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 #1

General comments

Song et al. investigated the variation, sources, and chemistry of atmospheric VOCs in Xi'an, China. Field observations were conducted in multiple representative sites in Xi'an. Results showed that vehicle emission was the largest VOC contributor, followed by industrial emissions. Results of backward trajectories coupled with potential source contribution function analysis indicated that Xi'an exhibited a strong local VOC source. In addition, the authors demonstrated that alkenes, aromatics, and OVOCs played dominant roles in the secondary transformation of ambient VOCs in Xi'an. The manuscript is very well written, and the results are clearly presented. Therefore, I would like to recommend its publication in Atmospheric Chemistry and Physics, subject to minor changes.

Response:

We would like to thank reviewer #1 for carefully reading our manuscript and for your valuable and constructive comments. We carefully revised and improved each part according to the reviewer's suggestions. Listed below are our point-by-point responses to reviewer's comments. Lastly, we would like to thank reviewer for the positive comments again.

Comments

1. Lines 75-80: GC analysis.

Please provide the details of GC procedures (e.g., oven temperature program) for the analyses of both low carbon number and high carbon number compounds.

Response:

We appreciate the reviewer's comments, and we have added more information on the GC analysis. Now it reads as follows:

The GC–MS/FID instrument utilized a dual gas path separation method. The sample gas, after water and CO_2 were removed, captured VOC components through an ultra-low temperature system (-160 °C), and the gas chromatography analysis system was utilized after thermal desorption. The oven temperature was programmed at 37 ℃ maintained for 5 min initially, then raised to 120 ℃ at 5 ℃ min^{-1} holding for 5 min and latter to 180 ℃ at 6 ℃ min^{-1} holding for 5 min. The low carbon number (C_2–C_5) compounds were separated on an Al_2O_3/KCl PLOT column and quantified using the FID (200 °C). The high carbon number (C_5–C_{10}) compounds were separated on a DB-624 column and quantified using MS (230 °C).

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2. Line 85: "VOC gridded sampling was performed at 7:00 China Standard Time (CST) and 15:00 (CST) on July 1 and July 14, 2019, respectively."

This sentence is confusing. Were the samples collected at both 7:00 and 15:00 on both July 1 and July 14? Or the samples were collected at 7:00 on July 1 and 15:00 on July 14? Please clarify.

Response:

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

VOC gridded samples were collected at each site for two days (July 1 and July 14, 2019) and twice a day at 7:00 China Standard Time (CST) and 15:00 (CST). A total of 80 ambient air samples with a frequency of 4 samples per site were collected and each sample was stored in a 3.2-L Silonite^{TM} canister (Entech Instrument, United States).

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3. Line 89: "Ambient air was sampled into a 3-L SiloniteTM 90 canister (Entech Instrument, United States)."

How long was the sampling time? Or what was the time resolution of the VOC sampling? How many samples were collected per site? Please clarify.

Response:

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

VOC gridded samples were collected at each site for two days (July 1 and July 14, 2019) and twice a day at 7:00 China Standard Time (CST) and 15:00 (CST). The gridded sampling site were chosen based on the technical regulations for selecting ambient air quality monitoring stations (HJ 664-2013) and method for selection of Photochemical Assessment Monitoring Stations (EPA). According to the prevailing wind direction and to ensure coverage of all urban areas in Xi'an, 20 gridded sampling sites were selected for this study (Figure 1). Detailed sampling site information is shown in Table 1. A total of 80 ambient air samples with a frequency of 4 samples per site were collected and each sample was stored in a 3.2-L Silonite^{TM} canister (Entech Instrument, United States). Before VOC gridded sampling, the Silonite^{TM} 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 2 min.

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4. Lines 116-117: "VOC tracers with a data integrity greater than 75% and greater than 65% valid data (concentration ⩾ MDL) were selected as the input species."

This sentence is confusing. Do you mean "VOC tracers with greater than 65% valid data"?

Please explain why 75% and 65% were used.

Response:

We appreciate the reviewer's comments. In order to ensure the accuracy of PMF model simulation, species with more than 25% missing samples or with more than 35% samples below the method detection limit (MDL) should be excluded in input files (Liu et al., 2020). Therefore, VOC tracers with a data integrity greater than 75% and valid data (concentration ⩾ MDL) greater than 65% were selected for this study.

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

VOCs tracers were selected according to the reported typical emission source profiles in China (He et al., 2015; Liu et al., 2008a; Song et al., 2018). Only those tracers which have data coverage greater than 75% during the campaign and have 65% measured concentrations above the MDL were included in the PMF analysis (c.f. Liu et al., 2020).

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5. Equation (4): please provide references for the uncertainty estimation.

Response:

We appreciate the reviewer’s comments. We have added references for the uncertainty estimation according to the reviewer’s suggestion. Now it reads as follows:

For the PMF input, data below the detection limit were assigned with MDL/2, and the missing data were substituted with median concentration. The uncertainty is calculated using Eq. (4) as follows (Brown et al, 2015; Liu et al, 2016a):

$$\mathrm{Unc}=\begin{cases}\sqrt{(\mathrm{Error\ Fraction}\times\mathrm{Conc.})^2+(0.5\times\mathrm{MDL})^2} & \mathrm{Conc.}>\mathrm{MDL}\\ \frac{5}{6}\times\mathrm{Conc.} & \mathrm{Conc.}\leq\mathrm{MDL}\\ 4\times\mathrm{median\ conc.} & \mathrm{Missing\ data}\end{cases}\qquad(4)$$

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6. Lines 172-176: the effects of temperature

As shown in Figure 2, the temperature during polluted periods could be 10-15 ◦C higher than that in the clean days. An increase in temperature can enhance both the emissions and the oxidation rates of VOCs. Can the authors estimate how much of the ozone increase was due to the increase of VOC emissions and how much was due to the enhancement of VOC oxidation rates during the polluted periods?

Response:

We appreciate the reviewer’s comments. We agree with reviewer that an increase in temperature can enhance the emissions and the oxidation rates of some VOCs (such as isoprene and solvent evaporation). Figure 3 shows 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.

We agree with the reviewer that the elevated concentration of OVOCs on O_3 pollution days could indicate the enhancement of VOC oxidation rates at this stage. However, quantifying the contribution of emission and meteorology (e.g., temperature) to O_3 formation would require detailed emission-based model analysis which is beyond the scope of this manuscript and will be discussed in a separate paper.

We have modified the Figure 3 and add the following discussion in the revised manuscript.

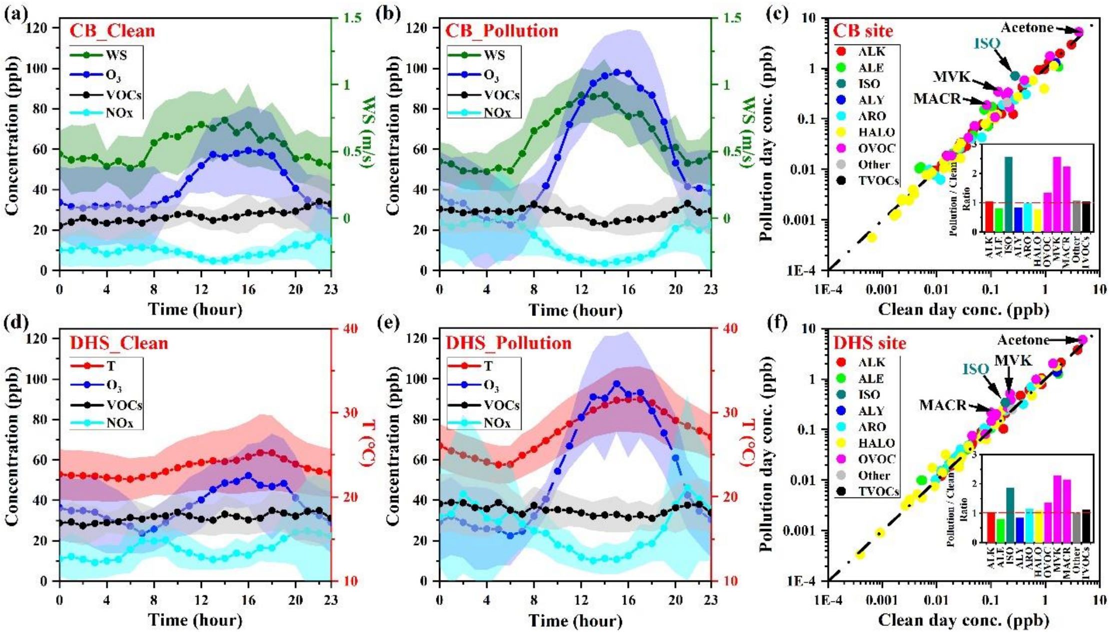

Figure 3: Diurnal variations in wind speed (WS), temperature (T), O$_3$, NOx, and TVOCs on clean and polluted days at the (a) and (b) CB and (d) and (e) DHS sites. Differences in VOC concentrations between clean and polluted days at the (c) CB and (f) DHS sites.

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. Figure 4: spatial variations of VOCs

Were the TVOC concentrations shown in Figure 4 two-day average values of July 1 and July 14? If no, please specify which date the figure represents. If yes, please explain why the author used the average concentrations. Following comment 2 above, if the sampling was conducted at 7:00 on July 1 and at 15:00 on July 14, were the meteorological conditions similar during the two sampling periods? Would the results be the same by analyzing the data collected on each individual day?

Response:

The TVOC concentrations shown in Figure 4 is two-day (4 samples) average values of July 1 and July 14. In this study, a total of 80 ambient air samples with a frequency of 4 samples per site were collected. From the Table S4 we can see the meteorological conditions similar during the two sampling periods. This table has been included in the revised Supplement.

Table S4. The weather parameter on July 1 and July 14 in Xi'an

Date	Area	WS (m/s)	WD (°)	T (℃)	RH (%)
2019/7/1	urban	0.6	205.4	28.9	53.3
2020/7/14		0.6	199.7	31.3	50.9
2020/7/1	rural	1.1	209.8	27.7	54.1
2020/7/14		1.5	201.1	29.8	50.6

Since the weather, emission and transmission conditions of the two days of sampling cannot be completely consistent (R1), in order to reduce the contingency of sampling, we used the method of average concentration to analyze the spatial variation.

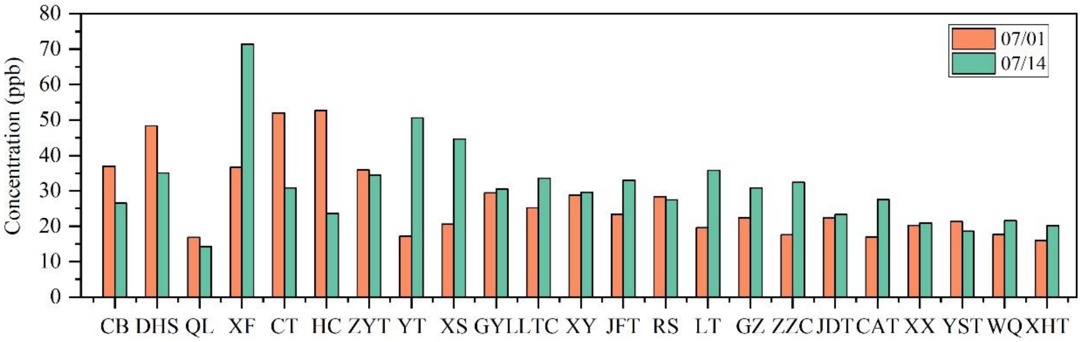

Figure R1: TVOCs concentrations in different sites in Xi'an on July 1 and July 14, 2019.

We appreciate the reviewer's comments. We have revised the caption in Figure 4 to clarify that the figure indicates the average concentration of TVOC at each sampling site. Now the sentence reads as follows:

Figure 4: (a) Proportions of seven VOCs groups and averaged TVOCs concentrations in different sites in Xi'an. (b) Spatial distribution of averaged TVOC concentrations in different sites in Xi'an.

We have also added the sampling information in the revised manuscript. Now it reads as follows:

VOC gridded samples were collected at each site for two days (July 1 and July 14, 2019) and twice a day at 7:00 China Standard Time (CST) and 15:00 (CST). A total of 80 ambient air samples with a frequency of 4 samples per site were collected and each sample was stored in a 3.2-L Silonite^{TM} canister (Entech Instrument, United States).

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8. Lines 192-194: “In addition, the contribution of OVOCs at the YT site was significantly higher than that of the other sites, indicating that the YT site may be significantly affected by ageing sources (Figure 4a).”

a) Please provide the VOC list identified in this study in the supporting information.

b) What were the OVOC composition measured in this study? Throughout the manuscript, the authors tended to attribute higher OVOC concentration to stronger atmospheric oxidation. Although this is reasonable to some extent, there is a possibility that OVOCs were directly emitted. For example, acetone can be emitted from sources such as solvent evaporation, biomass burning, and vehicle emission, as also shown in Figure 8.

Can the authors comment on the primary emissions of OVOCs during the campaign?

And how will this affect the conclusion regarding OVOCs in this study?

Response:

a) We appreciate the reviewer’s comments. We add a list of measured VOCs in the supporting information. The description of VOC measurement in the manuscript is revised as following.

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). 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).

b) 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:

$$[\mathrm{OVOCs}]=k_0+k_1\times[\mathrm{Ethyne}]+k_2\times[\mathrm{PAN}]+k_3\times[\mathrm{Isoprene}] \qquad \text{(R1)}$$

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.

It can be seen from the figure that 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). We therefore infer that the source of OVOCs at this site is most likely from aging sources.

In addition, 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.

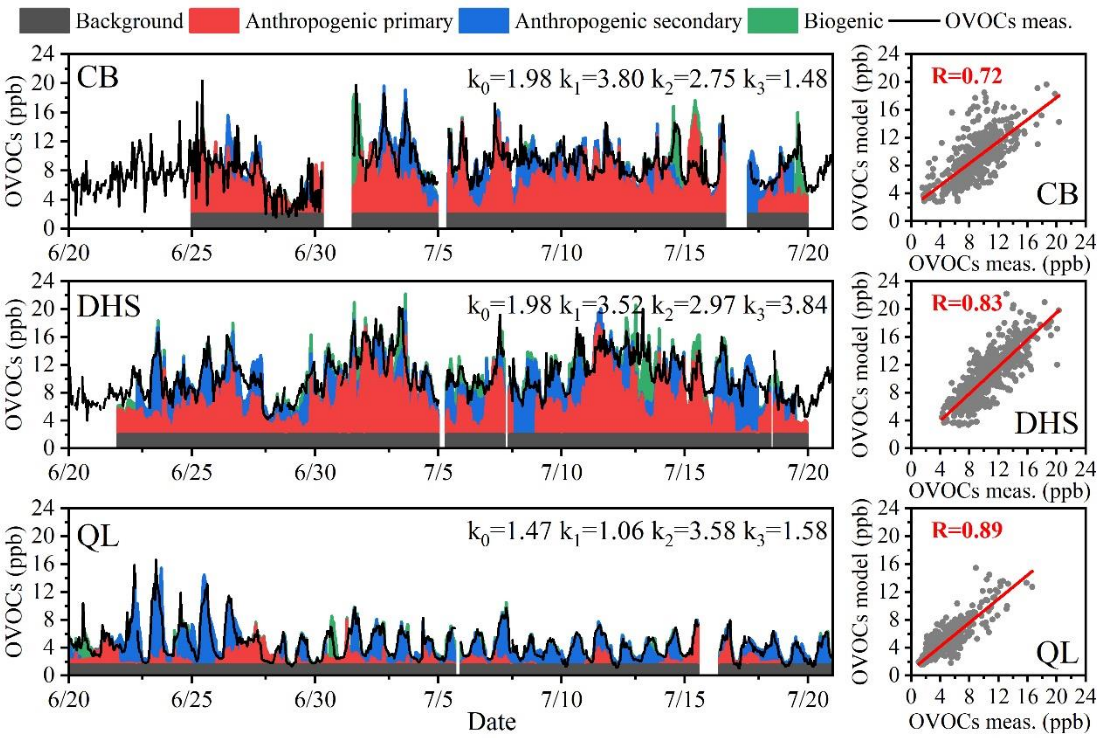

Figure S1. Time series of measured OVOCs concentrations and OVOCs calculated from the multi-linear regression model.

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.

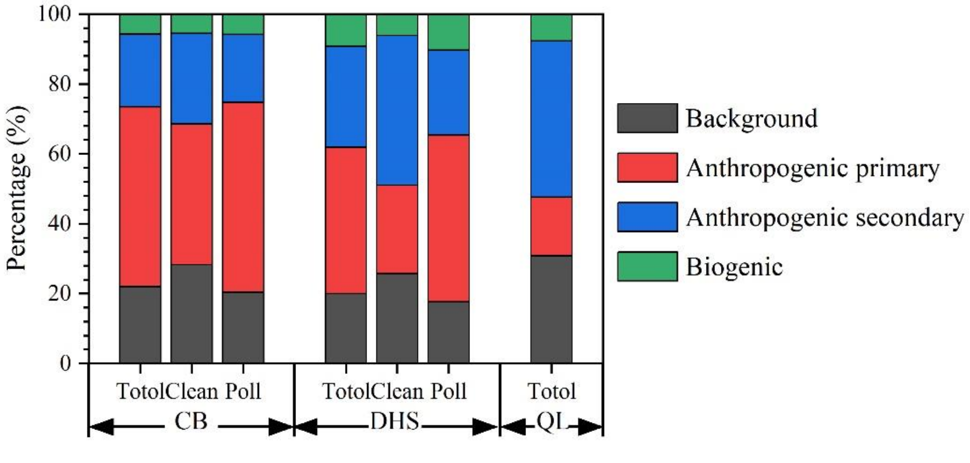

Figure S2. Contributions of different sources of OVOCs in different sites in Xi'an base on the multi-linear regression model.

Figure R2. Geographic environment map of TY site.

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9. Section 3.2.1 Specific VOC Ratios

The methodology using VOC ratios to investigate potential sources provides useful insights. However, the uncertainty may be huge. For example, the authors mentioned that in the industrial region, the concentration ratio of toluene to benzene ranged from 3.0 to 6.9, using the results obtained from Zhengzhou city in China (Li et al., 2019a), the Pearl River Delta region (Chan et al., 2006), and several other developed coastal regions in China (Zhang et al., 2015). I would expect that the industry type and composition are likely different between Xi'an and the cities/areas mentioned in the references (e.g., coastal regions). How does the T/B ratio vary from location to location? How will this affect the conclusions of this study?

Similar issues may exist in the T/B ratios for other sources. For example, the T/B ratio for vehicle emissions can be strongly influenced by vehicle type and fuel composition.

Please discuss the uncertainty of using these ratios.

Response:

We appreciate the reviewer's comments. We agree with reviewer that the T/B ratio vary from different industry type and composition. We summarized the T/B ratios of different types of sources in different regions based on a large number of source emission references during recently years (Tsai et al., 2008; Liu et al., 2008a; Yuan et al., 2010; Li et al., 2011; Qiao et al., 2012; Dai et al., 2013; Wang et al., 2013; Yao et al., 2013; Zhang et al., 2013; Zheng et al., 2013; Wang et al., 2014; Mo et al., 2015; Shi et al., 2015; Yao et al., 2015b; Mo et al., 2016; Yao et al., 2015a; Deng et al., 2018), as shown in Table S5.

According to the Report on the China Statistical Yearbook-2020 released by the National Bureau of Statistics of China (http://www.stats.gov.cn/tjsj/ndsj/), Xi'an's industries mainly include petrochemical industry, chemical industry and power plant. As can be seen from the Table S5, the ratio of T/B ranged from 1.4 ± 0.8 to 5.8± 3.4 by different process unit in petrochemical industry, chemical industry and power plant emissions (Mo et al., 2015; Shi et al., 2015). In vehicle source emission researches, the ratio of T/B ranged from 0.9 ± 0.6 to 2.2± 0.5 by different vehicle type and fuel composition (Qiao et al., 2012; Dai et al., 2013; Wang et al., 2013; Yao et al., 2013; Zhang et al., 2013; Yao et al., 2015b; Mo et al., 2016; Yao et al., 2015a; Deng et al., 2018). However, vehicle emissions include both diesel vehicles emissions and gasoline vehicles emissions in the atmospheric environment. Moreover, according to the Report on the China Statistical Yearbook-2020 released by the National Bureau of Statistics of China (http://www.stats.gov.cn/tjsj/ndsj/), there is no obvious difference in the composition of vehicles in various provinces of China (Figure R3). Thus, the ratio of T/B in the traffic source should be closer to the results of the tunnel experiments which approximately 1.5 ± 0.1 (Liu et al., 2008a; Deng et al., 2018). In addition, the ratio of T/B was greater than 8.8 ± 6.5 by different solvent use process in paint solvent usage source emission researches (Yuan et al., 2010; Wang et al., 2014; Zheng et al., 2013), and the T/B ratio was approximately 0.3 ± 0.1 in different combustion process and raw materials (Liu et al., 2008a; Li et al., 2011; Mo et al., 2016).

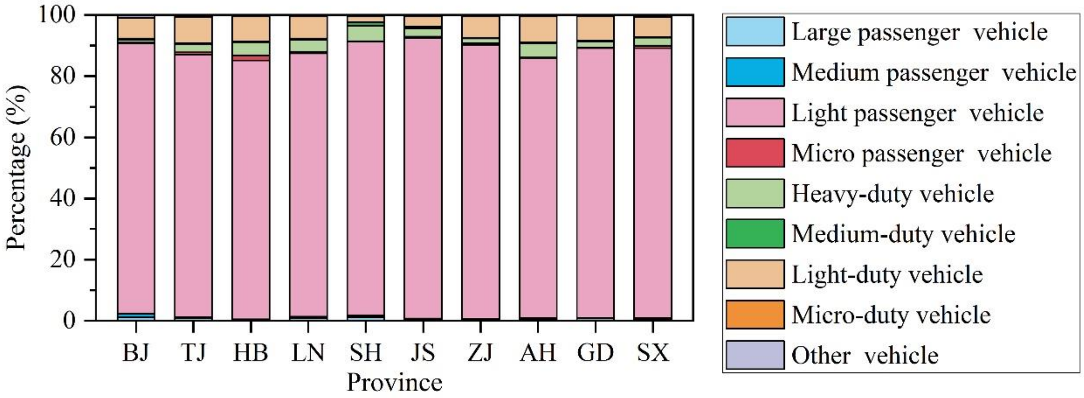

Figure R3. The composition of vehicles in various provinces of China.

Note. BJ=Beijing, TJ=Tianjin, HB=Hebei, LN=Liaoning, SH=Shanghai, JS=Jiangsu, ZJ=Zhejiang, AH=Anhui, GD=Guangdong, SX=Shanxi. The fuel of large passenger vehicle and heavy-duty vehicles is generally diesel. The fuel of light passenger vehicle is generally gasoline.

Then, we marked the T/B range of industrial sources, vehicle sources, paint solvent usage sources, and burning source in the Figure 5. In addition, 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).

Table S5. Toluene to benzene ratio (T/B) of different source profiles in different researches (unit: ppb/ppb).

Category	Sub Category	Location	T/B	Reference	Sub Category avgerage	Min	Max
Transportation	Gasoline vehicle exhaust	Tianjin	1.08	Wang et al.,2013; Dai et al.,2013	1.08	0.93	2.21
	Motorcycle exhaust	Taiwan	1.46	Yao et al,2013	1.46		
	Diesel vehicle exhaust	Beijing	1.77	Yao et al,2015a	0.93		
		Beijing	1.04	Yao et al,2015a			
		Beijing	1.05	Yao et al,2015a			
		Beijing	1.28	Yao et al,2015a			
		Xiamen	0.21	Mo, et al.,2016			
		Xiamen	0.22	Mo, et al.,2016			
	LPG vehicle exhaust	Shanghai	1.05	Qiao et al..,2012	1.05		
	Rural vehicle exhaust	Beijing	2.21	Yao et al.,2015b	1.64		
		Beijing	1.07	Yao et al.,2015b			
	Fuel evaporation	Guangzhou	1.71	Zhang et al.,2013	2.21		
		Guangzhou	2.71	Zhang et al.,2013			
	Tunnel	Hefei	1.52	Deng et al., 2018	1.48		
		Hefei	1.48	Deng et al., 2018			
		Hefei	1.31	Deng et al., 2018			
		Hefei	1.56	Deng et al., 2018			
		PRD	1.52	Liu et al., 2008a			
Burning	Coaling burning	Beijing	0.24	Mo, et al.,2016	0.24	0.23	0.38
	Coaling burning	Beijing	0.38	Liu et al.,2008a	0.38		

	Wheat	Beijing	0.23	Mo, et al.,2016	0.23		
	Maize	Beijing	0.30	Mo, et al.,2016	0.30		
	Wood	Beijing	0.27	Li et al., 2011	0.27		
Solvent use	Architecture paint	Shanghai	15.34	Wang et al.,2014	8.82	8.82	51.43
		Beijing	2.30	Yuan et al.,2010			
	Furniture paint	Beijing	32.44	Yuan et al.,2010	31.35		
		Shanghai	42.13	Wang et al.,2014			
		PRD	15.08	Zheng et al.,2013			
		PRD	34.68	Zheng et al.,2013			
		Beijing	32.44	Yuan et al.,2010			
	Surface paint	PRD	8.17	Zheng et al.,2013	12.63		
		PRD	17.09	Zheng et al.,2013			
	Paint manufacturing	PRD	6.10	Zheng et al.,2013	15.94		
		PRD	25.78	Zheng et al.,2013			
	Shoemaking	PRD	21.28	Zheng et al.,2013	25.38		
		PRD	29.47	Zheng et al.,2013			
	Printing	PRD	38.15	Zheng et al.,2013	51.43		
		PRD	64.71	Zheng et al.,2013			
Industrial processes	Petrochemical industry	YRD	0.95	Mo, et al.,2015	1.37	1.37	5.76
		YRD	2.20	Mo, et al.,2015			
		YRD	3.20	Mo, et al.,2015			
		YRD	0.42	Mo, et al.,2015			
		YRD	0.95	Mo, et al.,2015			
		YRD	1.88	Mo, et al.,2015			

	YRD	0.39	Mo, et al.,2015	
	YRD	0.98	Mo, et al.,2015	
	YRD	1.80	Mo, et al.,2015	
	YRD	1.98	Mo, et al.,2015	
	YRD	1.13	Mo, et al.,2015	
	YRD	0.75	Mo, et al.,2015	
	YRD	1.21	Mo, et al.,2015	
Chemical industry	YRD	2.37	Mo, et al.,2015	5.76
	YRD	9.14	Mo, et al.,2015	
Power plant	Liaoning	2.89	Shi et a..,2015	3.39
	Liaoning	5.29	Shi et a..,2015	
	Liaoning	0.48	Shi et a..,2015	
	Liaoning	4.89	Shi et a..,2015	

Note. PRD = Pearl River Delta, YRD=Yangtze River delta.

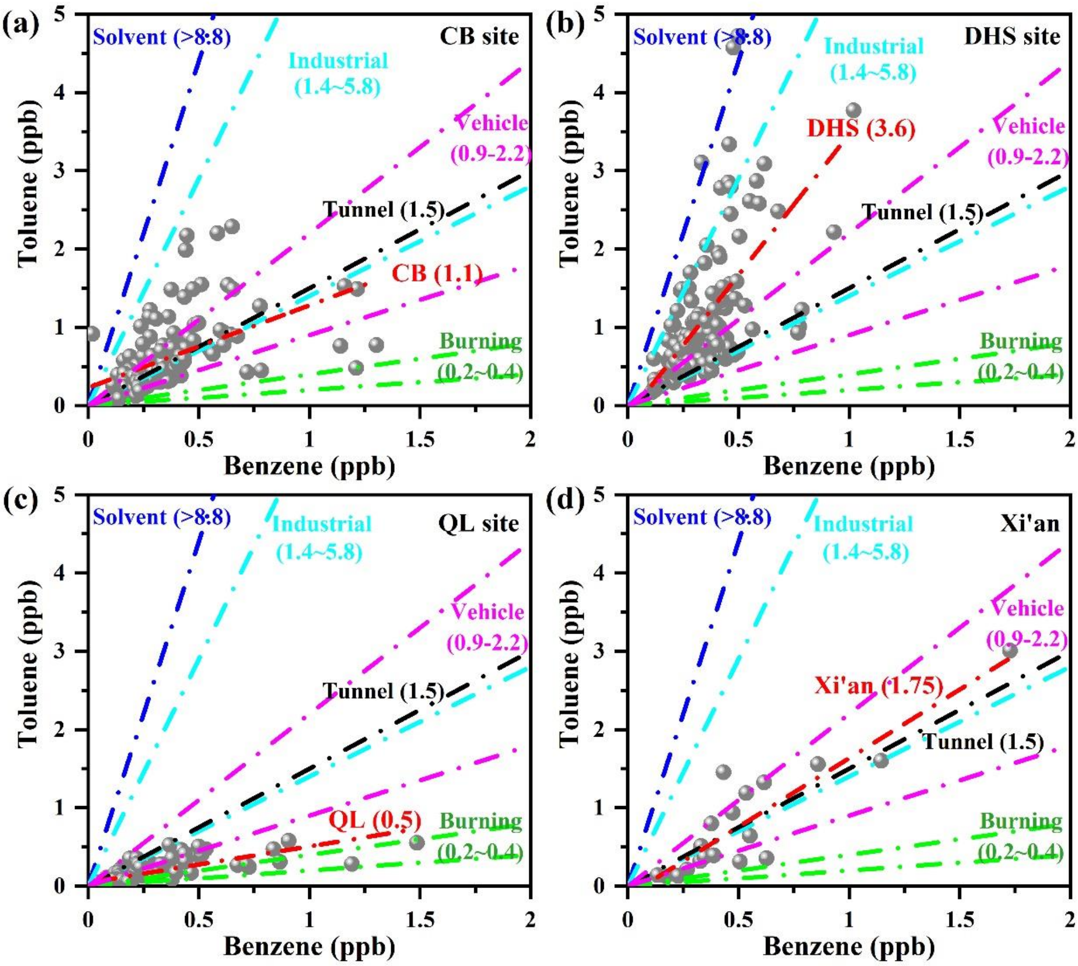

Figure 5: Linear correlations between toluene and benzene at the CB, DHS, QL, and gridded sampling sites between 3:00-7:00 during the observation period.

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

The T/B ratio is clearly different for various source profiles (Table S5). In industrial source emission researches, the ratio of T/B ranged from 1.4 ± 0.8 to 5.8± 3.4 by different industry type and process unit (Mo et al., 2015; Shi et al., 2015). In traffic source emission researches, the ratio of T/B ranged from 0.9 ± 0.6 to 2.2± 0.5 by different vehicle type and fuel composition (Qiao et al., 2012; Dai et al., 2013; Wang et al., 2013; Yao et al., 2013; Zhang et al., 2013; Yao et al., 2015b; Mo et al., 2016; Yao et al., 2015a; Deng et al., 2018). However, vehicle emissions include both diesel vehicles emissions and gasoline vehicles emissions in the atmospheric environment. Thus, the ratio of T/B in the traffic source should be closer to the results of the tunnel experiments which approximately 1.5 ± 0.1 (Liu et al., 2008a; Deng et al., 2018). In paint solvent usage source emission researches, the ratio of T/B was greater than 8.8 ± 6.5 by different solvent use process (Yuan et al., 2010; Wang et al., 2014; Zheng et al., 2013). In burning source emission researches, the T/B ratio was approximately 0.3 ± 0.1 in different combustion process and raw materials (Liu et al., 2008a; Li et al., 2011; Mo et al., 2016). 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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10. Figures 6a-6c: what are the green lines?

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:

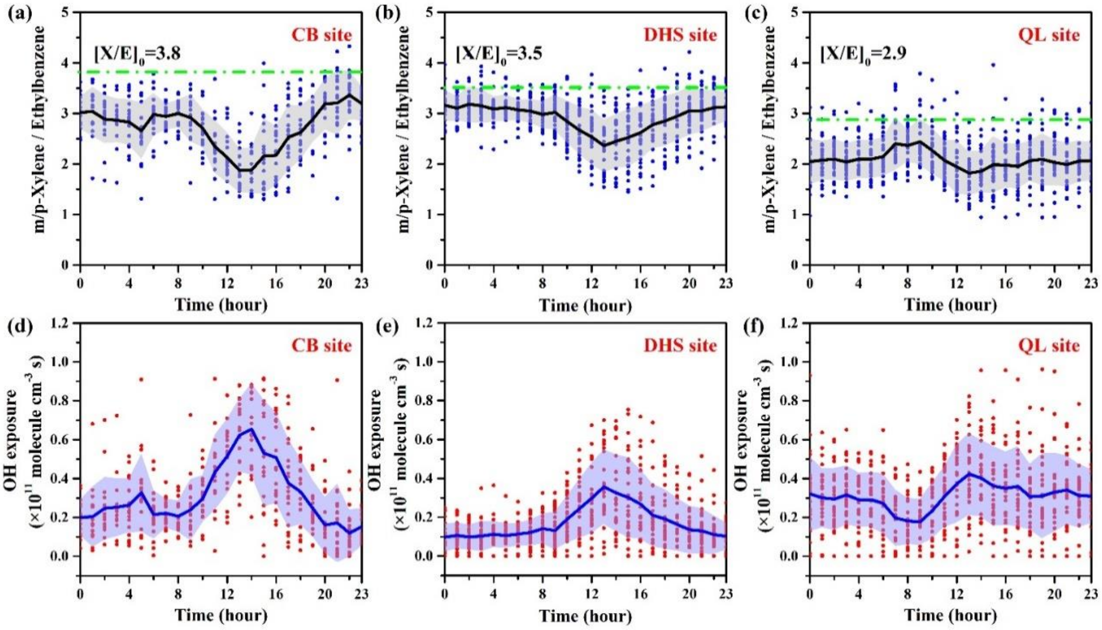

Figure 6: Diurnal variations in m/p-xylene to ethylbenzene and OH exposure at the CB, DHS, QL, and gridded sampling sites.

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

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11. Lines 297-301: "There were two trajectory clusters from the southeast direction, the southeast short distance trajectories (Cluster 2) and southeast medium-long distance trajectories (Cluster 4), accounting for 35.2% and 23.5%, respectively. This result indicated that the VOC concentration in the CB site was significantly affected by the southeast trajectory from the junction of the Shaanxi Province, Hubei

Province, and Henan Province in addition to local sources.”
The PSCF analysis was based on the results of the 24-h backward trajectories. The lifetimes of different VOCs are different in the atmosphere, as also indicated in Table2. For example, some OVOC species can have much longer lifetimes than reactive alkenes such as ethylene. The long-lived OVOC species may survive through atmospheric oxidation and get transported to Xi’an over 24 h from surrounding provinces.
However, reactive species such as ethylene may not be able to.
Can the authors incorporate the lifetime information of different categories of VOCs into the PSCF analysis?

Response:

We appreciate the reviewer’s comments. Because of the chemical lifetime of most VOCs in the atmosphere is much shorter than that of $PM_{2.5}$. Thus, the air mass tracing time should be considered when these methods are applied to the study of VOC contaminants. After compare the chemical lifetime of alkanes (32-253 h), alkenes (3-10 h), aromatics and others (12-228 h) we used a shorter air mass tracing time of 24 hour to analysis the PSCF of TVOCs in this study (Cai et al., 2010). However, when PSCF analysis is performed on VOCs species with different chemical lifetime, the air mass tracking time should be different. We agree with reviewer and have added the lifetime information of different tracer VOCs species into the PSCF analysis in the revised manuscript. Now it reads as follows:
Based on the PSCF analysis for Xi’an (Figures 10a, 10c, and 10e), in the urban sites, high PSCF values were mainly observed to the east and south of Xi’an, and in rural sites, the high PSCF values were primarily observed to the east of Xi’an. Different air mass tracking time (6h, 12h, 24h) were used in the PSCF analysis of different VOC species (Figure S3). Strong chemically active species (e.g., ethylene and xylene) had shorter air mass tracks, with high PSCF values appeared in areas near sites. However, the high PSCF values of long lifetime species (acetone) were found not only near the site but also in the eastern and southern regions of the site. The highest PSCF values of TVOCs appeared in areas near the CB, DHS, and QL sites, which indicated that Xi'an has a strong local source.

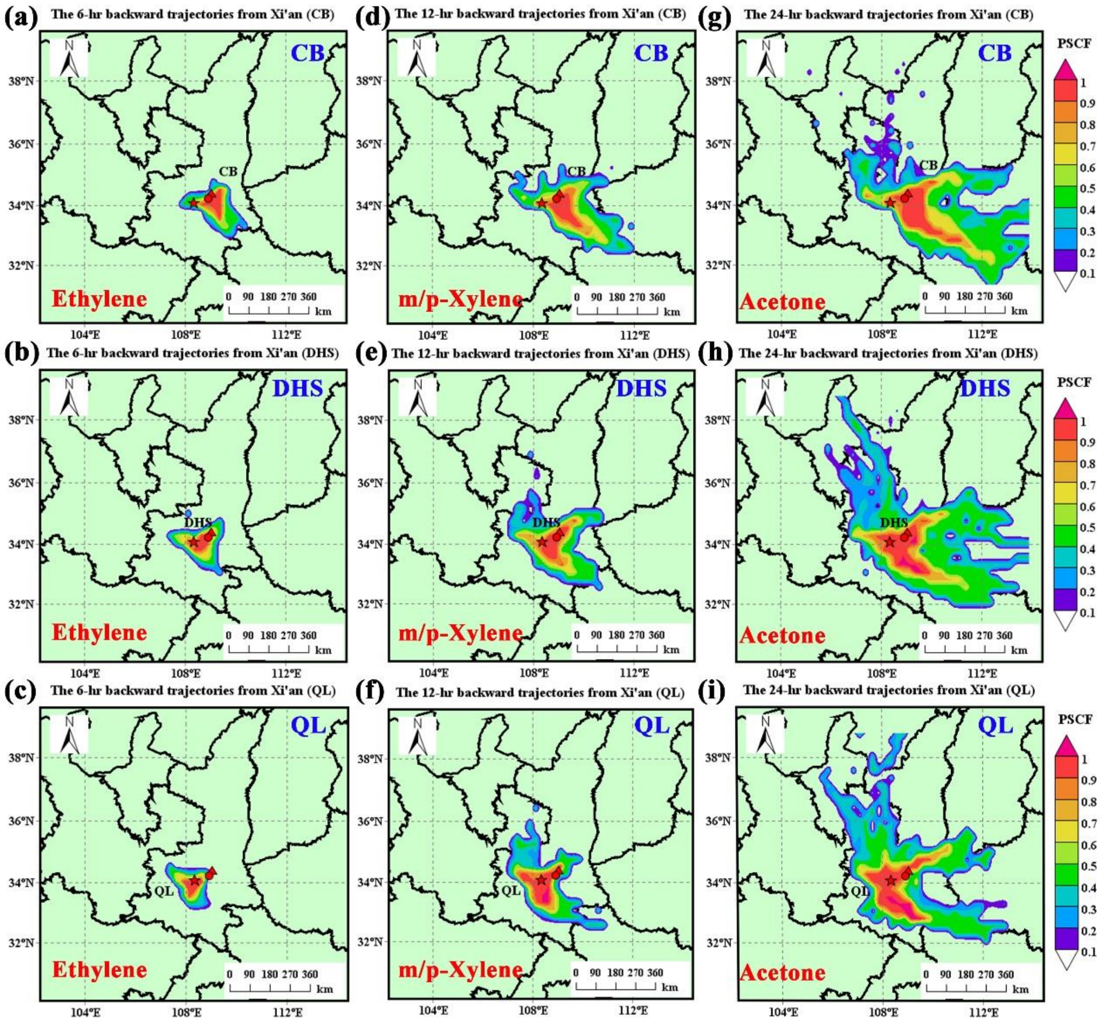

Figure S3: (a)-(c) 6-h backward trajectory PSCF analysis of ethylene in the CB, DHS, and QL sites, (d)-(f) 12-h backward trajectory PSCF analysis of m/p-Xylene in the CB, DHS, and QL sites, (g)-(i) 24-h backward trajectory PSCF analysis of acetone in the CB, DHS, and QL sites.

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12. Lines 349-350: “the O3 350 concentration in Xi’an urban areas (CB and DHS) often exceeded the national hourly standard of 200 µg/m3 (approximately 101.9 ppb).”

In lines 43-48, the author used a different national standard (i.e., 160 µg/m3). Please be consistent throughout the manuscript.

Response:

We have used the same national standard of O$_3$ in the manuscript. According the Technical Regulation on Ambient Air Quality Index released by the Ministry of Ecology and Environment of the People’s Republic of China (http://www.mee.gov.cn/ywgz/fgbz/bz/bzwb/dqhjbh/dqhjzlbz/201203/t20120302_224165.shtml), the annual evaluation standard of O$_3$ is 160 $\mu g/m^3$ and the hourly evaluation standard of O$_3$ is 200 $\mu g/m^3$.

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13. NOx concentration

This study demonstrated that high VOC concentration is a major concern in reducing ozone pollution in Xi’an. However, in addition to VOCs, NOx also plays an indispensable role in tropospheric ozone *production. NOx concentration was measured in this study. However, there was little discussion on the effects of NOx concentration on ozone and the interplay among NOx, VOC, and ozone. With the measurement data available, can the authors briefly comment on which regime (VOC-limiting or NOx limiting) was discussed in this study (e.g., in the urban sites and the rural sites) and corresponding implications?*

Response:
We appreciate the reviewer's comments. We have added the discussion on the interplay among NOx, VOC, and ozone in the section 3.4.2 of the revised manuscript. Now it reads as follows:

2.6 Empirical Kinetic Modelling Approach

The traditional empirical kinetic modelling approach (EKMA) is a model sensitivity tests of observation based box model and often used to evaluate the photochemical nonlinear relationship between ozone and precursors NOx and VOCs. The box model is based on the Regional Atmospheric Chemical Mechanisms version 2 (Goliff et al., 2013) updated with Leuven Isoprene Mechanism (Peeters et al., 2009). The definition and mechanism of the observation based box model is described elsewhere in detail (Tan et al., 2017; Tan et al., 2018).

The EKMA curve can be used as a theoretical basis for designing emission reduction strategies to obtain the best ozone pollution reduction method (Jiang et al. 2018, Tan et al. 2018). The model input parameters include temperature, pressure, humidity, photolysis rate constant, NO_2, VOCs, etc. In this model, the ozone production rate P (O_3) is calculated by the ozone formation rate F (O_3) minus the ozone loss rate D (O_3), as shown in Eq. (7). The ozone formation rate F (O_3) and the ozone loss rate D (O_3) can be calculated using Eq. (8) and (9) as follows:

$$\mathrm{P_{O_3} = F_{O_3} - D_{O_3}} \tag{7}$$

$$\mathrm{F_{O_3} = k_{HO_2+NO}[HO_2][NO] + k_{(RO_2+NO)_{eff}}[RO_2][NO]} \tag{8}$$

$$\mathrm{D_{O_3} = [O^1D][H_2O] + k_{O_3+OH}[O_3][OH] + k_{O_3+HO_2}[O_3][HO_2] + k_{O_3+alkenes}[O_3][alkenes] + k_{OH+NO_2}[OH][NO_2]} \tag{9}$$

where $\mathrm{k_{HO_2+NO}}$ is represent rate coefficients for the reaction of the NO with HO_2 radical (8.5 × 10^{-12} molecule^{-1}·cm^{3}·s^{-1}, 298K); $\mathrm{k_{(RO_2+NO)_{eff}}}$ is represent effective rate coefficients for the reaction of the NO with RO_2 radical (8.5 × 10^{-12} molecule^{-1}·cm^{3}·s^{-1}, 298K); $\mathrm{k_{O_3+OH}}$ is represent rate coefficients for the reaction of the O_3 with OH radical (7.3 × 10^{-14} molecule^{-1}·cm^{3}·s^{-1}, 298K); $\mathrm{k_{O_3+HO_2}}$ is represent rate coefficients for the reaction of the O_3 with HO_2 radical (1.9 × 10^{-15} molecule^{-1}·cm^{3}·s^{-1}, 298K); $\mathrm{k_{O_3+alkenes}}$ is represent rate coefficients for the reaction of the O_3 with alkenes (2.0 × 10^{-17} molecule^{-1}·cm^{3}·s^{-1}, 298K); $\mathrm{k_{OH+NO_2}}$is represent rate coefficients for the reaction of the NO_2 with OH radical (1.1 × 10^{-11} molecule^{-1}·cm^{3}·s^{-1}, 298K).

In this study, the average parameters of the entire observation period were used as the input parameters of the model to calculate the ozone concentration in the baseline scenario. Afterwards, the activity change array of VOCs and NO_X were generated by changing each parameter in equal distance steps. The P (O_3) contours under these different VOCs and NO_X reactivity conditions are called EKMA curves.

3.4.2 VOCs-NOx-O_3 Sensitivity

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.

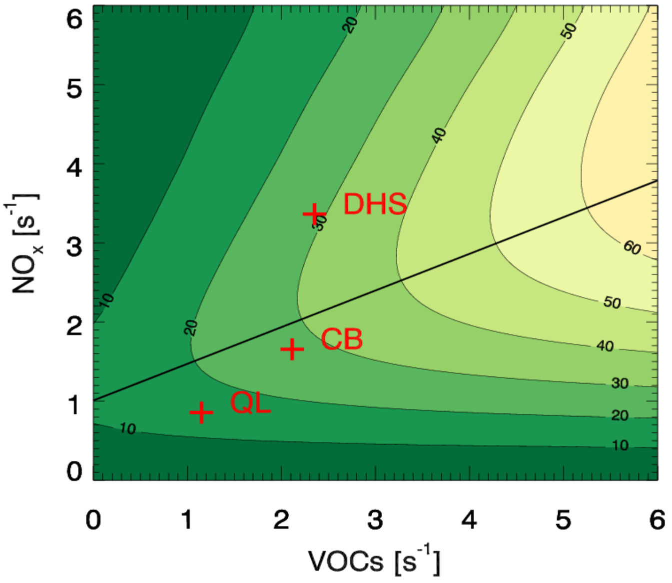

Figure 12. The ozone production rate (P (O_3)) contours diagram versus anthropogenic VOCs (AVOCs) and NOx using Empirical Kinetic Modelling Approach at CB, DHS, and QL sites.

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.

Technical comments

1. Line 11: "as a critical precursors of ozone…", remove "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 76: change "low-carbon" and "high-carbon" to "low carbon number" and "high carbon number"

Response:

We appreciate the reviewer's comments. We have change "low-carbon" and "high-carbon" to "low carbon number" and "high carbon number" in the revised manuscript. Now it reads as follows:

The low carbon number (C_2–C_5) compounds were separated on an Al_2O_3/KCl PLOT column and quantified using the FID. The high carbon number (C_5–C_{10}) compounds were separated on a DB-624 column and quantified using MS.

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3. Line 187: "Of the sites, XF site exhibited the highest VOC concentration of 54 ppb, followed by CT, HC, with concentrations of 41.4, and 38.2 ppb, respectively"

Please keep consistent the number of significant figures throughout the manuscript.

Response:

We appreciate the reviewer's comments. We have keep consistent the number of significant figures throughout the manuscript. Now it reads as follows:

Of the sites, XF site exhibited the highest VOC concentration of 54.0 ppb, followed by CT, HC, with concentrations of 41.4, and 38.2 ppb, respectively.

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4. Line 199: missing "to" between "used" and "preliminarily"

Response:

We appreciate the reviewer's comments. We are sorry for our mistakes, and we have added "to" *between "used" and "preliminarily"* in this sentence.

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