The impact of gaseous degradation on the ~~equilibrium state of~~ gas~~/~~-particle partitioning of methylated polycyclic aromatic hydrocarbons~~semi-volatile organic compounds~~

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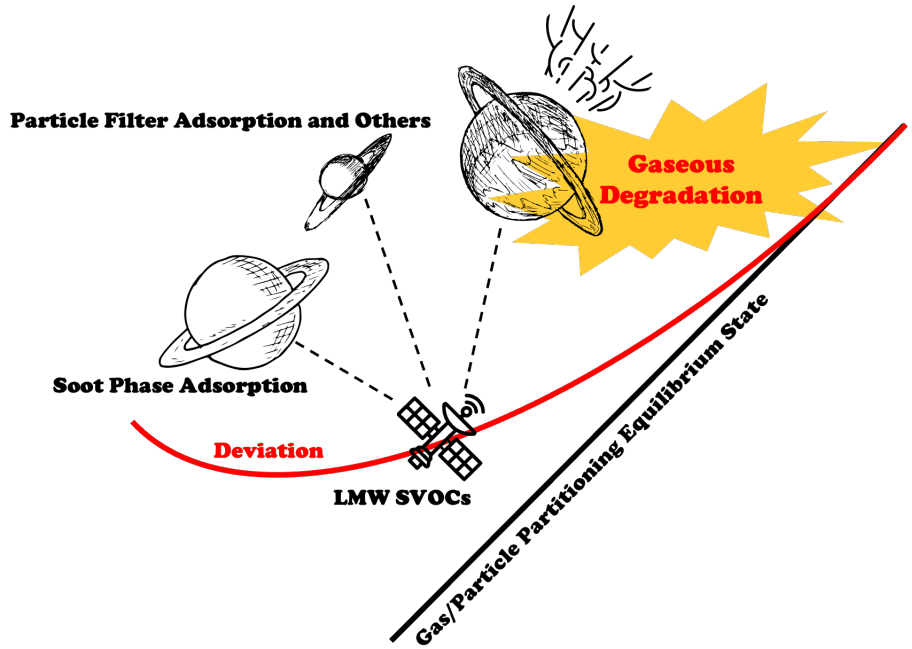
Abstract

The partitioning of semi-volatile organic compounds (SVOCs) between gas and particle phases plays a crucial role in their long-range transport and health risk assessment. However, the accurate predicting of the gas–particle (G–P) partitioning quotient (K_P') remains a challenge, especially for the light molecular weight (LMW) SVOCs due to their upward deviation from the equilibrium state. In this study, the phenomenon with the influence of gaseous degradation on G–P partitioning was observed. Based on the diurnal study of concentrations and K_P' values for methylated polycyclic aromatic hydrocarbons (Me-PAHs), it was found that the K_P' values of methylated naphthalenes (Me-Naps, one type of LMW SVOCs) during daytime were higher than that during nighttime, and the regression lines of log K_P' versus log K_{OA} (octanol-air partitioning coefficient) for daytime and nighttime were non-overlap, which were different with other Me-PAHs. Compared with other diurnal influencing factors, the higher gaseous degradation of Me-Naps in the daytime than that in the nighttime should partially explain their special diurnal variation of K_P', which provided a new explanation for the non-equilibrium behavior of K_P' of LMW SVOCs. Moreover, the influence of gaseous degradation on the deviation of K_P' from the equilibrium state was deeply studied based on a steady-state G–P partitioning model that considering particulate proportion in emission (ϕ_0). The increasing times of K_P' influenced by the gaseous degradation deviated from the equilibrium state can be calculated by $1 + 13.2\phi_0 \times k_{deg}$ (gaseous degradation rate). The K_P' increase along with the increasing of k_{deg}

proved that higher gaseous degradation in the daytime could increase K_P' value. ~~It was found that the deviation occurred when $\phi_0 F_{GR}$ (F_{GR}, degradation flux of gas phase) cannot be ignored when compared with F_{GP} (flux from gas phase to particle phase). It can be concluded that the deviation was not only related to the gaseous degradation rate (k_{deg}), but also related to ϕ_0.~~ Furthermore, an amplification of K_P' ranging from 1.10 to ~~8.4~~5.58 times (90% confidence interval: 1.01 to 14.4) under different ϕ_0 (0 to 1) in the temperature range of −50 to 50℃ was ~~estimated based on the individual degradation rates of Me-Naps and three LMW PAHs~~estimated by the Monte Carlo ~~a~~Analysis. In summary, it can be concluded that the influence of gaseous degradation should also be considered for the ~~G/P~~G–P partitioning models of SVOCs, especially for the LMW SVOCs, which provided new insights into the related fields.

Keywords: Equilibrium state; Upward deviation; Light molecular weight SVOCs; Diurnal variation; Methylated polycyclic aromatic hydrocarbons

55 **Graphic abstract**



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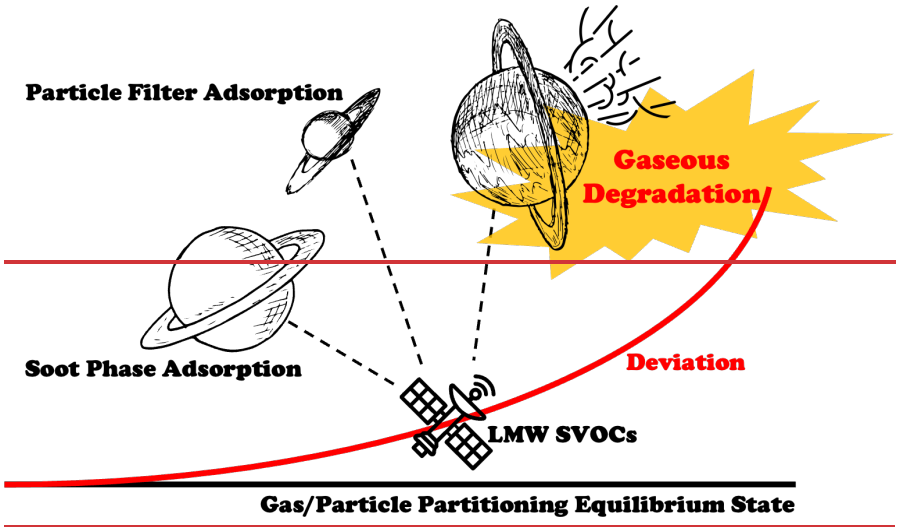

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1. Introduction

The partitioning of semi-volatile organic compounds (SVOCs) between gas and particle phases, known as gas–particle (G–P) partitioning, is a crucial process for their long-range atmospheric transport (Li et al., 2020; Zhu et al., 2021b) and their entry pathway into the human body (Hu et al., 2021). To investigate the G–P partitioning mechanism of SVOCs, researchers have widely employed the correlation between the G–P partitioning coefficient (K_P) at equilibrium state and the octanol-air partition coefficient (K_{OA}) (Ma et al., 2019; Harner and Bidleman, 1998). The prediction of K_P based on K_{OA} was conducted in previous studies, which deduced some G–P partitioning models (Qiao et al., 2020). The Harner-Bidleman (H-B) model (Harner and Bidleman, 1998) and the Dachs-Eisenreich (D-E) model (Dachs and Eisenreich, 2000) were successfully applied in the prediction of K_P for different SVOCs using the equilibrium-state theory (Wang et al., 2011; Sadiki and Poissant, 2008). In addition, the Li-Ma-Yang (L-M-Y) model (Li et al., 2015) was established based on the steady-state theory, which exhibited good performance for predicting the G–P partitioning quotient (K_P') at steady state, particularly for high molecular weight (HMW) SVOCs (Qiao et al., 2020; Li et al., 2017; Hu et al., 2020).

Previous studies had found that the K_P' deviated from the equilibrium state for both HMW SVOCs (i.e., high log K_{OA} value) (Li et al., 2015; Li and Jia, 2014) and light molecular weight (LMW) SVOCs (Ma et al., 2020; Dachs and Eisenreich, 2000). For the HMW SVOCs, the particulate SVOCs were either deposited or removed through dry and wet depositions of particles before reaching equilibrium state, as demonstrated by both the theoretical study (L-M-Y model) and the monitoring study (Mackay et al., 2019; Li et al., 2015), which can be used to explain the deviation. For the LMW SVOCs, the K_P' deviated upward from the equilibrium state,

~~that~~and the deviation could be multiple orders of magnitude, such as LMW polycyclic aromatic hydrocarbons (PAHs) (Ma et al., 2020; Ma et al., 2019). Several explanations have been proposed for this deviation. First, the artifacts resulting from the adsorption of gaseous PAHs onto particle filters during atmospheric sampling can increase K_P' values (Zhang and Mcmurry, 1991; Hart et al., 1992; Hart and Pankow, 1994). In an early study, the double filters sampling method demonstrated that gas adsorption onto filters would cause an overestimation of K_P' by a factor of 1.2 to 1.6 times (Hart and Pankow, 1994). However, the overestimation is much lower than the deviation ~~observed in the monitoring data~~with multiple orders of magnitude. Second, the enhanced adsorption of gaseous SVOCs onto various phases (e.g., soot phase and inorganic phases) within particles has been extensively documented (Shahpoury et al., 2016; Dachs and Eisenreich, 2000). Some ~~G/P~~G–P partitioning models were established with the consideration of the enhanced adsorption, such as the D-E model and the poly-parameter linear free energy relationships (pp-LFER) model (Shahpoury et al., 2016; Dachs and Eisenreich, 2000). However, these models ~~still~~ cannot fully explain the deviation from the equilibrium state for the LMW SVOCs, such as some LMW PAHs (acenaphthylene (Acy), acenaphthene (Ace), and fluorene (Flu)) (Ma et al., 2020).

A recent study delved into the non-equilibrium interplay of ~~G/P~~G–P partitioning resulting from chemical reactions of SVOCs (Wilson et al., 2020). The study found that when the chemical loss of SVOCs in the gas or particle phase exceeded the replenishment from the particle or gas phase, the K_P' values could deviate from the equilibrium state (Wilson et al., 2020). According to the findings, the upward deviation of LMW SVOCs from the equilibrium state might be caused by the faster chemical loss of SVOCs in the gas phase than the replenishment from the particle phase. However,

109 further studies are required to confirm this hypothesis. Our previous study provided
110 new insights into the deviation from the equilibrium state for several LMW PAHs by
111 studying the diurnal variation of K_P' values (Zhu et al., 2022). The study found that the
112 K_P' values for the three LMW PAHs (Acy, Ace, and Flu) were higher in the daytime
113 than those in the nighttime (Zhu et al., 2022). In addition, the chemical reactions of
114 SVOCs were different between the daytime and nighttime (Ohura et al., 2013).
115 Therefore, the study on the diurnal variation of ~~G/P~~G–P partitioning between the
116 daytime and nighttime can be considered as a special case for deep understanding the
117 deviation of LMW SVOCs from the equilibrium state.

118 In order to comprehensively investigate the deviation of the K_P' value from the
119 equilibrium state for LMW SVOCs, the diurnal variation of concentrations and K_P'
120 values for methylated PAHs (Me-PAHs) was conducted in this study. Furthermore, the
121 influence of the gaseous degradation on the deviation of K_P' from the equilibrium state
122 was quantified based on the theoretical model for both LMW Me-PAHs and PAHs,
123 which provided new insights into the ~~G/P~~G–P partitioning of SVOCs.

124

125 **2. Materials and methods**

126 **2.1. Sampling method**

127 The detailed information for the sampling method and site can be found in our
128 previous study (Zhu et al., 2022; Zhu et al., 2021a). In brief, the sampling program was
129 conducted at an urban location on the rooftop of a 14-meter-high building in Harbin
130 City in northeastern China. Harbin City has an obvious seasonal variation, with the
131 heating season from 20th October to 20th April and the non-heating season from 20th
132 April to 20th October. A total of 32 pairs of air samples during daytime (9:00 a.m. to
133 5:00 p.m.) and nighttime (9:00 p.m. to 5:00 a.m.) were collected every 10 days from

December 2017 to November 2018, which minimized the impact of heavy traffic. The glass fiber filters (GFFs) and polyurethane foam plugs (PUFs) were used to collect particulate and gaseous samples, respectively, using a high-volume air sampler (TE-1000, Tisch Environmental, Ohio, USA) with an air flow rate of 0.24 std m^3/min. The GFFs and PUFs were carefully sealed and stored in a refrigerator at −20℃ prior to treatment.

2.2. Analysis procedure of Me-PAHs

The analysis procedure for Me-PAHs was identical to that of PAHs (Zhu et al., 2022; Zhu et al., 2021a). In brief, the Soxhlet extraction and active silica gel column were used to extract and purify the GFFs and PUFs samples. Prior to extraction, four surrogates (naphthalene-D8, fluorene-D10, pyrene-D10, and perylene-D12) were added to all samples. The extractions were then solvent-exchanged into isooctane, concentrated to 1 mL in GC vials with 200 ng quantitation standard (phenanthrene-D10). A total of 49 Me-PAHs were analyzed by an Agilent 7890B gas chromatograph coupled with an Agilent 5977 mass spectrometer detector, with the electron-impact ionization and selected ion monitoring mode. Chromatographic resolution was achieved with a DB-5 MS capillary chromatographic column (60 m × 0.25 mm i.d. × 0.25 μm film thickness, J&W Scientific). Ultrapure helium gas (>99.9999%) was used as the carrier gas at a constant flow rate of 1 mL/min. An aliquot (2 μL) of the sample was injected into the multi-mode inlet of the GC/MS at 280ºC via the pulsed splitless mode. The column-oven temperature program was as follows: hold at 100ºC for 1 min, ramp to 200℃ at 40℃ /min, hold for 13 min, ramp to 300℃ at 80℃ /min, hold for 22 min, ramp to 310℃ at 50℃ /min, hold for 11 min with the post run of 310℃, hold for 3 min. The transfer line temperature was maintained at 280 ℃. For the mass

spectrometer, the MS source and quadrupole temperatures were set at 230℃ and 150℃, respectively. Detailed information and mass spectrometry parameters for the 49 Me-PAHs are summarized in **Table S1, supporting information (SI)**. A representative chromatogram is depicted in **Fig. S1, SI**.

2.3. Quality assurance/quality control

In order to minimize the errors, rigorous quality assurance/quality control procedures were implemented in the present study. Prior to sampling, GFFs were subjected to a cleaning process involving baking at 450℃ for 6 hours, while PUFs were extracted via Soxhlet extraction using dichloromethane for 24 hours and hexane for an additional 24 hours. All glassware utilized in the experimental process was cleaned with dichloromethane and hexane prior to use. Field blanks were conducted on a monthly basis, and laboratory blanks were added for every 11 samples. The quantitation standard was utilized to correct fluctuations of the corresponding instrument signal. The average recoveries of the four surrogates ranged from 70% to 110% for all samples, which were deemed acceptable for the utilization of concentration data without correction via surrogate recoveries. The instrument detection limit (IDL) was calculated as three times of the signal to noise, with IDLs for all Me-PAHs ranging from 0.0154 ng to 0.951 ng (**Table S1, SI**), utilizing a constant injection volume of 2 μL. Concentrations below IDLs were excluded from further calculations. The recoveries of all Me-PAHs with spiked blank samples ranged from 94% to 107%. The final reported concentrations were corrected by the blanks, but not corrected with recoveries of spiked blank samples and surrogates. A five-point calibration curve was established using concentrations of 5, 10, 50, 100, and 500 ng/mL, with a correlation coefficient (r^2) exceeding 0.99.

2.4. ~~G/P~~G–P partitioning quotient

The K_P' ($m^3/\mu g$) was calculated based on the following equation:

$$K_{P}' = C_{P}/(C_{G} \times TSP) \quad (1)$$

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

In general, the value of log K_{OA} can be calculated using the following equation:

$$\log K_{OA} = A + B/T \quad (2)$$

where, T is the ambient temperature (K); A and B are constants.

For most Me-PAHs, the values of A and B were estimated through the utilization of the pp-LFER equation, which relied on the solute descriptors obtained from the UFZ-LSER database (Baskaran et al., 2021; Ulrich et al., 2017). The calculation methods and corresponding parameters have been concisely summarized in **Tables S2 and S3, SI**. By utilizing the values of A and B, the value of K_{OA} for Me-PAHs can be obtained by Eq. (2) at any temperature.

2.5. Data analysis method

The statistical analysis was conducted using the SPSS Software (Version 24.0). Prior to analysis, the normal distribution test was performed via the One-Sample Kolmogorov-Smirnov Test. The Paired Sample t-test was utilized for difference analysis in datasets exhibiting normal distribution, while the Wilcoxon Signed Rank Test was employed for the non-normal distribution datasets. Results were considered as statistically significant if the p-value was less than 0.05.

3. Results and discussion

3.1. Diurnal variation of concentration

Among the 49 Me-PAHs, 30 Me-PAHs were frequently detected with detection rates exceeding 30% (**Table S1, SI**), ~~which~~and they were considered for further

discussion. As depicted in **Fig. 1a**, the total concentrations of 30 Me-PAHs (ΣMe-PAHs) in total phase (particle phase + gas phase) were compared between daytime and nighttime in different seasons. A clear diurnal variation with higher concentrations of Me-PAHs during nighttime as compared to daytime was observed. The geometric mean (GM) concentrations (range of 25th% to 75th%) of ΣMe-PAHs were 12.0 ng/m^3 (4.51 to 34.6 ng/m^3) and 23.6 ng/m^3 (7.97 to 69.9 ng/m^3) in daytime and nighttime, respectively. ~~These concentrations were comparable with those in air of urban (mean, 29.8 ng/m^3) and semi-urban areas (mean, 23.0 ng/m^3) in Toronto City, Canada (Moradi et al., 2022).~~ Furthermore, the concentrations of ΣMe-PAHs in total phase during nighttime were significantly higher than those during daytime ($p < 0.05$), with the GM value of nighttime/daytime (N/D) ratios of 1.97 for the whole sampling period. Although studies on the diurnal variation of Me-PAHs are limited, similar diurnal variations have also been observed in some previous studies for other PAHs, such as PAHs, chlorinated-PAHs, nitrated~~nitro~~-PAHs, and oxygenated~~oxy~~-PAHs (Cao et al., 2018; Ohura et al., 2013; Zhang et al., 2018; Zhu et al., 2022). It was found that the diurnal variations of emission sources, emission intensity, atmospheric reactions, and meteorological effects were responsible for the diurnal variation of SVOCs concentrations (Ohura et al., 2013; Zhang et al., 2018).

Moreover, it is noteworthy that distinctly diurnal variations were observed among different phases (gas and particle) and different seasons (heating and non-heating) (**Fig. 1b and Fig. 1c**). Notably, a significant increase of ~~nighttime~~ concentrations during nighttime compared to that during daytime was observed for the gas phase ($p < 0.01$), while no significant diurnal variation was observed for the particle phase in all seasons and in heating season. Additionally, the N/D ratios were higher in the non-heating season compared to the heating season. For instance, in the non-heating season, the GM

N/D ratios were 2.14 and 2.15 for the total and gas phases, respectively. However, in the heating season, the GM N/D ratios were 1.80 and 1.96 for the total and gas phases, respectively. These findings suggested that gaseous Me-PAHs exhibited more obviously diurnal variation than particulate Me-PAHs, and Me-PAHs in the non-heating season displayed more prominent diurnal variation than that in the heating season.

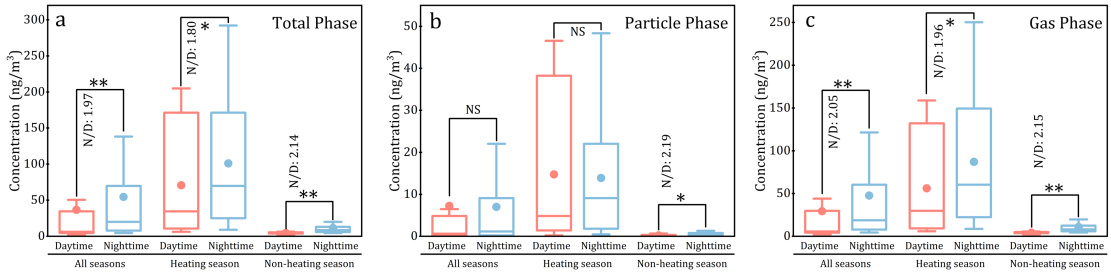


Fig. 1. Comparison with the concentrations of the ΣMe-PAHs between daytime and nighttime in different seasons for different phases (Note: * and ** represent that the differences are significant at 0.05 level and 0.01 level, respectively; NS represents no significant difference; N/D represents the geometric mean value of nighttime/daytime ratio for concentration.)

Furthermore, it is interesting to note that individual Me-PAHs also exhibited different diurnal variations. The N/D ratios, and the GM values of N/D ratios for individual Me-PAHs are presented in **Table S4 and Fig. S2, SI**. The GM values of N/D ratios varied considerably among different Me-PAHs, ranging from 0.347 to 7.30. Regarding to the seasonal differences in diurnal variation (**Table S4, SI**), the results for most individual Me-PAHs were consistent with those for ΣMe-PAHs, with higher GM values of N/D ratios in the non-heating season than the heating season. With respect to the phase differences in diurnal variation (**Table S4 and Fig. S2, SI**), the GM values of N/D ratios in the gas phase for Me-naphthalenes (Me-Naps, one type of LMW SVOCs) were ~~significantly~~ higher than those in the particle phase for individual Me-Naps in all seasons. This result with Me-Naps was consistent with that of ΣMe-PAHs, which could be attributed to the high contribution of Me-Naps to ΣMe-PAHs (mean value: 63%).

However, for other Me-PAHs (**Table S4 and Fig. S2, SI**), the N/D ratios in the particle phase were similar or even a little higher than those in the gas phase.

3.2. Diurnal variation of ~~G/P~~G–P partitioning

In general, the different diurnal variations with the concentrations of SVOCs between the gas phase and particle phase could cause the diurnal variations of K_P' values. As depicted in **Fig. 2**, compared with other Me-PAHs, several LMW Me-PAHs (such as Me-Naps) exhibited significantly higher log K_P' values in the daytime compared to the nighttime ($p < 0.05$). However, the other Me-PAHs, like 3-MeBcP, 5&6&4-MeChr, and 3&5-MeBaA, had higher log K_P' values in the nighttime than those in the daytime ($p < 0.05$). The special diurnal variations of the log K_P' of ~~these~~ Me-Naps can be attributed to the different diurnal variations of their concentrations between the two phases. For example, the N/D ratios of concentrations in the gas phase were significantly higher than those in the particle phase for Me-Naps, which was different from other Me-PAHs (**Fig. S2, SI**).

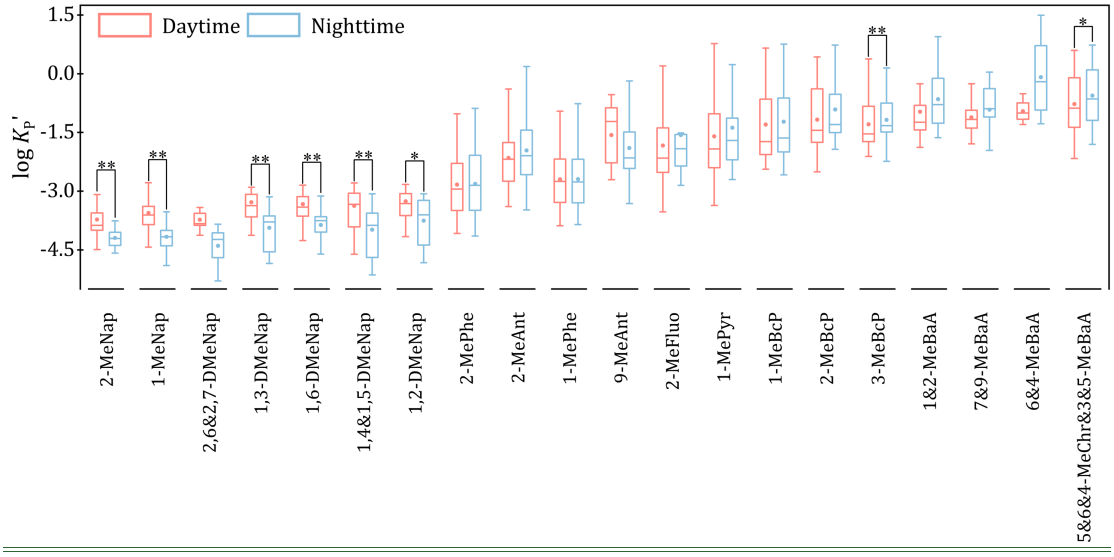


Fig. 2. Comparison of the values of log K_P' for individual Me-PAHs between daytime and nighttime (Note: * and ** represent that the differences are significant at 0.05 and 0.01 level, respectively.)

In order to deeply investigate the diurnal variations of ~~G/P~~G–P partitioning quotient, the regression lines of log K_P' against log K_{OA} were compared between daytime and nighttime. In general, the diurnal variations were also observed for the relationships between log K_P' and log K_{OA} for Me-Naps. Interestingly, for these Me-Naps, the regression lines also had obvious diurnal variations as being higher during daytime compared to nighttime (**Fig. 3**). In contrast, no significant differences were observed in the regression lines for the total Me-PAHs (**Fig. S3, SI**) and other individual Me-PAHs (**Fig. S4, SI**) between daytime and nighttime. Given the lower ambient temperatures during nighttime, higher K_P' values during nighttime compared to daytime and the overlap of the two regression lines between daytime and nighttime were expected, just like the total Me-PAHs (**Fig. S3, SI**) and other individual Me-PAHs (**Fig. S4, SI**). However, the different phenomenon with the regression lines of log K_P' against log K_{OA} was observed for Me-Naps (**Fig. 3**).

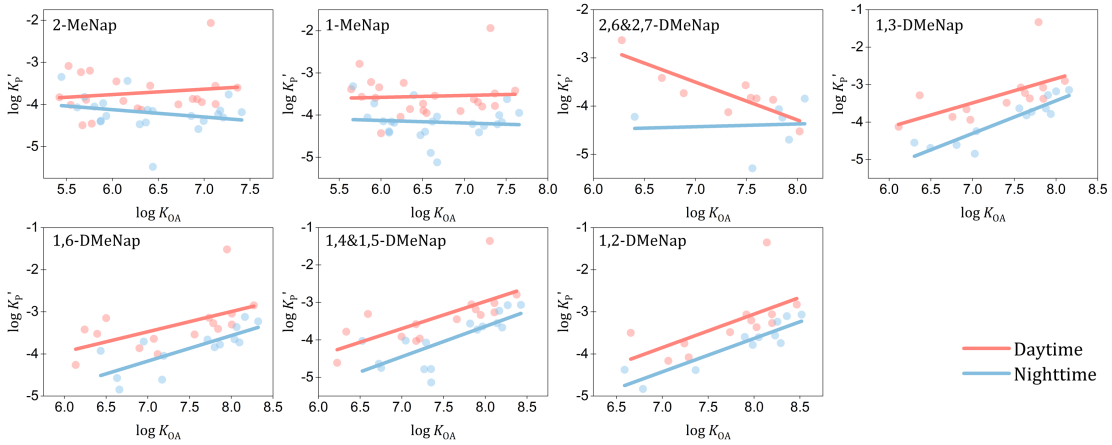


Fig. 3. The regression lines of log K_P' against log K_{OA} between daytime and nighttime for Me-Naps

The specific relationships with concentrations between daytime and nighttime~~K_P' and concentrations~~ for these Me-Naps can be elucidated by the following equations~~s~~:

$$C_{P,N}/C_{P,D} < C_{G,N}/C_{G,D} \rightarrow C_{P,N}/C_{G,N} < C_{P,D}/C_{G,D} \quad (3)$$

where, ~~N/D_P and N/D_G are the N/D ratios of particle phase and gas phase, respectively;~~ $C_{P,N}$ 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.

In addition, no significant difference was observed for *TSP* concentrations between daytime and nighttime (GM: 94.5 μg/m^3 in the daytime and 90.5 μg/m^3 in the nighttime). Therefore, the following relationship can be derived:

$$C_{P,N}/C_{G,N}/TSP_N < C_{P,D}/C_{G,D}/TSP_D \rightarrow K'_{P,N} < K'_{P,D} \quad (4)$$

where, TSP_N and TSP_D are the *TSP* concentrations during nighttime and daytime, respectively; $K'_{P,N}$ and $K'_{P,D}$ are the K_P' values during nighttime and daytime, respectively.

When Eqs. (3), ~~(4),~~ and (4) were considered together, ~~therefore,~~ it can be found that the higher N/D ratios of concentrations in the gas phase than those in the particle phase could caused ~~the~~ higher K'_P values during daytime than those during nighttime. Therefore, the higher log K_P' values in the daytime than the nighttime for Me-Naps (**Fig. 2**) can be explained by the findings with the values of N/D ratios between particle phase and gas phase (**Fig. S2 in SI**). The clarification of the influence factors in the special diurnal variation of the concentrations of these Me-Naps, would help to understand the diurnal variation of G–P partitioning of LMW SVOCs.

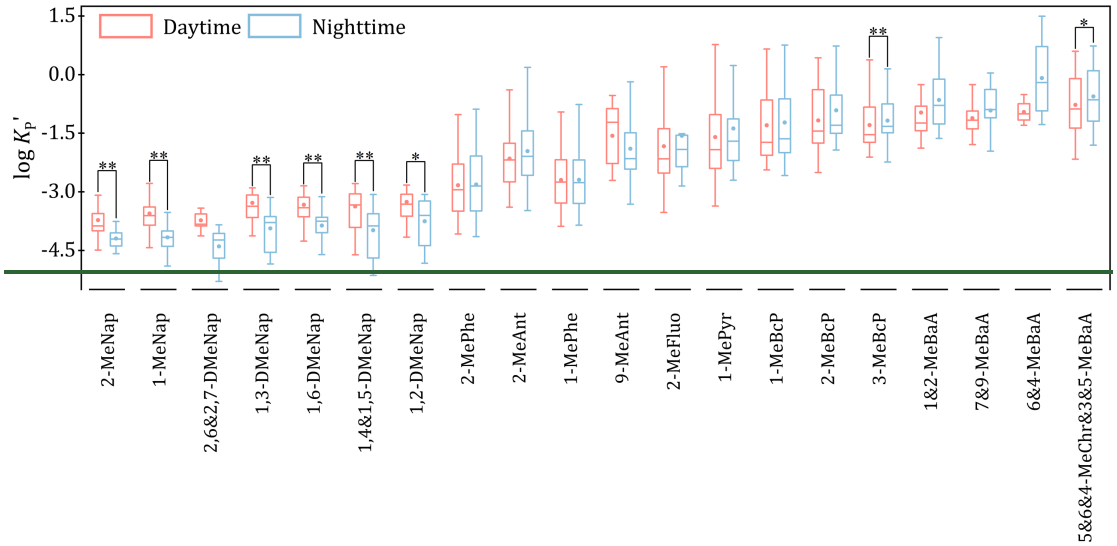


Fig. 2. Comparison of the values of log K_P' for individual Me-PAHs between daytime and nighttime (Note: * and ** represent that the differences are significant at 0.05 and 0.01 level, respectively.)

In order to deeply investigate the diurnal variations of G/P partitioning, the regression lines of log K_P' against log K_{OA} were compared between daytime and nighttime. In general, diurnal variations were also observed for the relationships between log K_P' and log K_{OA} for Me-Naps. Interestingly, for these Me-Naps, the regression lines also had obvious diurnal variations as being higher during daytime compared to nighttime (**Fig. 3**). In contrast, no significant differences were observed in the regression lines for the total Me-PAHs (**Fig. S3, SI**) and other individual Me-PAHs (**Fig. S4, SI**) between daytime and nighttime. Given the lower ambient temperatures during nighttime, higher K_P' values compared to daytime and the overlap of the two regression lines between daytime and nighttime were expected, just like the total Me-PAHs (**Fig. S3, SI**) and other individual Me-PAHs (**Fig. S4, SI**). However, the different phenomenon was observed for Me-Naps (**Fig. 3**). These findings suggested that the diurnal variations of G/P partitioning for Me-Naps may be also influenced by other environmental parameters beyond ambient temperature.

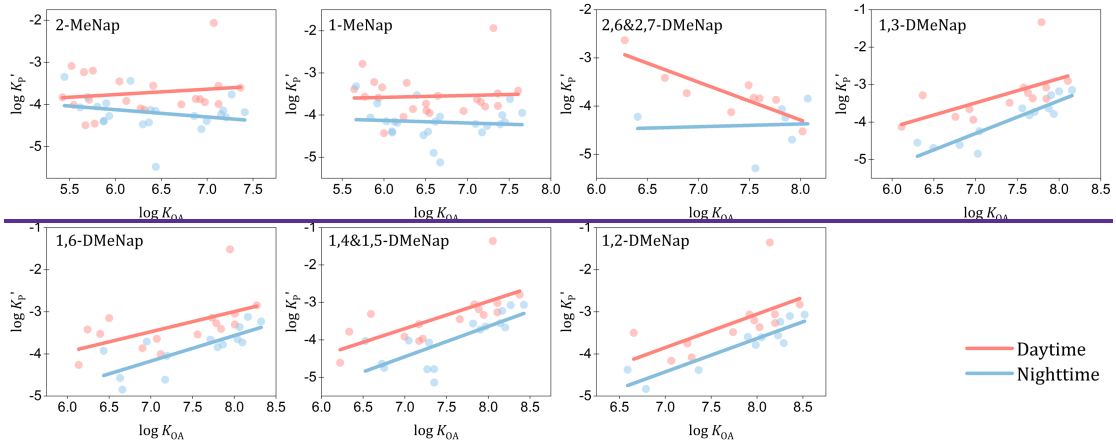


Fig. 3. The regression lines of log K_P' against log K_{OA} between daytime and nighttime for Me-NapsAs noted in previous studies, the concentrations of SVOCs are influenced by emission intensity, atmospheric reactions, and meteorological effects (Ohura et al., 2013; Zhang et al., 2018)(Ohura et al., 2013; Zhang et al., 2018). In general, emission intensity can impact the concentration of SVOCs in the total phase (gas phase plus particle phase), while they cannot affect the distribution between the two phases when the steady state has been reached. In other words, this factor cannot cause the diurnal variation of the G/PG–P partitioning for Me-Naps. Among meteorological parameters, temperature is the key factor on the G/PG–P partitioning of SVOCs, which could result in the higher K_P' values during nighttime than those during daytime. However, the opposite results were observed for Me-Naps in this study, which suggested the influences of other factors. As mentioned in previous studies, the higher atmospheric reactions in the daytime resulted in the lower concentrations of SVOCs in the daytime than those in the nighttime (Ohura et al., 2013; Reisen and Arey, 2005)(Ohura et al., 2013; Reisen and Arey, 2005), which might also be responsible for the special diurnal variations of the K_P' values of Me-Naps. Previous studies also suggested that when the rate of chemical loss is faster than the process of G/PG–P partitioning (or the degradation in the gas phase exceeded the replenishment from the particle phase), the G/PG–P partitioning maybe deviate from the equilibrium state

(Wilson et al., 2020)~~20)~~. In addition, the value of K_P' increased along with the increase of the chemical loss rate (Wilson et al., 2020). Therefore, it can be concluded that the higher gaseous degradation during daytime than that during nighttime might result in higher K_P' values during daytime. The observation of the higher K_P' for these Me-Naps in the daytime than those in the nighttime provided the new insight into the deviation of K_P' from the equilibrium state for LMW SVOCs.

3.3. Influence of gaseous degradation on K_P' of LMW SVOCs

~~**3.3. Influence of gaseous degradation on the deviation of LMW SVOCs from equilibrium state**~~

~~As noted in previous studies, the diurnal variations of SVOCs concentrations are influenced by emission intensity, atmospheric reactions, and meteorological effects (Ohura et al., 2013; Zhang et al., 2018). In general, emission intensity can impact the concentration of SVOCs in the total phase (gas phase plus particle phase), while they cannot affect the distribution between the two phases when the steady state has been reached. In other words, this factor cannot cause the diurnal variation of the G/P partitioning for Me-Naps. Among meteorological parameters, temperature is the key factor on the G/P partitioning of SVOCs, which could result in the higher K_P' values during nighttime than those during daytime. However, the opposite results were observed for Me-Naps in this study, which suggested the influences of other factors. Therefore, tAs mentioned in previous studies, the atmospheric reactions was responsible for the er concentrations of SVOCs in the ime than those in the time (Ohura et al., 2013; Reisen and Arey, 2005), which might also be responsible for the diurnal variations of the K_P' values of Me-Naps (Ohura et al., 2013; Reisen and Arey, 2005). Previous studies have also suggested that when the rate of chemical loss is faster than the process of G/P partitioning (or the degradation in the gas phase exceeded the~~

~~replenishment from the particle phase), the G/P partitioning maybe deviate from the equilibrium state (Wilson et al., 2020). In addition, the value of K_P' increased along with the increase of the chemical loss rate (Wilson et al., 2020). Therefore, it can be concluded that the higher gaseous degradation during daytime than that during nighttime, might result in the higher K_P' values during daytime than that during nighttime.~~ ~~In the above section, it was found that the higher gaseous degradation during daytime than that during nighttime might result in the higher K_P' values during daytime than that during nighttime.~~ ~~Furthermore~~Therefore, ~~we can deduce that the gaseous degradation might result in the upward deviation of K_P' from equilibrium state.~~ ~~Here~~In this section, the ~~fugacity model~~new steady-state G–P partitioning model (Zhu et al., 2023) was applied for better understanding the impact of gaseous degradation on the deviation of K_P' from equilibrium state. Based on the model, for the LMW SVOCs, the K_P' values can be obtained using the following simplified equation, and more detailed information about the equation were presented in **Text S1, SI**~~)~~:

~~$$\log K_P' = \log K_{P\text{-}HB} + \log\left(f_P/f_G\right) \quad (65)$$~~

~~where, $K_{P\text{-}HB}$ represents the predicted G/P partitioning coefficient from the H-B model (the equilibrium state model, $\log K_{P\text{-}HB} = \log K_{OA} + \log f_{OM} = 11.91$, f_{OM} is the fraction of the organic matters in particles) (Harner and Bidleman, 1998); f_P is the fugacity for particle phase; and f_G is the fugacity for gas phase.~~

~~According to the Eq. (65), K_P' will upward deviate from $K_{P\text{-}HB}$ (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. (76), when the steady state is reached between gas phase and particle phase:~~

~~$$\frac{f_P}{f_G} = \frac{D_{GP} + \phi_0 D_{GR}}{D_{GP} + (1-\phi_0)(D_{PD} + D_{PW})} \quad (76)$$~~

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, SI**) can be ignored , then the Eq. (76) can be expressed as follows:

$$\frac{f_P}{f_G} = 1 + \frac{\phi_0 D_{GR}}{D_{GP}} \quad (87)$$

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.

By simplifying the Eq. (76) and adding to Eq. (56), the new steady-state G/P partitioning model can be obtained (Zhu et al., 2023):

$$\log K'_{P-NS} = \log K_{P-HB} + \log(1 + 13.2\phi_0 \times k_{deg}) \quad (985)$$

where, $K'_{P\text{-}NS}$ is the predicted G/PG–P partitioning quotient of the new steady-state G/PG–P partitioning model; $K_{P\text{-}HB}$ is the G–P partitioning coefficient calculated from the H-B model (the equilibrium-state model, $\log K_{P\text{-}HB} = \log K_{OA} + \log f_{OM} - 11.91$, f_{OM} is the organic matters in the particles) (Harner and Bidleman, 1998); ϕ_0 is the particulate proportion of SVOCs in emission; k_{deg} is the degradation rate of SVOCs in gas phase (h^{-1}).

Based on Eq. (985), 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 nighttimevalues of K_P'. Therefore, the application of Eq. (5) can demonstrate that

the gaseous degradation of Me-Naps could be ~~the~~ part of reason for the higher K_P' in the daytime than that in the nighttime.

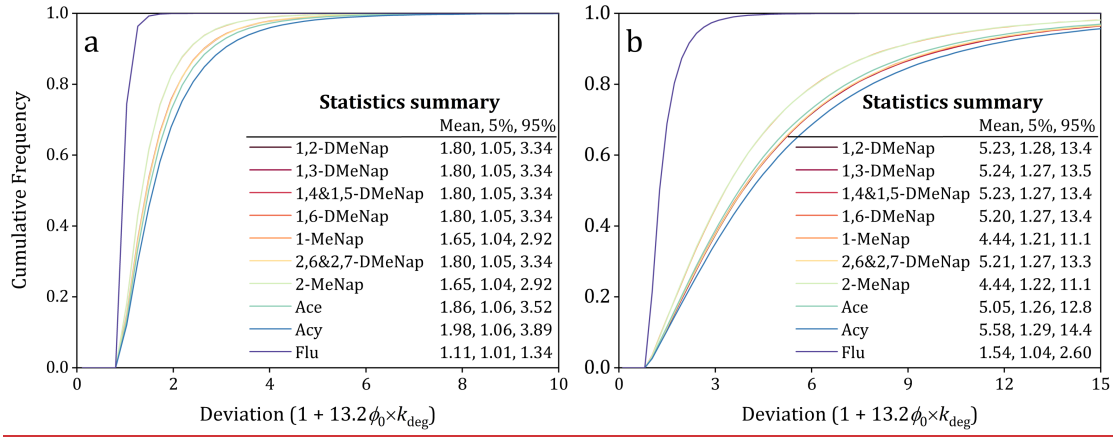
~~The exact the influence of gaseous degradation on G/P partitioning for LMW SVOCs can be comprehensively studied by~~Based on the new steady-state G/P partitioning model (Eq. (8)). ~~Therefore, it can be concluded that the deviation~~ with K_P' ~~from the equilibrium state for LMW SVOCs can be expressed as log $(1 + 13.2\phi_0 \times k_{deg})$, which was related to k_{deg} and ϕ_0. The impact from gaseous degradation on G/P partitioning was quantified using the theoretical method (Eq. (9)).~~ Furthermore, the deviation with K_P' from the equilibrium state (log $K_{P\text{-}HB}$) caused by the gaseous degradation for LMW SVOCs can be estimated using the equation of log $(1 + 13.2\phi_0 \times k_{deg})$, which was related to k_{deg} and ϕ_0. The k_{deg} values under 25℃ for the Me-Naps and the three LMW PAHs (Acy, Ace, and Flu) were calculated using their half-lives from the Estimation Programs Interface (EPI) Suite (**Table S5, SI**). Then, the k_{deg} values under different temperature (−50 ~~to~~ and 50℃) were calculated using the following equation:

$$k_{deg\_T} = k_{deg\_0} \exp\left(\frac{E_{aA}}{R\left(\frac{1}{T_0} - \frac{1}{T}\right)}\right) \quad (~~10~~96)$$

where, k_{deg_T} is the k_{deg} value at temperature T; k_{deg_0} is the k_{deg} value at 25℃; E_{aA} is the activation energy in air (J/mol); R is the universal gas constant (8.314 J·K/mol); T and T_0 (25℃) are temperature (K). The minimum and maximum k_{deg} values for these PAHs under ~~the~~ different temperature ~~range of −50 to 50℃~~ were summarized in **Table S5, SI**.

The increasing times of K_P' ~~values~~ 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. ~~Considering the influence of ϕ_0 on the gaseous degradation, the minimum impact of k_{deg} on K_P' deviation occurred when ϕ_0 was set to 0. On the other hand, the maximum impact of k_{deg} on K_P' deviation was observed when ϕ_0 was set to 1.~~ 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 ~~was~~ 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℃ and 50℃, 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. ~~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.~~



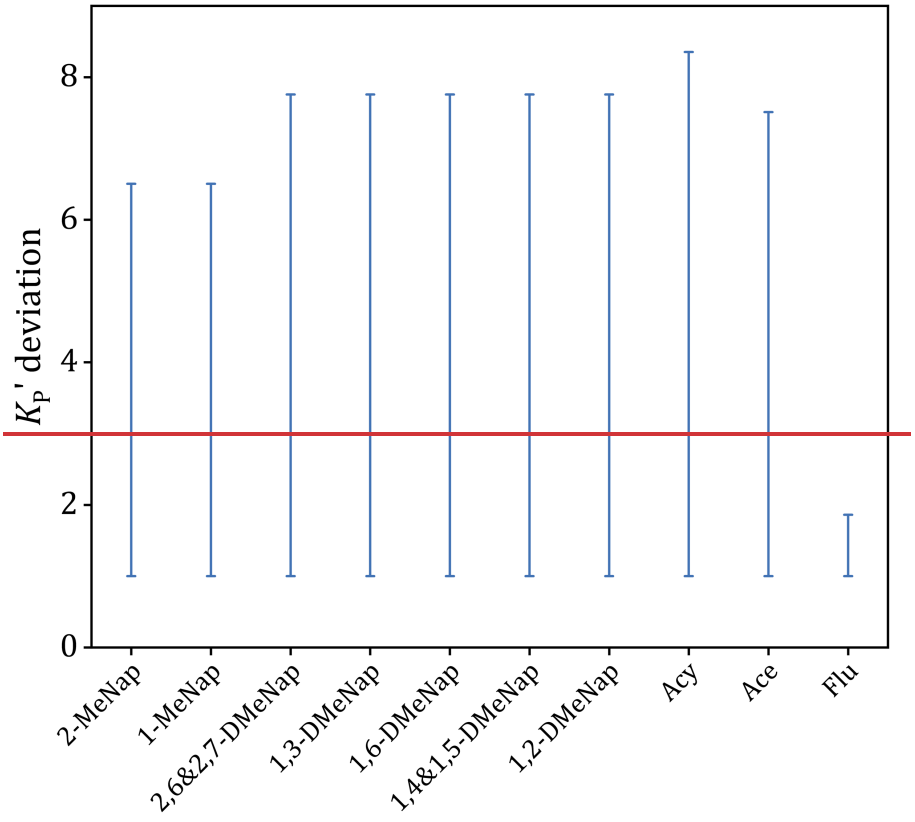


Fig. 4. The impact of the gaseous degradation on ~~the time of deviation of~~ K_P' deviat~~ed~~ion from the equilibrium state ~~calculated~~ estimated based on the Monte Carlo Analysis at ~~condition of~~ −50℃ (a) and 50℃ (b). ~~Eq. (9)~~(Note: The following variables with their distribution patterns and confidence factors (CF) were considered: ϕ_0: uniform distribution, 0 to 1; k_{deg}, lognormal distribution~~,~~; CF = 3 (Wania and Dugani, 2003).)

4. Implications

According to previous studies, adsorption of gaseous SVOCs onto filters during sampling (Hart and Pankow, 1994) and enhanced adsorption of gaseous SVOCs onto various phases (e.g., soot phase) (Dachs and Eisenreich, 2000) both can influence the equilibrium state of ~~G/P~~G–P partitioning. Additionally, the present study revealed that the gaseous degradation also caused the deviation of K_P' from the equilibrium state. Therefore, in the present study, the deviation of K_P' from the equilibrium state caused by these factors were estimated and compared in order to deeply understand the influence of gaseous degradation. As mentioned in above section, the mean deviation resulting from gaseous degradation was estimated (K_P': 1.10 to ~~8.4~~5.58 times increased)~~,~~ ~~with the logarithmic deviation of K_P' in the range of 0 to 0.925~~. The deviation caused by the influence of the soot phase within the particles was estimated by averaging the difference between the predictions of the H-B model (Harner and Bidleman, 1998) and the D-E model (Dachs and Eisenreich, 2000) for LMW SVOCs with the range of log K_{OA} from 5 to 9. The ~~logarithmic deviation~~increasing times of K_P' caused by the influence of the soot phase within the particles was in the range of ~~0.429~~2.68 to ~~0.887~~7.70 times ~~(K_P': 2.68 to 7.70 times increased)~~. A previous study pointed out that the effect of the adsorption of gaseous SVOCs onto filters could ~~cause the logarithmic deviation of~~increase K_P' ~~in a range of~~about ~~0.079~~2.1.2 to 1.6~~0.204~~ times ~~(K_P': 1.2 to 1.6 times increased)~~ (Hart and Pankow, 1994). Therefore, it can be found that, the deviation of K_P' from the equilibrium state caused by the gaseous degradation was comparable with that caused by the adsorption of the soot phase, which were both higher than that caused by the adsorption of gaseous SVOCs onto filters. Therefore, it can be concluded that the influence of gaseous degradation should also be considered for the ~~G/P~~G–P partitioning models of SVOCs, especially for the LMW SVOCs~~,~~.

~~It is worth noting that the present study only considered the gaseous degradation related to the reaction with hydroxyl radicals, however did not consider the gaseous degradation routes resulting from other atmospheric oxidation pathways and photodegradation were not included, which may lead to an underestimation of the impact of the total gaseous degradation. In addition, previous studies have demonstrated that PAHs can be entrapped within highly viscous, partially forming secondary organic aerosol particles during particle formation , which could cause the non-exchangeable SVOCs within particles. However, the presence and influence of the non-exchangeable SVOCs within particles on the G/P partitioning behavior were not conclusively demonstrated until now. Therefore, it is imperative to conduct studies for other influencing factors on the G/P partitioning behavior of SVOCs in future If the influence of the total gaseous degradation and the non-exchangeable SVOCs within particles on G/P partitioning were all considered, the comprehensive understanding of the influencing factors on the deviation of K_P' from the equilibrium state might be clarified.~~

5. Limitation

In this study, the gaseous degradation was speculated as the reason for the difference of K_P' for Me-Naps between the daytime and nighttime, which might result in the deviation of K_P' from equilibrium state for LMW SVOCs. In addition, the new steady state G-P partitioning model was used, which demonstrated that the gaseous degradation could deviate the K_P' from equilibrium state. However, there were some limitations in this study. Firstly, the different breakthrough values might occur between the daytime and nighttime, considering their different temperature. The influence of the breakthrough on K_P' was calculated, that could result in~~to~~ 1.20 to 1.27 times higher for K_P' in the daytime than in the nighttime, if the breakthrough (17% to 21%) only occurred in the daytime, not in the nighttime. However, the increasing of K_P' caused by the breakthrough cannot fully explain the observed diurnal variation with K_P' between

daytime and nighttime in this study (2.95 to 4.65 times). Secondly, the present study only considered the gaseous degradation related to the reaction with hydroxyl radicals. ~~h~~However, the gaseous degradation routes, like the other atmospheric oxidation pathways and photodegradation were not included, which may lead to an underestimation of the impact of the total gaseous degradation. Thirdly, the previous studies have demonstrated that PAHs can be entrapped within highly viscous, partially forming secondary organic aerosol particles during particle formation (Zelenyuk et al., 2012; Shrivastava et al., 2017), which could cause the non-exchangeable SVOCs within particles. However, the presence and influence of the non-exchangeable SVOCs within particles on the G–P partitioning behavior were not considered in this study. Therefore, it is imperative to conduct studies for other influencing factors on the G–P partitioning behavior of SVOCs in future, such as the total gaseous degradation, the non-exchangeable SVOCs within particles, and the advection of air masses, among others.

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Author contributions

Fu-Jie Zhu: Conceptualization, Methodology, Investigation, Writing – original draft. Zi-Feng Zhang: Writing – review & editing. Li- Yan Liu: Writing – review & editing. Pu-Fei Yang: Writing – review & editing. Peng-Tuan Hu: Writing – review & editing.

Geng-Bo Ren: Writing – review & editing. Meng Qin: Writing – review & editing. Wan-Li Ma: Conceptualization, Methodology, Writing – review & editing.

Appendix A. Supplementary data

Supplementary data for this article can be found at

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