Dear editor:

Here we submit our revised manuscript for consideration to be published on **Atmospheric Chemistry and Physics**. The further information about our manuscript is as follows:

Topic: Measurement report: Ambient volatile organic compounds (VOCs) pollution at urban Beijing: characteristics, sources, and implications for pollution control

Type of Manuscript: article

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We acknowledge the suggestions of the editor, and are also grateful to your efficient serving. We have updated the manuscript on the basis of these valuable comments. Our responses were listed as following:

Reviewer 1: Cui et al. conducted a campaign of comprehensive field observations at an urban site in Beijing. The composition, sources, and secondary transformation potential of VOCs were also identified. Overall, the study is very interesting and shows some new findings. However, the manuscript still suffers from many flaws especially the language expression. Furthermore, section 3.2.1 is not well-organized and needs major revisions. The detailed comments are as follows:

Comment 1: Why not perform the hourly measurement of VOCs? To the best of my knowledge, the daily resolution for VOCs measurement is too coarse. Especially, the PMF model needs substantial observation data, which ensures the model's reliability.

Response: In this work, the VOCs samples were collected using the summa canisters and then measured by the GC-MS technique. Although on-line monitoring techniques such as PTR-TOF-MS show high time resolution (e.g., a few minutes), they cannot detect certain hydrocarbons such as alkanes which are widely in air. Therefore, we chose to measure the VOCs concentrations using the GC-MS technique. In this work, the air samples were collected during December 2018 and November 2019 with a total of 123 effective sampling days. Three groups of samples were collected each day, i.e., daytime samples, nighttime samples and all-day samples. Therefore, 369 sets of data were obtained, which is enough for PMF analysis. The PMF model showed the lowest Q (robust) and Q (true) values, and thus the result of PMF model is robust.

Comment 2: The authors need to add the detailed QA/QC of VOCs and other criteria pollutants in section 2.1. The information is very important otherwise the study might be meaningless.

Response (Lines 110-114, 121-122): Thanks for the reviewer's suggestion. The QA/QC of VOCs has been described in the manuscript, as shown in lines 110-114:

"Quality assurance and quality control, including method detection limit (MDL) of each compound, laboratory and field blanks, retention time, accuracy and duplicate measurements of samples were performed according to USEPA Compendium Method TO-15 (USEPA 1999). The correlated coefficients of the calibration curves for all the compounds were > 0.95. The relative standard deviation (RSD) for all of compounds of triplicates were 0.5%-6.0%."

The other pollutants including $PM_{2.5}$, NO_X and O_3 were analyzed using oscillating balance analyzer (TH-2000Z, China), the NO–NO_2-NO_X Analyzer (Thermo Fisher Scientific USA, 17I), and the Ozone Analyzer (Thermo Fisher Scientific USA, 49I), respectively. The quality assurance of NO_2, O_3, and $PM_{2.5}$ was conducted based on HJ 630-2011 specifications.

Comment 3: Section 2.3: Why do you use RF model rather than other decision tree model or chemical transport model (CTM)? The predictive performance of RF model might be worse than GBDT and XGBoost. Meanwhile, CTM is a process-based model, which could clearly explain the contribution of many VOC species to O_3 Moreover, the hyperparameter of RF model should be added.

Response: The impact of meteorology and emission on $PM_{2.5}$ and O_3 can be separated by both statistical methods and CTMs. Although CTMs have the advantage of simulating the atmospheric processes of pollutants, these model simulations require considerable computation resources. Besides, the uncertainties of model inputs (emission inventory and meteorology) will lead to simulation deviation, and researchers' selection of chemical reaction mechanisms as well as parameter optimization leads to varying results (Chen et al., 2020). Increasing more studies use statistic methods (e.g., multiple linear regression, GAM and machine-learning models, etc.) to separate the contributions of meteorology and emission to air pollution variations (Xiao et al., 2021; Grange et al., 2018; Vu et al., 2019; Zhang et al., 2020; Qu et al., 2020). RF model is a typical machine learning method and has shown good performance in separating the impacts of meteorology and emission on air pollutants (Li et al., 2021). In the present study, the coefficients of determination (R^2) for the RF model in predicting $PM_{2.5}$ and O_3 are 0.85 and 0.91, respectively, suggesting that the RF model is reliable.

Comment 4: Section 2.4: The BS, DISP, and BS-DISP tests should be also added.

Response (Lines 162-167): Thanks for the reviewer's suggestion. The BS, DISP, and BS-DISP tests of the PMF analysis has been added in the revised version:

"During the PMF analysis, the bootstraps (BS) method, displacement (DISP) analysis, and the combination of the DISP and BS (BS–DISP) were used to evaluate the uncertainty of the base run solution. A total of 100 bootstrap runs were performed, and acceptable results were gained for all factors (above 90%). Based on the DISP analysis, the observed drop in the Q value was below 0.1 %, and no factor swap occurred, confirming that the solution was stable. The BS–DISP analysis showed that the observed drop in the Q value was less than 0.5 %, demonstrating that the solution was useful."

Comment 5: Section 2.5: I think the PSCF analysis is not important in this study and could be removed.

Response: The reviewer's suggestion is reasonable. The PSCF analysis has been deleted in the revised version.

Comment 6: Section 3.2.1: Why not distinguish the meteorological and emission contributions to each VOC species?

Response: We tried to distinguish the meteorological and emission contributions to each VOC species by both RF and GBDT models. The results showed that the two models showed poor performance for predicting aromatics, halocarbons and OVOC species, with $R^2 < 0.4$ for most species, and we have not found the optimal proxy for predicting these species. In future studies, we hope add more useful variables to elevate the modelling performance of these VOC species.

Comment 7: Section 3.3: The source identification method of each source based on VOC fingerprint should be added in this part. I think this part is too rough and should be rewritten.

Response (Lines 297-319): Thanks for the reviewer's suggestion. The source identification method of each source based on VOC fingerprint has been added in the revised version as below.

"3.3.1 Indication from tracers

"The great changes in the mixing ratios of VOCs species are mainly affected by the photochemical processing and the emission inputs, and ambient ratios for VOCs species having similar atmospheric lifetimes are indicators of different sources (Li et al., 2019a;

Raysoni et al., 2017 Song et al., 2021). The ratio of *i*-pentane to *n*-pentane are widely used to examine the impact of vehicle emissions, fuel evaporation and combustion emissions, within the i/n-pentane ratios of ranging between 2.2–3.8, 1.8–4.6 and 0.56-0.80, respectively (McGaughey et al., 2004; Jobson et al., 2004; Russo et al., 2010; Wang et al., 2013b; Yan et al., 2017). As shown in Fig. 6, the i/n-pentane ratios during the $PM_{2.5}$-polluted months were mostly within the range of 0.3-2.0, suggesting the pentanes were from the mixed sources of coal combustion and fuel evaporation. During the non-$PM_{2.5}$-polluted months, the i/n-pentane ratios were distributed in the range of 1.3-3.4, indicating strong impacts from vehicle exhaust and fuel evaporation. During the O_3-polluted months, most of the i/n-pentane ratios (1.5-2.5) were distributed within the reference range of vehicle exhaust and fuel evaporation, whereas most of the i/n-pentane ratios during the non-O_3-polluted months ranged between 1.7-2.1, suggesting the significant impact of fuel evaporation.

The toluene/ benzene (T/ B) ratio, a widely used indicator for sources of aromatics. In areas heavily impacted by vehicle emissions, the T/B ratio lies in the range of 0.9–2.2 (Qiao et al., 2012; Dai et al., 2013; Wang et al., 2013c; Yao et al., 2013; Zhang et al., 2013; Yao et al., 2015a; Mo et al., 2016; Deng et al., 2018). Higher T/B ratios were reported for solvent use (greater than 8.8) (Yuan et al., 2010; Wang et al.,2014b; Zheng et al., 2013) and industrial processes (1.4-5.8) (Mo et al., 2015; Shi et al.,2015). In burning source emission studies, the T/B ratio was below 0.6 in different combustion process and raw materials (Tsai et al., 2003; Akagi et al., 2011; Mo et al., 2016). Most of the T/B ratios during the $PM_{2.5}$-polluted and non-$PM_{2.5}$-polluted months were within the range of 1.1-1.8 and 0.8-2.2, whereas the T/B ratios were mostly distributed within the range of 0.8-2.2 and 0.9-1.9 during the O_3-polluted and non-O_3-polluted months, respectively, suggesting the significant impact of vehicle and industrial emissions. ”

Comment 8: Conclusion is too long and should be shorten and reorganized.

Response: Thanks for the reviewer’s suggestion. The conclusion has been rewritten in the revised version, as shown below.

“In this work, the field sampling campaign of VOCs was conducted at urban Beijing during December 2018 and November 2019. The VOCs concentrations ranged from 5.5 to 118.7 ppbv with mean value of 34.9 ppbv. Alkanes, OVOCs and halocarbons were the dominant chemical groups, accounting for 75-81% of the TVOCs across the sampling months. By excluding the meteorological impact, the emission-driven O_3 level during the O_3-polluted months were higher than that during the non-O_3-polluted months, and similar pattern was found for $PM_{2.5}$. The molar ratio of VOCs to NO_X indicated that O_3 formation was limited by VOCs during both the O_3-polluted non-O_3-polluted months, and thus reducing VOCs emission is essential for alleviation of O_3 pollution. The contributions of coal/biomass combustion, solvent use, industrial sources, oil/gas evaporation, gasoline exhaust, and diesel exhaust were identified based on PMF analysis. Considering both the concentration and maximum incremental reactivity of individual VOC species for each source, fuel use and diesel exhaust sources were identified as the main contributors of O_3 formation during the O_3-polluted months, particularly the VOCs species of toluene, xylenes, trans-2-butene, acrolein, methyl methacrylate, vinyl acetate, 1-butene and 1-hexene, illustrating the necessity of conducting emission controls on these pollution sources and species for alleviating O_3 pollution. VOCs from diesel vehicles and combustion were found to be the dominant contributors for SOAFP, particularly the VOC species of toluene, 1-hexene, xylenes, ethylbenzene and styrene, and top priority should be given to these for the alleviation of haze pollution."

Comment 9: Data availability: I suggest the authors open the VOC dataset and it is very valuable to some researchers engaged in air quality modelling.

Response: The VOC dataset will be upload to the Supplementary Information.

Comment 10: The English throughout the manuscript should be significantly revised.

Response: Thanks for the reviewer's suggestion. In the revised version, the English throughout the manuscript has been checked carefully.

Reviewer 2: The research focused on ambient volatile organic compounds pollution at urban Beijing, and analyzed their characteristics, sources, and control effects. This study is of interest to the atmospheric scientists and suitable for the ACP. The observation data were detailed presented, the chemical composition and emission sources were analyzed aiming at different months and different O3- or PM2.5- pollution days, and the VOCs decline was found through comparing with reference results to support the control effects. However, I have a few concerns that should be addressed before the acceptance of the manuscript.

Major comments:

Comment 1: In introduction section, the air pollution status has greatly changed in past several years in Beijing, due to the strict control measures implemented. However, the corresponding introductions were outdated and can't present the current pollution characteristics. For example, line42 about SOA fraction in $PM_{2.5}$, line 48 about SOA contribution to haze pollution, line 56 about the contribution of biogenic and anthropogenic sources, and so on. The recent references and their conclusions should be referred to.

Response (Lines 41-45,49-51, 53-55): Thanks for the reviewer's suggestion. The recent references and their conclusions have been added in the revised version is as below.

Lines 41-45: "Besides, haze pollution occurred in urban sites in recent years were commonly characterized by enhanced formation of secondary organic aerosols (SOA) in fine particles, e.g., the fraction of SOA in organic aerosols has reached 58% in Xi'an during winter 2018, and 53% in urban Beijing during winter 2014 (Kuang et al., 2020; Li et al., 2017b; Sun et al., 2020; Xu et al., 2019)."

Lines 49-51: “Besides, the VOCs compounds including aromatics and biogenic species have significant impact on SOA formation which play an important role in haze formation (Huang et al., 2014; Tong et al., 2021).”

Lines 53-55: “VOCs in ambient air can be emitted by a variety of sources including both anthropogenic and biogenic sources. While biogenic emissions are significantly greater than anthropogenic emissions globally (Doumbia et al., 2021; Sindelarova et al., 2022), ”

Comment 2: Methodology section, VOCs detection system should be GC-MS, but not GC (as mentioned in lines 95-96), for Agilent 5975 uses mass spectrometry detector. If the detector only included MSD but not included FID, C2 hydrocarbons would not be detected but they widely exist in atmosphere. This point should be illustrated. In addition, the efficiency of this analyze system for aldehydes should be well discussed. Because various monitoring standards don’t explicitly recommend the “canister sampling-GC/MS analyzer” to detect aldehydes.

Response (105-107, 114-116): Thanks for the reviewer’s suggestion. In the revised version, the point that GC-MS cannot detect VOCs compounds (C2-C3) with low boiling point (i.e., ethane, ethene, acetylene, and propane) has been illustrated. The efficiency of the GC-MS system for aldehydes was also discussed in the revised version.

Comment 3: This study used the fact that O_3 or $PM_{2.5}$ pollution event happening to define high-O_3 months (Apr, May, Jun, Jul and Sep) and high-$PM_{2.5}$ months (April, May, Oct, Nov, Dec, Jan). It seems weird. For example, although O_3 event never happened in Aug, but ozone level was also relatively higher in Aug than in Apr and Sep. So Aug should be considered as the high-O_3 month, comparing with Apr and Sep. And then, in the results of PMF, the source apportionment in low-O_3 months (Oct, Nov, Dec, Jan) was different with that in high-$PM_{2.5}$ months (April, May, Oct, Nov, Dec, Jan), but similar to that in low-$PM_{2.5}$ months (Jun, Jul and Aug). This conclusion was unreasonable to a certain extent.

Response: We agree with the reviewer's suggestion. In the revised version, the months with O_3 pollution events (days with maximum 8-h average O_3 exceeding 160 μg m^{-3}) were defined as the O_3-polluted months, and with $PM_{2.5}$ pollution events (daily average $PM_{2.5}$ exceeding 75 μg m^{-3}) were defined as the $PM_{2.5}$-polluted months.

In the initial version, the source appointment during the "low-$PM_{2.5}$ months" was confused with that on "clean days of high-$PM_{2.5}$ months". In the revised version, the error has been corrected in both the main text and Figure 8.

Comment 4: When using PSCF to explore the spatial potential sources of VOCs in urban Beijing, 24h was considered for all species. However, the lifetimes of various VOCs species were greatly different, several hours for alkenes, but several days for some alkanes and halocarbons. I suggest various groups of VOCs should be individually considered, to give the lifetime hours in backward trajectories.

Response: Thanks for the reviewer's suggestion. According to the comments of the first reviewer, the PSCF analysis is not important and could be removed. In the revised version, the contents about the PSCF analysis have been deleted.

Minor comments:

Comment 1: Abstract: "O_3/$PM_{2.5}$" frequently appeared but without an explicit definition. It is hard to understand the "high and low-O_3/$PM_{2.5}$ months", "O_3/$PM_{2.5}$ polluted days", and "high O_3/$PM_{2.5}$ levels", etc.

Response: Thanks for the reviewer's suggestion. In the revised version, the different pollution periods have been clearly defined, i.e., the months with O_3 and $PM_{2.5}$ pollution events were defined as the O_3-polluted and $PM_{2.5}$-poluted months, whereas the months without O_3 and $PM_{2.5}$ pollution events were defined as the non-O_3-polluted and non-$PM_{2.5}$-poluted months, respectively. During the O_3-polluted months, the days with maximum 8-h average O_3 exceeding 160 μg m^{-3} and below 160 μg m^{-3} were defined as the O_3 pollution days of the O_3-polluted months and O_3 compliance days of the O_3-polluted months, respectively. During the $PM_{2.5}$-polluted months, the days with average $PM_{2.5}$ exceeding 75 μg m^{-3} and below 75 μg m^{-3} were defined as the $PM_{2.5}$ pollution days of the $PM_{2.5}$-polluted months and $PM_{2.5}$ compliance days of the $PM_{2.5}$-polluted months, respectively.

Comment 2: Lines 32-34: “The positive matrix factorization (PSCF) analysis showed that O_3 and $PM_{2.5}$ pollution was mainly affected by local emissions.” PSCF was conducted for VOCs, but not for ozone and $PM_{2.5}$. No evidence to support this conclusion.

Response: Thanks for the reviewer’s suggestion. According to the first reviewer’s suggestion, the contents about the PSCF analysis have been deleted in the revised version.

Comment 3: Line 47: VOCs chemistry in ozone formation involves gas-phase reaction, but not multiphase reaction.

Response (Line 45-46): Thanks for the reviewer’s suggestion. The error has been corrected in the revised version.

Comment 4: Line 104: the “coefficient” should be coefficients; “was” should be “were”

Response (Line 112-113): Thanks for the reviewer’ rigorous. The error has been corrected in the revised version.

Comment 5: Line 111-112: air pressure appeared twice.

Response (Line 123): It’s our overlook. One of the “air pressure” has been deleted in the revised version.

Comment 6: More detailed model performance verifications (RF) are necessary, although R^2 has provided in Fig. S2.

Response: The reviewer's suggestion is reasonable. In the revised version, the RMSE and MAE of the RF model in predicting $PM_{2.5}$ and O_3 have been added in Fig. S2.

Comment 7: Line 191-193: I cannot figure out the sentence, suggesting checking out syntax rules.

Response (213-215): Thanks for the reviewer's suggestion. The sentence has been rewritten in the revised version.

Comment 8: Line 234: Fig. S3 was mentioned, however, there is not Fig. S3 in the supplement of this passage.

Response: Thanks for the reviewer's suggestion. The Fig. S3 has been added in the supporting information.

Comment 9: line 243-244: "Alkenes, aromatics and OVOCs were the three contributing chemical groups to O3 formation", should be "the three biggest contributors".

Response (269): Thanks for the reviewer's suggestion. This sentence has been revised.