

Dear Prof. Wang,

We would like to thank the anonymous reviewer for the great efforts. On the basis of the reviewer's suggestions, we have updated this manuscript greatly. We greatly appreciate those comments and valuable suggestions from the reviewer. Also, we are grateful to your efficient serving for this manuscript.

Here we submit our revised manuscript "**Measurement report: VOC characteristics at different land-use types in Shanghai: spatio-temporal variation, source apportionment, and impact on secondary formations of ozone and aerosol**" (Manuscript number: **acp-2022-250**). In the attachments, a point-by-point response to each point raised from the reviewer was uploaded. The revised version marked for reviewing and the clean version for editing were supplied, respectively.

Yours sincerely,

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Response to the reviewer

General Comments:

The authors have made lots of efforts to revise this manuscript according to the comments from reviewers. Additional information and discussions were provided, and the English writing was improved. However, some of the questions were not fully elaborated in terms of the research highlight, the rationality of the methods, and the result interpretations. Therefore, I think the current manuscript is not ready for publication until the below comments are addressed.

Response:

We appreciate the thoughtful and valuable suggestions by the reviewer, which are helpful for us to improve the MS quality greatly. We have updated the manuscript based on these valuable suggestions. The updated version has provided more elaborations on the research highlight, the rationality of the methods, and the result interpretations. We also made efforts to smooth the English writing thoroughly.

Comment 1: The authors emphasized that the VOCs characteristics and their impacts on O₃ and SOA under different land-use types remained a gap and highlighted that the multi-site measurements would be able to fill this gap. In fact, the abundance, compositions, sources, and the O₃ and SOA chemistry have been extensively investigated not only in Shanghai but also around the globe. Several studies have measured VOCs in the same locations (line 240-244). Despite the different TVOC concentrations, the results in this study were consistent with previous studies, including the VOC compositions and source contributions. Therefore, I wonder what new insight this work would bring in addition to comparing the reported results. What's more, a similar study has been published, which measured VOCs at the same 3 sites concurrently and investigated the VOC characteristics, sources, and secondary formation potentials (Wang et al., 2022).

Response:

Thank you for your valuable suggestions. Indeed, several field-based VOC observations have been performed in the same locations. However, the research times and objectives of previous studies were different from those in this study. Cai et al.

(2010a) did not study the VOC sources, SOA formation potentials and the sensitivity of VOCs to PM_{2.5} at the PD site. The previous study at the JS site did not calculate the SOA formation potentials and the sensitivity of VOCs to PM_{2.5} which was the single-site measurement (Zhang et al., 2018). The study of Zhang et al. (2020) at the QP site did not determine VOC sources, ozone and SOA formation potentials and the sensitivity of VOCs to PM_{2.5} which was also the single-site measurement. The policy of “one factory, one strategy”, targeted at mitigating VOC emissions, was published by the Shanghai government in 2018. Our study could reflect the variations of VOC characteristics since the implementation of the policy.

The main objectives of Wang et al. (2022) were to study VOC concentrations, sources and O₃ and SOA formation potentials at three sites, rather than the horizontal comparisons among multiple sites. Especially, the study mentioned did not discuss the effects of land-use types on VOC characteristics, sources, and the sensitivity of VOCs to PM_{2.5}. Thus, the scientific problems concerned by Wang et al. (2022) and this work were different greatly, especially based on the measurement data at different time spans. In this study, the concurrent multiple-site and high-time resolution measurement of VOCs with the typical land-use types in Shanghai for their concentrations, sources, ozone and SOA formation potentials and sensitivity of VOCs to PM_{2.5} were performed. The results shown herein highlight that the simultaneous multiple-site measurements with the different land-use types at a megacity or city cluster level could be more appropriate to fully understand the VOC characteristics, which could provide more information on the accurate air-quality control inside a megacity worldwide.

Comment 2: The causation between land-use type and VOC source was confusing. For example, in line 63-64, “the land-use types influence not only the VOC concentrations but also the sources, especially the anthropogenic sources”. Actually, the spatial variations of VOC abundance and compositions were due to the different major emission sources in different land-use types. Meanwhile, the definition of different land-use types in this study was based on the functional types of the areas, which include different source sectors inside. Thus, the results in this study are mostly

attributable to different emission sources, and they can hardly be concluded to the impacts of the different land-use types directly as in the Discussion section. Besides, though the term “land-use” was repeatedly emphasized throughout the manuscript, the relation between the findings and the land-use types was weak.

Response:

Thank you for your comments. The fundamental reason that caused the spatial variations of VOC abundance, sources, and sensitivity to the O₃ and SOA formation was the land-use type which was one of the objectives of this study. In detail, the JS site is located in the Second Jinshan Industrial Area of Shanghai as the industrial district and is surrounded by many chemical factories. The PD site is located in the Pudong New Area as the residential and commercial mixed district and is surrounded by residences and administrative areas. The QP site is located near the southeast of Dianshan Lake as the background district and is surrounded by many farmlands and forests. The land-use types of the JS and PD sites led to high anthropogenic emissions which resulted in the fact that the VOC concentrations were approximately twice higher than those at the QP site. Moreover, the distinct land-use types among the sampling sites also led to the difference in VOC sources. The vehicle exhaust was determined as the predominant source at the three sites. The second largest VOC contributor was identified as industrial production at the JS and PD sites, whereas it proved to be the fuel production and evaporation at the QP site. The limited influence of industrial sources at the QP site was observed which was related to the land-use type of this site. Relative to the QP site, JS and PD sites were less affected by biomass burning which was consistent with the regional characteristics of anthropogenic activities dominated by land-use types. Additionally, the O₃ and SOA formations were strongly affected by the land-use types. The higher OFPs (50.85 ± 2.63 and 33.94 ± 1.52 ppb) and SOAFPs (1.00 ± 2.03 and 0.46 ± 0.88 $\mu\text{g m}^{-3}$) at the JS and PD sites relative to those at the QP site (24.26 ± 1.43 ppb for OFPs and 0.41 ± 0.58 $\mu\text{g m}^{-3}$ for SOAFPs, respectively) were observed, in connection with the land-use types. Further, the VOCs-PM_{2.5} sensitivity analysis showed that VOCs at the QP site showed a more rapid increment along with the increase of PM_{2.5} values compared with the

other two sampling sites. Of the four VOC categories, aromatics at the JS and PD sites and alkanes at the QP site were more sensitive to PM_{2.5}. Therefore, the findings in this study were greatly related to the land-use types. We have rewritten the description in the revised manuscript.

Page 2, lines 63-65:

“Besides, the land-use types were also related to the VOC sources, especially the anthropogenic sources (Yoo et al., 2015; Chen et al., 2017; Wang et al., 2017; Jookjantra et al., 2022).”

Comment 3: Line 150-152: The meteorological parameters were measured at one weather station, while the meteorological factors were different among the 3 sites in the results (Figure 1). The authors need to clarify the data source.

Response:

Thank you for your comments. The data source has been revised.

Page 5, lines 150-151:

“The meteorological variables including temperature, RH and wind speed were acquired from each air monitoring station.”

Comment 4: The COD values were used to estimate the divergence of TVOC concentrations among sites. What were the thresholds of high and low similarity? The values 0.20, 0.33, and 0.36 seem to be small, as CODs of 0.269 and 0.783 were used to determine the similar and dissimilar sites in the cited paper (Wongphatarakul et al., 1998).

Response:

Thank you for your comments. There was no clear definition of high and low similarity thresholds. The values of COD can evaluate the degree of air pollutant concentration difference between two different sampling sites, which varies with the study areas and times (Ma et al., 2019). A greater COD value means less redundancy of the data between two sites (Ma et al., 2019). Wongphatarakul et al. (1998) found that the COD between Taipei and downtown Los Angeles (COD = 0.783) was higher than that between Teplice and downtown Los Angeles (COD = 0.269), illustrating that the most dissimilar and the greatest similar at the corresponding two sites were

observed. Meanwhile, Song et al. (2017) found that there were spatial variations of PM_{2.5} (COD = 0.34), NO₂ (COD = 0.34), PM₁₀ (COD = 0.45) and CO (COD = 0.32) among different Chinese cities. Similarly, the COD values herein between the JS-QP, PD-QP and JS-PD were 0.36, 0.33 and 0.20, respectively, indicating that the spatial heterogeneity of VOCs between the JS and PD sites was narrow, while the QP site was largely different from other two sites. We added the description in the revised manuscript.

Page 18, lines 549-552:

“ Note that the distinct spatial heterogeneity of VOCs was also observed with the highest value of the coefficient of divergence (COD = 0.36) between the JS and QP sites, followed by the PD and QP sites (COD = 0.33), with that between the JS and PD sites (COD = 0.20) being the lowest. A greater COD value means less redundancy of the data between two sites (Ma et al., 2019).”

Comment 5: The sensitivity analysis is confusing. Firstly, why were background values needed in the calculation? What were the “specific PM_{2.5} gradients” in line 213? What were the “corresponding VOC concentrations” in line 220? Secondly, how to derive equations 14 and 15? Which parameter in the calculation indicates sensitivity? Most importantly, why do we need to analyze the sensitivity of VOCs to PM_{2.5} instead of the other way around? Line 220-221: “the concentration of VOCs was greatly affected by the variations of PM_{2.5} concentration.” And Line 229.

Response:

Thank you for your suggestions. The method of calculating the sensitivity of VOCs to PM_{2.5} was used for the gradient model (Eq. 11), which needed the background levels.

$$VOCs-S_{PM_{2.5}} = \frac{\Delta_{VOCs} / B_{VOCs}}{\Delta_{PM_{2.5}} / B_{PM_{2.5}}} \quad (11)$$

The “specific PM_{2.5} gradients” in line 212 was the five levels of PM_{2.5}: clean level (PM_{2.5} < 35 μg m⁻³), slight pollution level (35 < PM_{2.5} < 75 μg m⁻³), medium pollution level (75 < PM_{2.5} < 120 μg m⁻³), heavy pollution level (120 < PM_{2.5} < 180 μg m⁻³) and extreme pollution level (PM_{2.5} > 180 μg m⁻³).

The “corresponding VOC concentrations” in line 219 was the VOC concentrations under the different PM_{2.5} values.

The x-axis was PM_{2.5}/B_{PM_{2.5}} and the y-axis was the values of VOCs-S_{PM_{2.5}}. We put the corresponding values into the Eq. (13).

$$\ln y = \ln a + b \cdot \ln x \quad (13)$$

We revised the Eq. (14) in line 224.

$$\ln VOCs - S_{PM_{2.5}} = \ln a + b \cdot \ln \frac{\Delta_{PM_{2.5}}}{B_{PM_{2.5}}} \quad (14)$$

According to the Eq. (11), we derived the Eq. (15). The evolution of calculation as follow.

$$\begin{aligned} \ln \frac{\Delta_{VOCs} / B_{VOCs}}{\Delta_{PM_{2.5}} / B_{PM_{2.5}}} &= \ln a + b \cdot \ln \frac{\Delta_{PM_{2.5}}}{B_{PM_{2.5}}} \\ \ln \frac{\Delta_{VOCs}}{\Delta_{PM_{2.5}}} &= \ln a + (1 + b) \cdot \ln \frac{\Delta_{PM_{2.5}}}{B_{PM_{2.5}}} \\ \ln \frac{\Delta_{VOCs}}{BVOCs} &= k \cdot \ln \frac{\Delta_{PM_{2.5}}}{B_{PM_{2.5}}} + c \end{aligned} \quad (15)$$

The values of VOCs-S_{PM_{2.5}} was the sensitivity between the VOCs and PM_{2.5}. The larger the VOCs-S_{PM_{2.5}} value, the more sensitive the VOC concentrations were to PM_{2.5}. We rewrote line 647 into “*The VOCs at the QP site showed a more rapid increment along with the increase of PM_{2.5} values.*”

We could quantitatively reveal patterns of variations between the VOCs and PM_{2.5}, and evaluate the degree by which VOCs were impacted by PM_{2.5} via analyzing the sensitivity of VOCs to PM_{2.5} under the different land-use types. Accordingly, the VOC-induced haze pollution could be efficiently controlled by decreasing corresponding VOC concentrations. Han et al. (2017) also calculated the sensitivity of VOCs to PM_{2.5} and showed that alkanes and alkenes were more sensitive to PM_{2.5} than aromatic compounds.

We have rewritten the description in detail in the revised manuscript.

Page 8, lines 219:

“The higher value of VOCs- $S_{PM_{2.5}}$, the more sensitive VOCs to the $PM_{2.5}$ concentrations.”

Page 8, lines 226-227:

“This method was appropriate for understanding the sensitivity of VOC concentrations to $PM_{2.5}$.”

Comment 6: As shown in Figure 1, two prominent peaks of VOC concentrations were observed at JS. Despite the peaks, the TVOC level at JS was comparable and even lower than that at PD. While the authors only discussed the mean TVOC concentrations at 3 sites, the special events were concealed.

Response:

Thank you for your valuable suggestions. The two prominent peaks of VOC concentrations were observed at the JS site on 23 January and 11 March, respectively. The highest VOC concentrations appeared on 11 March. There was leaking of the chemical factories *via* inquiring about the local workers. Therefore, the highest VOC concentration on 11 March might be attributed to the leaking of the chemical factories. The second highest VOC concentration was observed on 23 January, which was due to the increased vehicle exhaust and industrial processes and the decreased wind speed. Based on the reviewer’s comments, we added the new discussions about the special events in the revised manuscript.

Page 9, lines 246-255:

“The two prominent peaks of VOC concentrations were observed at the JS site on 23 January and 11 March, respectively. The highest VOC concentration appeared on 11 March with a value of 84.49 ppb. This phenomenon might be attributed to the leaking of chemical factories. The second highest VOC concentration was observed on 23 January with a value of 77.71 ppb which was 38.85 and 57.07 % higher than those at the PD and QP sites, respectively. According to the Shanghai Municipal Bureau of Statistics (<http://tjj.sh.gov.cn>), the traffic flow in January was ~ 10 % higher than that in the following two months. Such scenario was likely due to the Spring Festival Travel rush, i.e., population travel intensively occurred around the Chinese Spring Festival.

Moreover, there were pronounced in the industrial production in January compared with those in February (~ 36 % uplift) and March (~ 6 % uplift) (<http://tjj.sh.gov.cn>). The phenomena could be responsible for the elevated VOC emissions. Additionally, the lowest WS was observed on 23 January with the value of 0.85 m s^{-1} , which was adverse to dispersive dilution and convection of VOCs, causing high concentrations of VOC at the JS site (Kumar et al., 2018)."

Comment 7: Line 248-249: Why were the average PM_{2.5} concentrations comparable among 3 sites, whereas the O₃ levels were higher at QP than at the other sites?

Response:

Thank you for your questions. The influence factors were different between the O₃ and PM_{2.5}. The O₃ concentrations were primarily affected by the values of precursors including VOCs, NO_x and CO (Hu et al., 2022), meteorological factors including light intensity and radiation, wind speed and temperature (Haberer et al., 2006), and the strength of anthropogenic emissions such as transportation and industrial sources (Yang et al., 2021). However, the PM_{2.5} levels are influenced by many factors which were related to the composition. The primary composition of PM_{2.5} is water-soluble ions such as SO₄²⁻, NO₃⁻ and NH₄⁺, all of which are closely correlated with the atmospheric SO₂, NO_x and NH₃ concentrations (Liang et al., 2019). The carbonaceous aerosols accounting for approximately 40-60% of PM_{2.5} which included element carbon and organic carbon are influenced by emissions from different combustion methods, biogenic sources, VOC and radical concentrations and light intensity (Yao, 2016; Ryou et al., 2018). The metal elements such as Ca, Si, Fe, Mg, Zn and Mn are also components of PM_{2.5} which varied with emission types (Zhao et al., 2021). For example, the dominating source of V and Ni is diesel and fuel oil combustion (Zhao et al., 2021), while the non-tailpipe emissions from motor vehicles are an important emission source of Cu, Ba and Sb (Nicolas, 2009).

Comment 8: Line 257: How to infer that “The termination and titration (NO + O₃ → NO₂ + O₂) were more efficient”?

Response:

Thank you for your comment. We rewrote the description in the revised manuscript.

Page 10, lines 265-266:

“Lots of factors including NO_x levels, sunshine duration, temperature and relative humidity not only the emission of precursors, impacted on the surface O₃.”

Comment 9: Line 250-260: Pearson correlation coefficient was applied to estimate the correlations of VOCs and O₃ and VOCs and PM_{2.5}. The Pearson correlation coefficient is to measure the linear correlation between two datasets. However, O₃ and PM_{2.5} have non-linear relationships with VOCs. Hence, the feasibility of this estimation should be justified.

Response:

Thank you for your comment. We analyzed the non-linear relationships of PM_{2.5} and O₃ with VOCs. The results showed the concentrations of VOCs were found to be positively correlated with that of PM_{2.5}, and the spearman correlation coefficients ($R_{Spearman}$) were 0.72, 0.74 and 0.34 at the JS, PD and QP sites, respectively. However, the VOC concentrations were negatively correlated with O₃ ($R_{Spearman} = -0.39$ at the JS site, $R_{Spearman} = -0.50$ at the PD site and $R_{Spearman} = -0.40$ at the QP site, respectively). We have written the description in detail in the revised manuscript.

Page 9, lines 258-259:

“VOCs was found to be positively correlated with PM_{2.5}, and the spearman correlation coefficients ($R_{Spearman}$) were 0.72, 0.74 and 0.34 at the JS, PD and QP sites, respectively.”

Page 10, lines 263-265:

“However, the VOC concentrations were negatively correlated with O₃ ($R_{Spearman} = -0.39$ at the JS site, $R_{Spearman} = -0.50$ at the PD site and $R_{Spearman} = -0.40$ at the QP site, respectively).”

Comment 10: Line 305-306: haze days were defined as “visibility < 10 km and RH > 80 %”. Given the high RH, how to distinguish haze from fog?

Response:

Thank you for your question. We have revised the statement in the revised manuscript.

Page 11, lines 312-313:

“Referring to the previous documents (Li et al., 2017; Hui et al., 2019), haze pollution was defined as the condition with visibility < 10 km and RH < 80 %.”

Comment 11: Line 313-314: Why JS and PD had stagnant weather while QP didn't? How to define stagnant weather, and what were the weather conditions on haze days?

Response:

Thank you for your question. Herein, the impacts of human activities at the JS and PD sites were heavier than that at the QP site because of the land-use types. This phenomenon caused the high emission of VOCs i.e., VOC concentrations at the JS (21.88 ± 12.58 ppb) and PD (21.36 ± 8.58 ppb) sites were approximately twice higher than that at the QP site (11.93 ± 6.33 ppb). Moreover, the wind speed at the QP site (4.37 ± 1.47 m s⁻¹) was 2.29 and 1.36 times higher than those at the JS (1.91 ± 0.49 m s⁻¹) and PD (1.30 ± 0.62 m s⁻¹) sites, respectively, which decreased the dilution and diffusion conditions at the latter two sites. The above phenomena resulted in the stagnant weather appearing at the JS and PD sites compared with the QP site. We have written the description in the revised manuscript.

Page 11, lines 319-321:

“Such scenario could be attributed to the locations of JS and PD sites which led to high anthropogenic emissions and low wind speed and implicated stagnant weather conditions, therefore inducing the severe haze pollution.”

The stagnate weather always accomplishes low wind speed for more than 24 h which could decrease dispersive dilution and convection phenomenon and greatly contribute to the formation of haze days (Zhang et al., 2016).

The weather conditions on haze days were visibility < 10 km and RH < 80 %. At the JS site, the average wind speed and temperature were 1.67 m s⁻¹ and 9.24 °C on haze days, respectively. At the PD site, the average wind speed and temperature were 1.20 m s⁻¹ and 9.21 °C on haze days, respectively. At the QP site, the average wind speed and temperature were 4.03 m s⁻¹ and 7.64 °C on haze days, respectively.

Comment 12: Line 316-317: The authors attributed the elevated VOC concentrations on haze days to enhanced emissions. Is there any evidence for the enhanced emissions, especially the vehicle exhausts?

Response:

Thank you for your comment. The concentrations of aromatics especially *m*-ethyltoluene, *p*-ethyltoluene, ethylbenzene and 1, 2, 4-trimethylbenzene were significantly higher than those on clean days at the JS and PD sites. Industrial production was characterized by high contributions of aromatics including *m*-ethyltoluene and *p*-ethyltoluene (Hui et al., 2019). Ethylbenzene was closely related to the painting/coating (Cai et al., 2010b; Ling et al., 2011; Hui et al., 2019). Trimethylbenzene was closely correlated to vehicle exhaust, furniture manufacturing and painting/coating (Chan et al., 2006; Ling et al., 2011; Liu et al., 2008; Hui et al., 2019). Thus, the elevated VOC concentrations on haze days were greatly influenced by enhanced emissions. We have written the description in the revised manuscript.

Page 11, lines 323-325:

“The above VOC compounds were related with the industrial production, painting/coating and vehicle exhaust, and elevated concentrations reflected the concentrated emission sources.”

Comment 13: Figure 5: How to define the different thresholds of VOC ratios? If the reference values were obtained from previous studies, are they comparable and suitable for this study?

Response:

Thank you for your valuable suggestions. The special VOC ratios were widely used to preliminary distinguish the VOC sources. The reference values were obtained from previous studies which were used widely by many following works. For example, the T/B ratios ranged from 1.4 ± 0.8 to 5.8 ± 3.4 by different industrial processes in the different studies (Mo et al., 2015; Shi et al., 2015; Song et al., 2021). Moreover, many previous studies found that the ratios of T/B ranging from 0.9 ± 0.6 to 2.2 ± 0.5 indicated traffic-related sources (Qiao et al., 2012; Dai et al., 2013; Wang et al., 2013; Yao et al., 2013; Zhang et al., 2013; Yao et al., 2015; Mo et al., 2016; Deng et al., 2018; Song et al., 2021). The special VOC ratios were distributed within the reference range of one source, indicating that the source contributed more VOCs than other sources. In this study, most ratios (68.89 and 84.15 %) distributed the range of 0.9-2.2

and 1.4-5.8, suggesting that vehicle emissions and industrial emissions exerted a significant impact on VOC concentrations at the JS and PD sites. Nearly half of T/B ratios (43.02 %) distributed the range of 0.9-2.2 and 0.2-0.4, suggesting that vehicle emissions and burning emissions contributed significantly to VOC pollution at the QP site.

Comment 14: Line 355 and 367: What do you mean by “during the VOC pollution”?

Response:

Thank you for your question. The “during VOC pollution” means “when the VOC concentrations were high”. We rewrote the description in the revised manuscript.

Page 13, lines 363-365:

“The P/P ratios were distributed within the range of 2.2-3.8 at the sampling sites when the VOC concentrations were high, indicating the great impact of vehicle emission on VOC pollution, which was in agreement with the report of Song et al. (2021).”

Page 13, lines 374-375:

“When the VOC concentrations were high, the X/E ratios were approximately 2.3, 2.5 and 1.8 at the JS, PD and QP sites, respectively.”

Comment 15: The source profiles apportioned from PMF results were highly doubtful. The problems are not limited to the followings. 1) Industrial source was not resolved at QP, while the biogenic source was not resolved at JS and PD. Are the source apportionment results comparable among these sites? 2) From Figure 6c, a high proportion of 1,2,3-trimethylbenzene was apportioned to the biogenic source at QP. The proportions of aromatics were even higher than isoprene in the biogenic source. 3) Isoprene, as a tracer for biogenic sources, was apportioned to the industrial source at JS and paint solvent usage at PD. 4) At QP, C₂ species were apportioned to vehicle exhausts, while they were also tracers for coal combustion. In addition, coal combustion at QP contained a large proportion of ethylbenzene, which was not explained. 5) Line 413-414: Fuel evaporation was identified by C₃-C₇ species. However, high proportions of aromatics, such as benzene at JS, and isopropylbenzene at PD, were also apportioned to this source. In addition, the contributions of fuel

evaporation to TVOC at QP (20.15%) were much higher than those of the other sites. What could be the reason for that? 6) How about the correlations between every two sources (G-Space plot)?

Response:

Thank you for your suggestions. 1) The anthropogenic source was the dominating source of VOCs at the JS and PD sites, and the impact of biomass burning on VOCs was limited because of the land-use types. The QP site is located near the southeast of Dianshan Lake as a city background site where the tracers of industrial sources were limited. Thus, the industrial emission and biomass burning source showed slight contributions to VOC concentrations at the QP and JS/PD sites, respectively. Song et al. (2021) studied the VOC sources at three sites in Xi'an, China, and found the biogenic source was not resolved at the CB site while the fuel evaporation was not resolved at the other two sites (DHS and QL sites).

2) We added new sentences in the revised manuscript.

Page 15, lines 434-438:

“Biomass burning was distinguished by the isoprene and some aromatics (Schauer et al., 2001; Liu et al., 2020; Yang et al., 2023). Factors that coincide with the specific characteristic were regarded as biomass burning in this study. Our analysis showed that the contribution of biomass burning to VOC concentrations was 11.39 % at the QP site. However, this emission factor could not be reproduced at the JS and PD sites, implying the limited impacts of biomass burning in the population- and industrialization-concentrated areas that were primarily controlled by the anthropogenic emissions.”

3) Wood combustion could be used in industrial processes. Meanwhile, wood was also regarded as the raw material in painting. Thus, the above sources could release the isoprene. The previous study also showed that a certain amount of isoprene could be found in the industrial source, vehicle exhaust and paint solvent usage (Song et al., 2021).

4) Previous studies showed that C₂ species like ethylene and ethyne could be found both in vehicle exhaust and coal combustion (Liu et al., 2008; Ling et al., 2011; Song et al., 2018; Song et al., 2021). We rewrote the description in the revised manuscript.

Page 14, lines 406-407:

“Coal combustion factor was characterized by C₂-C₃ alkenes such as ethylene and propylene, some alkanes, ethyne, benzene and ethylbenzene (Liu et al., 2008; Ling et al., 2011; Song et al., 2018).”

5) We rewrote the description in the revised manuscript after consideration.

Page 14, lines 420-428:

“Fuel production and evaporation could be identified by C₃-C₇ alkanes, especially n-pentane and iso-pentane (Zheng et al., 2020), the C₃-C₅ alkenes such as trans/cis-2-butene (Geng et al., 2009; Hui et al., 2018; Zhang et al., 2018a; Zheng et al., 2020) and some aromatics (Liu et al., 2008; Xiong et al., 2020). There were high contributions of n-pentane (37.94, 25.20 and 71.95 %), iso-pentane (41.45, 28.18 and 23.16 %) and butene (26.73, 70.83 and 22.52 %) at the JS, PD and QP sites, respectively. The contributions of some aromatics such as benzene at the JS site (44.08 %), isopropylbenzene at the PD site (66.71 %) and 1, 2, 4-trimethylbenzene at the QP site (32.90 %) were also high. It was well documented that alkanes like n-pentane and iso-pentane were gasoline tracers, and some alkanes and aromatics could evaporate from the unburned fuels (Guo et al., 2004; Liu et al., 2008; Wang et al., 2013; Xiong et al., 2020). The VOC contributions from fuel production and evaporation were calculated to be 4.62, 10.35 and 20.15 % at the JS, PD and QP sites, respectively.”

The QP site is located around Dianshan Lake which is a tourist attraction, with large contributions of fuel production and evaporation from vehicles and gas stations (Chen et al., 2021).

6) There were no correlations between the two sources.

Table 1: The correlations between two sources at the JS, PD and QP sites.

JS site	Source 1	Source 2	Source 3	Source 4	Source 5
Source 2	-0.15				
Source 3	-0.27	-0.25			
Source 4	-0.14	-0.64	-0.16		
Source 5	-0.08	-0.13	-0.14	-0.29	
Source 6	-0.20	-0.29	-0.20	-0.30	-0.13

PD site	Source 1	Source 2	Source 3	Source 4	Source 5
Source 2	-0.25				
Source 3	0.09	-0.24			
Source 4	-0.24	-0.16	-0.18		
Source 5	0.05	-0.26	0.14	-0.19	
Source 6	-0.03	0.10	-0.15	-0.22	-0.09

QP site	Source 1	Source 3	Source 4	Source 5	Source 6
Source 3	-0.24				
Source 4	-0.13	-0.21			
Source 5	-0.15	-0.25	-0.13		
Source 6	0.18	-0.24	-0.11	-0.28	
Source 7	-0.16	0.17	-0.26	-0.12	-0.25

*Source 1: Vehicle exhaust; Source 2: Industrial source; Source 3: LPG usage; Source 4: Paint solvent usage; Source 5: Fuel production and evaporation; Source 6: Coal combustion; Source 7: Biomass burning

Comment 16: According to the PSCF results, regional transport of VOCs, especially from northern regions, also contributed to the VOC concentrations at 3 sites. While the VOCs were apportioned to local sources in the PMF model, which part of the VOCs was accountable for the regional transport?

Response:

Thank you for your comments. The region with high PSCF levels indicates high potential regional transport sources (Hui et al., 2018). Based on the PSCF results, at the JS and QP sites, high values were observed in the north of Shanghai. At the PD site, high values were observed in the northeast of Shanghai. All three sampling sites presented that the highest PSCF levels appeared in areas near the JS, PD and QP sites, suggesting that local source was a significant contributor to the VOC pollution compared with regional transport. Similarly, Song et al. (2021) studied the PSCF values at three different sites in Xi'an, China, and also showed that Xi'an had a strong local source, which was also consistent with the findings in Wuhan, China (Hui et al., 2018; Hui et al, 2019), suggesting that local source was a significant contributor to the VOC pollution. We added the description in the revised manuscript.

Page 16, lines 473-475:

“All three sampling sites presented that the highest PSCF levels appeared in areas near the JS, PD and QP sites, suggesting that local source was a significant contributor to the VOC pollution compared with regional transport.”

Comment 17: Line 472-473 and 497: How to quantify the percentage of OFP and SOAFP to O₃ and PM_{2.5} concentrations?

Response:

Thank you for your comments. The percentages of OFP and SOAFP to O₃ and PM_{2.5} concentrations could be calculated by the equations as followed.

$$\text{OFP to O}_3 = \frac{[\text{OFP}]}{[\text{O}_3]}$$
$$\text{SOAFP to PM}_{2.5} = \frac{[\text{SOAFP}]}{[\text{PM}_{2.5}]}$$

where [OFP] and [SOAFP] were the values of OFP and SOAFP, the [O₃] and [PM_{2.5}] were the O₃ and PM_{2.5} concentrations. We added the description in the revised manuscript.

Page 16, lines 481-482:

“The photo-induced transformation of VOCs could account for 69.15, 59.05 and 24.43 % of the O₃ concentrations in the above sampling sites (OFP values/O₃ concentrations).”

Page 17, lines 506-508:

“The SOAFP values accounted for 2.19, 0.95 and 1.02 % of the PM_{2.5} concentrations at the above sampling sites (SOAFP values/PM_{2.5} concentrations), all of which were lower than the results in Nanjing, China (3.46 %) (Mozaffar et al., 2020) and Wangdu, China (8.4 and 17.84 % under high-NO_x and low-NO_x conditions, respectively) (Zhang et al., 2020b).”

Comment 18: As discussed in line 500-504, large uncertainty existed for the SOAFP method. Indeed, the OFP and SOAFP methods are only based on the reference reactivity of VOCs, which species with high reactivity tend to have larger secondary yields. The results herein are rather general and widely known. It is hard to tell what new findings we can get from this method.

Response:

Thank you for your comment. The objective of this study was not to calculate the values of OFP and SOAFP. One of the purposes of this study was to determine the effects of VOCs under the different land-use types on O₃ and SOA formation *via* calculating the OFP and SOAFP values. We deleted the uncertainties of the SOAFP in the revised manuscript. The results herein showed that the predominate OFP contributors were alkenes and aromatics, and the relevant emission sources, which are thought to be the industrial production and vehicle exhaust at the sampling sites, should be controlled in priority. Meanwhile, we found that the OFP values were closely related to the land-use types i.e., the higher OFPs at the JS and PD sites (50.85 ± 2.63 and 33.94 ± 1.52 ppb) relative to that at the QP site (24.26 ± 1.43 ppb) were observed. Under the high OFPs, the concentrations of O₃ at the JS and PD sites (73.59 ± 23.59 and 57.48 ± 20.49 $\mu\text{g m}^{-3}$) were unexpectedly lower than that at the QP site (99.30 ± 24.00 $\mu\text{g m}^{-3}$). In term of SOAFP values, the aromatics especially toluene was determined to be the main SOA contributor, and the SOAFP value at the JS site was significantly higher than those at the PD and QP sites due to the effect of land-use types. Because the close associations between VOCs and SOA could induce the sensitive response of VOC concentrations to the different pollution degrees of PM_{2.5}, we further explored the influence of VOCs on the atmospheric PM_{2.5} abundance *via*

analyzing VOCs-PM_{2.5} sensitivity. The results showed that the VOCs at the QP site showed a more rapid increment along with the increase of PM_{2.5} values. The four groups of VOCs displayed similar linkages with VOCs, and the higher values of *k* were attributed to the aromatics at the JS and PD sites, while the alkanes at the QP site. Thus, the optimal choices for controlling VOC species varied with the land-use types.

Lastly, we would again express our appreciation to the reviewer and editor for their warmhearted help. Thank you very much!

References

- Cai, C., Geng, F., Yu, Q., An, J., Han, J.: Source apportionment of VOCs at city centre of Shanghai in summer, *Acta Sci. Circumst.*, 30 (5), 926-934, <https://doi.org/10.1631/jzus.A1000244>, 2010b.
- Cai, C., Geng, F. H., Tie, X. X., Yu, Q., and An, J. L., Characteristics of ambient volatile organic compounds (VOCs) measured in Shanghai, China, *Sensors*, 10, 7843-7862, <https://doi.org/10.3390/s100807843>, 2010a.
- Chan, L., Chu, K., Zou, S., Chan, C., Wang, X., Barletta, B., Blake, D.R., Guo, H., and Tsai, W.: Characteristics of nonmethane hydrocarbons (NMHCs) in industrial, industrial urban, and industrial-suburban atmospheres of the Pearl River Delta (PRD) region of south China. *J. Geophys. Res.* 111 (D11304), 2005JD006481, <https://doi.org/10.1029/2005JD006481>, 2006.
- Chen, C., Wang, L. R., Zhang, Y. J., Zheng, S. S., and Tang, L. L.: Spatial and Temporal Distribution Characteristics and Source Apportionment of VOCs in Lianyungang City in 2018, *Atmosphere*, 12, 1598, <https://doi.org/10.3390/atmos12121598>, 2021.
- 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, <https://doi.org/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 Air Qual. Res.*, 18, 3025-3034, <https://doi.org/10.4209/aaqr.2018.07.0248>, 2018.
- Haberer, K., Jaeger, L., and Rennenberg, H.: Seasonal patterns of ascorbate in the needles of Scots Pine (*Pinus sylvestris* L.) trees: Correlation analyses with atmospheric O₃ and NO₂ gas mixing ratios and meteorological parameters, *Environ. Pollu.*, 139, 224-231, <https://doi.org/10.1016/j.envpol.2005.05.015>, 2006.
- Han, D. M., Wang, Z., Cheng, J. P., Wang, Q., Chen, X. J., and Wang, H. L.: Volatile organic compounds (VOCs) during non-haze and haze days in Shanghai: characterization and secondary organic aerosol (SOA) formation, *Environ. Sci. Pollut. Res.*, 24, 18619-18629, <https://doi.org/10.1007/s11356-017-9433-3>, 2017.
- Hu, J., Zhao, T. L., Liu, J., Cao, L., Wang, C. G., Li, Y. Q., Shi, C. C., Tan, C. H., Sun, X. Y., Shu, Z. Z., and Li, J.: Exploring the ozone pollution over the western Sichuan Basin, Southwest China: The impact of diurnal change in mountain-plains solenoid, *Sci. Total Environ.*, 839, 156264, <https://doi.org/10.1016/j.scitotenv.2022.156264>, 2022.

Hui, L. R., Liu, X. G., Tan, Q. W., Feng, M., An, J. L., Qu, Y., Zhang, Y. H., and Cheng, N. L.: VOC characteristics, sources and contributions to SOA formation during haze events in Wuhan, Central China, *Sci. Total Environ.*, 650, 2624-2639, <https://doi.org/10.1016/j.scitotenv.2018.10.029>, 2019.

Hui, L. R., Liu, X. G., Tan, Q. W., Feng, M., An, J. L., Qu, Y., Zhang, Y. H., and Jiang, M. Q.: Characteristics, source apportionment and contribution of VOCs to ozone formation in Wuhan, Central China, *Atmos. Environ.*, 192, 55-71, <https://doi.org/10.1016/j.atmosenv.2018.08.042>, 2018.

Liang, X. X., Huang, T., Lin, S. Y., Wang, J. X., Mo, J. Y., Gao, H., Wang, Z. X., Li, J. X., Lian, L. L., and Ma, J. M.: Chemical composition and source apportionment of PM₁ and PM_{2.5} in a national coal chemical industrial base of the Golden Energy Triangle, Northwest China, *Sci. Total Environ.*, 659, 188-199, <https://doi.org/10.1016/j.scitotenv.2018.12.335>, 2019.

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 (10), 2310-2319, <https://doi.org/10.1016/j.envpol.2011.05.001>, 2011.

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

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, 1-12, <https://doi.org/10.1016/j.envpol.2019.113599>, 2020.

Ma, T., Duan, F., He, K., Qin, Y., Tong, D., Geng, G., Liu, X., Li, H., Yang, S., Ye, S., Xu, B., Zhang, Q., and Ma, Y.: Air pollution characteristics and their relationship with emissions and meteorology in the Yangtze River Delta region during 2014-2016, *J. Environ. Sci.*, 83, 8-20, <https://doi.org/10.1016/j.jes.2019.02.031>, 2019.

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, <https://doi.org/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, *Sci. Total Environ.*, 533, 422-431, <https://doi.org/10.1016/j.scitotenv.2015.06.089>, 2015.

Nicolas, B.: Real-world emission factors for antimony and other brake wear related trace elements: size-segregated values for light and heavy duty vehicles, *Environ. Sci. Technol.*, 21, 8072e8078, <https://doi.org/10.1021/es9006096>, 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.

Ryou, H. G., Heo, J. B., and Kim, S. Y.: Source apportionment of PM₁₀ and PM_{2.5} air pollution, and possible impacts of study characteristics in South Korea, *Environ. Pollut.*, 240, 963-972, <https://doi.org/10.1016/j.envpol.2018.03.066>, 2018.

Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of emissions from air pollution sources. 3. C-1-C-29 organic compounds from fireplace combustion of wood, *Environ. Sci. Technol.*, 35, 1716e1728, <https://doi.org/10.1021/es001331e>, 2001.

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, *Sci. Total Environ.*, 515, 101-108, <https://doi.org/10.1016/j.scitotenv.2015.02.034>, 2015.

Song, C. B., Wu, L., Xie, Y. C., He, J. J., Chen, X., Wang, T., Lin, Y. C., Jin, T. S., Wang, A. X., Liu, Y., Dai, Q. L., Liu, B. S., Wang, Y. N., and Mao, H. J.: Air pollution in China: Status and spatiotemporal variations, *Environ. Pollut.*, 227, 334-347, <https://doi.org/10.1016/j.envpol.2017.04.075>, 2017.

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(17), 9741-9763, <https://doi.org/10.1029/2018JD028479>, 2018.

Song, M. D., Li, X., Yang, S. D., Yu, X. N., Zhou, S. X., Yang, Y. M., Chen, S. Y., Dong, H. B., Liao, K. R., Chen, Q., Lu, K. D., Zhang, N. N., Cao, J. J., Zeng, L. M., and Zhang, Y. H.: Spatiotemporal variation, sources, and secondary transformation potential of volatile organic compounds in Xi'an China, *Atmos. Chem. Phys.*, 21, 4939-4958, <https://doi.org/10.5194/acp-21-4939-2021>, 2021.

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, *Sci. Total Environ.*, 445, 110-116, <https://doi.org/10.1016/j.scitotenv.2012.12.044>, 2013.

Wang, S., Zhao, Y., Han, Y., Gao, S., Li, R. and Fu, H. B.: Spatiotemporal variation, source and secondary transformation potential of volatile organic compounds (VOCs) during the winter days in Shanghai, China, *Atmospheric Environment*, 286, 119203, <https://doi.org/10.1016/j.atmosenv.2022.119203>, 2022.

Wongphatarakul, V., Friedlander, S. K., and Pinto, J. P: A comparative study of PM_{2.5} ambient aerosol chemical databases. *Journal of Aerosol Science*, 29, S115-S116. [https://doi.org/10.1016/S0021-8502\(98\)00164-5](https://doi.org/10.1016/S0021-8502(98)00164-5), 1998.

Xiong, Y., and Du, K.: Source-resolved attribution of ground-level ozone formation potential from VOC emissions in Metropolitan Vancouver, BC, *Sci. Total Environ.*, 721, 137698, <https://doi.org/10.1016/j.scitotenv.2020.137698>, 2020.

Yang, M. R., Li, F. X., Huang, C. Y., Tong, L., Dai, X. R., and Xiao, H.: VOC characteristics and their source apportionment in a coastal industrial area in the Yangtze River Delta, China, *J. Environ. Sci.*, 127, 483-493, <https://doi.org/10.1016/j.jes.2022.05.041>, 2023.

Yang, X. Y., Wu, K., Lu, Y. Q., Wang, S. G., Qiao, Y. H., Zhang, X. L., Wang, Y. R., Wang, H. L., Liu, Z. H., Liu, Y. L., and Lei, Y. : Origin of regional springtime ozone episodes in the Sichuan Basin, China: Role of synoptic forcing and regional transport, 278, 116845, <https://doi.org/10.1016/j.envpol.2021.116845>, 2021.

Yao, L.: Chemical composition, source and secondary generation of atmospheric PM_{2.5} in typical areas of Shandong Province [D]. Shandong University, 2016.

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

Zhang, H. D., Lü, M. Y., Zhang, B. H., An, L. C., and Rao, X., Q.: Analysis of the stagnant meteorological situation and the transmission condition of continuous heavy pollution course from February 20 to 26, 2014 in Beijing-Tianjin-Hebei, *Acta Sci. Circumst.*, 36, 4340-4351, 2016.

Zhang, K., Li, L., Huang, L., Wang, Y. J., Huo, J. T., Duan, Y. S., Wang, Y. H., and Fu, Q. Y.: The impact of volatile organic compounds on ozone formation in the suburban area of Shanghai, *Atmos. Environ.*, 232(137617), 1-11, <https://doi.org/10.1016/j.atmosenv.2020.117511>, 2020.

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, <https://doi.org/10.1016/j.atmosenv.2013.06.029>, 2013.

Zhang, Y. C., Li R., Fu H. B., Zhou D., and Chen J. M.: Observation and analysis of atmospheric volatile organic compounds in a typical petrochemical area in Yangtze River Delta, China, *J. Environ. Sci.*, 71, 233-248, <https://doi.org/CNKI:SUN:HJKB.0.2018-09-022>, 2018.

Zhao, S., Tian, H. Z., Luo, L. N., Liu, H. J., Wu, B. B., Liu, S. H., Bai, X. X., Liu, W., Liu, X.Y., Wu, Y. M., Lin, S. M., Guo, Z. H., Lv, Y. Q., and Xue, Y. F.: Temporal variation characteristics and source apportionment of metal elements in PM_{2.5} in urban Beijing during 2018-2019, *Environ. Pollut.*, <https://doi.org/10.1016/j.envpol.2020.115856>, 2021.