CB and (d) and (e) DHS sites. Differences in VOC concentrations between clean and polluted days at the (c) CB and (f) DHS sites.

Note: ALK = alkanes, ALE = alkenes (except isoprene), ISO = isoprene, ALY = alkynes, ARO = aromatics, HALO = Halohydrocarbons, MVK = Methyl Vinyl Ketone, and MACR = Methacrolein.

We have also modified this part in the revised manuscript. Now it reads as follows:

As shown in Figure 3, isoprene concentrations at urban sites increased significantly during the O_3 pollution day, which could due to the stronger plant emission at elevated temperature (Guenther et al., 1993; Guenther et al., 2012; Stavrakou et al., 2014). Concentrations of isoprene oxidation products (i.e., MVK and MACR) as well as most OVOCs also increased in the same period. However, similar concentrations of anthropogenic VOCs are found in clean and polluted days. This indicates a stronger photochemical conversion of VOCs existed in O_3 pollution days, which could due to the more favorable meteorological conditions (i.e., higher temperature and solar radiation).

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7. Based on Figure 3, the increase in the concentration of OVOC on O3 pollution days is largely driven by the increased concentration of acetone. The authors also show in section 3.2.2 that acetone is mainly from vehicle exhaust and industrial sources. Both primary emission and/or secondary transformation may contribute to the increase of OVOC. Can the authors estimate the contribution from primary emissions?

Response:

We appreciate the reviewer's comments. The sources of OVOCs can be divided into anthropogenic primary sources, anthropogenic secondary sources, biogenic sources and background sources (Li et al., 2014; Wang et al., 2015). The multi-linear regression model was used to analyse the sources of OVOCs in different sites in Xi'an. Ethyne, PAN and isoprene were selected as the tracers of the anthropogenic primary source, the anthropogenic secondary source and the biogenic sources respectively. The equation of the multi-linear regression model is as follows:

$$[OVOCs]=k_0+k_1\times[Ethyne]+k_2\times[PAN]+k_3\times[Isoprene] \quad (R1)$$

where [Ethyne] represents the concentration of Ethyne, [PAN] represents the concentration of PAN, [Isoprene] represents the concentration of isoprene, k_0 represents the background concentration, k_1, k_2 and k_3 are the corresponding coefficients.

Based on the analysis of the multi-linear regression model, we have a deeper understanding of the source of OVOCs during the ozone pollution period. From Figure S1 and S2 we found that the contribution of anthropogenic primary sources to OVOCs on O_3 pollution days is more significant.

We have carefully revised this statement in the revised manuscript. Now it reads as follows:

The specialty of OVOCs is that in addition to the primary emissions, OVOCs can also be formed through photochemical oxidation with alkenes and aromatics (Birdsall and Elrod 2011). The sources of OVOCs can be divided into anthropogenic primary sources, anthropogenic secondary sources, biogenic sources and background sources (Li et al., 2014; Wang et al., 2015). Base on the multi-linear regression model results (Figure S1 and S2) we found that the contribution of anthropogenic primary sources to OVOCs on O_3 pollution days is more significant.

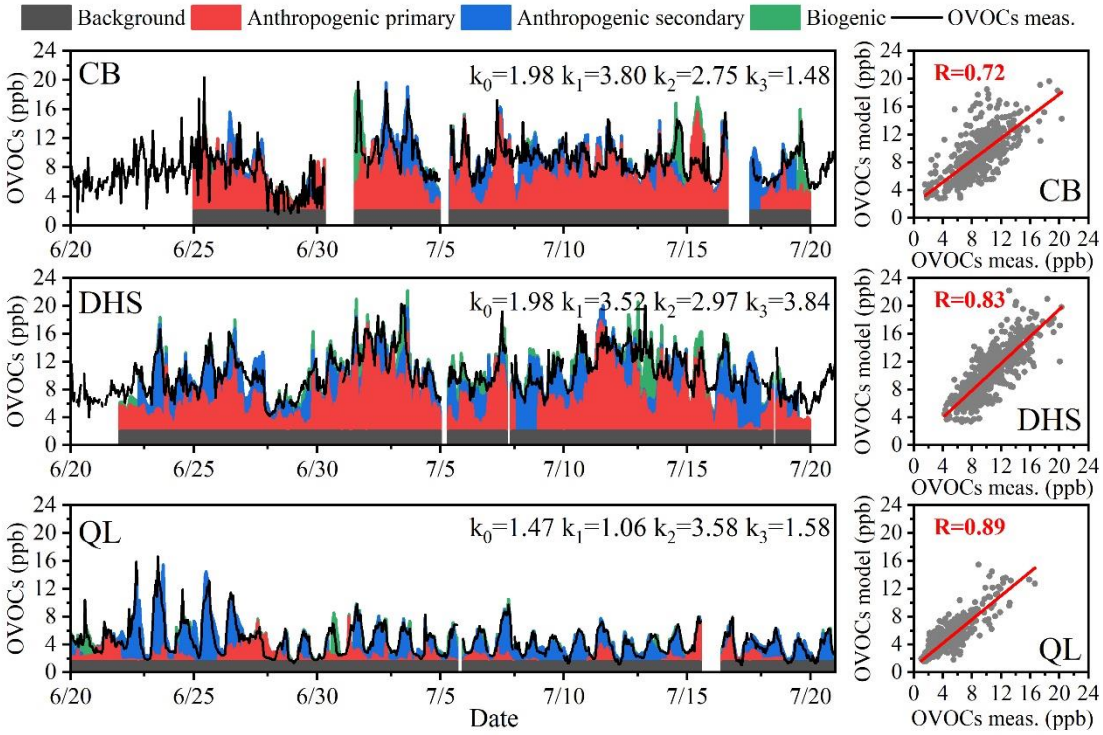

Figure S1. Time series of measured OVOCs concentrations and OVOCs calculated from the multi-linear regression model.

Note. The equation of the multi-linear regression model is:

$$[OVOCs]=k_0+k_1\times[Ethyne]+k_2\times[PAN]+k_3\times[Isoprene]$$

where [Ethyne] represents the concentration of Ethyne, [PAN] represents the concentration of PAN,

[Isoprene] represents the concentration of isoprene, k_0 represents the background concentration, k_1, k_2 and k_3 are the corresponding coefficients, meas. represents measure.

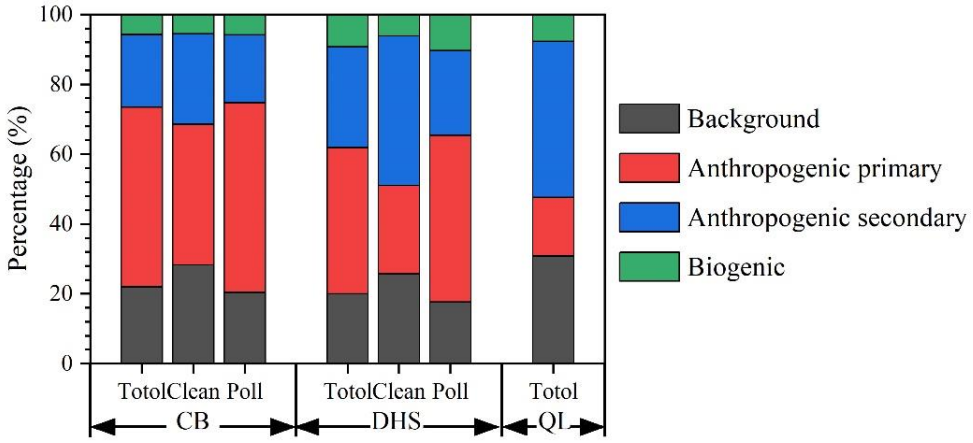

Figure S2. Contributions of different sources of OVOCs in different sites in Xi'an base on the multi-linear regression model.

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8. Did the NOx concentration change during the polluted and clean days? Did NOx play a role in increasing the O3 concentration on polluted days?

Response:

We appreciate the reviewer's comments. Compared with clean days, the NOx concentration at CB and DHS sites on polluted days increased by 5.8 and 10.3 ppb, respectively. However, before analyzing the influence of NOx changes on ozone, a VOCs-NOx-O_3 sensitivity analysis is needed. We have added VOCs-NOx-O_3 sensitivity analysis in section 3.4.2. Now it reads as follows:

The relationship between the ozone production rates (P (O_3)), anthropogenic VOCs (AVOCs) reactivity and NOx reactivity of the CB, DHS, and QL sites during the observation period was shown in Figure 12. The black curve in the Figure 12 represents the P (O_3) contour, and the black straight line represents the connection line of the P (O_3) turning point (ridgeline), whose slope represents the photochemical parameter k_{NOx}/k_{AVOCs} (Jiang et al., 2018). When the site's k_{NOx}/k_{AVOCs} value is located above the ridgeline, it means that ozone formation is under VOCs-limited regime, otherwise it means that ozone formation is under NOx-limited regime. It can be seen from Figure 12 that the ozone generation of QL site is located in the NOx-limited regime, and reducing NOx can effectively control ozone generation. The ozone generation of DHS site is located in the VOCs-limited regime, and reducing VOCs can effectively control ozone generation. However, CB site is located in the transition regime between VOC- and NOx-limited regimes. Therefore, simultaneous reduction of VOCs and NOx concentration should be considered at CB site to achieve the purpose of controlling O_3.

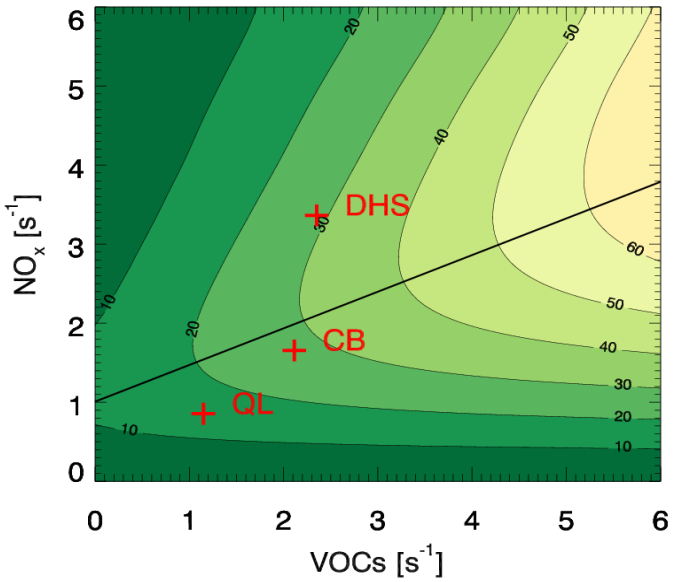

Figure 12. The ozone production rate (P (O_3)) contours diagram versus anthropogenic VOCs (AVOCs) and NOx using Empirical Kinetic Modelling Approach at CB, DHS, and QL sites.

We also have added this part of the results in the conclusion section. Now it reads as follows:

The VOCs-NOx-O_3 sensitivity analysis results showed that the ozone generation of DHS site is located in the VOCs-limited regime, CB in the transition regime between VOC- and NOx-limited regimes, and QL sites is located in the NOx-limited regime. Therefore, reducing VOCs concentration at DHS site, reducing VOCs and NOx concentration at CB site, and reducing NOx concentration at QL site can effectively control ozone generation.

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9. Line 184: It is recommended to provide the VOC list and the grid sampling data in the supporting information.

Response:

We appreciate the reviewer's comments. We agree with reviewer and added VOC list and the grid sampling data of the grid sampling sites in the supporting information. Now it reads as follows:

In the VOC grid sampling, 106 VOCs were measured, including 29 alkanes, 11 alkenes, 1 alkyne, 17 aromatics, 35 halohydrocarbons, 12 OVOCs, and carbon disulfide (Table S2-S3).

Table S2: Measured VOC species in VOC grid sampling sites.

Classification	VOC Species		
Alkanes	Ethane	3-Methylpentane	Methylcyclohexane
	Propane	n-Hexane	2,3,4-Trimethylpentane
	Iso-butane	2,4-Dimethylpentane	2-Methylheptane
	n-Butane	Methylcyclopentane	3-Methylheptane
	Cyclopentane	2-Methylhexane	n-Octane
	Iso-pentane	Cyclohexane	n-Nonane
	n-Pentane	2,3-Dimethylpentane	n-Decane
	2,2-Dimethylbutane	3-Methylhexane	n-Undecane
	2,3-Dimethylbutane	2,2,4-Trimethylpentane	n-Dodecane

	2-Methylpentane	n-Heptane	
Alkenes	Ethene	Cis-butene	Isoprene
	propene	1,3-Butadiene	cis-2-Pentene
	Trans-2-butene	1-Pentene	1-Hexene
	1-Butene	trans-2-Pentene	
Alkynes	Ethyne		
Aromatics	Benzene	iso-Propylbenzene	1,2,4-Trimethylbenzene
	Toluene	n-Propylbenzene	1,2,3-Trimethylbenzene
	Ethylbenzene	m-ethyltoluene	m-diethylbenzene
	m/p-Xylene	p-ethyltoluene	p-diethylbenzene
	o-Xylene	1,3,5-Trimethylbenzene	Naphthalene
	Styrene	o-Ethyltoluene	
Halohydro-carbons	Freon114	Tetrachloromethane	Bromodicloromethane
	Freon11	1,2-Dichloroethane	Benzyl chloride
	Freon113	Trichloroethylene	1,2-Dichlorobenzene
	Chloromethane	1,2-Dichloropropane	trans-1,2-Dichloroethylene
	Vinylchloride	cis-1,3-Dichloropropene	Freon12
	Bromomethane	trans-1,3-Dichloropropene	Trichloromethane
	Chloroethane	1,2,4-trichlorobenzene	Dibromo-monochloro-methane
	1,1-Dichloroethene	1,1,2-trichloroethane	Tribromomethane
	Dichloromethane	Tetrachloroethene	1,1,2,2-tetrachloroethane
	1,1-Dichloroethane	1,2-Dibromoethane	1,3-Dichlorobenzene
	cis-1,2-Dichloroethylene	Chlorobenzene	Hexachloro-1,3-butadiene
	1,1,1-Trichloroethane	1,4-Dichlorobenzene	
OVOCs	Acrolein	2-Propanol	Tetrahydrofuran
	Methyl isobutyl ketone	Vinyl Acetate	Methyl methacrylate
	Acetone	Methyl Ethyl Ketone	1,4-Dioxane
	MTBE	Ethyl Acetate	2-Hexanone
Others	Carbon Disulfide		

Table S3: Concentrations of seven VOCs groups in VOC grid sampling sites.

site	Alkanes	Alkenes	Alkynes	Aromatics	Halohydrocarbons	OVOCs	Others	TVOCs
XF	19.2	8.4	2.3	4.4	4.9	14.6	0.2	54.0
CT	16.1	3.6	1.8	3.3	5.1	11.5	0.1	41.4
HC	15.2	2.4	1.2	2.8	4.5	12.1	0.1	38.2
ZYT	13.7	5.0	1.8	3.0	2.0	9.7	0.1	35.4
YT	8.7	3.3	1.1	1.1	3.4	16.1	0.2	33.9
XS	12.3	2.4	1.2	2.6	3.5	10.5	0.2	32.6
GYL	10.1	2.5	1.3	2.5	3.6	9.8	0.1	29.9

LTC	10.5	4.8	2.3	2.4	2.4	6.7	0.1	29.4
XY	11.6	2.7	1.5	1.7	3.4	8.3	0.1	29.1
JFT	9.8	2.8	1.1	1.4	2.5	10.6	0.1	28.2
RS	10.6	2.4	1.4	1.3	3.5	8.6	0.1	27.9
LT	8.7	3.2	0.9	0.9	3.4	10.5	0.2	27.7
GZ	10.1	2.6	1.4	1.7	3.6	7.2	0.1	26.6
ZZC	9.8	2.0	1.2	1.2	2.5	8.3	0.1	25.0
JDT	7.5	2.9	1.1	1.3	2.9	7.0	0.1	22.8
CAT	7.3	2.3	0.8	0.9	2.7	7.9	0.1	22.2
XX	8.0	1.8	1.3	0.9	2.9	5.5	0.1	20.6
YST	5.8	1.9	1.1	1.3	2.7	7.0	0.1	19.9
WQ	7.3	0.9	0.8	0.6	3.1	6.8	0.1	19.6
XHT	5.9	1.7	1.0	0.9	2.1	6.3	0.1	18.0

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10. Line 190: Did "the overall level" mean "the average concentration"?

Response:

We appreciate the reviewer's comments. We apologize for the vague expression and carefully revised the statement in the revised manuscript. Now it reads as follows:

Compared with the results of the field observation campaign, the VOC concentration at the CB site was closer to the average concentration in Xi'an, and the VOC concentration at the DHS site was significantly higher than the average concentration.

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11. Lines 192-194: Are there any specific industrial sources near YT? Again, the contribution of primary emissions to OVOCs should be excluded to draw this conclusion.

Response:

We appreciate the reviewer's comments. Based on the analysis of the multi-linear regression model, the anthropogenic secondary sources are more significant for OVOCs in rural sites. The YT site is a rural site and does not have many primary sources of VOCs (Figure R2), so the source of OVOCs is more from aging sources.

Figure R2. Geographic environment map of TY site.

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12. Lines 209-210: These numbers are the slopes of the fitting lines, not the correlation coefficients. Please also revise other places accordingly.

Response:

We appreciate the reviewer's comments. We agree with reviewer and carefully revised the statement according to the reviewer's suggestion. Now it reads as follows:

The ratios of toluene to benzene at the CB, DHS, QL, and gridded sampling sites were 0.7 ($R_{Pearson}$=0.5), 2.3 ($R_{Pearson}$=0.6), 0.5 ($R_{Pearson}$=0.6), and 1.2 ($R_{Pearson}$=0.9), respectively.

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13. Lines 215-217: For the grid sampling, only samples at 7:00 and 15:00 were collected. It is reasonable that vehicle exhaust greatly contributed to the overall VOCs because of the sampling time. The authors should state the weakness of the sampling as a caveat.

Response:

We appreciate the reviewer's comments. We agree with reviewer that the sample time may affect the ratio of T/B. In order to reduce the influence of sample time and photochemical reaction on the ratio of benzene to toluene, this study selected the weaker photochemical reaction period (3:00-7:00) for the analysis of toluene and benzene (Figure 5).

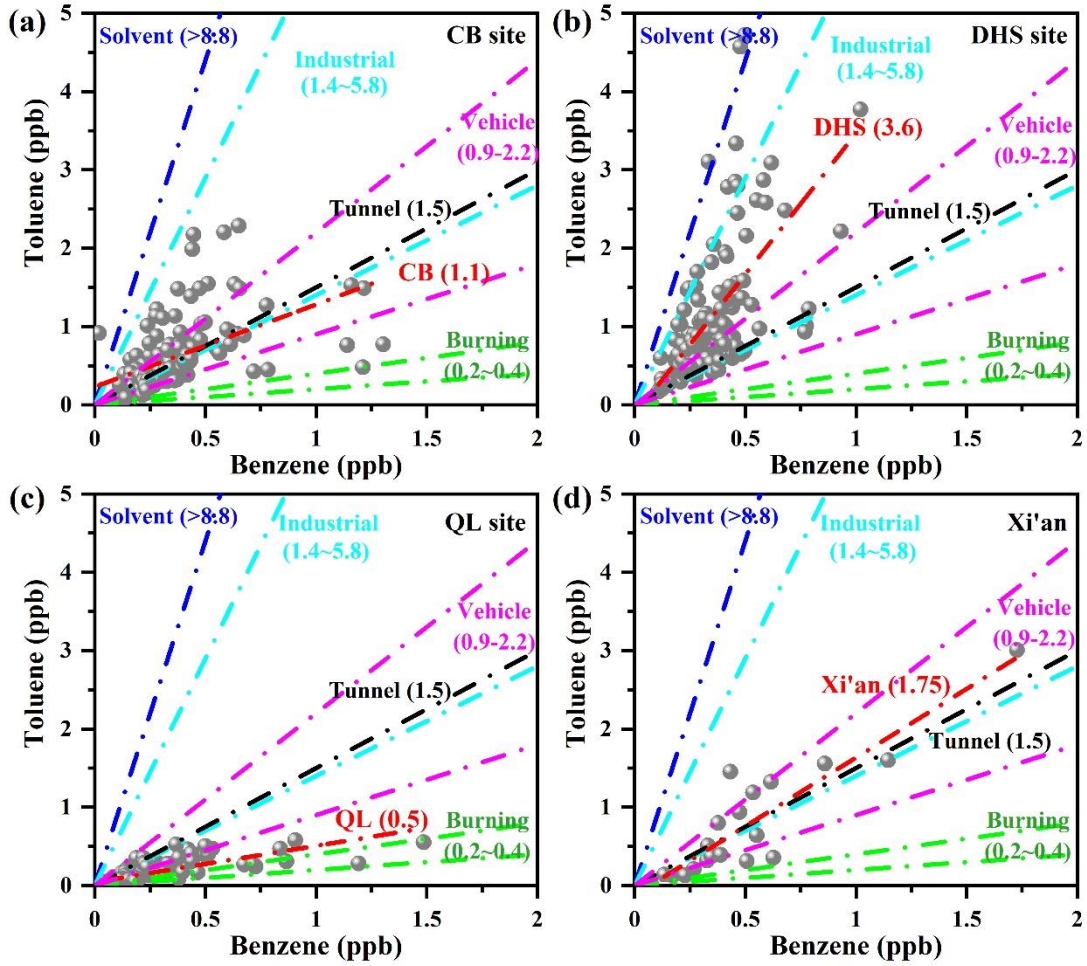

Figure 5: Linear correlations between toluene and benzene at the CB, DHS, QL, and gridded sampling sites between 3:00-7:00 during the observation period.

We agree with reviewer and carefully revised the statement in the revised manuscript. Now it reads as follows:

In order to reduce the influence of photochemical reaction on the ratio of benzene to toluene, this study selected the weaker photochemical reaction period (3:00-7:00) for the analysis of toluene and benzene (Figure 5). Figure 5 shows that the ratios of toluene to benzene at the CB, DHS, QL, and gridded sampling sites were 1.1 ($R_{Pearson}$=0.5), 3.6 ($R_{Pearson}$=0.6), 0.5 ($R_{Pearson}$=0.8), and 1.75 ($R_{Pearson}$=0.9), respectively. In the urban areas (CB and DHS sites), most of the T/B ratios were distributed within the reference range of vehicle emissions and industrial emissions (Figure 5a, 5b), implying that vehicle sources and industrial sources contribute significantly to the VOCs in Xi'an urban area. In addition, the T/B value of some samples is greater than 5.8 in urban area which may affected by paint solvent usage source (Figure 5b). However, the detailed source contribution needs to be obtained through PMF source analysis results (Section 3.2.2). In the rural area (QL site), most of the T/B ratios were distributed within the reference range of vehicle emissions and burning emissions (Figure 5c), implying that vehicle sources and burning sources contribute significantly to the VOCs in Xi'an rural area. In the gridded sampling sites, the T/B ratio was predominately concentrated around 1.5, indicating that vehicle exhaust sources may greatly contributed to the overall VOCs in Xi'an (Figure 5d).

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14. MVK is a photochemical product of isoprene. Why are most of the MVK attributed to vehicle exhaust at the CB site?

Response:

We appreciate the reviewer's comments. As the photooxidation product of isoprene, MVK could be emitted from secondary sources. However, the tunnel and vehicular exhaust emissions measurements have indicated that MVK could be emitted from vehicle exhaust sources including gasoline and diesel vehicles (Biesenthal and Shepson, 1997;Kean et al., 2001;Ling et al., 2019). In urban site with less affected by biological sources, MVK may more affected by anthropogenic emissions

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15. Figure 1: it is recommended to mark Feiwei plain.

Response:

We appreciate the reviewer's comments. We agree with reviewer and marked the Feiwei plain in Figure1. Now it reads as follows:

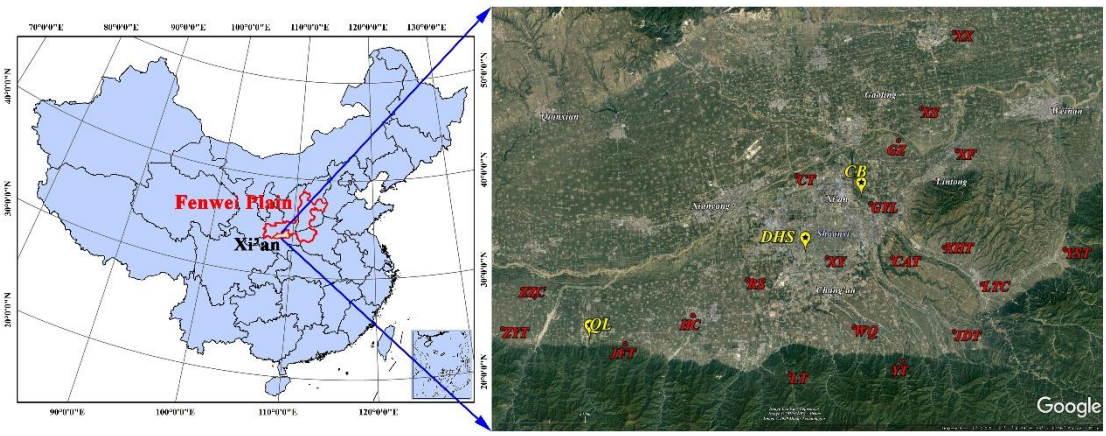

Figure 1: VOC field observation and grid sampling sites in Xi'an.

Note: The topographic image was obtained from Google Earth.

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16. Figures 5 and 7: Linear correlations are shown, not correlation coefficients.

Response:

We appreciate the reviewer's comments. We agree with reviewer and carefully revised the statement according to the reviewer's suggestion. Now it reads as follows:

Figure 5: Linear correlations between toluene and benzene at the CB, DHS, QL, and gridded sampling sites.

Figure 7: Linear correlations between (a) iso-pentane and n-pentane and (b) propane and ethane at the CB (red), DHS (orange), QL (blue), and gridded sampling sites (light blue).

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17. Figure 6: What does the green line represent?

Response:

We appreciate the reviewer's comments. The green line represents the initial emission ratio of m/p-xylene and ethylbenzene, which can be replaced by the highest concentration ratio in periods where the photochemical reaction is weak.

We have added the green line description in the caption in the revised manuscript. Now it reads as follows:

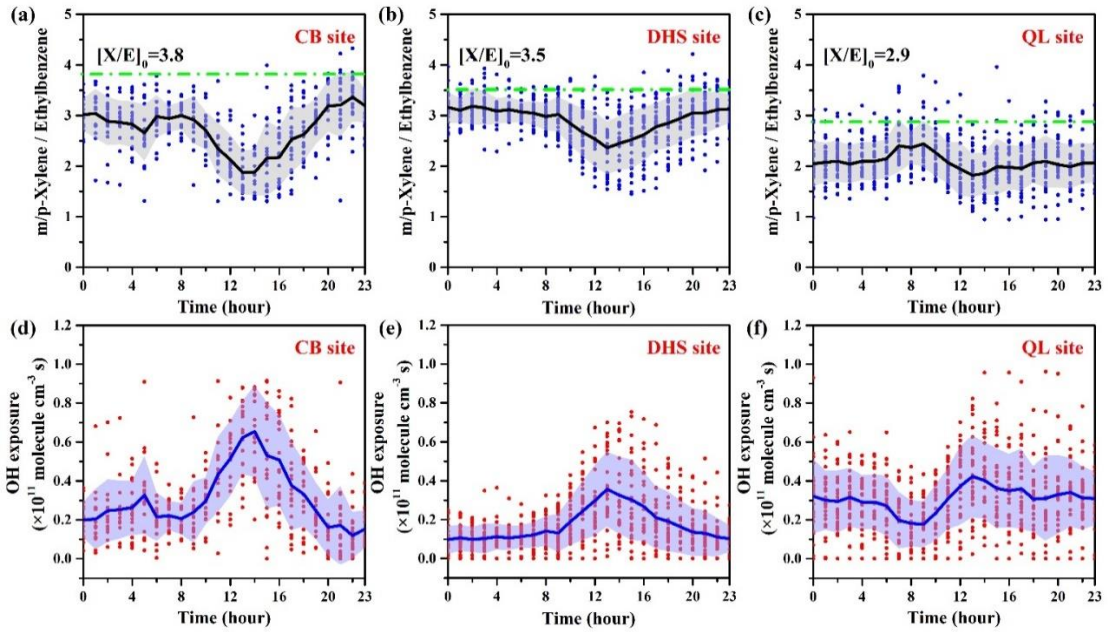

Figure 6: Diurnal variations in m/p-xylene to ethylbenzene and OH exposure at the CB, DHS, QL, and gridded sampling sites.

Note: Time is expressed in CST. The green line represents the initial emission ratio of m/p-xylene and ethylbenzene.

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18. Figure 8: What do the bars and dots represent? Please explain in the caption.

Response:

We appreciate the reviewer's comments. We agree with reviewer and add the explanation in the caption.

Now it reads as follows:

Figure 8: Source profiles and contributions of VOCs in the CB, DHS, and QL sites during the observation period.

Note. Bars represent the concentration of each species apportioned to the factor, and black dots represent the percent of each species apportioned to the factor.

Technical comments

1. Line 10: "a critical precursors"... delete "a".

Response:

We appreciate the reviewer's comments. We are sorry for our mistakes, and we have removed "a" in this sentence.

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2. Line 23: References are missing.

Response:

We appreciate the reviewer's comments, and we have added references in this sentence in the revised manuscript. Now it reads as follows:

Atmospheric pollution in China is characterized by frequent secondary pollution, which is primarily reflected by the yearly increasing ozone (O_3) concentrations and proportion of secondary organic components (SOA) in $PM_{2.5}$ (Lu et al., 2018; Huang et al., 2014).

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3. Line 35: "source" should be "sources"

Response:

We appreciate the reviewer's comments. We are sorry for our mistakes, and we have change *"source" to "sources"* in this sentence.

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4. Line 36: "indicates" should be "indicate"

Response:

We appreciate the reviewer's comments. We are sorry for our mistakes, and we have change *"indicates" to "indicate"* in this sentence.

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5. Equation 1, lines 98 and 100: the rate coefficient is typically represented by the lowercase k.

Response:

We appreciate the reviewer's comments. We are sorry for our mistakes, and we have change the rate coefficient K by the lowercase k in the revised manuscript.

Lastly, we would again express our appreciation to the reviewers and editor for their warm-hearted help. Thank you very much!!!!

References

An, J., Wang, J., Zhang, Y., and Zhu, B.: Source Apportionment of Volatile Organic Compounds in an Urban Environment at the Yangtze River Delta, China, Arch. Environ. Contam. Toxicol., 72, 335-348, 10.1007/s00244-017-0371-3, 2017.

Biesenthal, T. A., and Shepson, P. B.: Observations of anthropogenic inputs of the isoprene oxidation products methyl vinyl ketone and methacrolein to the atmosphere, Geophysical Research Letters, 24, 1375-1378, 10.1029/97gl01337, 1997.

Biesenthal, T. A., and Shepson, P. B.: Observations of anthropogenic inputs of the isoprene oxidation products methyl vinyl ketone and methacrolein to the atmosphere, Geophysical Research Letters, 24, 1375-1378, 10.1029/97gl01337, 1997.

Brown, S. G., Eberly, S., Paatero, P., and Norris, G. A.: Methods for estimating uncertainty in PMF solutions: Examples with ambient air and water quality data and guidance on reporting PMF results, Sci. Total. Environ., 518, 626-635, 10.1016/j.scitotenv.2015.01.022, 2015.

Chen, C.-H., Chuang, Y.-C., Hsieh, C.-C., and Lee, C.-S.: VOC characteristics and source apportionment at a PAMS site near an industrial complex in central Taiwan, Atmos. Pollut. Res., 10, 1060-1074, 10.1016/j.apr.2019.01.014, 2019.

Dai, P., Ge, Y., Lin, Y., Su, S., and Liang, B.: Investigation on characteristics of exhaust and evaporative emissions from passenger cars fueled with gasoline/methanol blends, Fuel, 113, 10-16, 10.1016/j.fuel.2013.05.038, 2013.

Deng, C. X., Jin, Y. J., Zhang, M., Liu, X. W., and Yu, Z. M.: Emission Characteristics of VOCs from On-Road Vehicles in an Urban Tunnel in Eastern China and Predictions for 2017-2026, Aerosol and Air Quality Research, 18, 3025-3034, 10.4209/aaqr.2018.07.0248, 2018.

Gao, Q., Yan, Y., Li, R., Xu, Y., Niu, Y., Liu, C., Xie, K., Chang, Z., Hu, D., Li, Z., and Peng, L.: Characteristics of Volatile Organic Compounds during Different Pollution Periods in Winter in Yuncheng, a Typical City in North China, Aerosol and Air Quality Research, 20, 97-107, 10.4209/aaqr.2019.08.0402, 2020.

Goliff, W. S., Stockwell, W. R., and Lawson, C. V.: The regional atmospheric chemistry mechanism, version 2, Atmos. Environ., 68, 174-185, 10.1016/j.atmosenv.2012.11.038, 2013.

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, Geosci. Model Dev., 5, 1471-1492, 10.5194/gmd-5-1471-2012, 2012.

Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K., and Fall, R.: Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses, J. Geophys. Res.: Atmosphere 98, 12609-12617, https://doi.org/10.1029/93JD00527, 1993.

Huang, R. J., Zhang, Y. L., Bozzetti, C., Ho, K. F., Cao, J. J., Han, Y. M., Daellenbach, K. R., Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z. S., Szidat, S., Baltensperger, U., El Haddad, I., and Prevot, A. S. H.: High secondary aerosol contribution to particulate pollution during haze events in China, Nature, 514, 218-222, 10.1038/nature13774, 2014.

Jiang, M., Lu, K., Su, R., Tan, Z., Wang, H., Li, L., Fu, Q., Zhai, C., Tan, Q., Yue, D., Chen, D., Wang, Z., Xie, S., Zeng, L., and Zhang, Y.: Ozone formation and key VOCs in typical Chinese city clusters, Chinese Science Bulletin, 63, 1130-1141, 2018.

Jiang, M., Lu, K., Su, R., Tan, Z., Wang, H., Li, L., Fu, Q., Zhai, C., Tan, Q., Yue, D., Chen, D., Wang,

Z., Xie, S., Zeng, L., and Zhang, Y.: Ozone formation and key VOCs in typical Chinese city clusters, Chinese Science Bulletin, 63, 1130-1141, 2018.

Kean, A. J., Grosjean, E., Grosjean, D., and Harley, R. A.: On-road measurement of carbonyls in California light-duty vehicle emissions, Environmental Science & Technology, 35, 4198-4204, 10.1021/es010814v, 2001.

Kean, A. J., Grosjean, E., Grosjean, D., and Harley, R. A.: On-road measurement of carbonyls in California light-duty vehicle emissions, Environmental Science & Technology, 35, 4198-4204, 10.1021/es010814v, 2001.

Li, B., Ho, S.S.H., Gong, S., Ni, J., Li, H., Han, L., Yang, Y., Qi, Y. and Zhao, D.: Characterization of VOCs and their related atmospheric processes in a central Chinese city during severe ozone pollution periods, Atmos. Chem. Phys., 19(1), 617-638, doi:10.5194/acp-19-617-2019, 2019a.

Li, J., Zhai, C., Yu, J., Liu, R., Li, Y., Zeng, L., and Xie, S.: Spatiotemporal variations of ambient volatile organic compounds and their sources in Chongqing, a mountainous megacity in China, Sci. Total. Environ., 627, 1442-1452, 10.1016/j.scitotenv.2018.02.010, 2018.

Li, M., Shao, M., Li, L.-Y., Lu, S.-H., Chen, W.-T., and Wang, C.: Quantifying the ambient formaldehyde sources utilizing tracers, Chinese Chemical Letters, 25, 1489-1491, 10.1016/j.cclet.2014.07.001, 2014.

Li, Q., Su, G., Li, C., Liu, P., Zhao, X., Zhang, C., Sun, X., Mu, Y., Wu, M., Wang, Q., and Sun, B.: An investigation into the role of VOCs in SOA and ozone production in Beijing, China, Sci. Total. Environ., 720, 10.1016/j.scitotenv.2020.137536, 2020.

Li, X.-h., Wang, S.-x., and Hao, J.-m.: Characteristics of Volatile Organic Compounds (VOCs) Emitted from Biofuel Combustion in China, Huanjing Kexue, 32, 3515-3521, 2011.

Ling, Z. H., and Guo, H.: Contribution of VOC sources to photochemical ozone formation and its control policy implication in Hong Kong, Environ. Sci. Policy., 38, 180-191, 10.1016/j.envsci.2013.12.004, 2014.

Ling, Z. H., Guo, H., Cheng, H. R., and Yu, Y. F.: Sources of ambient volatile organic compounds and their contributions to photochemical ozone formation at a site in the Pearl River Delta, southern China, Environ. Pollut., 159, 2310-2319, 10.1016/j.envpol.2011.05.001, 2011.

Ling, Z., He, Z., Wang, Z., Shao, M., and Wang, X.: Sources of methacrolein and methyl vinyl ketone and their contributions to methylglyoxal and formaldehyde at a receptor site in Pearl River Delta, J. Environ. Sci., 79, 1-10, 10.1016/j.jes.2018.12.001, 2019.

Ling, Z., He, Z., Wang, Z., Shao, M., and Wang, X.: Sources of methacrolein and methyl vinyl ketone and their contributions to methylglyoxal and formaldehyde at a receptor site in Pearl River Delta, J. Environ. Sci., 79, 1-10, 10.1016/j.jes.2018.12.001, 2019.

Liu, B., Liang, D., Yang, J., Dai, Q., Bi, X., Feng, Y., Yuan, J., Xiao, Z., Zhang, Y., and Xu, H.: Characterization and source apportionment of volatile organic compounds based on 1-year of observational data in Tianjin, China, Environ. Pollut., 218, 757-769, 10.1016/j.envpol.2016.07.072, 2016a.

Liu, Y., Shao, M., Fu, L., Lu, S., Zeng, L. and Tang, D.: Source profiles of volatile organic compounds (VOCs) measured in China: Part I, Atmos. Environ., 42(25), 6247-6260, doi:10.1016/j.atmosenv.2008.01.070, 2008a.

Liu, Y., Song, M., Liu, X., Zhang, Y., Hui, L., Kong, L., Zhang, Y., Zhang, C., Qu, Y., An, J., Ma, D., Tan, Q. and Feng, M.: Characterization and sources of volatile organic compounds (VOCs) and their related changes during ozone pollution days in 2016 in Beijing, China, Environ. Pollut., 257, 113599,

doi:10.1016/j.envpol.2019.113599, 2020.

Lu, S., Bai, Y., Zhang, G., and Ma, J.: Study on the Characteristics of VOCs Source Profiles of Vehicle Exhaust and Gasoline Emission, Acta Scientiarum Naturalium Universitatis Pekinensis, 39, 507-511, 2003.

Lu, X., Hong, J., Zhang, L., Cooper, O. R., Schultz, M. G., Xu, X., Wang, T., Gao, M., Zhao, Y., and Zhang, Y.: Severe Surface Ozone Pollution in China: A Global Perspective, Environmental Science & Technology Letters, 5, 487-494, 10.1021/acs.estlett.8b00366, 2018.

Mo, Z., Shao, M., and Lu, S.: Compilation of a source profile database for hydrocarbon and OVOC emissions in China, Atmos. Environ., 143, 209-217, 10.1016/j.atmosenv.2016.08.025, 2016.

Mo, Z., Shao, M., Lu, S., Qu, H., Zhou, M., Sun, J., and Gou, B.: Process-specific emission characteristics of volatile organic compounds (VOCs) from petrochemical facilities in the Yangtze River Delta, China, Science of the Total Environment, 533, 422-431, 10.1016/j.scitotenv.2015.06.089, 2015.

Peeters, J., Nguyen, T. L., and Vereecken, L.: HOx radical regeneration in the oxidation of isoprene, Physical Chemistry Chemical Physics, 11, 5935-5939, 10.1039/b908511d, 2009.

Qiao, Y.-z., Wang, H.-l., Huang, C., Chen, C.-h., Su, L.-y., Zhou, M., Xu, H., Zhang, G.-f., Chen, Y.-r., Li, L., Chen, M.-h., and Huang, H.-y.: Source Profile and Chemical Reactivity of Volatile Organic Compounds from Vehicle Exhaust, Huanjing Kexue, 33, 1071-1079, 2012.

Shen, L., Wang, Z., Cheng, H., Liang, S., Xiang, P., Hu, K., Yin, T., and Yu, J.: A Spatial-Temporal Resolved Validation of Source Apportionment by Measurements of Ambient VOCs in Central China, Int. J. Env. Res. Pub. He., 17, 10.3390/ijerph17030791, 2020.

Shi, J., Deng, H., Bai, Z., Kong, S., Wang, X., Hao, J., Han, X., and Ning, P.: Emission and profile characteristic of volatile organic compounds emitted from coke production, iron smelt, heating station and power plant in Liaoning Province, China, Science of the Total Environment, 515, 101-108, 10.1016/j.scitotenv.2015.02.034, 2015.

Song, M., Tan, Q., Feng, M., Qu, Y., Liu, X., An, J., and Zhang, Y.: Source Apportionment and Secondary Transformation of Atmospheric Nonmethane Hydrocarbons in Chengdu, Southwest China, J. Geophys. Res.-Atmos., 123, 9741-9763, 10.1029/2018jd028479, 2018.

Stavrakou, T., Müller, J. F., Bauwens, M., De Smedt, I., Van Roozendael, M., Guenther, A., Wild, M., and Xia, X.: Isoprene emissions over Asia 1979–2012: impact of climate and land-use changes, Atmos. Chem. Phys., 14, 4587-4605, 10.5194/acp-14-4587-2014, 2014.

Tan, Z., Fuchs, H., Lu, K., Hofzumahaus, A., Bohn, B., Broch, S., Dong, H., Gomm, S., Haeseler, R., He, L., Holland, F., Li, X., Liu, Y., Lu, S., Rohrer, F., Shao, M., Wang, B., Wang, M., Wu, Y., Zeng, L., Zhang, Y., Wahner, A., and Zhang, Y.: Radical chemistry at a rural site (Wangdu) in the North China Plain: observation and model calculations of OH, HO2 and RO2 radicals, Atmos. Chem. Phys., 17, 663-690, 10.5194/acp-17-663-2017, 2017.

Tan, Z., Lu, K., Jiang, M., Su, R., Dong, H., Zeng, L., Xie, S., Tan, Q., and Zhang, Y.: Exploring ozone pollution in Chengdu, southwestern China: A case study from radical chemistry to O3-VOC-NOx sensitivity, Science of The Total Environment, 636, 775-786, https://doi.org/10.1016/j.scitotenv.2018.04.286, 2018.

Tsai, J. H., Lin, K. H., Chen, C. Y., Lai, N., Ma, S. Y., Chiang, H. L.: Volatile organic compound constituents from an integrated iron and steel facility, Journal of Hazardous Materials, 157, 569-578, 10.1016/j.jhazmat.2008.01.022, 2008.

Wang, H. L., Chen, C. H., Wang, Q., Huang, C., Su, L. Y., Huang, H. Y., Lou, S. R., Zhou, M., Li, L., Qiao, L. P., and Wang, Y. H.: Chemical loss of volatile organic compounds and its impact on the

source analysis through a two-year continuous measurement, Atmos. Environ., 80, 488-498, 10.1016/j.atmosenv.2013.08.040, 2013.

Wang, H., Qiao, Y., Chen, C., Lu, J., Dai, H., Qiao, L., Lou, S., Huang, C., Li, L., Jing, S., and Wu, J.: Source Profiles and Chemical Reactivity of Volatile Organic Compounds from Solvent Use in Shanghai, China, Aerosol and Air Quality Research, 14, 301-310, 10.4209/aaqr.2013.03.0064, 2014.

Wang, J., Jin, L., Gao, J., Shi, J., Zhao, Y., Liu, S., Jin, T., Bai, Z., and Wu, C.-Y.: Investigation of speciated VOC in gasoline vehicular exhaust under ECE and EUDC test cycles, Science of the Total Environment, 445, 110-116, 10.1016/j.scitotenv.2012.12.044, 2013.

Wang, M., Chen, W., Lu, S. and Shao, M.: Ratios of Volatile Organic Compounds in Ambient Air of Various Cities of China, Huanjing. Kexue., 39(10), 4393-4399, doi:10.13227/j.hjkx.201801291.html, 2018.

Wang, M., Chen, W., Shao, M., Lu, S., Zeng, L., and Hu, M.: Investigation of carbonyl compound sources at a rural site in the Yangtze River Delta region of China, J. Environ. Sci., 28, 128-136, https://doi.org/10.1016/j.jes.2014.12.001, 2015.

Wang, S., Wei, W., Du, L., Li, G. and Hao, J.: Characteristics of gaseous pollutants from biofuel-stoves in rural China, Atmos. Environ., 43(27), 4148-4154, doi:10.1016/j.atmosenv.2009.05.040, 2009.

Yan, Y., Peng, L., Li, R., Li, Y., Li, L. and Bai, H.: Concentration, ozone formation potential and source analysis of volatile organic compounds (VOCs) in a thermal power station centralized area: A study in Shuozhou, China, Environ. Pollut., 223, 295-304, doi:10.1016/j.envpol.2017.01.026, 2017.

Yang, Y., Ji, D., Sun, J., Wang, Y., Yao, D., Zhao, S., Yu, X., Zeng, L., Zhang, R., Zhang, H., Wang, Y., and Wang, Y.: Ambient volatile organic compounds in a suburban site between Beijing and Tianjin: Concentration levels, source apportionment and health risk assessment, Sci. Total. Environ., 695, 10.1016/j.scitotenv.2019.133889, 2019.

Yao, Y.-C., Tsai, J.-H., and Wang, I. T.: Emissions of gaseous pollutant from motorcycle powered by ethanol-gasoline blend, Applied Energy, 102, 93-100, 10.1016/j.apenergy.2012.07.041, 2013.

Yao, Z., Shen, X., Ye, Y., Cao, X., Jiang, X., Zhang, Y., and He, K.: On-road emission characteristics of VOCs from diesel trucks in Beijing, China, Atmos. Environ., 103, 87-93, https://doi.org/10.1016/j.atmosenv.2014.12.028, 2015a.

Yao, Z., Wu, B., Shen, X., Cao, X., Jiang, X., Ye, Y., and He, K.: On-road emission characteristics of VOCs from rural vehicles and their ozone formation potential in Beijing, China, Atmos. Environ., 105, 91-96, 10.1016/j.atmosenv.2015.01.054, 2015b.

Yuan, B., Shao, M., Lu, S. and Wang, B.: Source profiles of volatile organic compounds associated with solvent use in Beijing, China, Atmos. Environ., 44(15), 1919-1926, doi:10.1016/j.atmosenv.2010.02.014, 2010

Zhang, J., Wu, Y., Li, H., Ling, D., Han, K., Li, J., Hu, J., Wang, H., Zhang, M., and Wang, S.: Characteristics and source apportionment of ambient volatile organic compounds in autumn in Langfang development zones, China Environmental Science, 39, 3186-3192, 2019a.

Zhang, Y., Wang, X., Zhang, Z., Lu, S., Shao, M., Lee, F. S. C., and Yu, J.: Species profiles and normalized reactivity of volatile organic compounds from gasoline evaporation in China, Atmos. Environ., 79, 110-118, 10.1016/j.atmosenv.2013.06.029, 2013.

Zhang, Y.-x., Yin, S.-s., Yuan, M.-h., Zhang, R.-q., Zhang, M., Yu, S.-j., and Li, Y.-d.: Characteristics and Source Apportionment of Ambient VOCs in Spring in Zhengzhou, Huanjing Kexue, 40, 4372-4381, 10.13227/j.hjkx.201902075, 2019b.

Zheng, J., Yu, Y., Mo, Z., Zhang, Z., Wang, X., Yin, S., Peng, K., Yang, Y., Feng, X., and Cai, H.:

Industrial sector-based volatile organic compound (VOC) source profiles measured in manufacturing facilities in the Pearl River Delta, China, Science of the Total Environment, 456, 127-136, 10.1016/j.scitotenv.2013.03.055, 2013.

Zhou, X., Li, Z., Zhang, T., Wang, F., Wang, F., Tao, Y., Zhang, X., Wang, F., and Huang, J.: Volatile organic compounds in a typical petrochemical industrialized valley city of northwest China based on high-resolution PTR-MS measurements: Characterization, sources and chemical effects, Sci. Total. Environ., 671, 883-896, 10.1016/j.scitotenv.2019.03.283, 2019.

Zhuang, Y., Cheng, C.-L., Weng, X., Chen, J.-S., Lyu, X.-P., Li, M., and Zhou, Z.: Characteristics and Source Apportionment of Atmospheric Volatile Organic Compounds During Emission Control Period in Xiamen, Chinese J. Anal. Chem., 47, 890-898, 10.19756/j.issn.0253-3820.181670, 2019.