***Point-by-Point Response to Review Comments by Anonymous Referee #1 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 and suggestions, which have helped us to supplement and consolidate our research findings. 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. For the ease of referencing, the line numbers mentioned in our response refer to those in the revised main text/SI documents.

**Response to Specific Comments:**

Line 128: More description/discussion on PMF analysis should be given. For example, did the authors performed seasonal PMF runs, or only yearly PMF runs, or only a single PMF run (six-year data all together)? Did the authors test more factors? Why not selecting more factors? How were those Q value variations?

**Response:** We thank the reviewer for reminding us to provide additional necessary details on the PMF analysis. The PMF-derived source contributions reported in this work is based on a single PMF run considering six-year data all together. For the sake of bootstrap uncertainty estimation, we also divided the whole dataset into three time-segments, each segment consists of one-third of the samples, and performed PMF for each time segment. This exercise and the relevant outcome have been discussed in line 132–135, and line 262–266, respectively.

As to the number of factors determined in the final solution, after considering the reviewer's comment, we added the Q-value metric (i.e., $Q_{true}/Q_{expected}$), which reflects the discrepancy between modeled and observed species concentrations (lower $Q/Q_{expected}$ means better fitting), to support the determination of factor number. The result, as shown in the new Figure S7, shows that increasing factor number from 3 to 4 and from 4 to 5 lowered the $Q_{true}/Q_{expected}$ value in a much greater extent when comparing to increasing the factor number from 5 to 6, 6 to 7 and 7 to 8. This indicates the 5-factor solution is most suitable for source interpretation.

Revisions is made as below:

Line 106 – 114: In this work, vehicular contributions to $PM_{2.5}$ are quantified by PMF analysis using the EPA PMF 5.0 software (Norris et al., 2014). PMF is a receptor model that solves the chemical mass balance of a speciated sample data matrix by decomposing it into factor profiles and factor contributions with non-negative constraints, with the objective to minimize the objective function Q (Paatero and Tapper, 1994; Paatero, 1997). The Q value represents the uncertainty weighted deviation between observed and modeled species concentrations.

Hourly concentrations of OC, EC, $NO_x$, CO and 12 selected VOC species from the entire monitoring period are considered in the PMF model for a single analysis. The VOCs, which were consistently detected above detection limit (> 80 % in each calendar year), include ethene, ethane, propane, propene, *i*-butane, *n*-butane, *i*-pentane, *n*-pentane, benzene, toluene, ethylbenzene and *m*-&*p*-xylene.

Line 232–236: Among various PMF solutions, the five-factor solution is the most interpretable for source identification and quantification. The drop in $Q_{true}/Q_{expected}$ value, which reflects the improvement in modeled species concentrations against measurements, is more significant when the factor number is increased by one from three to five compared to from five to eight (Fig. S7). This implies five factors are sufficient and suitable to explain the variations of input species data.

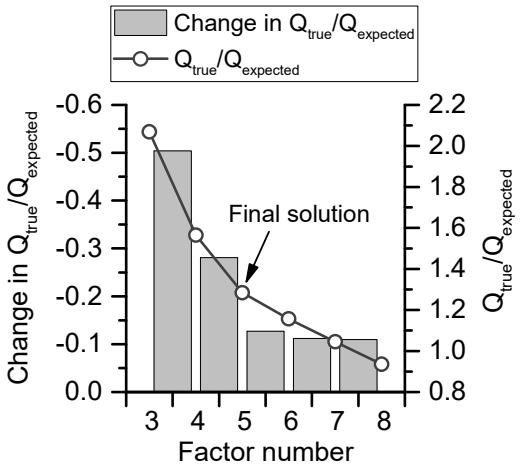


**Figure S7.** PMF performance in terms of the fitting between modeled and measured species concentrations expressed in $Q_{true}/Q_{expected}$ values, considering different factor numbers. Columns show the change in $Q_{true}/Q_{expected}$ values as the factor number increases by one (left axis). Markers show the $Q_{true}/Q_{expected}$ values in individual runs (right axis). The final solution of 5-factor run is indicated by an arrow.

Line 160, section 2.4: the author defined that the vehicle PM is the sum of total ambient EC and vehicle OC. Was there contribution of any solid-fuel burning (and cooking to OC) to EC and OC? If yes, how did the authors isolate these fractions using this vehicle OC/EC method, and assuming that total ambient EC was only from vehicle emissions? In addition, the authors simply considered the minimum OC/EC ratio as the vehicle OC/EC method. This part should be more clearly described, for example what this ratio is, how many selected samples associated with such minimum ratio, did the authors filter the potential influence of biomass burning and/or cooking (if applicable), etc.? These points should be discussed here.

**Response:** Study on source apportionment of EC at our roadside monitoring site has not been reported in the past. Certain amount of EC at this site could originate from nonvehicular sources such as biomass burning and coal combustion, but their contributions should be limited given the observed seasonal and diurnal patterns. Our PMF analysis shows that local vehicles contribute to 80–100% of EC in most sampling months, which further support this notion (Fig. S12b). Biomass burning and coal combustion are rare in our city area and their contributions are typically associated with regional transport in cold seasons. To isolate EC contributions from nonvehicular sources, measurement of additional chemical tracers is needed, which was not available in the study period. Still, given the strong evidence that EC at our roadside site is dominated by local traffic sources (e.g. based on diurnal variation patterns and PMF result), we believe the assumption that ambient EC is equivalent to vehicular EC is reasonable.

Details on the determination of $[OC/EC]_{vehicle}$ ratio and evidence to support its reliability have been given in section 3.2. Briefly, the minimum OC/EC ratios are determined on a monthly basis considering summer month data. The ratios range from 0.30 to 0.47, with $R^2$ between 0.56–0.96 (sample size $n$ = 18–33). These ratios mostly occur during morning rush hour, when contribution from nearby cooking emissions is minimal.

We also make revision as below to clarify the use of the minimum OC/EC method:

Line 145–149: The $[OC/EC]_{vehicle}$ is determined using the minimum OC/EC ratio approach, in which the ambient OC in a certain lowest percentage range by OC/EC ratio are regressed on ambient EC, and the slope obtained represents the target ratio (Lim and Turpin, 2002). This minimum ambient OC/EC ratio is perceived to be of minimal contributions from secondary formation and nonvehicular primary sources, which typically have higher OC/EC ratio than VE (e.g. cooking emissions and biomass burning).

Line 180, section 3.1: For trend analysis/discussion in the manuscript, they could be further performed with statistical approach, for instance, the Mann-Kendall trend test. By using that, the magnitude of change rate for the trend can be quantified, along with the significance levels. Overall, it seems there were increasing trends during the beginning years, while the decreasing trends have been observed since around 2013? In addition, it seems that there was a rapid decrease in those trends during around 2013-2015 (?), while a slowdown decrease in those trends were observed during recent years. Therefore, those points might be further discussed and explain possible reasons.

**Response:** We thank the reviewer for the suggestion of using statistical approach to examine the trends reported in this work. The Mann-Kendall test can indicate whether a monotonic increasing/decreasing trend exist at certain confidence interval, while the Sen's slope can subsequently be used to estimate the rate of change of the monotonic trend if it exists. However, the OC/EC time series presented in this study appear to consist of both upward and downward trends in different periods where the transition point is difficult to locate, thus isolation of a specific period for statistical analysis would be arbitrary, so does the statistical results. We therefore attempt to only describe the distinctive features of the trends without further performing the statistical analysis.

We believe what the reviewer referring to is the trends for EC and $NO_x$ shown in Fig. 1. We agree that there could be a slight increase in concentration from 2011 to 2013, followed by a rapid drop by the end of 2014. While we are unclear about the reason behind the change in the beginning years, the sudden drop near the end of 2014 (especially for $NO_x$) could be attributed to road blockage of several major roads near MK AQMS for ~2 months due to a major protest. It is also surprising to notice the EC level rebound in the last two months. Unfortunately, the monitoring has ceased since that period, and we are unsure whether that reversing trend continued or not. Twenty four-hour filter-based speciation data from this site as part of Hong Kong's $PM_{2.5}$ network in recent years (have not been released to the public yet) will help fill in this gap.

Lines 186 – 190: I think air mass back-trajectory analysis could be applied here to support those statements. By this method, the authors will be able to investigate the different concentration levels and/or sources of OC and EC associated with different air mass origins/clusters.

**Response:** Hong Kong is located in the coastal area facing the South China Sea to the south and mainland China to the north. This geographical feature gives Hong Kong a typical monsoon climate that results in contrasting prevailing wind directions in different seasons, and therefore seasonal characteristics in level and composition of $PM_{2.5}$, including elevated organic mass during winter. This feature has been validated by air mass backward trajectory analysis and documented in a number of past studies (e.g. Louie et al., 2005; Hagler et al., 2006; Huang et al., 2014). We therefore do not repeat the analysis in this work. Instead, we provide the references to allow interested readers to look for further details.

Revision is made in the main text as below:

Line 160–162: 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 (Louie et al., 2005; Hagler et al., 2006; Huang et al., 2014).

Lines 190 – 192: Did the authors have any evidence to prove these reasons?

**Response:** We thank the reviewer for raising this question. We do observe the seasonal variation in mixing height in Hong Kong as shown in Figure R1 below. However, as we re-examine the OC/EC data, the EC does not exhibit discernible seasonal variation over the years. This lack of seasonality is also reported in Louie et al. (2005). These pieces of evidence suggest the variation in mixing height is indeed unlikely to produce sufficiently large impact on the OC concentration in our study area.

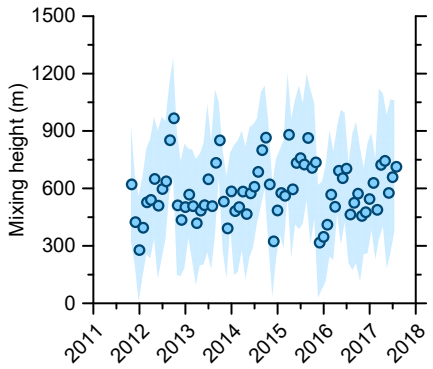


**Figure R1.** Trend in mixing height in Hong Kong during 11:00 (local time) recorded by the Global Telecommunication System of the World Meteorological Organization. Each data point represents the monthly average. Shaded area represents one standard deviation for the hourly data.

As for the effect of partitioning of SVOC, while we do not have direct measurement-based evidence for support, Lee et al.'s (2017) work does show that submicron vehicle-related organic aerosol (VE-OA) in the same study location tends to partition in the gas phase during summer, contributing to a 40% reduction in VE-OA mass compared to spring (2.0 vs. 3.5 $\mu g\ m^{-3}$). This implies gas-particle partitioning of SVOC could be an important factor contributing to the seasonal variation in OC concentration.

Revision is made in the main text as below:

Line 162–167: Another plausible reason for the elevated OC observed in wintertime is the enhanced partitioning of semivolatile organic compounds (SVOCs) into particle phase due to lower temperature and higher organic aerosol loading. Previous study at the same monitoring site shows that VE-related organic aerosol (derived from PMF analysis of organic aerosol mass spectra) decreases by 40 % in summer relative to spring despite consistency in traffic flow volume, pointing to a sizable influence of gas-particle partitioning of SVOCs (Lee et al., 2017).

Lines 192 – 193: It could help to further support the OC trend driven by wintertime OC when you separately show the six-year trends of monthly data for winter (DJF), spring (MAM), summer (JJA), and fall (SON). Did the authors find seasonal characterization for those OC and EC trends over the six-year period? Those new plots can be presented in supplement.

**Response:** We thank the reviewer for the suggestion. The trends during different seasons are added as the new Figure S3, which is also shown below. Instead of separating the seasons according to the reviewer's suggestion (i.e., DJF, MAM, etc.), we defined the seasons based on the subtropical climate feature of our location, which has longer summer and winter and shorter, transitional spring and fall (Louie et al., 2005). The new plot more clearly shows that the magnitude of OC reduction from 2011 to 2017 was the highest in winter.

Revision is made in the main text as below:

Line 168–169: It is noted that the winter OC had larger improvement than summer OC over the monitoring period, as shown in the season-specific trend plot in Fig. S3.

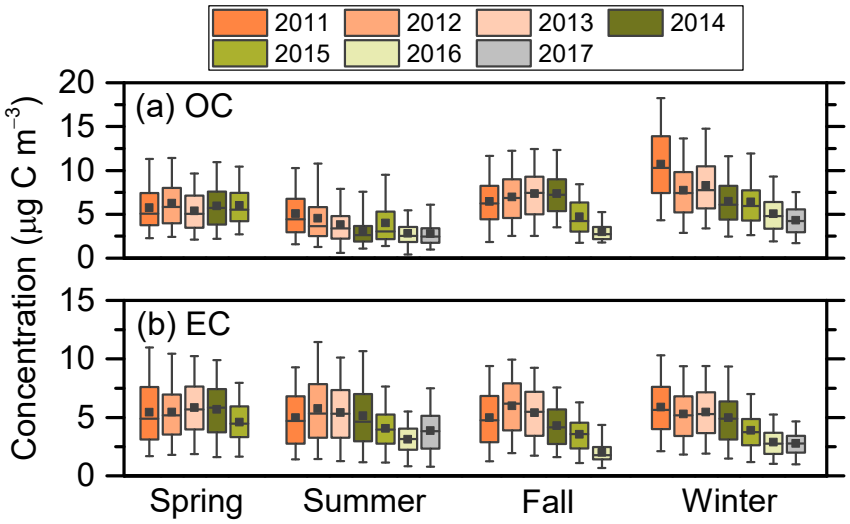


**Figure S3.** Inter-annual trends of (a) OC and (b) EC at MK AQMS from 2011 to 2017 during spring (mid-March to mid-May), summer (mid-May to mid-September), fall (mid-September to mid-November) and winter (mid-November to mid-March of next year). The measurement did not cover spring 2016 and 2017 and fall 2017, thus their results are not shown. Square marker and horizontal line within the box represent mean and median, respectively. Lower and upper bound of the box represent 25$^{th}$ and 75$^{th}$ percentile. Whiskers represent 5$^{th}$ and 95$^{th}$ percentile.

Lines 202-203: Based on these discussions above, it seems not fully convinced to conclude the less regional source influence on EC loadings rather than local traffic emissions. I guess, the similar EC diurnal cycles between work days and holidays/Sundays might reflect similar rush hours between the two types of days during a week. This could not sufficiently prove that the EC was more coming from local emissions. The different concentration levels of EC between the two types of days were also observed, however they weren't discussed. These similar diurnal patterns, along with different concentration levels, would be due to reduction in the total amount of traffic emissions over local and/or small-regional scales, however rush hours were overall not changed. In addition, as the NOx data was available in this work, it would be interesting to show correlations of EC versus NOx during work days and holidays, respectively. As commented above, air mass back trajectory analysis could also help to understand if there would have significant influence of regional sources on EC observed at the receptor site. Therefore, further discussions to support your statements should be extended.

**Response:** We thank the reviewer for the careful examination of the arguments. The main reason we think regional sources were not important to EC is that EC did not show seasonal variation as OC did. This implies regional air mass, which transports to our study area more frequently during winter, is enriched in OC to a much greater extent than EC, and thus the regional contribution to EC would be low. We add some description on the diurnal and workday–holiday patterns of EC observed during our long-term monitoring period to support VE as the major sources of EC. The revisions are as below:

Line 176–177: The absence of seasonal variation indicates local emissions dominated EC at this roadside site, and the impact of regional sources on EC, as opposed to OC, was limited.

Line 179–183: Such correlations persisted over the years, as shown in Fig. S4. Specifically, during workdays, EC concentration increased 4-fold from its minimum during small hours to ~ 4–8 μg C m$^{-3}$

during daytime. The corresponding increase was 2-fold for holiday period, consistent with the reduced traffic flow volume. These multiple lines of evidence indicate that EC at the site was mainly affected by local VE sources and less impacted by regional sources.

As suggested by the reviewer, we make scatter plot comparison between $NO_x$ and EC separately for workdays and holidays data, as shown below in Fig. R2. The two species had moderate correlation in both workdays and holidays. But since this correlation has been indirectly reflected by the similarity in their six-year trends shown in Fig. 1 in the main text, we will leave these plots in this response document for future reference only.

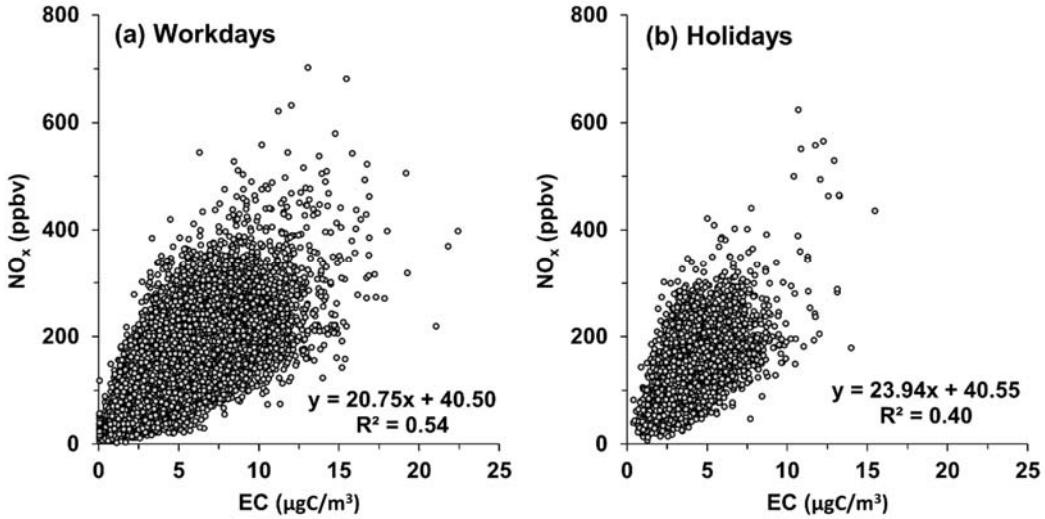


**Figure R2.** Scatter plot comparison between $NO_x$ and EC during (a) workdays and (b) holidays.

As mentioned in the previous response, the EC contributions from regional sources could be evaluated through comparing the EC concentrations in summer and winter given these two seasons have contrasting air mass origins associated with the prevailing wind direction. Again, the lack of seasonality in EC concentration supports that regional sources have a limited impact on EC concentration at our site. In addition, as our roadside site is surrounded by tall buildings, the wind information recorded at this micro-environment is subjected to uncertainty resulting from the heterogeneity in land surface, which would create bias in air mass backward trajectory analysis.

Line 241: It's not easy to justify the seasonality only based on time series of monthly data. It would be better if the authors could show monthly cycles and/or perform a seasonality significance test.

**Response:** The monthly cycles of *n*-butane concentration during 2011–2012 and 2014–2017 are shown in Fig. S5. Data from 2013 is not included because a major catalytic converter replacement program for LPG-fueled vehicles was undergoing and *n*-butane showed a precipitous drop during that year. From the figure, it is observed that the concentration remained almost the same throughout all months, supporting the seasonality is minimal. Revision is made in the main text as below:

Line 205–207: As shown in Fig. 1e, the *n*-butane level did not show obvious monthly variation over the years, supporting this species was predominantly emitted by local LPG vehicles (box-plot statistics of the monthly concentration are shown in Fig. S5).

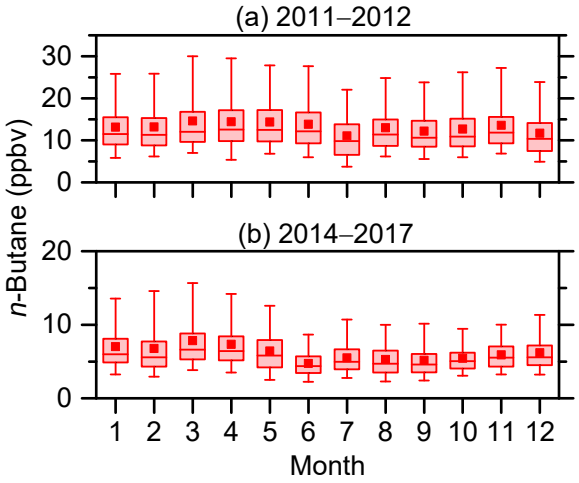


**Figure S5.** Monthly variation of *n*-butane concentration during (a) 2011–2012 and (b) 2014–2017 at MK AQMS. Data from 2013 is not included because a major catalytic converter replacement program for LPG-fueled vehicles was undergoing and *n*-butane showed a precipitous drop during that year. Square marker and horizontal line within the box represent mean and median, respectively. Lower and upper bound of the box represent 25$^{th}$ and 75$^{th}$ percentile. Whiskers represent 5$^{th}$ and 95$^{th}$ percentile.

Lines 257-259: It would be also good to show diurnal variations of the OC/EC ratio to support the lowest ratios associated with the rush hours. As shown in Fig. S3, EC presents high concentration starting from around 7 AM – 6 PM. Could this suggest rush hours for EC spanning this time period? It might be also useful to check and discuss diurnal variations of OC concentrations, NOx and OC/EC ratios.

**Response:** We plot the study-wide diurnal variation of OC/EC ratio by season, as shown below in Fig. R3. It can be seen that the ratio is the lowest during the 7:00–10:00 am period. Indeed, the lowest 5 % OC/EC ratio data are mostly derived from this morning period. Although EC presents high concentration during 7 am–6 pm, the lowest OC/EC ratio mainly occurs during the morning rush hours because cooking emissions, which represent an important OC source at our site, are insignificant during this period. During mealtime in the afternoon and evening, OC/EC ratio increases sharply despite the consistently high EC level because of the OC contribution from cooking emissions. The OC/EC ratio from these time segments are therefore not suitable to represent VE.

The diurnal variation of OC has been given in Fig. S10 for the purpose of evaluating the PMF result, while that for $NO_x$ is given below as Fig. R4. These diurnal patterns (including OC/EC ratio as well) are very similar to those reported in our previous publication (Huang et al., 2014), which characterizes the impact of VE at the same roadside location for the first time. Given the focus of this extended work is on long-term trend analysis and separating VE contributions for different vehicle types, we tend to leave out the discussion on diurnal variation of various species. We will refer interested readers to our previous publication for detailed analysis and discussion of the diurnal variation patterns.

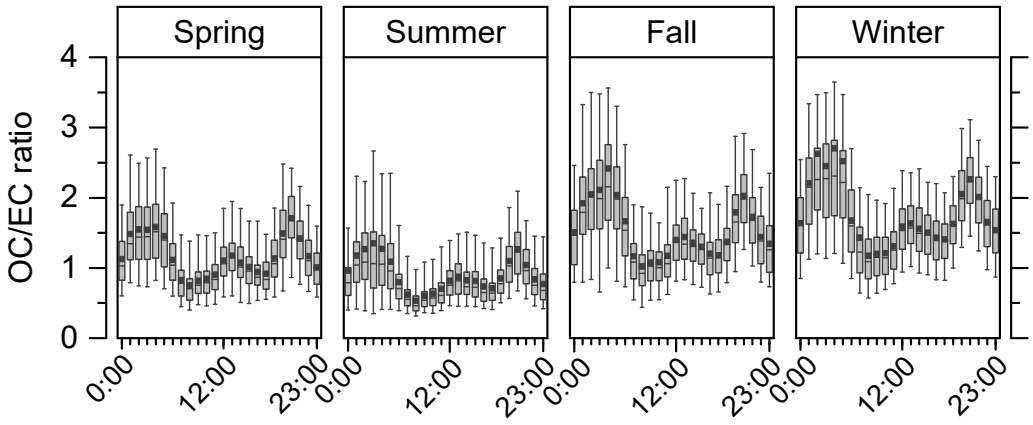


**Figure R3.** Diurnal variation of OC/EC ratio at MK AQMS during spring, summer, fall and winter. Square marker and horizontal line within the box represent mean and median, respectively. Lower and upper bound of the box represent 25$^{th}$ and 75$^{th}$ percentile. Whiskers represent 5$^{th}$ and 95$^{th}$ percentile.

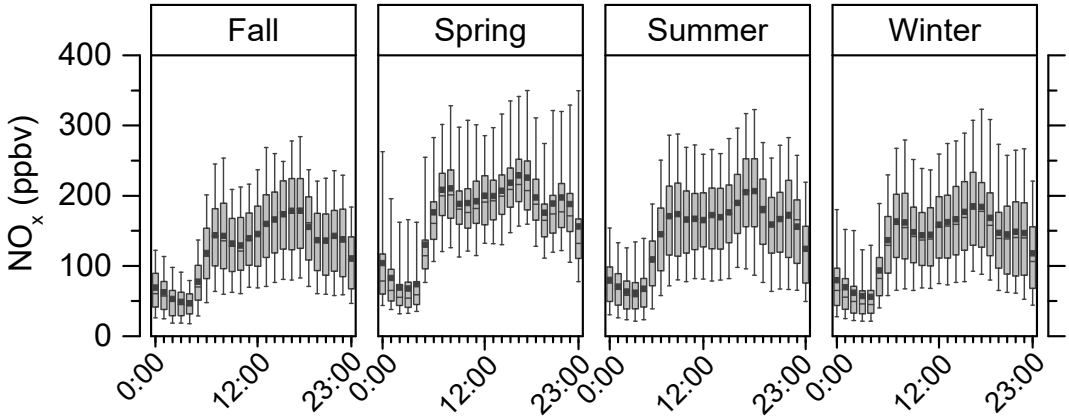


**Figure R4.** Diurnal variation of $NO_x$ at MK AQMS during spring, summer, fall and winter. Square marker and horizontal line within the box represent mean and median, respectively. Lower and upper bound of the box represent 25$^{th}$ and 75$^{th}$ percentile. Whiskers represent 5$^{th}$ and 95$^{th}$ percentile.

Line 278: As commented above, did the authors perform only a single PMF run? Did you have any other PMF run tests, e.g., using seasonal runs? Based on these runs, did the authors have the same solution? And were the results from seasonal PMF runs consistent with the present results? Did the authors try to increase the number of PMF factors? How were those PMF solutions based these tests?

**Response:** The VE source contributions reported in this work is based on a single PMF run, which considers all data collected from the entire study period. We also performed the PMF analysis on subset of samples (by dividing the samples into three groups of equal sample size). The results from these additional PMF runs are consistent with the base PMF result, as discussed in sect. 3.3.2 (Fig. S9 and Fig. S11). We attempted to perform PMF analysis using winter and summer data separately. Five factors resembling those in the base PMF run are resolved in both seasons. However, the winter PMF did not apportion any OC and EC to the gasoline VE factor, which is not the case in the base PMF. This issue is not observed in summer PMF. A comparison in VE contributions between the base PMF and summer PMF is summarized in Fig. R5. Overall, the contributions derived from both PMF runs show excellent correlation ($R^2$ = 0.98 as shown in Fig. R5a–5f). The diesel contributions derived from the two PMF runs are comparable, while the gasoline contributions are higher in the summer PMF. From the summer PMF, the diesel contribution dominates the $PM_{vehicle}$ contribution as shown in Fig. R5g, in agreement

with the base PMF result. The reason why OC and EC are absent in gasoline VE factor in winter PMF warrant further investigation, but based on our PMF analyses, certainly considering all available data in PMF would yield most reasonable results.

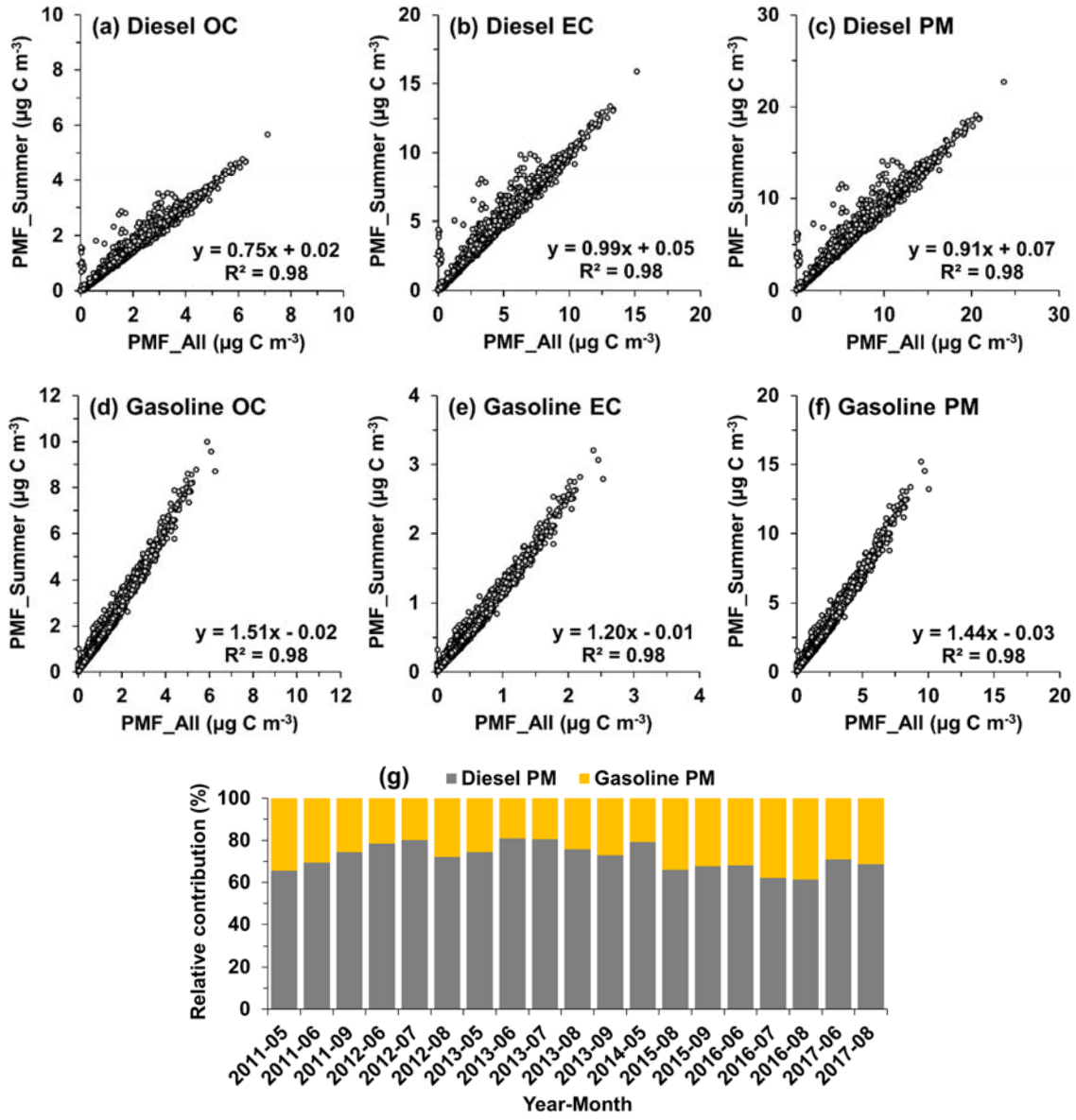


**Figure R5.** Comparison of VE source contributions derived from PMF considering all data and PMF considering summer data only. Figure (a)–(c) show the results for diesel OC, EC and PM, respectively. Figure (d)–(f) show the results for gasoline OC, EC and PM, respectively. Figure (g) shows the relative contributions between diesel and gasoline VE to $PM_{vehicle}$, derived from summer PMF.

As mentioned earlier, we tested the PMF performance using a range of factor number from 3 to 8. We found that further increasing the factor number beyond 5 would not give significant improvement in $Q_{true}/Q_{expected}$ value. The additional factors resolved are also ambiguous. Take the 8-factor solution as an example, the additional factors include an *m*-/*p*-xylene factor, a toluene factor, and an unidentified factor. The presence of these excessive and unidentified factors hinders our interpretation of source analysis.

## References

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