

Review 2 for “Uncertainties in the effects of organic aerosol coatings on polycyclic aromatic hydrocarbon concentrations and their estimated health effects” by Lou et al.

In this study the authors compared three BaP degradation approaches with different treatment of the effects of organic aerosol coatings on the particle-phase BaP reactivity. The simulated gas-phase BaP and oxidized BaP based on the three approaches were compared with observations. As BaP has significant health effects, accurate representation of BaP concentrations over a global scale is highly needed. This manuscript is clearly written and is helpful for future modelling studies to improve the PAHs simulations. I recommend the publication of this work after the authors could address my comments below.

Thank you for your valuable comments and suggestions. We have carefully addressed each point as follows.

Major comments:

(1) My major concern is that how to simulate the effects of organic aerosol coating, namely, the viscosity, on the gas-particle partitioning of BaP and the heterogeneous degradation coherently. Viscosity affects both partitioning and reactivity. Therefore, if the BaP degradation in the particle phase has considered the effects of viscosity in the Shielded approach and ROI-T approach as what the author did, for coherence, the effect of viscosity on gas-particle partitioning of BaP should be also included. Does the ppLFER model the authors applied for gas-particle partitioning of BaP specifically considered the viscosity of the organic shell and its effect on partitioning?

Response:

Thank you for your insightful comment. As you correctly pointed out, viscosity of the organic aerosol coating is an important factor that could influence both BaP gas-particle partitioning and the heterogeneous degradation reactivity.

In this study, the pp-LFER approach considers the effects of BaP partitioning to a two-phase organic system consisting of liquid water-soluble/organic soluble organics, and solid/semisolid organic polymers. In this sense, this approach considers the impacts of water-soluble organics and organic polymers (formed by accretion reactions) on BaP partitioning. However, further experiments that measure the partitioning of BaP on liquid-like SOA and polymeric SOA systems are needed to constrain pp-LFER model predictions.

The viscosity of OA affects the atmospheric lifecycle of BaP in two ways: (1) through gas-particle partitioning of SOA that also impacts gas-particle partitioning of BaP (pp-

LFER approach), and (2) by altering BaP heterogeneous degradation kinetics with ozone. From the first perspective, we handle viscosity differently across the three approaches. In the NOA simulation, we use the FragSVSOA treatment described in Shrivastava et al. (2015), assuming SOA as semi-volatile liquid-like well-mixed solution throughout its atmospheric lifetime, which does not consider the effects of viscosity on gas-particle partitioning of SOA. In contrast, the Shielded and ROI-T approaches use the FragNVSOA treatment, which assumes that SOA, once formed, is transformed to a highly viscous non-volatile semi-solid SOA within the same global model timestep (30 min) due to particle-phase oligomerization reactions within SOA [Shrivastava et al., 2015]. The FragNVSOA treatment also assume that any further gas-phase organic oxidation products that condense do not form a solution with pre-existing OA. This assumption is consistent with recent experimental studies, which show a short aging timescale of ~20 min that causes oligomer and organosulfate formation within isoprene SOA causing non-equilibrium partitioning behavior and phase transition to semi-solid SOA [Chen et al., 2023].

From the second perspective, both the Shielded and ROI-T approaches incorporate the effects of SOA viscosity on BaP degradation kinetics with ozone. The Shielded approach, based on Shrivastava et al. (2017), assumes that thick OA coatings ( $> 20$  nm) completely shield particle-bound BaP oxidation under cool (temperature  $< 296$  K) and dry (RH  $< 50\%$ ) conditions, thus providing an upper bound of the impact of viscous SOA on BaP degradation, however this approach moderately underestimates the oxidation rate in urban areas. The ROI-T approach models the multiphase degradation of BaP with ozone, incorporates both mass transport and chemical reactions of particle-bound species in the bulk phase and at the surface. The first-order decay rates of BaP, as presented in Table S3 of Mu et al. (2018), are parameterized values that already account for the impact of changing SOA viscosity as a function of temperature and RH on BaP degradation, though this may overestimate the oxidation rate in remote areas (Fig. 7).

Our assumption of a globally constant 30-minute particle-phase reaction and oligomerization timescale for SOA (converting it to semi-solid SOA) is consistent with the recent experimental study [Chen et al., 2023]. However, future studies are needed to measure the phase transition timescale of different SOA types under varying temperature and relative humidity conditions. Previous modeling studies have suggested that the phase state of OA varies significantly with environmental factors such as temperature, RH in different SOA systems [Pye et al., 2017; Shiraiwa et al., 2017; Zhang et al., 2019; Li et al., 2020; Schmedding et al., 2020]. However, experimental measurements of the phase transition timescales of atmospherically relevant SOA are needed, similar to the study by Rasool et al. (2021). In addition, water associated with organics has been suggested to be the primary predictor of OA viscosity [Rasool et al., 2021]. The effects of phase separation within SOA-water mixtures and variability in the water uptake ability of SOA as a function of its aging and gas-particle partitioning, and the resulting impacts on BaP reaction kinetics need to be considered in future studies.

We acknowledge that incorporating the viscosity of the organic shell could provide a more comprehensive representation of gas-particle partitioning, and we have revised the “conclusion and discussion” section to address this comment.

(2) My another concern is that the section of “Conclusion and Discussion” is too much rephrasing the results with little discussion. I recommend that the authors can give a clearer conclusion. For the discussion, the following aspects may be helpful. First, what are the limitations of the Shielded and ROI-T approaches and how to improve these kinds of methods for future modelling studies? For example, BaP and ROI-T have not considered the phase state of the organic coatings varied with RH, T, and organic aerosol chemical composition, which, however, has been parameterized since 2017 (Li et al., 2020; Shiraiwa et al., 2017; Zhang et al., 2019) and included in chemical transport models (Shrivastava et al., 2022; Zhang et al., 2024). Second, would phase separation affect BaP gas-particle partitioning and heterogeneous degradation (Pye et al., 2017; Schmedding et al., 2020)?

**Response:**

Thank you for your valuable comment. We appreciate your suggestion to improve the “Conclusion and Discussion” section. In response, we have summarized the conclusion for better clarity. Additionally, we have expanded the discussion to address the potential impact of the phase state of organic coatings on BaP gas-particle partitioning and heterogeneous degradation. Relevant references, such as Shiraiwa et al. (2017), Li et al. (2020), and others, have been incorporated to highlight the recent developments in this area. Please refer to the updated section “Conclusion and Discussion” for further details.

**Specific comments:**

(1) Some recent modeling work on PAH should be cited and the simulated BaP concentrations are better compared (Wu et al., 2024).

**Response:**

Thanks for the comment. We have added the following sentence in main text: “Our simulated seasonal BaP concentrations, particularly for the ROI-T approach, align with a previous study using the same emissions and particulate-BaP degradation approach [Wu et al., 2024].” Please refer to lines 328-329.

(2) Line 164 at Page 5, why the authors did not include the gas-phase reaction of BaP with O<sub>3</sub> and NO<sub>3</sub>?

**Response:**

According to Keyte et al. (2013), most BaP and its oxidized products are observed as particulate phase. Their study also indicates that gas-phase PAHs primarily react with OH, O<sub>3</sub>, and NO<sub>3</sub>. Keyte et al. (2013) also summarized the chemical reactivity of PAHs, noting that the second-order reaction rate coefficients for gas-phase reactions of PAHs

with OH radicals are typically around  $10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , while the reaction rate with O<sub>3</sub> is six orders of magnitude slower ( $10^{-18} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ). Additionally, no measured value is available for the gas-phase reaction of BaP with O<sub>3</sub> in Keyte et al. (2013). Therefore, in this study, we only consider the gas-phase reaction oxidation of BaP by OH.

(3) Line 348-350 at Page 11, the authors wrote that a large portion of the total BaP was still oxidized though the effect of organic coating had been considered in bulk diffusion of BaP in the ROI-T scheme, which was surprising. Again, referring to my major comment 1, the authors should clarify that the effect of viscosity on gas-particle partitioning and BaP degradation rate is related to two different processes. Did the ROI-T scheme consider the phase state effect on bulk diffusivity of BaP in your simulation? I think the result showed in Line 348-350 is not surprising as the reaction rate of BaP with ozone in the particle phase was dependent on RH and T, thus the viscosity of organic shell, which resulted in limited effect of organic coating on BaP degradation in areas with low viscous particles.

Response:

Thank you for your valuable comment.

The ROI-T approach, which models the multiphase degradation of BaP with ozone, incorporates both mass transport and chemical reactions of particle-bound species in the bulk phase and at the surface. The first-order decay rates of BaP, as presented in Table S3 of Mu et al. (2018), are parameterized values that already include the influence of SOA viscosity on bulk diffusivity of BaP.

As mentioned above, we acknowledge that incorporating the viscosity of the organic coatings could provide a more comprehensive representation of gas-particle partitioning, and we have revised the “conclusion and discussion” section to address this comment.

(4) Line 198-200 on Page 6, please double check. I did not see this from Table S3 in Mu et al. (2018).

Response:

Thank you for your comment. The statement “First-order reaction rate coefficients for BaP ozonolysis are sensitive to both temperature and RH below room temperature (296 K), but are only temperature sensitive above room temperature [Mu et al., 2018]” is not from Table S3 in Mu et al. (2018), but from Figure 1A in the same study. As shown in Figure 1A, when the temperature is below 296 K, there is a significant deviation in the first-order multiphase degradation rate coefficient, and its value can differ by 1-2 orders of magnitude under different humidity conditions (temperature < 253 K). In contrast, above 296 K, the degradation rate coefficients remain consistent within the same order

of magnitude. We have added Table S1 for comparing the first-order reaction rate coefficients ( $k$ ,  $s^{-1}$ ) across the three approaches.

## References

Chen, Y., Zaveri, R. A., Vandergrift, G. W., Cheng, Z., China, S., Zelenyuk, A., and Shilling, J. E.: Nonequilibrium behavior in isoprene secondary organic aerosol, *Environ. Sci. Technol.*, 57, 38, 14182-14193, <https://doi.org/10.1021/acs.est.3c03532>, 2023.

Keyte, I. J., Harrison, R. M., and Lammel, G.: Chemical reactivity and long-range transport potential of polycyclic aromatic hydrocarbons—a review, *Chem. Soc. Rev.*, 42(24), 9333-9391, <https://doi.org/10.1039/C3CS60147A>, 2013.

Li, Y., Day, D. A., Stark, H., Jimenez, J. L., and Shiraiwa, M.: Predictions of the glass transition temperature and viscosity of organic aerosols from volatility distributions, *Atmos. Chem. Phys.*, 20, 8103-8122, 10.5194/acp-20-8103-2020, 2020.

Liu, Y., Shilling, J. E., Schneider, J., Schulz, C., Zöger, M., Martin, S. T., Ye, J., Guenther, A., Souza, R. F., Wendisch, M., and Pöschl, U.: Tight Coupling of Surface and In-Plant Biochemistry and Convection Governs Key Fine Particulate Components over the Amazon Rainforest, *ACS Earth and Space Chemistry*, 6, 380-390, 10.1021/acsearthspacechem.1c00356, 2022.

Mu, Q., Shiraiwa, M., Octaviani, M., Ma, N., Ding, A., Su, H., Lammel, G., Poschl, U., and Cheng, Y.: Temperature effect on phase state and reactivity controls atmospheric multiphase chemistry and transport of PAHs, *Sci. Adv.*, 4(3), doi:10.1126/sciadv.aap7314, 2018.

Pye, H. O. T., Murphy, B. N., Xu, L., Ng, N. L., Carlton, A. G., Guo, H., Weber, R., Vasilakos, P., Appel, K. W., Budisulistiorini, S. H., Surratt, J. D., Nenes, A., Hu, W., Jimenez, J. L., Isaacman-VanWertz, G., Misztal, P. K., and Goldstein, A. H.: On the implications of aerosol liquid water and phase separation for organic aerosol mass, *Atmos. Chem. Phys.*, 17, 343-369, 10.5194/acp-17-343-2017, 2017.

Rasool, Q. Z., Shrivastava, M., Octaviani, M., Zhao, B., Gaudet, B., and Liu, Y.: Modeling volatility-based aerosol phase state predictions in the Amazon rainforest, *ACS Earth and Space Chem.*, 5, 10, 2910-2924, <https://doi.org/10.1021/acsearthspacechem.1c00255>, 2021.

Schmedding, R., Rasool, Q. Z., Zhang, Y., Pye, H. O. T., Zhang, H., Chen, Y., Surratt, J. D., Lopez-Hilfiker, F. D., Thornton, J. A., Goldstein, A. H., and Vizuete, W.: Predicting secondary organic aerosol phase state and viscosity and its effect on multiphase chemistry in a regional-scale air quality model, *Atmos. Chem. Phys.*, 20, 8201-8225, 10.5194/acp-20-8201-2020, 2020.

Shiraiwa, M., Li, Y., Tsimpidi, A. P., Karydis, V. A., Berkemeier, T., Pandis, S. N., Lelieveld, J., Koop, T., and Pöschl, U.: Global distribution of particle phase state in atmospheric secondary organic aerosols, *Nat. Commun.*, 8, 15002, 10.1038/ncomms15002, 2017.

Shrivastava, M., Rasool, Q. Z., Zhao, B., Octaviani, M., Zaveri, R. A., Zelenyuk, A., Gaudet, B., Wu, Z., Chen, X., Wang, Z., Chen, H., Wang, Z., Mu, Q., Wu, L., Wang, W., Tang, X., Li, J., Li, Y., Wu, Q., Wang, Y., Zou, Z., and Jiang, Z.: Modeling of polycyclic aromatic hydrocarbons (PAHs) from global to regional scales: model development (IAP-AACM\_PAH v1.0) and investigation of health risks in 2013 and 2018 in China, *Geosci. Model Dev.*, 17, 8885-8907, 10.5194/gmd-17-8885-2024, 2024.

Zhang, Y., Nichman, L., Spencer, P., Jung, J. I., Lee, A., Heffernan, B. K., Gold, A., Zhang, Z., Chen,

Y., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., Onasch, T. B., Surratt, J. D., Chandler, D., Davidovits, P., and Kolb, C. E.: The Cooling Rate and Volatility Dependent Glass Forming Properties of Organic Aerosols Measured by Broadband Dielectric Spectroscopy, *Environmental Science & Technology*, 10.1021/acs.est.9b03317, 2019.

Zhang, Z., Li, Y., Ran, H., An, J., Qu, Y., Zhou, W., Xu, W., Hu, W., Xie, H., Wang, Z., Sun, Y., and Shiraiwa, M.: Simulated phase state and viscosity of secondary organic aerosols over China, *Atmos. Chem. Phys.*, 24, 4809-4826, 10.5194/acp-24-4809-2024, 2024.