Authors' response to community 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.

(1) Previous studies have shown that high volume samplers equipped with PUF are unsuitable for measuring LMW PAHs (for example, 2-, 3-ring PAHs) due to high breakthrough (Hart et al., 1992; Peters et al., 2000). The observed breakthrough values of 2-methyl NAP and 1-methyl NAP are around 50% (Peters et al., 2000), indicating excessive breakthrough. Therefore, the measurement results of this work may not reasonably show the gas/particle partitioning of methylated NAPs, and the diurnal variations of their $K_{\rm P}$ ' are most likely ascribed to the variations of breakthrough due to temperature changes. In section 2.3, did the author evaluate the breakthrough of LMW PAHs when sampling gasses?

RE: Thanks for the comment.

We agree with the opinion "the breakthrough of LMW SVOCs occurred with high volume air samplers equipped with PUF". In our study, we made the breakthrough test during the sampling program, and we also found the breakthrough phenomenon. However, according to the following discussion, the influence of only breakthrough cannot cause so large diurnal variations of $K_{\rm P}$ ' between daytime and nighttime. Therefore, we don't agree with the opinion "the diurnal variations of their $K_{\rm P}$ ' are most likely ascribed to the variations of breakthrough due to temperature changes". The reasons can be found as follows:

1) According to previous studies, it was found that the breakthrough is significantly related with sampling volume and sampling flow rate. In our study, the sampling flow rate was maintained at $0.24 \text{ m}^3/\text{min}$, and the sampling time was set for 8h, therefore the sampling volume was around 115 m³. Compared to the sampling programs in the above

literatures (500 - 700 m³ and 170 m³) (Peters et al., 2000; Hart et al., 1992), the sampling volume is not too much in our study. During the sampling program in our study, the breakthrough test was also conducted, and the results indicated that the breakthrough values are around 17 - 21% for Me-Naps. Therefore, it can be found that the breakthrough phenomenon is not significant. In addition, if the breakthrough only occurred in the daytime (17% to 21%) not in the nighttime, the breakthrough could cause $K_{P'}$ in the daytime 1.20 to 1.27 times higher those in the nighttime. Even if the breakthrough values reached 50% in the above literatures (Peters et al., 2000; Hart et al., 1992), the impact on $K_{P'}$ is only 2 times, which was much lower than the observed diurnal variation with $K_{P'}$ between daytime and nighttime in our study. In our study, the mean values of $K_{P'}$ in the daytime were higher than those in the nighttime for 2.95 to 4.65 times.

2) In addition, the breakthrough phenomenon occurred for both daytime and nighttime sampling. Therefore, the influence of breakthrough on $K_{\rm P}$ ' can occurred for both daytime and nighttime. Therefore, the influence of breakthrough on $K_{\rm P}$ ' would not cause so large difference between daytime and nighttime.

3) Based on the above discussion, we agree with the opinion "the different breakthrough values of LMW SVOCs between daytime and nighttime can influence the diurnal variation of K_P ". However, the diurnal variation of K_P ' between the daytime and nighttime cannot be fully explained by the breakthrough. In addition, the major objective of our study was to deeply study the impact of gaseous degradation on the deviation of the equilibrium state of gas/particle partitioning of SVOCs other than the diurnal variation of K_P ' between daytime and nighttime. Therefore, the topic with the impact of breakthrough was not deeply discussed in the manuscript.

Related references:

Hart, K. M., Isabelle, L. M., and Pankow, J. F.: High-volume air sampler for particle and gas sampling. 1. Design and gas sampling performance, Environ. Sci. Technol., 26, 1048-1052, 10.1021/es00029a027, 1992.

Peters, A. J., Lane, D. A., Gundel, L. A., Northcott, G. L., and Jones, K. C.: A comparison of high volume and diffusion denuder samplers for measuring semivolatile

organic compounds in the atmosphere, Environ. Sci. Technol., 34, 5001-5006, 2000.

(2) Section 3.3. The gaseous degradation of LMW PAHs was not directly observed, but inferred from existing theories and empirical calculations.

RE: Thanks for the comment.

According to current atmospheric sampling technology, the gaseous degradation of PAHs cannot be directly measured. Therefore, in this study, the impact of gaseous degradation on the deviation of the equilibrium state of gas/particle partitioning of PAHs was comprehensively studied based on model. In addition, the results from model were also verified by the measured PAHs degradation data from related studies, which confirmed the conclusions of this study. On the other hand, in the final section of the manuscript we also mentioned that the actual degradation of PAHs was complicated, and further investigations are needed for better understanding the topic.