Response to Reviewer #2

We sincerely appreciate the valuable comments provided by the reviewer, which greatly contributed to enhancing the quality of the paper. Detailed responses are shown below. The reviewer's comments are in regular font, and the author's responses are in red. The changes made to the text are highlighted in blue. The corresponding contents have been updated in the manuscript.

Reviewer 2:

Ye et al. applied CMAQ model, incorporating revised Naphthalene (Nap) and methylnaphthalene (MN) emissions, as well as including new secondary organic carbon (SOC) formation pathway through 1-MN, to investigate the importance of Nap and MN for SOC formation. They found the model well-reproduced the Nap and MN if using revised emission and one-product SOC formation pathway. Additionally, the findings indicated the oxidation of Nap and MN has negligible effects on regional ozone and radical levels. The draft is well-written, and the topics fit the scope of ATMOS CHEM PHYS journal. I enjoy reading the draft, and I only have a few minor comments.

Response: Thank you very much for taking the time to thoroughly review our manuscript. We truly appreciate your valuable comments, which have been instrumental in improving the quality of our work. Several changes have been made to enhance the clarity of the manuscript. We renamed 'base1' as 'base_zeroNapMN'. Additionally, we conducted a new scenario (base_zeroMN) where the emissions of 1-methylnaphthalene (1-MN) and 2-methylnaphthalene (2-MN) in case-1product were set to zero to quantify the individual impacts of naphthalene (Nap) and methylnaphthalene (MN). The manuscript has been updated with results based on corrected Nap and MN emissions from transportation and residential sources in the MEIC inventory for the surrounding area of YRD. The conclusions remain unchanged. Our study emphasizes the importance of Nap and MN in contributing to secondary organic aerosol (SOA) formation, even with only a small amount emitted into the atmosphere. Although their regional impacts on SOC, ozone, and HO_x radicals may not be substantial, it is crucial to consider their impacts in areas with high emissions such as Shanghai and southern Jiangsu. We have carefully considered all your comments and made revisions accordingly. Detailed point-to-point responses are shown below.

Minor comments:

1. Line 105: Figure S1 is important for understanding the paper method framework. I checked Figure S1 several times to understand the results. I would recommend moving this figure to the main text. Also, for the SOC formation pathway, the two new added pathways are all about 1-MN. Are there any new pathway for 2-MN in this work? If not, is there any default SOC formation pathway through 2-MN?

Response: Thank you for the advice. Figure S1 has been moved to the main text and labeled as Figure 1 (Figure R1). The SOC formation pathways for 1-MN and 2-MN are similar and both are newly added to the CMAQ model. We have revised the figure to

include the SOC formation pathways of 2-MN. Additionally, the reaction of Nap with chlorine radicals has been excluded from the SOC-Nap scheme since it is not considered in the current CMAQ model. The updated figure is shown below:

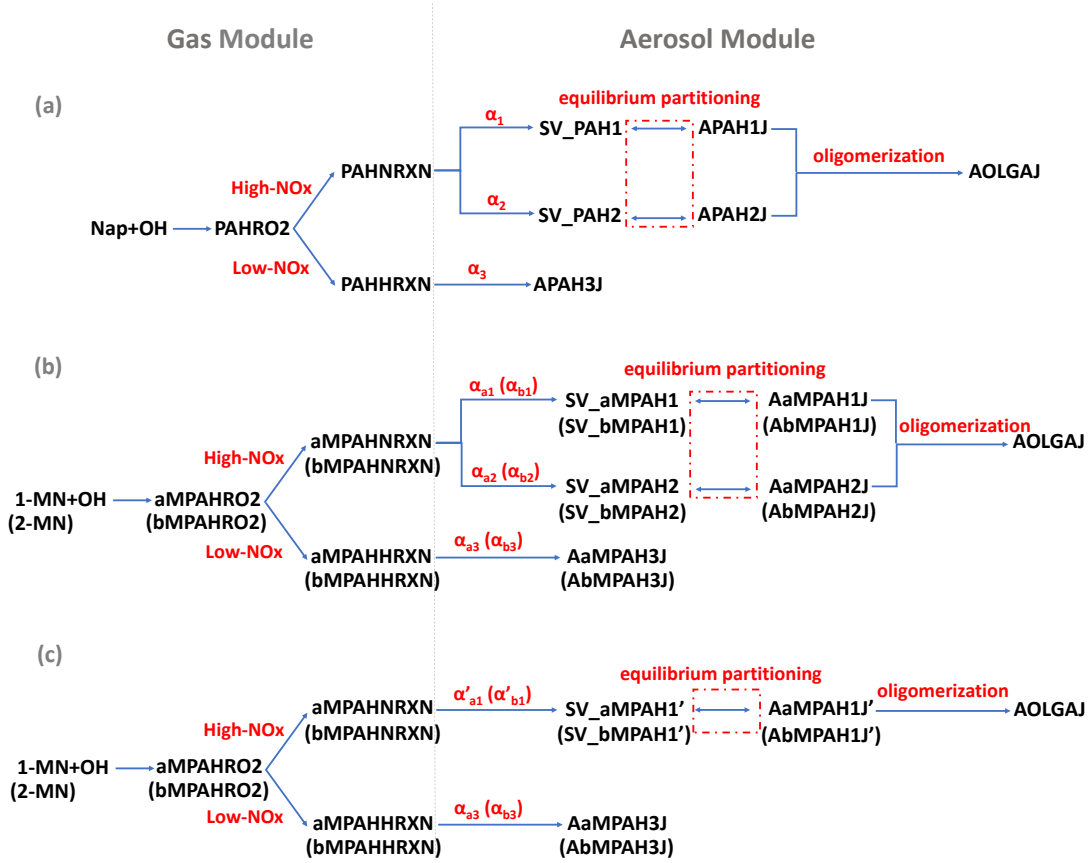

Figure R1. SOA schemes for naphthalene (Nap), 1-methylnaphthalene (1-MN), and 2-methylnaphthalene (2-MN) in the updated CMAQ model. (a) pre-existing Nap-derived SOA formation pathways fitted by two products under high NO_x; (b) newly added SOA formation pathways for 1-MN and 2-MN fitted by two products under high NO_x; (c) newly added SOA formation pathways for 1-MN and 2-MN fitted by one product under high NO_x. SOA formation from Nap and MN oxidation by OH radicals under low-NO_x conditions is represented by a fixed yield. Parameters for 2-MN are indicated in brackets in (b) and (c). The values of α refer to Table S1.

2. Line 166: I recommend moving table S3 to the main text. Additionally, should there be a solid case-1product-orig and base1, and case-1product and case-2product-orig?

Response: Thanks for the advice. Table S3 (Table R1) has been moved to the main text and labeled as Table 1. Generally, the scenarios can be divided into three categories based on Nap and MN emissions. The first type (emis-orig), i.e. case-1product-orig and case-2products-orig, used default Nap emissions from the YRD inventory and estimated emissions for Nap in the rest of the domain and MN in the whole domain based on source profiles from the SPECIATE database. To improve modeled Nap and MN concentrations, their anthropogenic emissions were adjusted (emis-adjust) according to observed/predicted concentration ratios from aforementioned cases,

named case-1product and case-2products, respectively. The difference between the two cases within each category is the representation of SOA formation from 1-MN and 2-MN, i.e., one-product (1product) or two-product (2products) scheme as shown in Figure R1(b-c). For the third type, i.e., base1, only the emissions of Nap and MN in the entire domain were set to zero on top of emis-adjust. To make this clear, we have renamed 'base1' as 'base_zeroNapMN'. A new scenario (base_zeroMN) was conducted to quantify the individual impacts of Nap and MN by setting the emissions of 1-MN and 2-MN to zero. The revised Table 1 and the text are shown as follows:

Lines 171-184: "Table 1 lists the scenarios conducted in this study. In case-1product-orig, the anthropogenic emissions were based on emis-orig, along with the SOA parameterization for MN fitted by a one-product method in Fig. 1c and that of Nap fitted by a two-product method in Fig. 1a under high-NO_x conditions. To assess the impacts of different SOA parameterizations, case-2products-orig adopted the same setting as case-1product-orig except for utilizing a two-product method for MN-derived SOA under high-NO_x conditions (Fig. 1b). For accurate representations of the fate of Nap and MN in the atmosphere, both case-1product and case-2products employed adjusted emissions (emis-adjust) along with different SOA parameterizations for MN. SOA formation from Nap and MN under low-NO_x conditions in the above cases were all characterized by a fixed yield as shown in Table S1. Overall, the contributions of Nap, 1-MN, and 2-MN to the aromatic SOC were estimated based on different emission inventories and SOA schemes. To evaluate the effects of Nap, 1-MN, and 2-MN on O_3, SOC, and radical concentrations, their emissions in case-1product were set to zero and named base_zeroNapMN. A case named base_zeroMN was conducted to quantify the individual effects of Nap and MN by setting the emissions of 1-MN and 2-MN to zero."

Table R1. Settings of the scenarios.

Case	Emission setting	SOA parameterization for MN
case-1product-orig	Nap emissions in the YRD were based on the 2017 YRD inventory; Nap emissions in the rest of the domain and MN emissions in the entire domain were calculated using sector-specific mass ratios and total emissions of non-methane volatile organic compounds (emis-orig)	one-product method
case-2products-orig		two-product method
case-1product	The anthropogenic emissions of Nap and MN in the entire domain from emis-orig were multiplied by 5 and 7, respectively (emis-adjust)	one-product method
case-2products		two-product method
base_zeroNapMN	Emissions of Nap and MN were set to zero based on emis-adjust	one-product method
base_zeroMN	Emissions of MN were set to zero based on emis-adjust	one-product method

3. Line 193: Why there are no results of case-1product and case-2products in figure 1 (c)-(e) and figure S4 (c)-(e)? Are they overlapped with the original emission simulations? Why do not show the results for the base1 simulation? I think comparisons with the base simulation can indicate the importance of the newly added 1-MN SOA formation pathway.

Response: Thanks for your insightful suggestion. Yes, the results of case-1product and case-2products (both in red lines) based on adjusted emissions of Nap and MN (emis-adjust) overlapped with those using emis-orig emissions (blue lines), due to minimal impacts on OC, O_3, and $PM_{2.5}$. We have added the explanation "Note that the red and blue lines overlap in (c)-(e)" in relevant figure captions (Figures R2 and R3).

We did not separately examine the impacts of Nap and MN on the formation of secondary pollutants since the focus is on the combined impacts of Nap and derivatives. Therefore, the emissions of Nap and MN were set to zero in base1. To clarify this point, we have renamed 'base1' as 'base_zeroNapMN' in the revised manuscript. Additionally, we conducted a sensitivity simulation by excluding 1-MN and 2-MN emissions in case-1product ('base_zeroMN'). The differences between case-1product and base_zeroMN represent the impacts of MN alone, as shown in Figure R4 (Figure S11 in the revised Supplement). Overall, the impacts of Nap on SOC, O_3, and radicals are significantly higher than those of MN. The importance of MN is summarized in the revised text as follows:

Lines 294-295: "The impact on O_3 was relatively limited, with a maximum increase of 0.3%, primarily attributed to Nap rather than MN (Fig. S11)."

Lines 307-308: "Similar to O_3, variations in $OH^{\cdot}$ and $HO_2^{\cdot}$ were primarily influenced by Nap rather than MN (Fig. S11)."

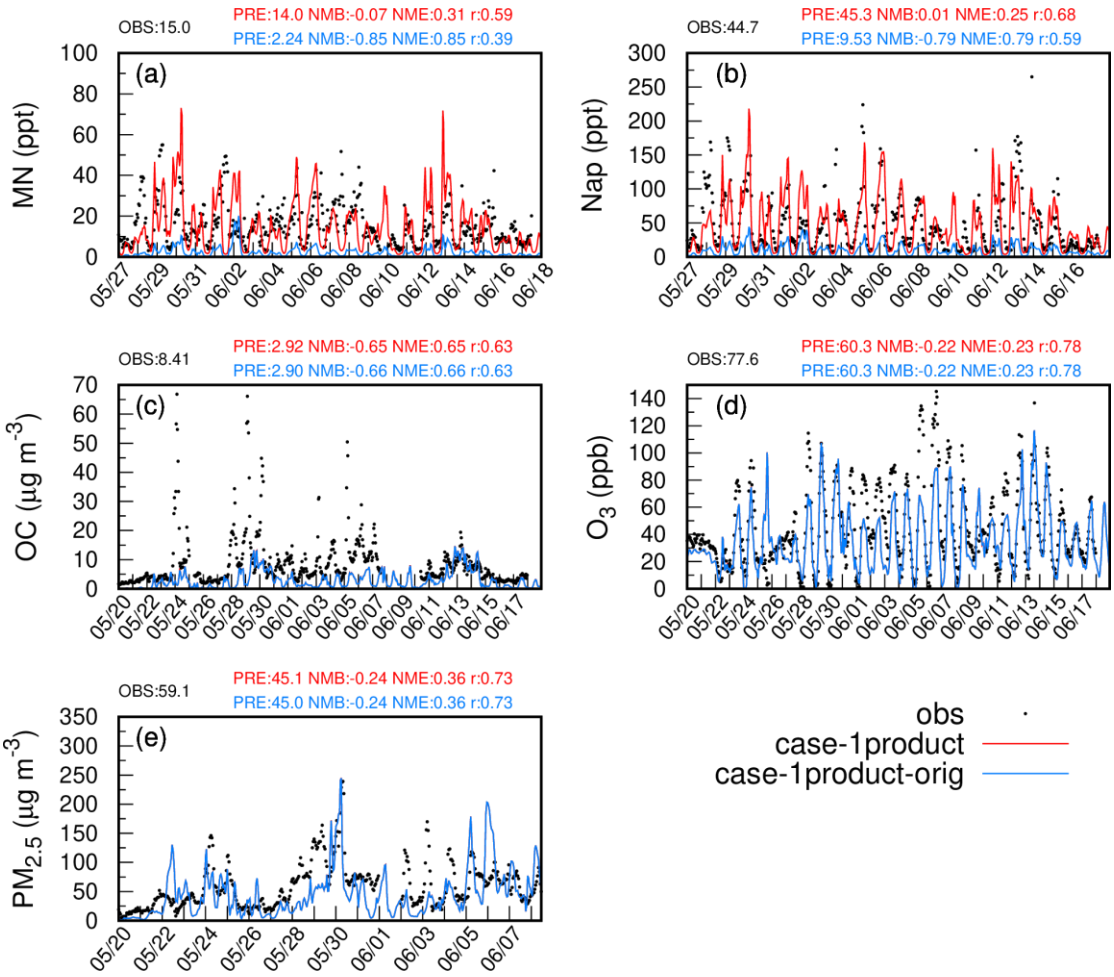

Figure R2. Observed and simulated hourly concentrations of MN, Nap, OC, $PM_{2.5}$, and O_3 based on emis-adjust (red) and emis-orig (blue) at the Taizhou site. Model performances for daily MN, Nap, OC, $PM_{2.5}$, and MDA8 O_3 are shown in blue for case-1product-orig and in red for case-1product. OBS and PRE represent the average of observations and predictions, respectively. Note that the red and blue lines overlap in (c)-(e).

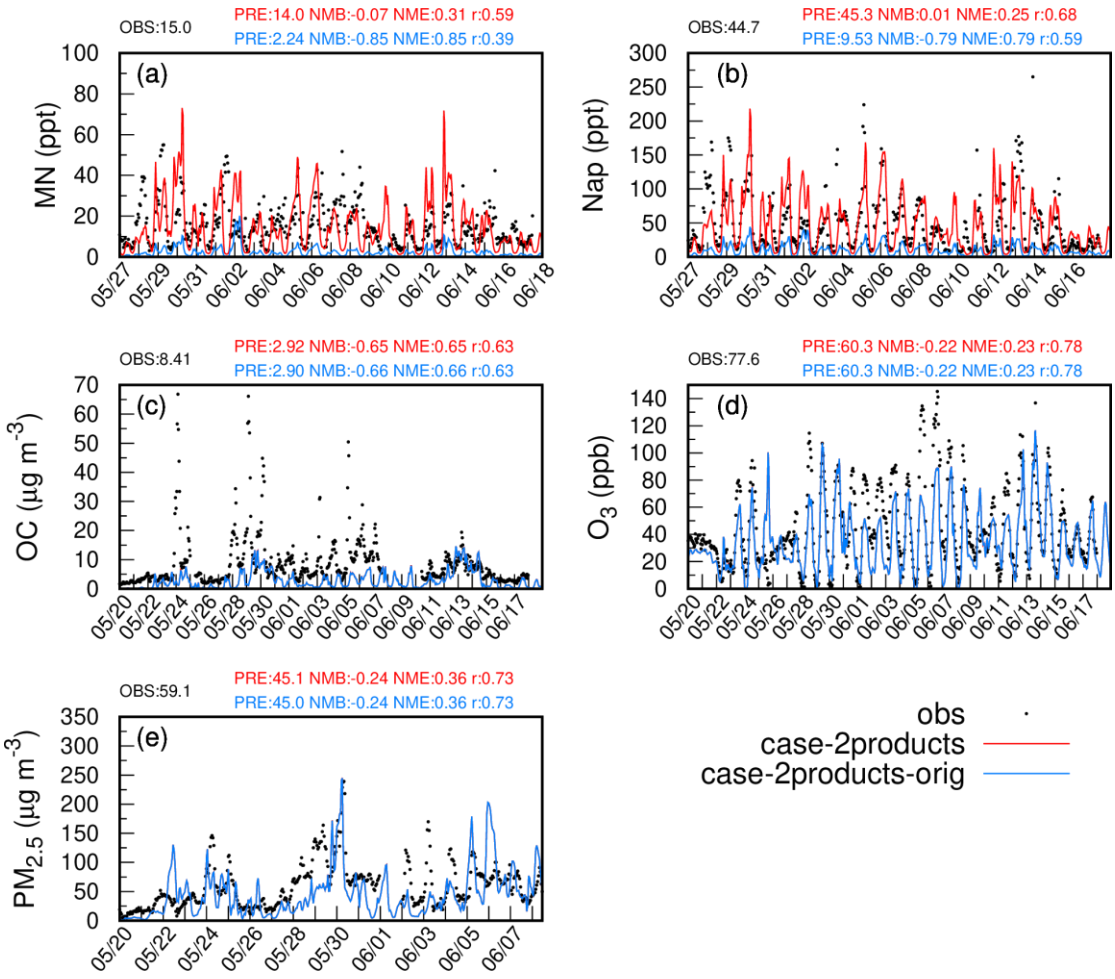

Figure R3. Observed and simulated hourly concentrations of MN, Nap, OC, $PM_{2.5}$, and O_3 based on emis-adjust (red) and emis-orig (blue) at the Taizhou site. Model performances for daily MN, Nap, OC, $PM_{2.5}$, and MDA8 O_3 are shown in blue for case-2products-orig and in red for case-2products. OBS and PRE represent the average of observations and predictions, respectively. Note that the red and blue lines overlap in (c)-(e).

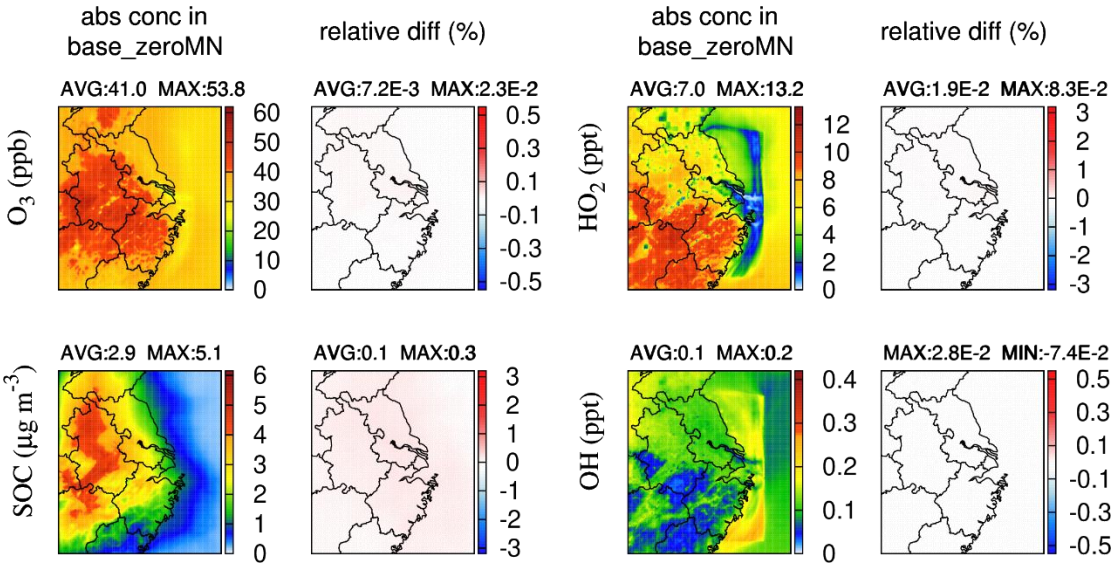

Figure R4. Average concentrations of SOC, O_3, OH·, and HO_2· in base_zeroMN and changes in case-1product relative to base_zeroMN.

4. Line 204: Why do you only show the metrics for case-1product in Tables S4 and S5? How about the other four cases? If the results from case-1product closely align with measurements, you can simply say that the correlations with observations are higher in case-1product than in the other four cases.

Response: Thanks for pointing this out. We evaluated scenarios implementing different Nap and MN emissions, i.e., emis-orig and emis-adjust, against observations. Among them, the results of cases using the same emissions but different SOA schemes for MN were very similar. Considering scenarios using different emissions, the metrics for the case exhibiting the best performances (case-1product) were presented, although the differences between case-1product and case-1product-orig were insignificant. We have included discussions in the text as follows:

Lines 217-218: "It should be noted that the influences of different SOA schemes for MN on the aforementioned species are negligible."

Lines 220-222: "The results of case-1product and case-2products using emis-adjust as the emission data were superior compared to the cases using emis-orig. These findings will be further discussed in the subsequent analysis."

5. Line 213: Figure 2 is interesting. Did you also check the SOC-Nap diurnal cycle in the base1 simulation? The current results show that more SOC formation pathways do not indicate more SOC formation. It also depends on the reaction rates of each pathway. So the default model scheme with only SOC-Nap pathway, which is also the most efficient pathway, may simulate more SOC.

Response: Thank you for your valuable advice. In base1, the emissions of Nap, 1-MN, and 2-MN were all set to zero so that there was no SOC formation from these PAHs.

To enhance clarity, we have renamed 'base1' as 'base_zeroNapMN'. The differences in SOC-MN between case-1product and case-2products are mainly attributed to the yields and equilibrium partitioning coefficients of SVOC products under high-NO_x conditions. When comparing the SOA yields under high-NO_x conditions, 2-MN and 1-MN employing one-product SOA schemes exhibit higher values than Nap (Figure R5). Additionally, the reaction rate of PAHs with OH radicals and their emission rates also affect SOC formation. Overall, among these compounds, Nap demonstrates the highest contribution to SOC. The text has been revised as follows:

Lines 240-247: "Apart from having the highest emissions, Nap also exhibits greater reactivity with OH·. Although its SOA yield under high-NO_x conditions is lower than that of MN fitted by the one-product scheme (Fig. S6), its SOA yield under low-NO_x conditions is the highest among the three PAHs (Table S1). Overall, Nap contributed the most to SOC. 2-MN demonstrates higher SOA yields than 1-MN under high-NO_x conditions in both cases, but a lower SOA yield under low-NO_x conditions. Considering the impact of a higher emission rate (Fig. 3a and 3c), 2-MN contributed two times more SOC compared to 1-MN."

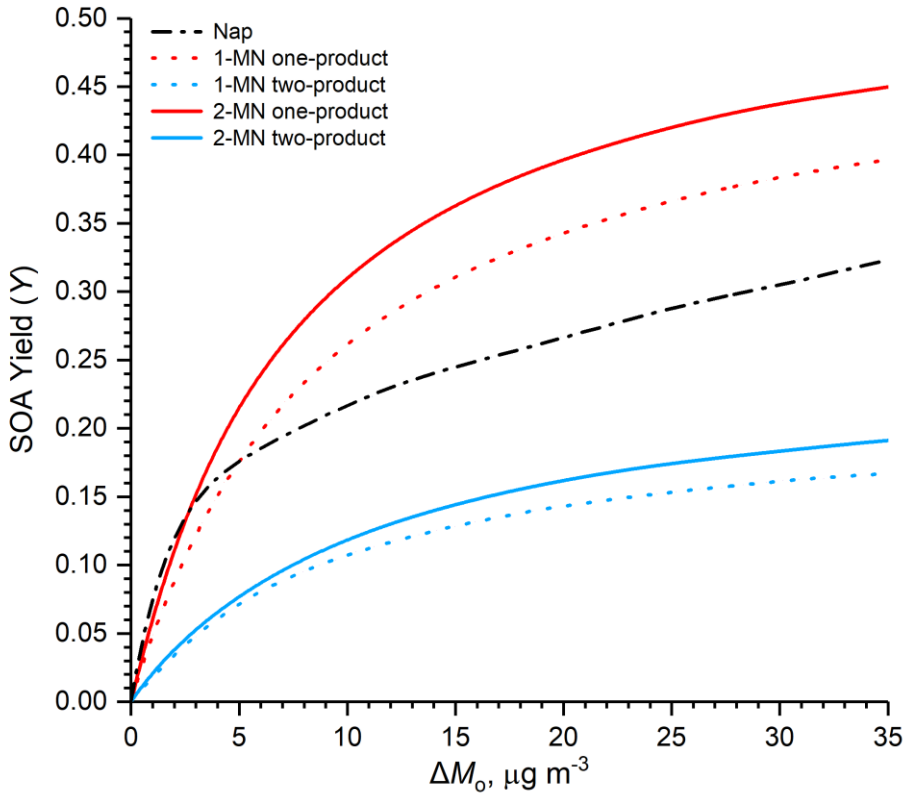

Figure R5. Comparison of fitted SOA yield curves of Nap, 1-MN, and 2-MN under high-NO_x conditions with different total organic mass concentrations (ΔM_o). SOA yield (Y) is calculated as $Y=\Delta M_o \sum_i \frac{\alpha_i K_{om,i}}{1+\Delta M_o K_{om,i}}$, where values of α and K_{om} come from Table S1.