We thank the reviewers for their careful review of our manuscript. The comments and suggestions greatly improve our manuscript. Following is our point to point responses to the comments:

Response to referee #2:

This manuscript described the composition, variation, and sources of gas-phase nitrated phenols in Beijing during winter 2018. A box model was used to simulate the formation of nitrophenols. A NMF model was used to determine the primary sources of nitrophenols. Given the ubiquity of nitrophenols and the potentially important roles they play in influencing climate, this manuscript will be of interest to the atmospheric chemistry community. However, substantial revisions need to be made before this manuscript can be considered for publication.

We thank the reviewer for his careful review of our manuscript. Following is our point to point response to the comments.

1. In general, I found the writing quality of the manuscript very poor. There were many parts of the manuscript where inappropriate words/terminology were used (e.g., “vicarious peaks” on line 238). There was also inconsistent use of tenses and punctuations. The poor writing made the manuscript very difficult (and frustrating) to read and understand. The writing has to be improved substantially. I strongly recommend the authors get someone with strong writing skills to help them improve the manuscript.

Thank you for your comment. We improve the writing substantially in the revised manuscript. In addition, we asked a native speaker to help us with the language editing.

2. It was not clear from the manuscript whether calibrations were performed throughout the study or only at the beginning/end of the study. If calibrations were only performed at the beginning or end, how can the authors be sure that the sensitivity of their instrument was the same throughout the study?

Thank you for your comment. The calibrations were performed at the end of the campaign. The detailed information can be found in line 58 – 61 in the revised supplementary information. We agree that the sensitivity of CIMS might vary throughout the campaign. However, as the signals of nitrated

phenols were all normalized by reagent ions (NO_3^-(HNO_3)$_{0-2}$), the fluctuations of sensitivity could be corrected in this way (Aljawhary et al., 2013; Duncianu et al., 2017).We added more description in the supplementary information. The details are as following:

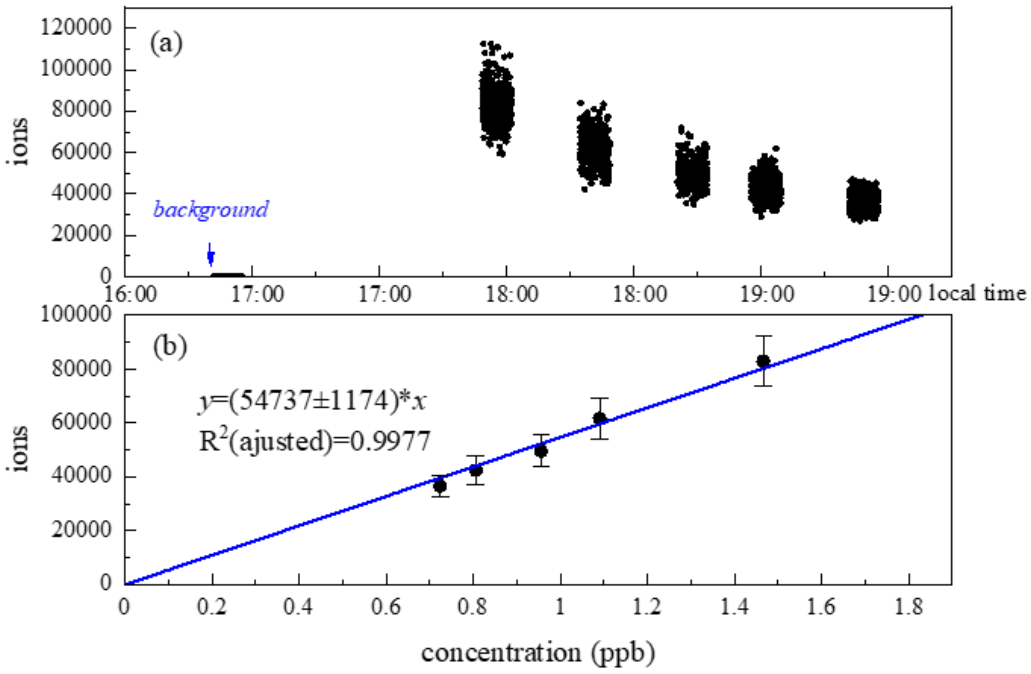

Figure S2. (a) Background ions and ions detected during the calibration period (calibrated at the end of the campaign, on Jan 26, 2019); (b) Calibration line of ions (*y*) and the standard gas-phase concentration of nitrophenol (*x*). The signals were normalized by reagent ions (NO_3^-(HNO_3)$_{0-2}$). Yuan et al. calibrated nitrophenol (NP), methylnitrophenol (MNP) and dinitrophenol (DNP) in the previous study utilizing nitrate-CIMS. The sensitivity of NP, MNP and DNP were 13.2, 16.6, 10.3 npcs ppt^{-1}, respectively (Yuan et al., 2016). The sensitivities of MNP and DNP ranged -26% and 22% from NP. Rebecca H. Schwantes et al. estimated sensitivity factors for CIMS operated in both negative and positive mode using CF_3O^- and $H_3O(H_2O)^+$. The estimated sensitivities of *o*-nitrophenol, 3-nitrocatechol, 4-methyl-2-nitrophenol were 1.48, 1.16 and 1.69, respectively. The sensitivities of NC and MNP ranged 22% and -14% from NP (Schwantes et al., 2017). Even though uncertainties remain, the addressed NPs calibrated by NP were correct in concentration levels and magnitudes. Besides, the secondary formation process simulated by the box model is constrained only by precursors of NPs measured by online GC-MS rather than the actual concentrations of NPs.

NMF model might be influenced by the uncertainties in the quantification. However, the high time resolution of CIMS increased sample inputs of the NMF model and reduced the uncertainties for this statistical approach. Even though the actual contrition of sources faces uncertainties, the proportion of source profiles is still reliable in this approach.

3. Why was only one nitrophenol used for calibration? I don't think this is appropriate since different nitrophenolic compounds will have different CIMS sensitivities. Have the authors done other calibration tests to determine how the sensitivities of nitrophenolic compounds can differ? Uncertainties in the quantification of ambient nitrophenols may have contributed to the differences between their ambient observations and model predictions.

We agree with the reviewer. Only one nitrophenol was used for calibration in this study, which could lead to uncertainty in quantifing other nitrophenols. We added uncertainty analysis in the SI to make the reader more clear about how much the uncertainty is.

Yuan et al. calibrated nitrophenol (NP), methylnitrophenol (MNP) and dinitrophenol (DNP) in the previous study utilizing nitrate-CIMS. The sensitivity of NP, MNP and DNP were 13.2, 16.6, 10.3 npcs ppt^{-1}, respectively (Yuan et al., 2016). The sensitivities of MNP and DNP ranged -26% and 22% from NP. Rebecca H. Schwantes et al. estimated sensitivity factors for CIMS operated in both negative and positive mode using CF_3O^- and $H_3O^+(H_2O)$. The estimated sensitivities of *o*-nitrophenol, 3-nitrocatechol, 4-methyl-2-nitrophenol were 1.48, 1.16 and 1.69, respectively. The sensitivities of NC and MNP ranged 22% and -14% from NP (Schwantes et al., 2017). Even though uncertainties remain, we tend to believe that the addressed NPs calibrated by NP were correct in concentration levels and magnitudes. Besides, the secondary formation process simulated by the box model is constrained only by precursors of NPs measured by online GC-MS rather than the actual concentrations of NPs. NMF model might be influenced by the uncertainties in the quantification. However, the high time resolution of CIMS increased sample inputs of the NMF model and reduced the uncertainties for this statistical approach. Even though the actual contrition of sources faces uncertainties, the proportion of source profiles is still reliable in this approach.

In addition, we add uncertainty analysis in the manuscript (line 103 – 104) as follows, "The

uncertainty in quantifying other NPs from the sensitivity of NP ranged from -26% to 22% (Schwantes et al., 2017; Yuan et al., 2016). The addressed NPs calibrated by NP were correct in concentration levels and magnitudes. See more detail in Figure S2". Figure S2 can be found as follows.

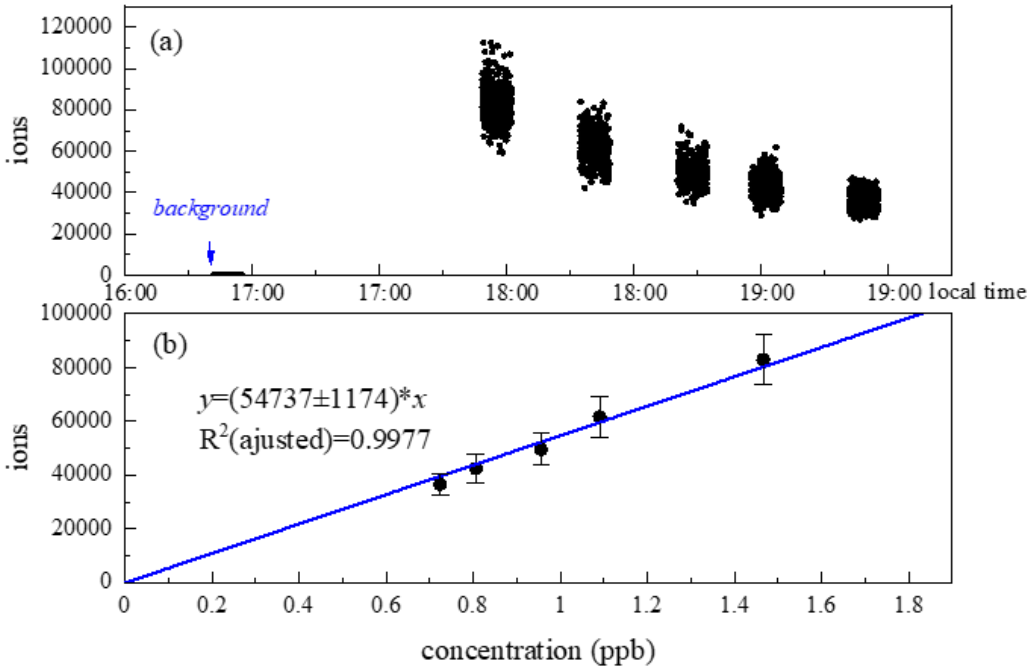

Figure S2. (a) Background ions and ions detected during the calibration period (calibrated at the end of the campaign, on Jan 26, 2019); (b) Calibration line of ions (*y*) and the standard gas-phase concentration of nitrophenol (*x*). The signals were normalized by reagent ions $(NO_3^-(HNO_3)_{0\text{-}2})$. Yuan et al. calibrated nitrophenol (NP), methylnitrophenol (MNP) and dinitrophenol (DNP) in the previous study utilizing nitrate-CIMS. The sensitivity of NP, MNP and DNP were 13.2, 16.6, 10.3 npcs ppt^{-1}, respectively (Yuan et al., 2016). The sensitivities of MNP and DNP ranged -26% and 22% from NP. Rebecca H. Schwantes et al. estimated sensitivity factors for CIMS operated in both negative and positive mode using CF_3O^- and $H_3O^+(H_2O)$. The estimated sensitivities of *o*-nitrophenol, 3-nitrocatechol, 4-methyl-2-nitrophenol were 1.48, 1.16 and 1.69, respectively. The sensitivities of NC and MNP ranged 22% and -14% from NP (Schwantes et al., 2017). Even though uncertainties remain, the addressed NPs calibrated by NP were correct in concentration levels and magnitudes. Besides, the secondary formation process simulated by the box model is constrained

only by precursors of NPs measured by online GC-MS rather than the actual concentrations of NPs. NMF model might be influenced by the uncertainties in the quantification. However, the high time resolution of CIMS increased sample inputs of the NMF model and reduced the uncertainties for this statistical approach. Even though the actual contrition of sources faces uncertainties, the proportion of source profiles is still reliable in this approach.

4. How can the authors be sure that the seven peaks they tracked were nitrophenols? The MS instrument only provides the m/z, not the molecular structure. Were nitrophenols also detected by the GCMS?

Thank you for your comment. The ToF-MS is excellent in identifying formulas of chemical compounds, not the molecular structure. However, we use several approaches to determine the molecular structure.

First, the data processing procedures were conducted following previous studies (Priestley et al., 2018; Yuan et al., 2016). Second, we compare the structure with GC×GC-qMS data to further determine the structure and make sure the identification more reliable.

The listed nitrated phenols in the study were the most possible compounds for these molecular ion peaks. For instance, the number of chemical structures of $C_6H_5NO_3$ in National Institute of Standards and Technology (NIST) library is 15, nevertheless, only nitrophenol (NP) is probable in gas-phase samples in Beijing. This was guaranteed by non-targeted measurement of >50 gas-phase samples in autumn of Beijing utilizing thermal desorption comprehensive two-dimensional gas chromatography-quadruple mass spectrometer (TD-GC×GC-qMS). The campaign was conducted from Sep. 1 to Oct. 31 in 2020. More than 3600 blobs were detected, including phenol, and isomers of NP, MNP, DMNP (Figure R1). The molecular weight of $C_6H_5NO_3$ (identified as NP in CIMS), $C_7H_7NO_3$ (identified as MNP in CIMS), $C_8H_9NO_3$ (identified as MNP in CIMS)was 139, 153, and 167, respectively. The select ion chromatograms (SIC) of 139, 153, and 167 were displayed in Figure R2, R3 and R4. Despite NP, MNP, and DMNP, the molecular ion peaks of other compounds including these select ions were not 139, 153, and 167. This demonstrated that other structures of these molecular ion peaks occurred in the library of mass spectrums, however, they were not

abundant in ambient air of Beijing. As a result, we identified seven peaks as nitrophenols in our study.

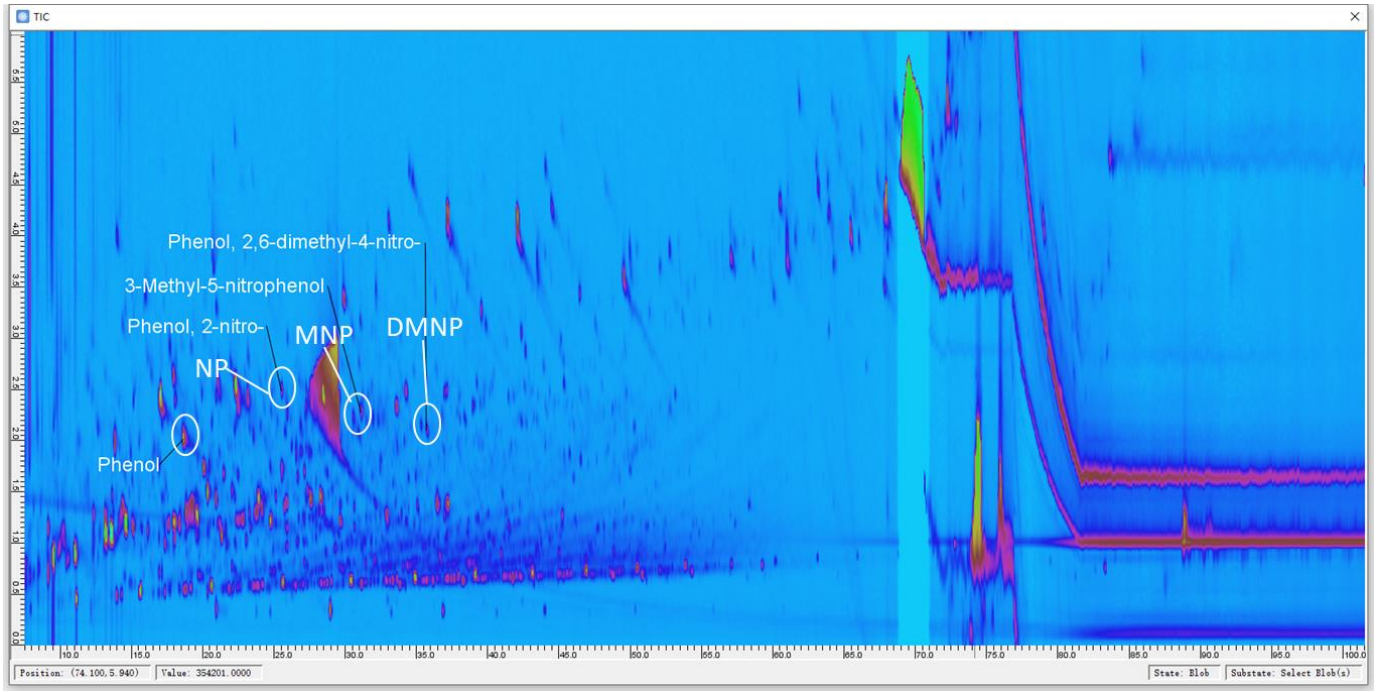

Figure R1. A typical chromatogram of gas-phase samples in Beijing analyzed by TD-GC ×GC-qMS.

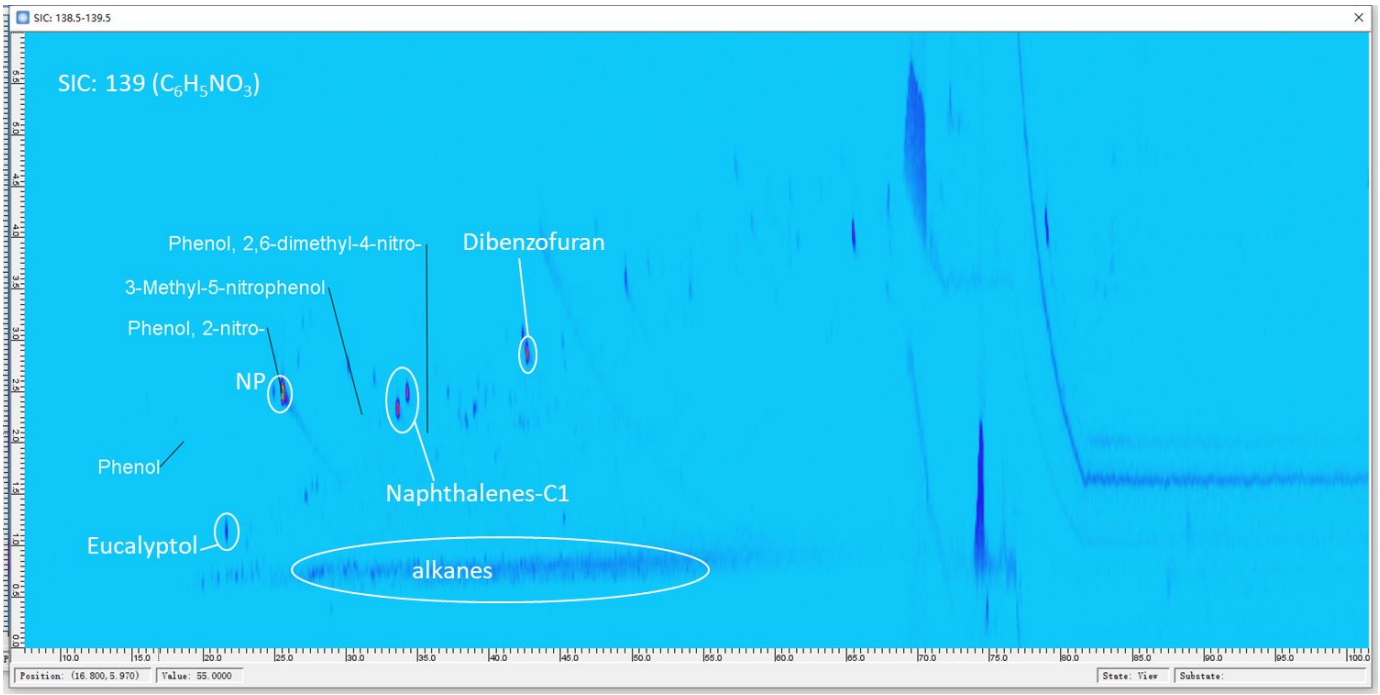

Figure R2. Select ion chromatogram ($C_6H_5NO_3$) of 139. Despite NP, the molecular ion peaks of eucapytol, naphthalenes, alkanes, and dibenzofuran were not 139.

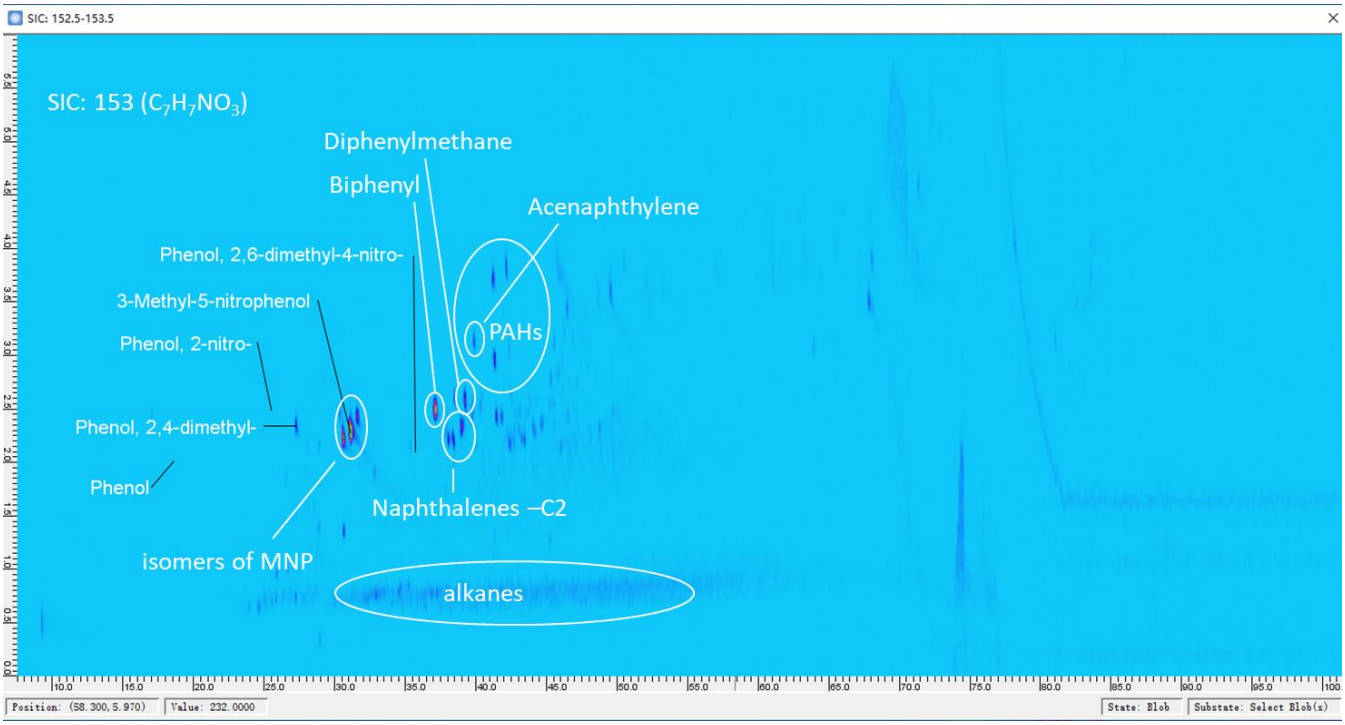

Figure R3. Select ion chromatogram ($C_7H_7NO_3$) of 153. Despite MNP, the molecular ion peaks of other compounds were not 153.

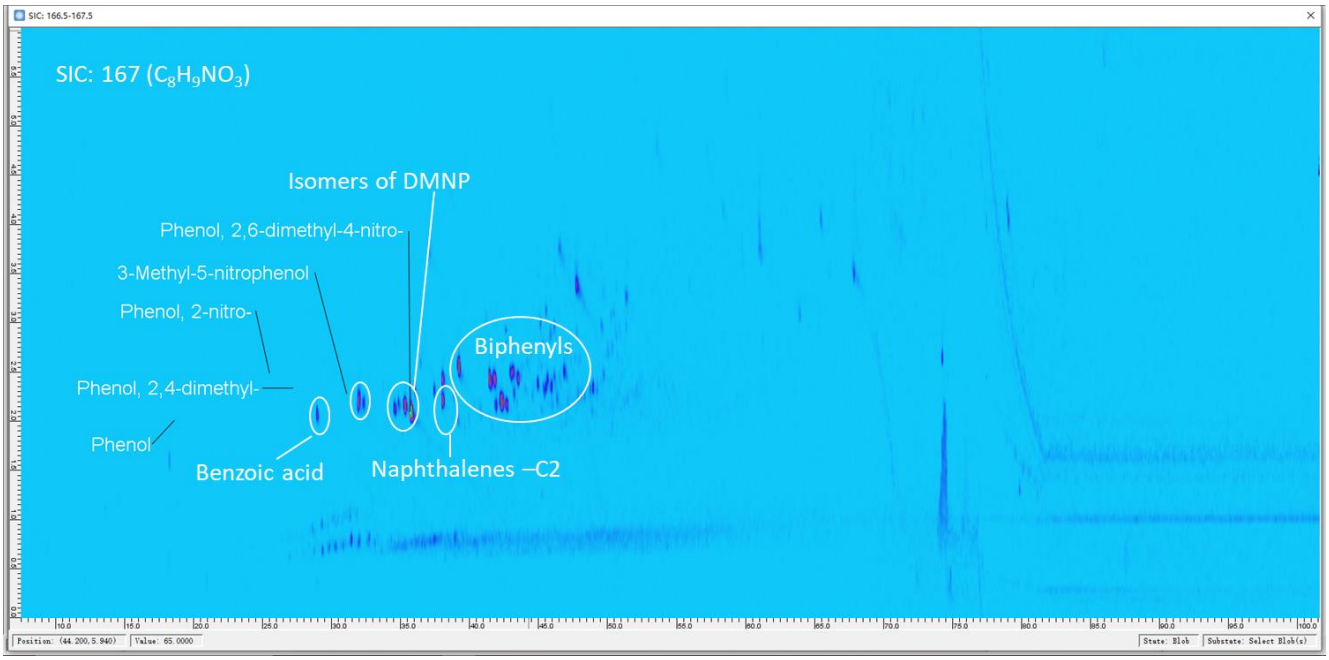

Figure R4. Select ion chromatogram ($C_8H_9NO_3$) of 167. Despite MNP, the molecular ion peaks of other compounds were not 167.

5. More information on the box model needs to be provided. For example, what branching ratios and rate constants were used in the model? Do the authors have any idea which reaction pathways are currently missing in their box model that may have contributed to differences between their ambient observations and model predictions?

Thank you for your comment. The branching ratios and rate constants of the box model were added to Figure 1 in the revised manuscript. Figure 1 can also be found as follows.

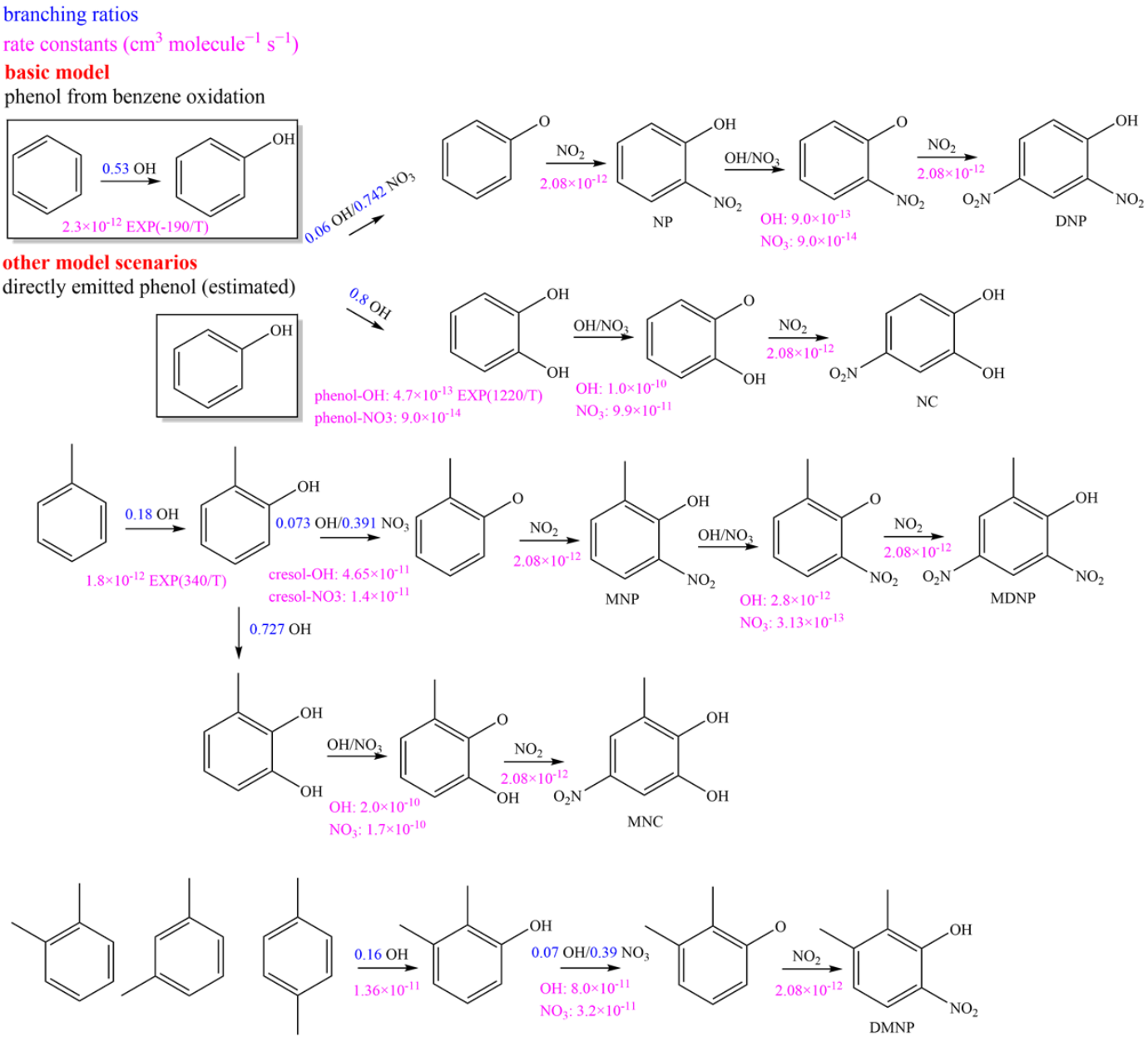

Figure 1. Mechanism related to the secondary formation of the nitrated phenols (NPs) in MCM 3.3.1 applied in this study. Different model scenarios differed in the constraints of the precursors. The basic model constrained the concentration of benzene by measurement from online GC-MS/FID. The

other model scenarios constrained primary phenol concentration rather than benzene estimated by the ratio of phenol/NOy or phenol/CO from fresh vehicle exhaust.

The main missing reaction pathway in this study is gas-particle partitioning of NPs. According to Wang et al., the estimated proportions of gas-phase NP, MNP, and DMNP in Beijing were 99.2%, 94.9%, and <1%, respectively (Wang et al., 2019). Simulation of NP and MNP without gas-particle partitioning pathways faced small uncertainties as they mainly occurred in the gas-phase. The small proportion of DMNP in gas-phase and rather low concentration in particle-phase (0.55 ng m^{-3}, (Wang et al., 2019)) made the missing pathway not important. Meanwhile, gas-phase DMNP mainly came from secondary formation in this study and the concentration level of DMNP could be well explained by the box model.

We revised our manuscript as following (line 293 - 299):

The main missing reaction pathway in this study is gas-particle partitioning of NPs. According to Wang et al., the estimated proportions of gas-phase NP, MNP, and DMNP in Beijing were 99.2%, 94.9%, and <1%, respectively (Wang et al., 2019). Simulation of NP and MNP without gas-particle partitioning pathways faced small uncertainties as they mainly occurred in the gas-phase. The small proportion of DMNP in gas-phase and rather low concentration in particle-phase (0.55 ng m^{-3}, (Wang et al., 2019)) made the missing pathway not important. Meanwhile, gas-phase DMNP mainly came from secondary formation in this study and the concentration level of DMNP could be well explained by the box model. As a result, the missing pathway of gas-particle partitioning may not be important in this study.

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