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.

Semi-volatile organic compounds (SVOCs) were typical pollutants in atmosphere. The gas and particle partitioning of SVOCs is important for their long-range atmospheric transport and health to human. Therefore, the study of gas and particle partitioning has attracted more attentions recently. However, the mechanism of the gas and particle partitioning for some types SVOCs was not well clarified. In this study, the impact of gaseous degradation of SVOCs on the equilibrium state of gas and particle partitioning was comprehensively discussed and studied. Some new findings were provided for this topic, which will improve our understanding of the mechanism of gas and particle partitioning.

RE: Thanks for the positive evaluation to our study.

I have some comments and suggestions to the study:

(1) In the title of the manuscript, semi-volatile organic compounds were used, however, in the main manuscript, only PAHs were studied and discussed. Therefore, semi-volatile organic compounds should be replaced by PAHs or Me-PAHs.

RE: Thanks for the suggestion. The "semi-volatile organic compounds" in the title was changed by "methylated polycyclic aromatic hydrocarbons".

(2) Abstract, what kind of theoretical model? More details should be added.

RE: Thanks for the suggestion. The "theoretical model" was changed by the "steady-state G-P partitioning model".

(3) Introduction Section, the authors mentioned the scientific problem was the deviation between the prediction of models and monitoring for K_P' with LMW SVOCs. The deviation or the problem needs to be quantified.

RE: Thanks for the suggestion. The following information was added in the Introduction Section of the revised manuscript.

"For the LMW SVOCs, the K_P' deviated upward from the equilibrium state, and the deviation could be multiple orders of magnitude, such as LMW polycyclic aromatic hydrocarbons (PAHs)."

(4) Section 3.1. for the comparison with other studies, the numbers and names of Me-PAHs should be mentioned. If different Me-PAHs were compared, the conclusion was not reasonable.

RE: Thanks for the suggestion. Because the numbers and names of Me-PAHs were different between our study and other previous studies, therefore, the related sentences were deleted in the revised manuscript.

(5) Fig. 1, if different seasons were separated for discussion. I don't think it is necessary for the figure of "All seasons".

RE: Thanks for the suggestion. According to the related Chinese Environmental Standards, the information for all seasons was important and necessary, such as the annual average concentrations. The all-season data help us to have a general understanding of the data and also facilitate the reading and citation of other readers. Therefore, the samples were collected for the whole year during the sampling program, and the basic information with Me-PAHs pollutions in different seasons were obtained. Therefore, the figure with all seasons was included, and the discussion on the related data was also conducted in the main section.

(6) Section 3.2, the equations of (3)-(5) were not easily for understanding.

RE: Thanks for the suggestion. The equations (3) to (5) was revised as follows for better understanding:

"The specific relationships with concentrations between daytime and nighttime can be elucidated by the following equation:

$$C_{P,N}/C_{P,D} < C_{G,N}/C_{G,D} \rightarrow C_{P,N}/C_{G,N} < C_{P,D}/C_{G,D} \tag{3}$$

where, $C_{P,N}$ and $C_{P,D}$ are the particulate concentrations during nighttime and daytime, respectively; $C_{G,N}$ and $C_{G,D}$ are the gaseous concentrations during nighttime and daytime, respectively."

(7) Section 3.3, for equation (6), more derivation process or steps are necessary for reading, or maybe in SI.

RE: Thanks for the suggestion. We added more detailed information in SI as follows:

"Text S1. The derivation of the log K_P' for LMW SVOCs based on the new steady-state G–P partitioning model

The G/P partitioning quotient (K_P') can be calculated as follows:

$$K_P' = (C_P/C_G)/TSP \tag{S1}$$

where, C_P (ng/m^3 air) and C_G (ng/m^3) are the concentrations of SVOCs in particle phase and gas phase, respectively, and TSP is the concentrations of total suspended particles (μg/m^3).

C_P can be transferred to C'_P (ng/m^3 particle) based the following equation:

$$C_P = C'_P \times TSP/10^9 \rho_P \tag{S2}$$

where, C'_P (ng/m^3 particle) is the concentrations in particle phase with different units, and ρ_P is the density of particles (kg/m^3).

Then, the Eq. (S1) can be expressed in different form:

$$K_P' = (C'_P/C_G)/10^9 \rho_P \tag{S3}$$

The ratio of C'_P to C_G can be calculated using the method from the multimedia fugacity model:

$$C'_P/C_G = f_P Z_P/f_G Z_G \tag{S4}$$

where, f_P and f_G are the fugacity for particle phase and gas phase, respectively, Z_P and Z_G are the fugacity capacity for particle phase and gas phase, respectively.

Z_P/Z_G equal to K_{PG} at equilibrium state, which can be calculated by the following

equation (Li et al., 2015):

$$K_{PG} = Z_P/Z_G = 10^9 \rho_P K_{P-HB} \quad (S5)$$

where, K_{P-HB} is the G/P partitioning coefficient calculated from the H-B model (the equilibrium-state model) (Harner and Bidleman, 1998).

Summarizing the equations above, $\log K_P$ can be expressed as following equation:

$$\log K_P' = \log K_{P-HB} + \log(f_P/f_G) \quad (S6)$$

According to the Eq. (5), K_P' will upward deviate from K_{P-HB} (or the equilibrium state) when $f_P > f_G$. Based on our previous study (Zhu et al., 2023), the fugacity ratio of the particle phase to the gas phase can be expressed as Eq. (S7), when the steady state is reached between gas phase and particle phase:

$$\frac{f_P}{f_G} = \frac{D_{GP} + \phi_0 D_{GR}}{D_{GP} + (1-\phi_0)(D_{PD} + D_{PW})} \quad (S7)$$

where, ϕ_0 is the particulate proportion of SVOCs in emission; D_{GP} is the intermedia D value between gas phase and particle phase; D_{GR} is the D value for the degradation of gas-phase SVOCs; D_{PD} and D_{PW} are the D values of the dry and wet depositions of particle-phase SVOCs, respectively.

For the LMW SVOCs, the dry and wet deposition fluxes of particle phase ($F_{PD} + F_{PW}$) (**Fig. S5**) can be ignored (Li et al., 2015; Zhu et al., 2023), then the Eq. (S7) can be expressed as follows:

$$\frac{f_P}{f_G} = 1 + \frac{\phi_0 D_{GR}}{D_{GP}} \quad (S8)$$

Based on the above equation, when $\phi_0 D_{GR}$ cannot be ignored compared with D_{GP}, f_P will be higher than f_G, and the K_P' values will deviate upward from equilibrium state. In other words, when $\phi_0 F_{GR}$ ($F_{GR} = f_G D_{GR}$, the degradation flux of gas phase) cannot be ignored compared with F_{GP} ($F_{GP} = f_G D_{GP}$, the flux from gas phase to particle phase), the K_P' values will deviate upward from equilibrium state. Therefore, it can be concluded that the deviation was affected by both the gaseous degradation and the particulate proportion of SVOCs in emission.

References:

Harner, T. and Bidleman, T. F.: Octanol-air partition coefficient for describing particle/gas partitioning of aromatic compounds in urban air, Environmental Science &

Technology, 32, 1494-1502, https://doi.org/10.1021/es970890r, 1998.

Li, Y., Ma, W., and Yang, M.: Prediction of gas/particle partitioning of polybrominated diphenyl ethers (pbdes) in global air: A theoretical study, Atmospheric Chemistry and Physics, 15, 1669-1681, https://doi.org/10.5194/acp-15-1669-2015, 2015.

Zhu, F. J., Hu, P. T., and Ma, W. L.: A new steady-state gas–particle partitioning model of polycyclic aromatic hydrocarbons: Implication for the influence of the particulate proportion in emissions, Atmospheric Chemistry and Physics, 23, 8583-8590, https://doi.org/10.5194/acp-23-8583-2023, 2023."

(8) Section 3.3, the last two sentences: "It can be found that, the impact caused by the gaseous degradation on K_P' deviation was in the range of 1 to 8.4 times under different ϕ_0 (0 to 1) in the temperature range of −50 to 50℃. However, due to the limited consideration of the gaseous degradation (only reaction with hydroxyl radicals) in this study, the actual impact of the gaseous degradation on K_P' deviation was expected to be higher than the range." I have two questions here: first, the uncertainty analysis of results is needed for the model; second, the two appearances with "the gaseous degradation" between the first sentences and the second sentence were confused for me, please modify the writing.

RE: Thanks for the suggestion.

1) For the first question: The uncertainty analysis of the model was conducted based on the Monte Carlo Analysis. And the following information was added in the revised manuscript:

"The increasing times of K_P' influenced by the gaseous degradation deviated from the equilibrium state can be calculated based on the equation: $1 + 13.2\phi_0 \times k_{deg}$. To evaluate the impact of the gaseous degradation on the K_P' deviated from equilibrium state, the sensitivity analysis at condition of −50℃ and 50℃ was separately conducted by the Monte Carlo Analysis with 100 000 trials employing the commercial software package Oracle Crystal Ball. Consequently, the range of the impact resulting from the gaseous degradation was calculated for individual PAHs, and the results are presented in **Fig. 4**. It can be found that, the mean impact caused by the gaseous degradation on

K_P' deviation for these PAHs were in the range of 1.10 to 1.98 times (90% confidence interval: 1.01 to 3.89) (**Fig. 4a**) and in the range of 1.54 to 5.58 times (90% confidence interval: 1.04 to 14.4) (**Fig. 4b**) at −50°C and 50°C, respectively. The influence from the gaseous degradation on the deviation of K_P' from the equilibrium state could approach to one order of magnitude, which cannot be ignored in the study of G–P partitioning of SVOCs."
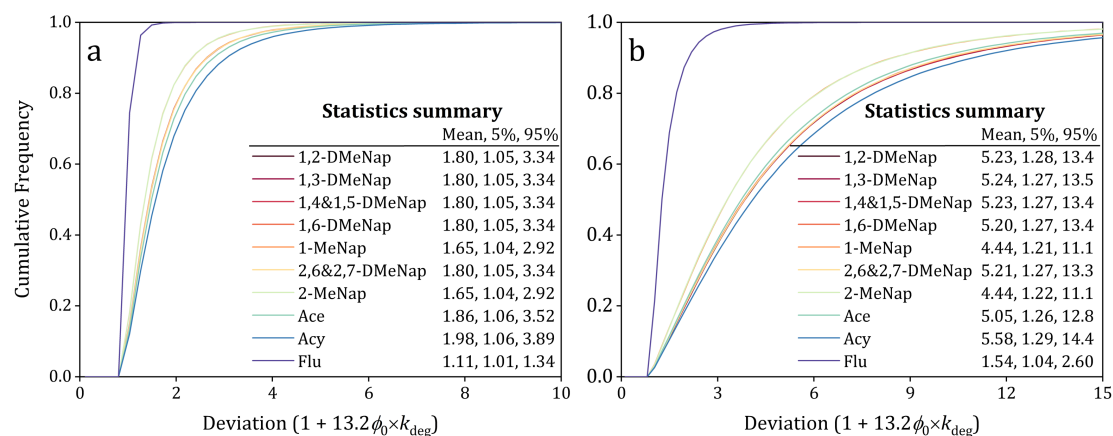

Fig. 4. The impact of the gaseous degradation on K_P' deviation from the equilibrium state estimated based on the Monte Carlo Analysis at −50°C (a) and 50°C (b). (Note: The following variables with their distribution patterns and confidence factors (CF) were considered: ϕ_0: uniform distribution, 0 to 1; k_{deg}: lognormal distribution; CF = 3 (Wania and Dugani, 2003).)

2) For the second question, in our study, only the gaseous degradation related to the reaction with hydroxyl radicals was considered. Actually, in real atmosphere, other gaseous degradation routes (like the other atmospheric oxidation pathways and photodegradation) also exist. Therefore, the second description of gaseous degradation was removed for better understanding in the revised manuscript.

Related references:

Wania, F. and Dugani, C. B.: Assessing the long-range transport potential of polybrominated diphenyl ethers: a comparison of four multimedia models, Environ. Toxicol. Chem., 22, 1252-1261, https://doi.org/10.1002/etc.5620220610, 2003.

(9) Fig. 4, the title of Y-axis is not clear.

RE: Thanks for the suggestion. The Fig. 4 was revised as follows in the revised manuscript:
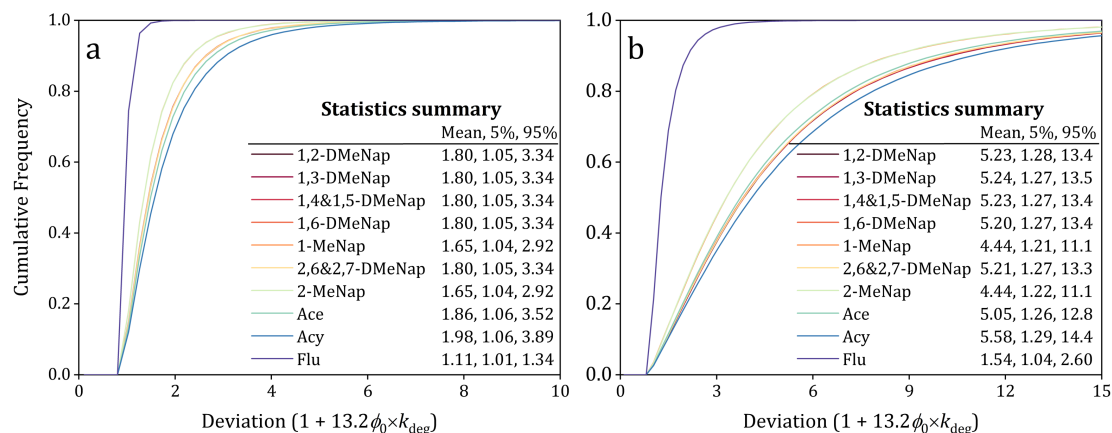

Fig. 4. The impact of the gaseous degradation on K_P' deviation from the equilibrium state estimated based on the Monte Carlo Analysis at −50℃ (a) and 50℃ (b). (Note: The following variables with their distribution patterns and confidence factors (CF) were considered: ϕ_0: uniform distribution, 0 to 1; k_{deg}: lognormal distribution; CF = 3 (Wania and Dugani, 2003).)

Related references:

Wania, F. and Dugani, C. B.: Assessing the long-range transport potential of polybrominated diphenyl ethers: a comparison of four multimedia models, Environ. Toxicol. Chem., 22, 1252-1261, https://doi.org/10.1002/etc.5620220610, 2003.

(10) This kind of writing was confused for reading: in the range of 0.429 to 0.887 (K_P': 2.68 to 7.70 times increased). Pleased modify the writing for the similar problem through the manuscript.

RE: Thanks for the suggestion.

The sentence was revised as follows: "The deviation of K_P' caused by the influence of the soot phase within the particles was in the range of 2.68 to 7.70 times". In addition, all the related sentences were revised in the manuscript.