Point-by-Point Response to Review Comments by Anonymous Referee #2 on "Tracking Separate Contributions of Diesel and Gasoline Vehicles to Roadside $PM_{2.5}$ Through Online Monitoring of Volatile Organic Compounds, $PM_{2.5}$ Organic and Elemental Carbon: A Six-Year Study in Hong Kong" by Yee Ka Wong et al.

Response to General Comments:

We thank the reviewer for the comments, which have helped us sharpen our understanding of the limitations of current work and the way forward in improving the accuracy of estimating vehicular emission contributions using PMF model. Each of the questions raised by the reviewer has been addressed and detailed in the ensuing point-by-point response. We have addressed all the other comments as well and offered detailed explanation where we disagree with the reviewers. Our response text is marked in blue in this document. The revised text in the main manuscript is also marked in blue. References cited in this response document are placed at the end.

"However, one major issue with this manuscript is that authors have not properly explained limitations of this method – can this approach be used in other air monitoring conditions where vehicle emissions are not the major source of PM or other locations outside of Hong Kong? Is the method only robust for data collected from near road sites in Hong Kong? Further guidance on caveats regarding application of this approach to other situations/locations is needed."

Response: In principle this PMF approach is applicable in places where vehicle emissions are not the major PM source. As long as vehicle-related tracer compounds are available (e.g. pentanes and EC), the vehicular contributions could be teased out using PMF model. As to whether the method is constrained to roadside environment (in Hong Kong), we opine that the method gives the most robust results in near roadside site condition where the speciated VOCs are freshly emitted and are less affected by photochemical degradation, as mentioned in line 117 of the original main text. However, the reactivity of VOCs should be taken care of when applying the method in area downwind of traffic emissions source region.

The following statement will be added to the revised main text:

Line 118: "However, for non-roadside environments, the effect of photochemical reactions should first be examined, and correction of VOCs input data should be made when needed to avoid bias in source apportioning (He et al., 2019)."

"The other related issue is that the method is heavily weighted towards primary vehicle emissions without accounting for temperature-dependent semivolatile organic partitioning to particle phase or including good tracers for regional air pollution or primary emissions from any other source. Therefore, it's not clear whether trends in OC seasonality are due to SVOC partitioning or regional transport. Further discussion of how to better address these method limitations (e.g. potential underestimation of vehicle related primary/secondary OC or inaccurate contribution of regional air pollution) to better inform regulatory action would be helpful."

Response: We agree that differentiating the effects of SVOC partitioning and regional transport on OC seasonality could be very useful for shaping policy development. Attaining this goal, however, is challenging at this stage due to constraints in available speciation data. Sulfate and water-soluble potassium have been demonstrated to be useful for tracking regional secondary aerosol formation and biomass burning, respectively, in our study region (e.g. Hu et al., 2010; Huang et al., 2014). We believe deployment of

additional monitoring system for online measurement of ionic and elemental compositions in the future would effectively allow us to gain a more comprehensive picture on the sources affecting the study region.

We also agree that SVOC partitioning would affect vehicular OC contributions. A possible means to examine this issue is through conducting the PMF analysis on subset of samples grouped by temperature and organic aerosol concentration. The effectiveness of this undertaking requires further investigation. Indeed, while this response document is being drafted, we are preparing another manuscript which incorporates gas-particle partitioning of organic aerosol and oxidation degradation of hopanes (molecular source tracers for vehicular emissions) into chemical mass balance model to quantify vehicular contributions to $PM_{2.5}$. We believe the study would provide further insights into the effect of atmospheric processes on PMF quantification of vehicular contributions. We have addressed the study limitations issue in the ensuing specific comments section.

Response to Specific Comments:

Lines 78-79. Clarify what is meant by "highly recommended".

Response: Revision is made as below for clarification:

Line 78: The methodology presented in this study for instrument deployment, data collection and analysis could help air quality management authorities to obtain measurement-based evidence from the routine monitoring dataset for evaluating effectiveness of control policies targeting VE.

Line 156. Is there a prevalent wind direction in other seasons?

Response: Yes, in summer the prevailing wind is from the south. Revision is made as follow:

Line 158: During the fall/winter monsoon season, the prevailing northeasterly wind transports pollutants from the continental area to HK, while in summer the prevailing southerly wind carries clean air mass from the sea (Hagler et al., 2006).

Line 161. The results presented here do not appear to explain these reductions in OC over time. Are there any suggested explanations? Could it be improvements in regional air pollution?

Response: Yes, we agree that the improvement especially during winter was largely due to reduced regional air pollution. Revision is made as follow:

Line 162: It is noted that the winter OC had larger improvement than summer OC over the monitoring period. The average OC concentration in winter dropped by 6.4 μg C m^{-3} (from 10.7 μg C m^{-3} in 2011 to 4.3 μg C m^{-3} in 2017), while the decrease in summer was 2.3 μg C m^{-3} (from 5.1 to 2.8 μg C m^{-3}) during the same period. Such difference demonstrates the benefit on local air quality through collaborative effort in reducing regional air pollution over the years.

Line 176. If vehicle exhaust is the main source of OC, why not use OC x 1.2 to estimate OM as was used with the EC Tracer Method?

Response: Though vehicle exhaust represents an important OC source at the site, the contributions from aged air mass and cooking emissions are non-negligible, which are more oxygenated and thus having higher OM/OC ratio. We therefore use 1.4 to estimate the overall OM.

Lines 183-187. Could these measurements be used in this PMF analysis as a tracer(s) for improve regional air pollution factor?

Response: The chemical composition data adopted here is from 24-h filter-based measurement, and thus are not compatible with the hourly data set for PMF analysis. Deployment of MARGA system for hourly monitoring of ionic species (e.g. sulfate, nitrate, K^+, etc) could expand the source apportionment capability of this site. Revision is made for clarification:

Line 187: Based on HKEPD's chemical speciation results for 24-h filter samples, these materials mainly consist of secondary inorganics (sulfate, nitrate and ammonium), followed by crustal material, and trace elements (Yu and Zhang, 2018).

Line 197. Do benzene and ethane have seasonality from their contribution in aged air mass?

Response: Yes, the two species showed seasonality in line with contribution of aged air mass, as shown in Figure R1 below. We attempt to focus on vehicle-related species and thus these VOCs were not discussed in detail in the main text.

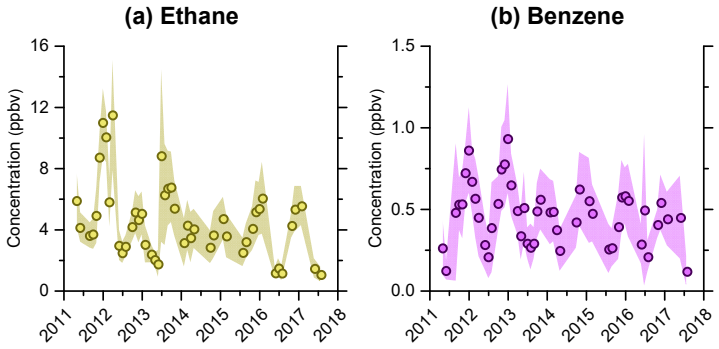

Figure R1. Trends in concentrations of (a) ethane and (b) benzene at MK AQMS. Each data point represents the monthly average of the hourly concentrations. Shaded areas represent one standard deviation for the hourly data.

Line 209. Could average ambient temperatures be plotted over this time period in the supplementary material so that partitioning could potentially be estimated?

Response: The average ambient temperatures are plotted in Figure R2. As shown in the figure, the temperature varied in a fairly constant manner over the years, which suggests the effect of temperature on partitioning should be largely consistent over the study period. This figure will be included in the supplementary material in our next revision.

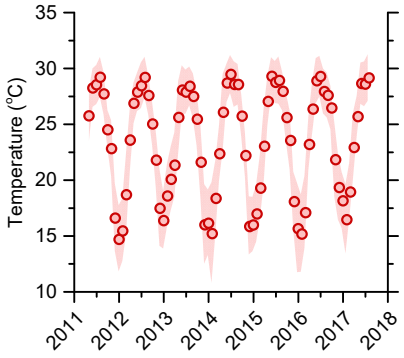

Figure R2. Trend in ambient temperature near MK AQMS. Each data point represents the monthly average of hourly data. Shaded area represents one standard deviation for the hourly data.

Line 214. How does this value compare to those determined in vehicle emissions studies or in emission inventories for representative vehicles in Hong Kong?

Response: Wang et al. (2018) reported that the OC/EC ratio measured from a tunnel in Hong Kong in 2015 winter was 0.7±0.2, which is higher than the $[OC/EC]_{vehicle}$ ratio determined by the minimum OC/EC ratio method in our study (i.e., 0.35±0.05). The higher ratio observed in Wang et al.'s work could potentially be attributed to lower temperature (measurement taken in winter vs. summer data adopted in our study) and the higher organic aerosol loading in tunnel (OC concentration was ~17 μg C m^{-3} in the tunnel vs. < 5 μg C m^{-3} at MK AQMS during summer), which favor the partitioning of SVOC into particle phase. The difference in prevailing driving conditions between the two sites may also contribute to the OC/EC ratio discrepancy. Vehicle emissions at our roadside site are more influenced by emissions from engine acceleration, due to the close proximity to several pedestrian crossings, which in turn gives higher EC emission compared to tunnel environment where vehicles are mainly traveling at constant speed (Lee et al., 2017).

Line 236. Are the relative VOC contributions in the fuel filling profile consistent with the local gasoline fuel composition?

Response: The relative VOC contributions in the fuel filling profile are in reasonable agreement with local gasoline and diesel fuel composition reported by Tsai et al. (2006). We will add Table S3 in the supplementary information for illustration and revise the main text as below.

Line 241: The VOCs characteristic ratios (e.g. ethylbenzene-to-*m*-&*p*-xylene ratio) of this profile are also in reasonable agreement with local fuel composition. Details of the comparison are given in Table S3.

Table S3. Comparison of VOCs characteristic ratios among fuel-filling process profile derived in this study and gasoline and diesel fuel profiles reported in Tsai et al. (2006)

	Fuel-filling process (This study)	Gasoline fuel (Tsai et al. 2006)	Diesel fuel (Tsai et al., 2006)
Toluene/Benzene	12.4	22.1±12.7	~10*
Toluene/*m*-&*p*-Xylene	1.8	6.3	~1*
Ethylbenzene/*m*-&*p*-Xylene	0.5	~0.5*	~0.25*

Note: The value is approximated from graphic information as no numerical values were provided in the publication.

Line 274. Is there a possible explanation for this deviation?

Response: We double check the result and confirm there is no erroneous data presentation. We compared the modeling performance of *i*-pentane for the two sets of PMF analyses and did not found any significant discrepancy, as shown in Figure R3, indicating the discrepancy was caused by other unknown reasons. Indeed, the apportioning of OC by the PMF method in this study is affected by a complex web of factors, including PMF modeling uncertainties, partitioning of SVOCs, and omission of source tracers of certain known sources (e.g. cooking emissions). Further work is needed to better constrain the vehicular OC contributions (both primary and secondary OC). Nevertheless, this work highlights that when both OC and EC are considered, diesel vehicles are the more important source of primary vehicular $PM_{2.5}$ than gasoline vehicles in the study area.

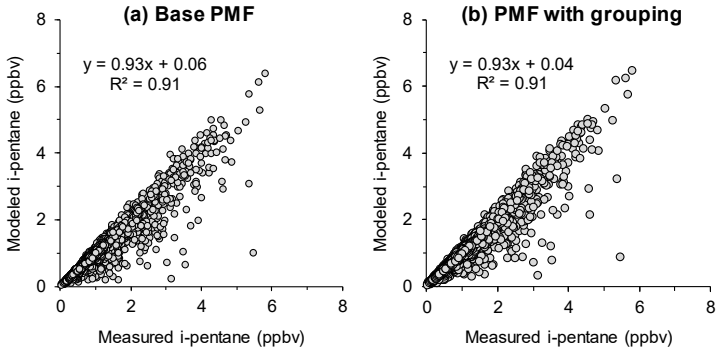

Figure R3. Scatter plot comparison of modeled versus measured *i*-pentane derived from (a) base PMF analysis and (b) PMF analysis with grouping.

Line 280. If OC from other factors are added, does the seasonality disappear?

Response: Figure S10 is re-plotted as Figure R4 in this response document by adding OC contributions from fuel-filling process and aged air mass factors (contribution from LPG vehicles are zero). As shown in the figure, the seasonality becomes much less significant after OC from other factors are added.

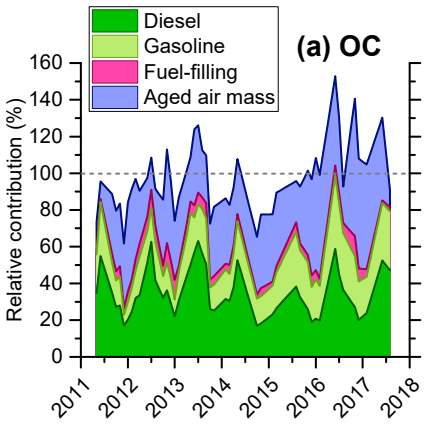

Figure R4. Relative contributions of diesel vehicles, gasoline vehicles, fuel-filling process and aged air mass to ambient OC at MK AQMS.

Line 305. This would be a good point to stress that limitations of this method in accurately estimating PMvehicle (does not take SOA formation, SVOC partitioning, or other emission sources into account) makes it difficult to make these types of policy recommendations.

Response: We thank the reviewer for the suggestion. The limitation of this method in taking SOA formation into consideration has been mentioned in line 357–362, whereas the challenge posed by SVOC partitioning has been mentioned in line 213–215. As this study focuses on vehicular emissions, we tend not to spend length on suggesting control measures for nonvehicular sources. However, we do touch upon the need to reduce secondary aerosol precursors based on the analysis of $PM_{2.5}$ composition, as given in line 189–191.

Line 334. The trends for the truck and bus time periods looks strikingly similar. Was this expected? Perhaps traffic patterns have changed since the traffic counting exercise?

Response: We double checked the data and confirm the trends in the figure are correct. We agree that the trends for the two traffic periods look similar and that traffic pattern could affect the vehicular contributions. One shared distinctive feature in the trends is the precipitous drop in contributions close to the end of 2014. This feature was the result of road blockage of several major roads near MK AQMS for ~2 months due to a major protest.

Figure 1. What is the air quality PM2.5 standard level?

Response: The prevailing Air Quality Objective for annual average $PM_{2.5}$ in Hong Kong is 35 μg m^{-3}, and the objective will soon be tightened to 25 μg m^{-3}.

Figure 3. It would be helpful to add Fig. S6 to this figure.

Response: We take the suggestion and will amend the figure and relevant figure captions.

Figure S10. It would be useful to see other factor contributions.

Response: We appreciate the suggestion, but given our focus is on vehicular contributions, we tend not to put additional information on the figure. Assigning aged air mass contribution to $PM_{2.5}$ in Figure c also involves making arbitrary assumption on the OM/OC ratio.

Figure S11. A time series of modelled and measured OC would be helpful to include.

Response: We take the suggestion and revise the figure as shown below. We will also revise the original plot for easier interpretation.

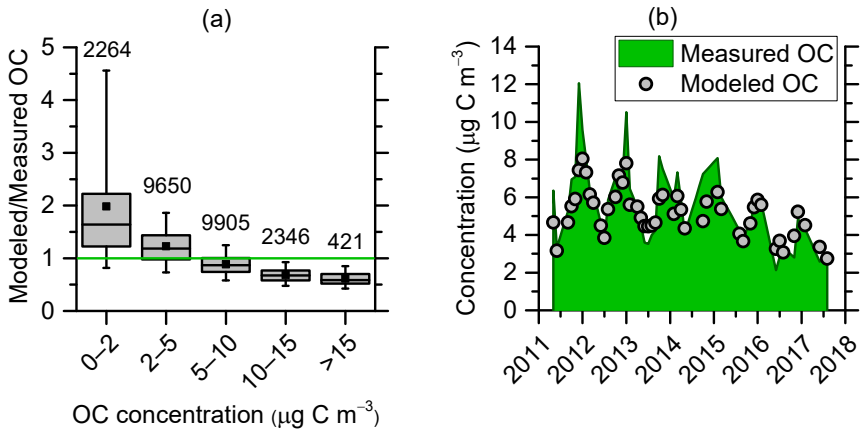

Figure S10. Comparison of PMF-derived and measured OC concentration at MK AQMS. Figure (a) presents the result as modeled-to-measured ratio in box-plot as a function of ambient OC concentration. Square marker and horizontal line within the box represent mean and median, respectively. Lower and upper bound of the box represent 25th and 75th percentile. Whiskers represent 5th and 95th percentile. The figures above each box diagram represent sample size. Figure (b) presents the comparison over time, with green area and grey markers representing measurement and modeling results, respectively.

References

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