A point-to-point response and relevant changes made in the revised manuscript

Ms. Ref. No.: egusphere-2025-229

Title: Investigating Influencing Factors of Gas-Particle Distribution of Oxygenated Organic Molecules in Urban Atmosphere and Its Deviation from Equilibrium Partitioning Using Random Forest Model.

Anonymous Referee #2

The manuscript by Wang et al. presents a well-executed study that integrates FIGAERO-CIMS measurements with a machine learning approach to understand the gas-particle partitioning of OOMs in urban environments. They identified key influencing factors such as relative humidity, liquid water content, and particle-phase composition. The authors showed how these factors affect the deviations from equilibrium partitioning, contributing significant knowledge to atmospheric aerosol science. I recommend publication after the authors address the following questions.

Response:

We sincerely thank the reviewer for their valuable comments and suggestions, which will significantly improve the quality of our manuscript.

1. *It would be better to add more details about the sampling site's characteristics, such as location and distances to pollution sources (e.g., traffic or industrial areas), and discuss how these factors influence OOM partitioning.*

Response:

We appreciate the reviewer's valuable suggestion. In lines 72-80, we have added more detailed information about the characteristics of the sampling site:

"Hourly measurements of OOMs in both gas and particle phases was conducted during a winter campaign from December 5th, 2022, to January 8th, 2023, using an iodide-based FIGAERO-CIMS (Aerodyne Research Inc., USA) at a suburban site in Wuhan, a megacity in central China (114.6157°E, 30.4577°N). The site is located in the campus of China University of Geosciences, which is surrounded by residential and agricultural mixed area. The nearest urban center and industrial area are about 25 km west to the measurement site. Nearest highways and major roads lie about 2 km north and south of the site. The site is the only provincial supersite operated by local environmental authority for monitoring air quality in Wuhan and can thus be regarded as a receptor site influenced by wide ranges of emission sources from neighboring regions."

In lines 441-443, we have also expanded our discussion on the influence of wind speed and direction on OOM partitioning:

"As shown in Figure 6a, wind speed and direction rank relatively low in terms of feature importance for the six OOMs. This suggests that while wind direction and speed might

influence the source areas of OOMs, they have a minimal impact on the G/P ratios of OOMs."

2. *The authors use different C^* parameterizations to estimate the equilibrium G/P ratios and compare them with the observed G/P ratios. However, these different C^* parameterizations may introduce significant uncertainty. Please provide a more detailed discussion of the advantages and limitations of each parameterization and explain why these specific methods were chosen.*

Response:

We appreciate the reviewer's suggestion. Based on the existing literature, we selected the parameterization methods to estimate C^* and compared their predictions. We have provided a more detailed discussion of the results from each method and explained the rationale behind our choice of these specific approaches in lines 283-306:

"Among all the methods, Mohr et al. (2019) predicts the steepest dependence of $(\frac{G}{P})_{eq}$ on MW. Their $(\frac{G}{P})_{eq}$ are higher than $(\frac{G}{P})_{obs}$ for the OOMs with n_C = 2-5 and lower than $(\frac{G}{P})_{obs}$ for the OOMs with n_C > 8 (Figure 1b). It has been recognized by Kurtén et al. (2016) and subsequent publications that SIMPOL-derived parameterizations predict a too steep dependence of C^* on Mw and oxygen content. Moreover, the parameterization of Mohr et al. (2019) likely produces C^* of pure compounds. Without considering the effect of particle matrix, it may be unrealistic to predict G/P ratios using their C^* parameterization. On the basis of thermal desorption temperature, Ren et al. (2022) predicts lower equilibrium G/P ratios than all other parameterizations and our observation. The weakness of Ren et al. (2022) is thermal desorption may result in the formation of decomposed fragments, which could be misidentified as OOM species. As a result, the T_{max} of OOM formulas tends to be overestimated and the C^* tends to be underestimated in their parameterization. Although Peräkylä et al. (2020) also predicted lower G/P ratios, their ratios are much closer to our observation than Ren et al. (2022). Among all the predictions, the prediction from Priestley et al. (2024) is most close to our observation. This is because their C^* parameterization is based on the measured gas and particle-phase concentrations of OOMs in fresh or aged residential wood-burning emissions. Their predicted G/P ratio is thus inherently consistent with the observed G/P ratios in our study. This also highlights the risks of estimating volatility (C^*) using the partitioning method, which is based on measuring equilibrium gas- and particle-phase concentrations of OOMs. Two key issues arise: (1) OOMs may not achieve the assumed equilibrium state in real atmospheric or chamber conditions, introducing substantial uncertainty into calculations of $(\frac{G}{P})_{eq}$; (2) The method fails for the compounds with extremely high or low volatility, as their gas- or particle-phase concentrations often fall below the detection limit of mass spectrometers. These limitations explain why the partitioning method typically reports a narrow volatility range (Voliotis et al., 2021; Chen et al., 2024)."

3. *The authors mentioned that the model is based on winter data and limited to specific OOM species. It is recommended that the authors clearly discuss the model's limitations, such as whether certain OOM types (e.g., highly volatile organics) were underrepresented, and how seasonal variations (e.g., summer heat or rainy season humidity) might affect model predictions. The authors should address these limitations and suggest future improvements, such as expanding the dataset to include different seasons or OOM species.*

Response:

We appreciate the reviewer's suggestion. We added the discussions about the limitations and future improvement direction in the end of the conclusion section.

"At last, the random forest models developed in this study have certain limitations. (1) Aerosol particle coating may serve as an inhibitory factor of gas/particle partitioning. However, the mixing state and morphology of aerosol particles were not considered in the model due to the challenges in quantifying these features with high resolution. (2) The OOMs with extremely high or low volatility might be underrepresented in this study, because their gas- or particle-phase concentrations often fall below the limit of quantification of FIGAERO-CIMS. (3) Isomers were not differentiated in the measurement of FIGAERO-CIMS in this study. The observed G/P ratio was contributed by isomers sharing the same chemical formula. The machine learning model built in this study did not account for the effect of isomerization on gas-particle distribution of OOMs. (4) The model was based solely on the data collected during the winter season and for specific groups of OOM species present in urban atmosphere. To enhance the robustness of the gas-to-particle partitioning model, future data collection under a broader range of atmospheric conditions is recommended."

4. *In the feature selection process, the authors identify essential features using the random forest model and explain them with SHAP analysis. It is recommended that the authors provide more statistical justification for the feature selection, such as significance tests or correlation analysis, to validate the importance of these features. Additionally, the SHAP interpretation could be enhanced by including quantitative analysis of how each feature's variation impacts the G/P ratio, not just the ranking of feature importance. Specifically, sensitivity curves for different features across ranges could visually show their contribution to the model output.*

Response:

We added a correlation analysis between the features and the observed G/P ratio of the six selected OOMs.

On lines 375-381, we added the following revision:

"All models show acceptable generalization ability (R^2 = 0.51-0.88). For all six OOMs, particle composition features dominate over meteorological and gaseous composition

features in predicting the G/P ratios (Figure 5). Particle composition features LWC, OC, K^+, SO_4^{2-} and pH, as well as RH, consistently play important roles in influencing the G/P ratios of these species. This is roughly in line with the correlation analysis between the features and the observed G/P ratios of the selected 6 OOMs (Figure S5), which show that pH, RH, LWC, and SO_4^{2-} exhibited strong positive or negative correlations with the G/P ratios."

In the supplementary materials, we add a new Figure S5.

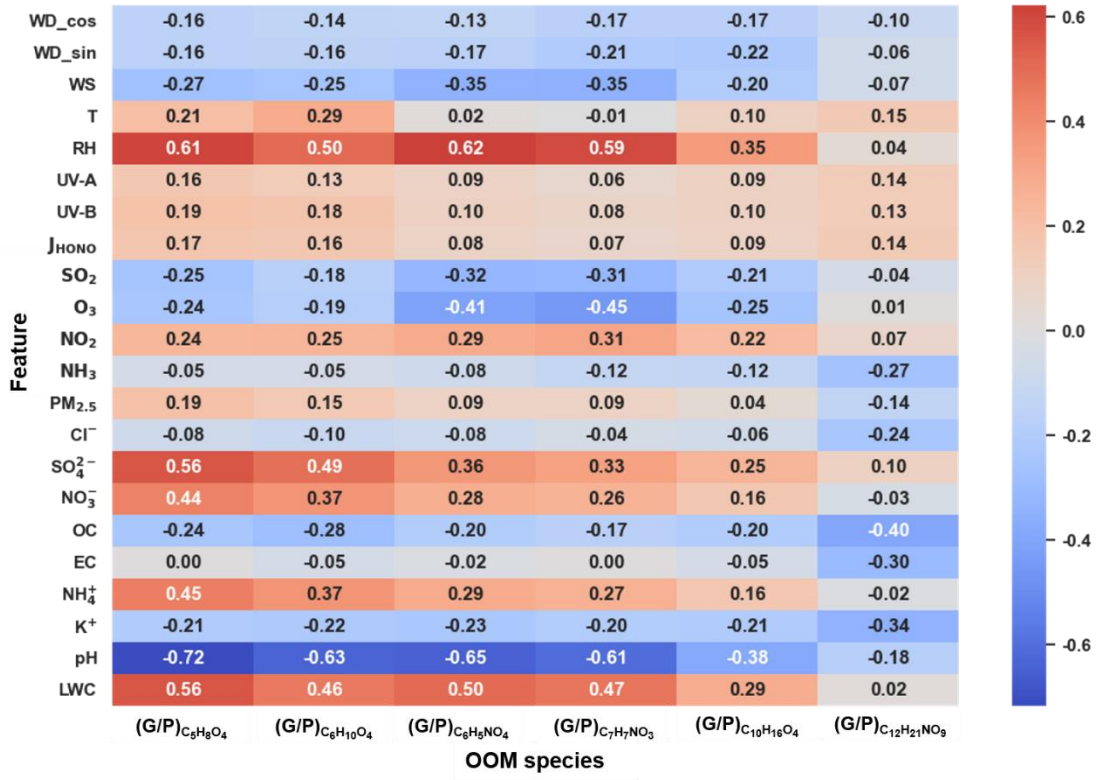

Figure S5. The correlation between the observed G/P ratios of the 6 selected species and various features.

We had shown the sensitivity curves of SHAP values versus features across different feature ranges visually by Figure 7. Now we added quantitative interpretation of the SHAP values and sensitive ranges of features in Section 3.2.2. The blue front below highlights our changes:

"pH is among the two most influential factors for the gas/particle partitioning of five species ($C_5H_8O_4$, $C_6H_{10}O_4$, $C_6H_5NO_3$, $C_7H_7NO_3$ and $C_{10}H_{16}O_4$) with a sensitive range of 3.5–4.5 (as illustrated for $C_6H_{10}O_4$ in Figure 7a). Within this range, the contribution to the G/P ratio decreases by 0.5 from pH 3.5 to 4.5. Beyond pH 4.5, the G/P ratio stabilizes at -0.1. An increase in pH results in a pronounced decrease of the G/P ratio. This phenomenon can be attributed to the enhanced partitioning of OOMs with acidic functional groups from gas to particles with elevated pH (Su et al., 2020).

RH has a positive effect, ranking among the top 5 significant features, on the G/P ratios

of three OOMs $C_6H_5NO_3$, $C_7H_7NO_3$, and $C_{10}H_{16}O_4$ (Figure 6a). SHAP value is sensitive to RH across the full RH range (20%-80%, illustrated by an example $C_6H_5NO_3$ in Figure 7b). LWC also has a significant positive effect for $C_5H_8O_4$, $C_6H_{10}O_4$, $C_6H_5NO_3$, and $C_7H_7NO_3$. For example, in the case of $C_5H_8O_4$, a sharp increase of 0.35 in the G/P ratio is observed within the LWC range below 20 μg m^{-3}. Above 20 μg m^{-3}, the contribution to the G/P ratio stabilizes at 0.15 (Figure 7c). The underlying mechanism of this behavior is unclear. One explanation is that the low RH and LWC in particles may facilitate the formation of reversible oligomers (Shen et al. (2018) and suppress their hydrolysis (Liu et al., 2012), thereby increasing the concentration of these OOMs in particle phase. It is also possible that the thermal desorption and subsequent detection of particle-bound OOMs were inhibited in aerosol particles with more moisture.

OC has a significant negative impact (i.e., rank among the top 5) on the G/P ratios of all six species, being consistent with Eq. (4), where the equilibrium G/P ratios are inversely proportional to C_{OA}. Taking $C_{12}H_{21}NO_9$ as example (Figure 7d), the SHAP values decrease monotonically with C_{OA} by 0.08 in the entire C_{OA} range (5-25 μg m^{-3}). For this compound, EC ranks as the second most influential factor, exerting a notable negative impact below 4 μg m^{-3}. A significant G/P decrease of 0.05 was observed in this range (Figure 7e).

SO_4^{2-} has a positive effect (i.e., rank among the top 5) on the G/P ratios of $C_5H_8O_4$, $C_6H_{10}O_4$, $C_{10}H_{16}O_4$ and $C_{12}H_{21}NO_9$. For example, in the case of $C_6H_{10}O_4$, the G/P ratio rises rapidly by 0.30 with increasing SO_4^{2-} concentrations below 6 μg m^{-3} (Figure 7f). Above 6 μg m^{-3}, the contribution to the G/P ratio stabilizes at 0.1. This may be partly related to the fact that SO_4^{2-} is a highly hydrophilic component (Thaunay et al., 2015), which makes its effect similar to that of LWC. In addition, an increase of sulfate in aerosols is often associated with enhanced acidity and a decrease in pH (Zhang et al., 2007), which drives OOM from particle to gas phase as we explained above.

K^+ has a negative effect on the G/P ratios of $C_5H_8O_4$, $C_{10}H_{16}O_4$, $C_6H_5NO_3$ and $C_7H_7NO_3$. Taking $C_{10}H_{16}O_4$ as example, the G/P ratio decreases rapidly by 0.15 with K^+ in the concentration range of below 1 μg m^{-3}. Above 1 μg m^{-3}, its contribution to the G/P ratio stabilizes at -0.03 (Figure 7g). K^+ is considered as a tracer of biomass burning. The increase of K^+ is generally associated with higher pollution levels and higher OC concentrations in the study region (Zhao et al., 2024). The effect of K^+ on the G/P ratio is thus similar to that of OC."

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