Authors' response to reviewers' feedback on "A new steady-state gas/particle partitioning model of PAHs: Implication for the influence of the particulate proportion in emissions"

We thank the anonymous reviewers for their time and effort engaging with our manuscript and providing us with valuable feedback. We edited our manuscript to address their feedback, below our respond in blue and manuscript revision in red to their reviews in black.

Referee 1

This paper presents a model which incorporates the extent of partitioning at emissions sources to explain observed non-equilibrium gas-particle partitioning trends for PAHs. Overall, I think the results are interesting and the paper highlights some interesting cases where the assumption of equilibrium partitioning at emissions is not valid – e.g. for coking when particles are being filtered out. I think that clarifying that this model is showing deviations from equilibrium K_P values rather than a "new" K_P value could maybe help here – along with more emphasis on comparing the measured results with a null-hypothesis of $\phi_0 = K_{PCa}$ (emissions are at equilibrium conditions is the default assumption in most fate and transport models) rather than setting arbitrary values.

RE: Thanks for your positive evaluation to our manuscript. In our previous studies, we made comprehensive studies on the G/P partitioning of PAHs, and we found that the previous G/P partitioning models were not suitable for PAHs. Therefore, in the present study, we want to develop a new G/P partitioning equation for the prediction of K_P. In order to evaluate the performance of the new model, we made the comparisons with the measured values of K_P and the predicted values of K_P by previous G/P partitioning models. The deviations with the new model from the measured results and the predicted results of other previous models were studied and the related reasons were also figured out. Furthermore, the limitations and implications of the new model were also pointed out for future studies. According to your suggestion, the manuscript was revised, which looks much better than the original one.

Abstract: I think parts of the abstract could be re-worded.

RE: Thanks for your suggestion. We revised the abstract based on your following comments, which looks much better than the original one.

Lines 21-23: here it would be more clear to describe the domains you observed

RE: Thanks for your suggestion. We added detailed description of the domains in the revied manuscript as follows

"Same with the previous steady-state model, three different domains with different G/P partitioning behaviors can be divided by the threshold values of log K_{OA} (octanol-air partitioning coefficient), and the slopes of the prediction line of the new model were 1, from 1 to 0, and 0 for the three domains, respectively."

Lines 25-29: I think rather than a description of results the actual results could be given, as the current form seems a little vague.

RE: Thanks for your suggestion. We added the description of actual results in the revised manuscript as follows.

"The comparison with the G/P partitioning of PAHs between the prediction result of the new steady-state model and the monitored results from 11 cities in China suggested different prediction performances under different values of ϕ_0 and the lowest root mean square error when ϕ_0 was set to 0.9 or 0.99."

Lines 53-61: Here and throughout the use of K_P throughout the manuscript is somewhat problematic, since K_P is an equilibrium constant but the model presented here is not at equilibrium. I think the authors should clarify the differences here, and use a different symbol (e.g. K'_P) for non-equilibrium distribution between gas and particle. I also think fundamentally the equilibrium models and the non-equilibrium models are describing different things, so they are not directly comparable. In this section, the authors could expand on why in the real-world assumptions of equilibrium are often not valid.

RE: Thanks for your suggestion.

(1) As we know, the G/P partitioning coefficient (K_P) is calculated by the measured concentrations of gas phase and particle phase SVOCs, and the total suspended particle concentration. In addition, some models and equations were developed for the prediction of the K_P without the monitoring program. Therefore, in order to make it more clearly understanding, the following symbols were used in our manuscript: $K_{P\text{-}M}$ for the measured value, $K_{P\text{-}HB}$ for the predicted value by the H-B model, $K_{P\text{-}LMY}$ for the predicted value by the L-M-Y model, $K_{P\text{-}NS}$ for the predicted value by the new steady-state model. All the related information were corrected in the revised manuscript.

(2) In our study, we developed a new steady state G/P partitioning model. In order to evaluate the performance of the model, we made the comparisons with the measured values of K_P and the predicted values of K_P by previous G/P partitioning models. Actually, the real condition with the G/P partitioning of PAHs was not clear, whether in equilibrium state or in steady state. Therefore, both the equilibrium state and steady state G/P partitioning models in previous studies were considered. Therefore, in our opinion, the comparison between different models should be conducted.

(3) As we know, many factors can influence the G/P partitioning of SVOCs, such as environmental factors, the physicochemical properties of SVOCs, the sources. Therefore, the G/P partitioning states for different SVOCs were not uniform. As for PAHs, according to the finding of the present study, both the equilibrium state and steady state G/P partitioning models were not suitable. Therefore, we developed the new steady state G/P partitioning model. In our opinion, all the G/P partitioning models can be used for some types of SVOCs other than for all types of SVOCs.

Lines 108-109: “it can be found…” This could be rephrased to be more direct e.g. “Four fluxes represented <XX% of overall mass transfer and were therefore removed from the system.” For instance, from Fig. S1 it looks like gaseous wet deposition becomes somewhat important for e.g. DahA, making up a pretty large portion of the overall flux. Did you have some threshold you defined here?

RE: Thanks for your suggestion. In general, it was believed that the ignored proportion for fluxes in each category was less than 10% of the total fluxes. However, for some

special fluxes, such as the flux of the gaseous wet deposition (F_{GW}) for DahA, proportion was higher than 10% of the total fluxes. In the present study, we want to establish a universal model for all the PAHs. Therefore, we did not consider the special situations. Finally, the four fluxes (F_{GWS_diff}, F_{WSG_diff}, F_{PR}, and F_{GW}) were removed from the model establishment. The following information was added in the revised manuscript:

"In the present study, in order to establish a universal and simple model, the four fluxes (F_{GWS_diff}, F_{WSG_diff}, F_{PR}, and F_{GW}) were removed from the system because their contributions were less than 10% of the total fluxes. In addition, the special situation was not considered, for example, even the contribution of the flux of F_{GW} for DahA was higher than 10%, the F_{GW} was also removed."

Line 120: This looks like a derivation based on the fugacity capacity (Z value) – is that correct?

RE: Thanks for your comment. After careful check, the calculation method was cited from the previous study (Li et al., 2015), which was based on the multimedia fugacity model.

References:

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.

Line 122: Again here I find the use of K_P I think this equation shows what you are doing – adjusting an equilibrium partition coefficient with a correction based on ϕ_0 – rather than creating a new equilibrium rate constant. I think expressing this as a departure from equilibrium could also help the discussion elsewhere – for instance around Fig. 2

RE: Thanks for your suggestion. In our study, the new steady state model was developed based on the previous steady state model (the L-M-Y model), therefore, the equation (3) in Line 122 was established. In order to make the difference more clearly understanding, the $K_{P\text{-}NS}$ was used.

Equation 4: You have simplified the equation such that it only depends on ϕ_0 nought and k_{deg} but it also has a dependence on the parameters used to set-up the fugacity model. In particular, I would be interested to see what this looks like at different rain rates – the value you use (9.7e-5 m/h) from Mackay (2001) is going to vary substantially depending on location (presumably it was parameterized for a temperate climate like Ontario, Canada). Also, what about the assumed windspeed/ventilation coefficient – presumably, if you have little turnover the equilibrium assumption for G/P partitioning would get more accurate, whereas faster turnover would mean the initial G/P ratio would dominate.

RE: Thanks for your suggestion. We agreed with your opinion that more exact and different values of parameters should be considered and discussed for Equation 4. However, the database for these parameters were not available, and even the measured values of these parameters were limited. For the development of the steady-state G/P partitioning model, the commonly used values of these parameters in our previous study were chosen (Li et al., 2015). Therefore, except for ϕ_0 and k_{deg}, the commonly used values for other parameters in Equation 4 were also applied in our study. In the section of validation, it can be observed that although the new model predicted well than other models, it still cannot accurately match the monitoring data. The reasons for these deviations might be caused by the deviation between these empirical values of these parameters and the actual situation. The new stead-state model is similar to the other models and is a catch-all model. For more accurate prediction, the model needs to be localized according to the actual situation. In addition, in order to optimize the new steady-state model, the actual values for other parameters should be considered in future.

Reference:

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.

Line 197: do you mean “deviation” here? Also, this is an interesting finding – are you assuming that degradation is only happening in the gas-phase?

RE: Sorry for the confusion. This is a writing mistake, the “derivation” was corrected to “deviation” in the revised manuscript. We did not make the assumption of that the degradation is only happening in the gas phase. As we know, the degradation happens in both gas phase and particle phase. However, the degradation flux of particle phase PAHs (F_{PR}) was removed from the system because they contributed less than 10% of all the fluxes. The result suggested that the loss from the degradation of PAHs in particle phase was less than that of the replenishment from the gas phase, which leaded to its ignored effect on the equilibrium state of PAHs. However, higher loss from the degradation of PAHs in gas phase than that of the replenishment from particle phase can result in the deviation from the equilibrium state of PAHs. Therefore, the following conclusion was obtained: based on the result of the new steady state model, the deviation was mainly caused by the degradation of PAHs in gas phase.

Line 235: wouldn’t most modeling approaches show these to be mostly in the particle-phase anyways? I think the null-hypothesis here would be to assume equilibrium G/P partitioning at the emissions source rather than an arbitrary value?

RE: Thanks for the comment.

(1) In our study, the ϕ_0 means the particulate phase proportion of PAHs in the emission sources. As we know, the ϕ_0 was considered in the G/P partitioning model for the first time. Therefore, other G/P partitioning models did not consider ϕ_0.

(2) In general, after the SVOCs were released from the sources, they would partition between gas phase and particle phase, and finally SVOCs would reach the final equilibrium state and/or the steady state between the two phases (Li et al., 2020). Furthermore, the particulate phase proportion was also changed compared with the original value (ϕ_0) in the emission sources. In the new model, only the value of ϕ_0 was considered, therefore, the G/P partitioning state (equilibrium or steady) was not necessary.

(3) Based on related studies (Mastral and Callén, 2000; Mu et al., 2014; Shen et al., 2011; Wang et al., 2018; Zhang et al., 2020), it was found that the values of ϕ_0 were quite different for different compounds and for different emission sources. PAHs with high values of log K_{OA} or the high molecular weight were mostly in the particle phase in the emission sources. In our study, when ϕ_0 is set to 0.9 or 0.99, the prediction of the new steady state model fit best with the monitoring data. The values of ϕ_0 were consistent with the related studies of PAHs in emission sources (Mastral and Callén, 2000; Mu et al., 2014; Shen et al., 2011; Wang et al., 2018; Zhang et al., 2020).

References:

Li, Y., Qiao, L., Ren, N., Macdonald, R. W., and Kannan, K.: Gas/particle partitioning of semi-volatile organic compounds in the atmosphere: Transition from unsteady to steady state, Sci. Total Environ., 710, 136394, https://doi.org/10.1016/j.scitotenv.2019.136394, 2020.

Mastral, A. M. and Callén, M. S.: A Review on Polycyclic Aromatic Hydrocarbon (PAH) Emissions from Energy Generation, Environ. Sci. Technol., 34, 3051-3057, https://doi.org/10.1021/es001028d, 2000.

Mu, L., Peng, L., Liu, X., Song, C., Bai, H., Zhang, J., Hu, D., He, Q., and Li, F.: Characteristics of polycyclic aromatic hydrocarbons and their gas/particle partitioning from fugitive emissions in coke plants, Atmos. Environ., 83, 202-210, https://doi.org/10.1016/j.atmosenv.2013.09.043, 2014.

Shen, G., Wang, W., Yang, Y., Ding, J., Xue, M., Min, Y., Zhu, C., Shen, H., Li, W., Wang, B., Wang, R., Wang, X., Tao, S., and Russell, A. G.: Emissions of PAHs from indoor crop residue burning in a typical rural stove: Emission factors, size distributions, and gas−particle partitioning, Environ. Sci. Technol., 45, 1206-1212, https://doi.org/10.1021/es102151w, 2011.

Wang, R., Liu, G., Sun, R., Yousaf, B., Wang, J., Liu, R., and Zhang, H.: Emission characteristics for gaseous- and size-segregated particulate PAHs in coal combustion flue gas from circulating fluidized bed (CFB) boiler, Environ. Pollut., 238, 581-589, https://doi.org/10.1016/j.envpol.2018.03.051, 2018.

Zhang, L., Yang, L., Zhou, Q., Zhang, X., Xing, W., Wei, Y., Hu, M., Zhao, L., Toriba, A., Hayakawa, K., and Tang, N.: Size distribution of particulate polycyclic aromatic hydrocarbons in fresh combustion smoke and ambient air: A review, Journal of Environmental Sciences, 88, 370-384, https://doi.org/10.1016/j.jes.2019.09.007, 2020.

Line 246 – Ok here I see where this might apply! I think giving more examples like this makes sense and helps show where this model would be most useful – places where the emissions would not be at equilibrium (e.g. if they are at high temperatures, if the particles are being removed, etc.)

RE: Thank for your suggestion. As a new developed model, we want to expand its applications. Therefore, the model was used for the special scenarios of PAHs in the prototype coking plant and PBDEs in E-waste site, which both indicated the good performance of the new model.

Line 265-266: what would be the equilibrium ϕ_0 value for these compounds – is it close to 1? If so, then is this result telling us anything new?

RE: Thank for your suggestion. According to related studies, the PBDEs were mainly in particle phase in the emissions in E-waste sites, therefore, the values of ϕ_0 can be considered close to 1. In our study, it was found that the new steady state model with ϕ_0 = 1 matched well with the measured results. Therefore, the results again demonstrated the importance of ϕ_0 in predicting the G/P partitioning of SVOCs and the good applicability of the new model.

Implications: I think more could be done here showing how these limitations would impact the model. Could the authors run some sensitivity analyses?

RE: Thanks for your suggestion. We conducted the sensitivity analysis for the parameters of ϕ_0, f_{OM}, and k_{deg}. And we added the following information in the revised manuscript and SI as follows:

(1) The following information was added in the revised manuscript:

"In order to evaluate the influence of the three parameters on the K_P in the new steady-state model, the sensitivity analysis was conducted by the Monte Carlo analysis with 100,000 trials using the commercial software package Oracle Crystal Ball. In order to obtain comprehensive results, the sensitivity analysis was conducted for different values of log K_{OA} from 6 to 16. As presented in **Fig. S8, SI**, it is interesting to note that three different ranges of log K_{OA} were observed according to the different characteristics. For the range of log K_{OA} from 6 to 10, the influence of ϕ_0 was the dominant followed by k_{deg} and f_{OM}. Furthermore, for each parameter, the influence was stable for different log K_{OA} in range. For the range of log K_{OA} from 10 to 12, the influence of ϕ_0 was also the dominant followed by k_{deg} and f_{OM}. In addition, the influence of ϕ_0 increased, while for the other two parameters the influence decreased. In the third range of log K_{OA} (12 to 16), the influences of the three parameters were also stable. In addition, the influence of ϕ_0 was also the dominant, and the influence of f_{OM} can be ignored. Actually, the three ranges of log K_{OA} were consistent with the three domains. It can be concluded that the different influences of the three parameters on K_P for different log K_{OA} should be considered for the new model."

(2) The following information was added in the revised SI:

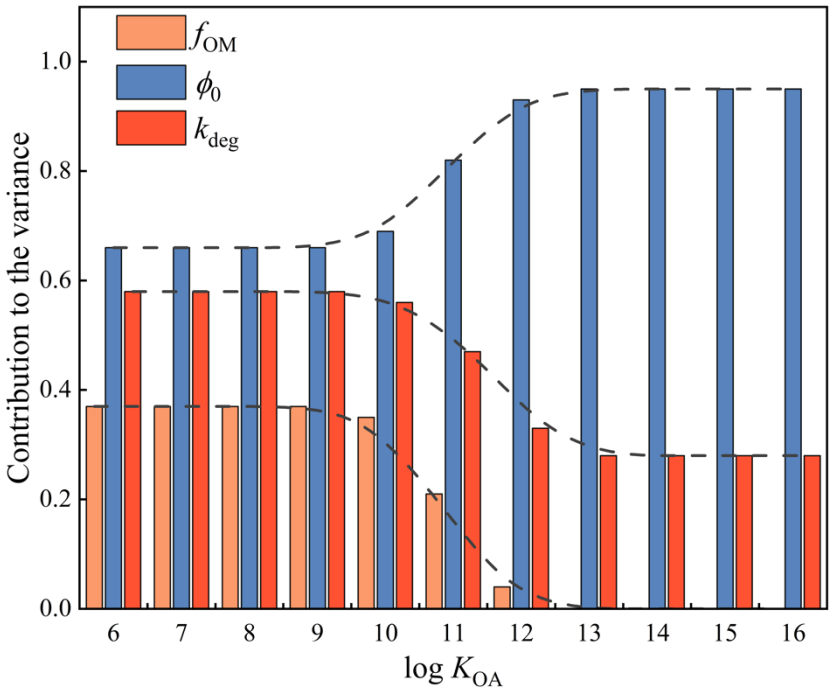

Fig. S8. Sensitivity analysis for the parameters of ϕ_0, f_{OM}, and k_{deg} in the new

steady-state model

(Note: Sensitivity analysis was conducted by the Monte Carlo analysis with 100,000 trials using the commercial software package Oracle Crystal Ball. The following three variables with their distribution patterns and confidence factors (CFs) were considered: ϕ_0: uniform distribution, 0 to 1; f_{OM}, lognormal distribution, mean = 0.21, CF = 1.5 (Mackay, 2001); k_{deg}, lognormal distribution, mean = 0.27, CF = 3 (Wania and Dugani, 2003).)

References:

Mackay, D.: Multimedia Environmental Models: the Fugacity Approach, Taylor & Francis, New York 2001.

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."

Referee 2

The manuscript in its present form (after revision) seems to meet the quality requisites to publish. Authors have made the changes/improvements required.

RE: Thanks to the reviewer for the positive evaluation to our manuscript.