**Authors' response to referee comments on "The impact of gaseous degradation on the equilibrium state of gas/particle partitioning of semi-volatile organic compounds"**

RE: We thank the reviewer for the time and effort engaging with our manuscript and providing us with valuable feedback. The manuscript was revised based on the following comments and suggestions, which looks much better than the original one. The detailed response and revisions can be found as follows.

In this manuscript, Zhu et al. reported their field observations, highlighting two interesting and important key findings: (1) significant diurnal variation in the gas-phase and particle-phase concentrations of methylated polycyclic aromatic hydrocarbons (Me-PAHs), and (2) remarkably higher gas-particle partitioning quotients (log $K_P'$) for lighter Me-PAHs during daytime compared to nighttime. To explain the latter observation, the authors propose that "the higher gaseous degradation of [Me-PAHs] during daytime than that during nighttime should be responsible for their special diurnal variation".

The authors arrived at this hypothesis as they investigated another hypothesis and found it insufficient for explaining the observed diurnal variation in log $K_P'$. For another hypothesis, they assessed whether the log $K_P'$ observed for the same chemical at different temperatures correlates with the calculated log $K_{OA}$ at those temperatures, where log $K_{OA}$ at different temperatures were calculated using a simple regression (A/T + B). The authors found no significant correlation (Figure 3), which led them to conclude that the temperature-dependent variability in log $K_{OA}$ does not adequately explain the observed diurnal variation in log $K_P'$. They then turned to an alternative hypothesis that the temperature-dependent variability in the gaseous degradation rate "should be responsible" for the observed diurnal variation in log $K_P'$, given that the temperature-dependent variability in the gaseous degradation rate can lead to a much more pronounced variation in log $K_P'$ (Figure 4).

Honestly, I do not believe the authors' reasoning is convincing. It is not logically sound to accept an alternative hypothesis as valid simply because another has been invalidated

- unless the two hypotheses are mutually exclusive. So my first recommendation is that the authors reframe their argument to state that "the temperature-dependent variability in log $K_{OA}$ does not sufficiently explain the observed diurnal variation in log $K_P$'", rather than asserting that "temperature-dependent variability in the gaseous degradation rate *should be responsible* for the observed diurnal variation in log $K_P$'". This adjustment would present their conclusion as a more measured interpretation of the data, rather than a definitive explanation (actually, it is only a speculation).

RE: Thanks for the suggestion.

In our study, three findings were obtained: (1) significant diurnal variation in the gas-phase and particle-phase concentrations of methylated polycyclic aromatic hydrocarbons (Me-PAHs) (Section 3.1), (2) remarkably higher gas-particle partitioning quotients (log $K_P$') for lighter Me-PAHs during daytime compared to nighttime (Section 3.2), (3) the influence of gaseous degradation on the deviation of $K_P$' from the equilibrium state was confirmed based on a new steady-state G/P partitioning model (Section 3.3).

**For the second finding:** remarkably higher gas-particle partitioning quotients (log $K_P$') for lighter Me-PAHs during daytime compared to nighttime, we applied two methods to study. Firstly, the direct comparison with the log $K_P$' values between daytime and nighttime was conducted. As showed in Fig. 2, Me-Naps exhibited significantly higher log $K_P$' values in the daytime compared to the nighttime. Secondly, the direct comparison with the regression lines of log $K_P$' against log $K_{OA}$ between daytime and nighttime was conducted. As showed in Fig. 3, the regression lines with Me-Naps also had obvious diurnal variations as being higher during daytime compared to nighttime. In order to figure out the reason for the finding, we found that the N/D ratios of concentrations in the gas phase were significantly higher than those in the particle phase for Me-Naps (Fig. S2 in SI). And the direct description was explained by Equations (3) and (4). Furthermore, the reasons for the finding were discussed based on previous studies (the last paragraph in the revised manuscript), and the conclusion "the higher gaseous degradation during daytime than that during nighttime might result in the higher $K_P$' values during daytime than that during nighttime" was obtained. Furthermore,

the conclusion was also confirmed based on the new steady-state G/P partitioning model in Section 3.3. Therefore, based on the above discussion, we did not apply one hypothesis to explain another hypothesis. In addition, the Section 3.2 was comprehensively revised for better reading and understanding, which can be found in detail in the revised manuscript.

Furthermore, the following sentence was added in the revised manuscript:

"Based on Eq. (5), the value of $K_P'$ will increase along with the increasing of $k_{deg}$. As we mentioned above, the gaseous degradation in the daytime was higher than those in the nighttime. Therefore, the application of Eq. (5) can demonstrate that the gaseous degradation of Me-Naps could be part of reason for the higher $K_P'$ in the daytime than that in the nighttime."

In addition, I don't even think the observed absence of correlation between the observed log $K_P'$ and log $K_{OA}$ at different temperatures can lead to any meaningful conclusions, as many sources of uncertainties may contribute to the deviation of the log $K_P'$-log $K_{OA}$ relationship. I just name a few:

(1) One critical assumption underlying the log $K_P'$-log $K_{OA}$ relationship is that lipid-like organics predominantly control the partitioning of chemicals into the particle phase. Although this assumption may hold for a variety of organochlorines and organobromines, it may not be universally applicable to Me-PAHs. This is because, for PAHs, carbonaceous components (such as black carbon) can sometimes exceed lipid-like organics as the principal sorbents (Cornelissen et al., Environ. Sci. Technol. 2005, 39, 18, 6881–6895). Of course, Cornelissen et al. focused on the significant role of carbonaceous materials in the sorption of PAHs onto sediments and soils, but it also gives the possibility of sorption of PAHs by carbonaceous components in aerosol. So, it should not be unexpected to see significant deviations from the log $K_P'$-log $K_{OA}$ relationship for Me-PAHs.

RE: Thanks for the suggestion.

We agree with the opinion, the sorption of PAHs by carbonaceous components was an important process for the G/P partitioning of these compounds. As we mentioned in the

manuscript, the D-E model introduced the sorption of soot phase in particles into the G/P partitioning model, which indicated that the additional sorption could increase $K_P'$ for about 2.68 to 7.70 times (Dachs et al., 2000, *Environ. Sci. Technol.*, 34 (17): 3690-3697):

$$\log K_{P-DE} = \log\left(\frac{K_{OA}f_{OM}}{0.82} + K_{SA}f_{EC}\right) - 12 \tag{1}$$

$$\log K_{SA} = 0.85 \log K_{OA} + 3.45 - \log(998/\alpha_{EC}) \tag{2}$$

where, $f_{OM}$ is the organic matter content of the particle; $f_{EC}$ is the fraction of the elemental carbon (EC) of the particle; $K_{SA}$ is the soot/air partition coefficient (L/kg); $\alpha_{EC}$ is the specific surface area of the elemental carbon (m$^2$/g).

As we mentioned in Sections of Introduction and 3.3, the additional sorption could increase the value of $K_P'$, which could result in the deviation from the equilibrium state. However, no evidence was reported for the difference of the sorption mechanism between the daytime and nighttime. Therefore, the regression lines of log $K_P'$ against log $K_{OA}$ can be used to figure out the difference between daytime and nighttime.


(2) Another potential reason for deviation is the uncertainties associated with the parameters in Equation 2. The values of A and B in this equation are derived from pp-LFER solute descriptors. However, Me-PAHs were not among the training chemicals used to develop these pp-LFER solute descriptors, and it is not sure whether these chemicals can be adequately predicted by these relationships.

RE: Thanks for the suggestion.

During the calculation of log $K_{OA}$ (Eq. (2)), the parameters of A and B were same for daytime and nighttime for each PAHs. And only the temperatures were different. The comparison for each compound with the regression lines of log $K_P'$ against log $K_{OA}$ was actually the comparison with the relationship of log $K_P'$ against temperature. Therefore, the uncertainties with A and B cannot influence the comparison.

(3) It has also been recognized that advection of air masses may also lead to deviation from the expected temperature dependence of log $K_P$'. See Wania et al. Environ. Sci. Technol. 1998, 32, 8, 1013–1021.

RE: Thanks for the suggestion.

We agree with the opinion that advection of air masses may also lead to deviation of log $K_P$'. However, the main objective of the present study was to clarify the influence of gaseous degradation on the deviation of $K_P$' from the equilibrium state. The other influence factors were not considered in the study. Therefore, in the Implication Section we pointed out that other influencing factors needed to be studied for better understanding the G/P partitioning of SVOCs. And the following sentence was added at the end of Section 5 in the revised manuscript:

"Therefore, it is imperative to conduct studies for other influencing factors on the G/P partitioning behavior of SVOCs in future, like the total gaseous degradation, the non-exchangeable SVOCs within particles, and the advection of air masses, among others."

Of course, we may also name another set of possibilities responsible for the absence of correlation between the observed log $K_P$' and log $K_{OA}$ at different temperatures. Clearly, all of these indicate a need for cautious interpretation of the use of the log $K_P$'-log $K_{OA}$ relationship, especially when applied to chemicals like Me-PAHs that may not align perfectly with the assumptions and parameters used in its derivation. As such, I do not think the manuscript has discussed and excluded these possible counterexamples to well justify the authors' interpretation of the deviation of the log $K_P$'-log $K_{OA}$ relationship. So my second recommendation is that the authors just end the manuscript with the statement that "the temperature-dependent variability in log $K_{OA}$ does not sufficiently explain the observed diurnal variation in log $K_P$'", stop overinterpreting its implications, and more importantly, acknowledge and discuss a wide array of possible reasons (including but not limited to those outlined above) that leads to such a deviation from the log $K_P$'-log $K_{OA}$ relationship.

RE: Thanks for the suggestion.

As we mentioned above, the relationship between log $K_P'$-log $K_{OA}$ was only used to figure out the difference between daytime and nighttime. The conclusions with the diurnal variation of Me-PAHs concentrations and $K_P'$ values were clear and confirmed based on the measurement. The influence of gaseous degradation on the deviation of $K_P'$ from the equilibrium state was also comprehensively studied based on a new steady-state G/P partitioning model. The conclusion with the influence of gaseous degradation on G/P partitioning was also confirmed. The findings of this study would provide new insight into the related field, which is the major implication of the study.

Overall, I believe the two key findings are very interesting and important and deserve publication. However, the authors' explanations and interpretations do not fully convince me. It may be beneficial for the authors to consider either dropping much of the speculative discussion in Section 3.2 and all of Section 3.3 or pivoting towards discussing the potential reasons behind these findings in a more thorough, comprehensive manner.

RE: Thanks for the suggestion. The manuscript was comprehensively revised according to your suggestions and comments, especially for Section 3.2 and Section 3.3. The details on the revisions can be found in the revised manuscript. The revised manuscript looks much better than the original one, which is much more suitable for reading and understanding.