Responses to reviewer's comments

We thank the reviewer for their detailed, helpful, and overall supportive comments. We have revised the manuscript to account for each comment. Responses to the individual comments are provided below. Reviewer comments are in bold. Author responses are in plain text. Modifications to the manuscript are in italics. Line numbers in the response correspond to those in the revised manuscript text file. All changes made in the revised manuscript have been highlighted in red font.

1. **Line 544-547, "This box model finding is supported...", the attribution to biomass burning is not sufficiently supported.**

The reviewer identified a paragraph that contained insufficient support of our statement and was rather confusing. We have revised the entire paragraph and provided supporting information in lines 628 to 638:

"We found that enhanced photolysis acts to increase particle-phase C6H5NO4 in particular, but that changes to influence from open biomass burning can exert a comparable change to particle-phase C6H5NO4 concentration. Seasonal changes in open biomass burning influence, represented by changed model influx rates, are supported by changes to air mass back trajectories in Zhang et al. (2022) that show a shift from maritime to continental influence from Yangon summer to Yangon winter. The simulated effect of changing precursor availability for Yangon is sufficiently great to indicate that varying precursor concentration could drive changes also seen in Mandalay, however we did not have the data to justify changing precursor influx rates between Mandalay simulations, in contrast to changes in photochemistry and RH that were justified for Mandalay"

2. **Could the RH dependence be influenced by precursor variability rather than partitioning?**

We thank the reviewer for this insightful comment. Our box modelling results for

Yangon include plausible precursor variability, finding it comparable, by magnitude of change to C6 and C8 products, to the influence of partitioning thermodynamics and photochemistry. In the absence of further constraint around precursor gas-phase concentrations, it is therefore plausible that precursor variability alone drives the observed variations in C6 and C8 products.

The reviewer therefore highlights a general issue with the wording in the paper that there is too much emphasis and conclusiveness around the effect of partitioning, and we have revised the abstract and implications appropriately. They now read:

"Two ubiquitous nitrophenols, nitrocatechol ($C_6H_5NO_4$) and dimethyl nitrocatechol ($C_8H_9NO_4$), showed strong covariance but a distinct relationship of their particle-phase $C_8H_9NO_4/C_6H_5NO_4$ ratio with RH. CHemistry with Aerosol Microphysics in Python (PyCHAM) box model simulations reveal that increasing RH enhances aerosol water content, to which $C_8H_9NO_4$ and $C_6H_5NO_4$ respond differently because of differences in their partitioning thermodynamics. Increased photochemistry in summertime further promotes $C_6H_5NO_4$ formation. These two processes, in addition to gas-phase precursor concentration, can explain the observed RH relationship and demonstrate that the $C_8H_9NO_4/C_6H_5NO_4$ ratio is sensitive, by comparable extents, to: partitioning thermodynamics, photochemistry and precursor supply" in lines 51 to 61.

And lines 619 to 638 in chapter "Atmospheric implications"

"By combining molecular-level observations with aromatic emission rates from combustion of varying biomasses and box model simulations, we show that variations in the formation of nitrophenolic compounds can be influenced by changing RH, variations in precursor concentrations, and seasonal changes to photochemistry. Our results are consistent with previous studies identifying biomass burning as an important source of aromatic precursors and nitrophenolic compounds (Salvador et al., 2021; Wang et al., 2020), whilst providing additional investigation of how RH and photochemical conditions can influence molecular-level partitioning and

transformation of nitrophenolic compounds in tropical urban atmospheres.

We found that enhanced photolysis acts to increase particle-phase $C_6H_5NO_4$ *in particular, but that changes to influence from open biomass burning can exert a comparable change to particle-phase* $C_6H_5NO_4$ *concentration. Seasonal changes in open biomass burning influence, represented by changed model influx rates, are supported by changes to air mass back trajectories in Zhang et al. (2022) that show a shift from maritime to continental influence from Yangon summer to Yangon winter. The simulated effect of changing precursor availability for Yangon is sufficiently great to indicate that varying precursor concentration could drive changes also seen in Mandalay, however we did not have the data to justify changing precursor influx rates between Mandalay simulations, in contrast to changes in photochemistry and RH that were justified for Mandalay."*

3. The model does not include transport processes.

We thank the reviewer for highlighting this point. We acknowledge that the PyCHAM box model does not explicitly include transport and mixing processes. However, the purpose of the model in this study is to isolate the coupled chemical and partitioning mechanisms governing nitrophenol formation and evolution.

By constraining the model with observed environmental parameters, we focus on mechanistic interpretation rather than reproducing absolute atmospheric concentrations.

Furthermore, lines 496-498 already state that "According to our previous study (Zhang et al., 2022), the backward trajectories during both winter and summer in Mandalay were highly similar, indicating that the observed RH differences cannot be attributed to variations in air-mass transport." Thereby excluding the influence of transport process on pollutant concentrations and the observed ratio.

The reviewer highlights that the exclusion of explicit transport processes from the model and the limitations thereby enforced are not currently sufficiently addressed in the article, therefore the Method now reads:

"The model does not explicitly include the organic oxidation products entering

the simulated box, similarly it cannot spatially distinguish between precursors of SOA that were emitted directly from sources within the box and those transported in from sources outside. Nevertheless, the model and its setup, including a non-zero air change rate for representative transport losses, allow investigation of the processes driving particle-phase organic composition in the observed areas. The results and implications below are therefore constrained to this ability." In lines 283 to 289.

4. The explanation based on solubility of $C_6H_5NO_4$ and $C_8H_9NO_4$ lacks support.

We agree that the original discussion did not sufficiently justify the assumed differences in solubility between $C_6H_5NO_4$ and $C_8H_9NO_4$. We have therefore revised the manuscript to clarify the basis for these inputs. The method now reads:

"The different particle-phase solubilities were not directly measured, but were represented through activity coefficients following previous studies of structurally similar aromatic nitro-compounds (Lee et al., 2000). The $C_6H_5NO_4$ molecule contains hydroxyl and nitro functional groups that enhance polarity and hydrogen-bonding interactions with aerosol water, and was therefore assumed to behave relatively close to ideal solution conditions. In contrast, $C_8H_9NO_4$ contains additional non-polar organic functionality, which is expected to increase non-ideal interactions and reduce effective aqueous-phase solubility. Solubility was assumed to vary linearly with particle water mole fraction, consistent with Kholod et al. (2011). Consequently, for both $C_6H_5NO_4$ and $C_8H_9NO_4$ the activity coefficient was assumed to be unity at zero particle water mole fraction, whilst for $C_6H_5NO_4$ diluted by water, the activity coefficient was set to 10, and for $C_8H_9NO_4$ it was set to 3000. The combination of different volatilities and solubilities of $C_6H_5NO_4$ and $C_8H_9NO_4$ in a thermodynamic simulation of gas-particle partitioning presents the potential for different sensitivities to varying particle-phase water content, which is quantitatively investigated in the results." In lines 267-282.

Furthermore, the Results section has been updated to quantitatively investigate how partitioning thermodynamics, including solubility, affects the two components ($C_6H_5NO_4$ and $C_8H_9NO_4$) differently:

"Considering first just the Mandalay results (Fig. 7a), for which the influx rates of $C_6H_5NO_4$ *and* $C_8H_9NO_4$ *precursors were constant across all RH, modelled* $C_8H_9NO_4/C_6H_5NO_4$ *changes from 0.69 to 0.54 as RH changes from 80 to 60 %, whilst observations report a change from 0.59 to 0.48. Because both 80 and 60 % were during the winter period, the modelled change is not due to changing actinic flux, similarly although the decrease in gas-phase water content from 80 to 60 % RH leads to a slight decrease in OH concentration, the change in consumption of the parent VOCs is negligible, therefore photochemistry does not explain the change in ratio. The only remaining explanation for the ratio changes available to the model is changes to the particle phase due to changed partitioning thermodynamics. The decrease in particle-phase concentration of* $C_8H_9NO_4$ *from 80 to 60 % RH is 30 %, whilst the decrease is 10 % for* $C_6H_5NO_4$*. Therefore, the greater sensitivity of* $C_8H_9NO_4$ *to changing partitioning thermodynamics, which results from changes to both absorptive particle concentration and particle-phase solubility, results in changed* $C_8H_9NO_4/C_6H_5NO_4$*. Variations in sensitivity are dependent on the product of component activity coefficient and vapour pressure, which gives an effective volatility or* c^*_{eff}*. For* $C_8H_9NO_4$*,* c^*_{eff} *changes from 2400 to 1800 µg* m^{-3} *between 80 and 60 % RH, whilst for* $C_6H_5NO_4$ c^*_{eff} *changes from 82 to 64 µg* m^{-3}*. These effective volatilities can be divided by the component molar masses to give units of mol* m^{-3} *and combined with the total absorptive molar concentration (*$c_{n,abs}$*) of the particle phase in an equation for equilibrium gas-particle partitioning (Pankow 1994) to demonstrate the different thermodynamic sensitivity of the two components:*

$$\xi_i = \left(1 + \frac{c^*_{n,i,eff}}{c_{n,abs}}\right)^{-1} , \qquad (3)$$

where ξ *is the equilibrium condensing fraction of component* i *and* n *is the molar concentration. Using the simulated* $c_{n,abs}$ *of* 3.59×10^{-6} *and* 7.28×10^{-6} *mol* m^{-3} *for the 60 and 80 % RH scenarios, respectively, gives a factor change in* ξ *(*$\xi_{i,80\%RH}/\xi_{i,60\%RH}$*) of 1.33 for* $C_8H_9NO_4$ *and 1.04 for* $C_6H_5NO_4$*."* In lines 529-555.

Because the new quantitative analysis finds that partitioning thermodynamics, not just solubility, drives the varying sensitivity to changing RH when photochemistry and emissions are constant, the Abstract and Implications sections have been updated accordingly:

Abstract: "CHemistry with Aerosol Microphysics in Python (PyCHAM) box model simulations reveal that increasing RH enhances aerosol water content, to which $C_8H_9NO_4$ *and* $C_6H_5NO_4$ *respond differently because of differences in their partitioning thermodynamics. Increased photochemistry in summertime further promotes* $C_6H_5NO_4$ *formation. These two processes, in addition to gas-phase precursor concentration, can explain the observed RH relationship and demonstrate that the* $C_8H_9NO_4/C_6H_5NO_4$ *ratio is sensitive, by comparable extents, to: partitioning thermodynamics, photochemistry and precursor supply."*

Implications: "Meanwhile, particle-phase $C_8H_9NO_4$ *concentrations were shown to be relatively sensitive to changing RH, via partitioning thermodynamics. These findings indicate the importance of accurately representing emissions, photochemistry, and gas-particle partitioning thermodynamics in predicting particle-phase composition and abundance in chemical transport models, and we note that the latter two processes are in principle represented by the BAT-VBS framework (Serrano Damha et al., 2024)."*

5. How generalizable are your findings?

Thank you for raising this point. Although this study was conducted in Myanmar, the mechanisms identified by the PyCHAM simulations are not location-specific. The effects of aerosol water content on gas-particle partitioning and of atmospheric oxidizing capacity on nitrophenol production are fundamental atmospheric processes expected to occur in many environments. Therefore, the observed sensitivity of the particle-phase $C_8H_9NO_4/C_6H_5NO_4$ ratio to RH and photochemical activity may also be relevant in other humid and photochemically active regions.

Nevertheless, our simulations also show that precursor concentrations can substantially influence the particle-phase $C_8H_9NO_4/C_6H_5NO_4$ ratio. Consequently, the sensitivity of this ratio to RH and atmospheric oxidizing capacity may differ between regions with different emission profiles, even though the underlying mechanisms remain the same. We modified the content in lines 644-656:

"While this study focuses on Myanmar, the identified controls of RH on gas-particle partitioning and of atmospheric oxidizing capacity on nitrophenol formation are fundamental atmospheric processes likely relevant to other humid and photochemically active regions. Nevertheless, regional differences in precursor abundance and emission profiles may modulate the sensitivity of particle-phase nitrophenolic compounds to these processes. As nitrophenolic compounds are important constituents of biomass-burning-derived brown carbon, the demonstrated sensitivity of their abundance to RH and photochemical conditions may also contribute to uncertainties in estimates of brown carbon radiative forcing. However, due to the limited availability of standards, quantitative analysis was only possible for few nitrophenolic compounds. Future work should include more comprehensive laboratory simulations to better constrain the effects of RH and OH on the formation and degradation of nitrophenolic compounds."

6. "demonstrate that varying precursor concentrations can substantially disrupt the relationship between $C_8H_9NO_4/C_6H_5NO_4$ and aerosol aging." in line 515-517, based on the analysis in Figure S7, I guess that RH is more likely to influence the relationship between $C_8H_9NO_4/C_6H_5NO_4$ and aerosol aging, and that the comparison of precursor concentrations does not have a significant effect.

We thank the reviewer for this insightful comment. We agree that variations in RH may also contribute to the scatter observed in Fig.S7 because our box-model simulations show that RH influences the particle-phase $C_8H_9NO_4/C_6H_5NO_4$ ratio through changes in aerosol water content and gas-particle partitioning.

Our intention was not to imply that the observed scatter can be attributed solely to precursor concentrations. Rather, the box-model results indicate that both RH and precursor abundance can affect the relationship between $C_8H_9NO_4/C_6H_5NO_4$ and aerosol aging. In particular, the simulations demonstrate that realistic variations in precursor concentrations can substantially modify the ratio and may even exceed the influence of photochemistry under some conditions.

We have revised the manuscript (line 593-597) to clarify that RH, precursor concentrations, and photochemical processing all contribute to the observed variability of $C_8H_9NO_4/C_6H_5NO_4$:

"However, the spread of points in Fig. S8, particularly for Yangon summer and Mandalay summer, indicates that aerosol aging alone cannot fully explain the variability in $C_8H_9NO_4/C_6H_5NO_4$. *The box-model simulations suggest that RH-dependent partitioning, precursor emissions, and photochemical processing all contribute to the observed variability."*

7. "variations in the formation of nitrophenolic compounds is influenced" in Line 539-540, "is" should be changed to "are"; "mass concentration of these two compounds were higher in the Mandalay samples than in Yangon" in line 405, "were" should be changed to "was".

Thank you for your suggestion. We have made the corresponding changes to the text.

8. The section on implications in the "Conclusions and Implications" chapter needs to be strengthened.

Thank you for your suggestion. We have modified in lines 622-656 of the main text as follows. In particular, we highlight generalizable and the importance of these findings for accurately estimating the radiative forcing of brown carbon.

"Our results are consistent with previous studies identifying biomass burning as an important source of aromatic precursors and nitrophenolic compounds (Salvador et al., 2021; Wang et al., 2020), whilst providing additional investigation of how RH and photochemical conditions can influence molecular-level partitioning and transformation of nitrophenolic compounds in tropical urban atmospheres.

We found that enhanced photolysis acts to increase particle-phase $C_6H_5NO_4$ *in particular, but that changes to influence from open biomass burning can exert a comparable change to particle-phase* $C_6H_5NO_4$ *concentration. Seasonal changes in open biomass burning influence, represented by changed model influx rates, are* *supported by changes to air mass back trajectories in Zhang et al. (2022) that show a shift from maritime to continental influence from Yangon summer to Yangon winter. The simulated effect of changing precursor availability for Yangon is sufficiently great to indicate that varying precursor concentration could drive changes also seen in Mandalay, however we did not have the data to justify changing precursor influx rates between Mandalay simulations, in contrast to changes in photochemistry and RH that were justified for Mandalay.*

Meanwhile, particle-phase $C_8H_9NO_4$ *concentrations were shown to be relatively sensitive to changing RH, via partitioning thermodynamics. These findings indicate the importance of accurately representing emissions, photochemistry, and gas-particle partitioning thermodynamics in predicting particle-phase composition and abundance in chemical transport models, and we note that the latter two processes are in principle represented by the BAT-VBS framework (Serrano Damha et al., 2024). While this study focuses on Myanmar, the identified controls of RH on gas-particle partitioning and of atmospheric oxidizing capacity on nitrophenol formation are fundamental atmospheric processes likely relevant to other humid and photochemically active regions. Nevertheless, regional differences in precursor abundance and emission profiles may modulate the sensitivity of particle-phase nitrophenolic compounds to these processes. As nitrophenolic compounds are important constituents of biomass-burning-derived brown carbon, the demonstrated sensitivity of their abundance to RH and photochemical conditions may also contribute to uncertainties in estimates of brown carbon radiative forcing. However, due to the limited availability of standards, quantitative analysis was only possible for few nitrophenolic compounds. Future work should include more comprehensive laboratory simulations to better constrain the effects of RH and OH on the formation and degradation of nitrophenolic compounds."*