

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

3

4 **Response to referee #1:**

5 This paper describes an interesting analysis of the sources and formation of nitrated phenolic
6 compounds in a Mega city. The material presented is original and the topics are well chosen. The
7 paper contains some model-based data analysis parts and a section about source apportionment by
8 NMF. While the latter is quite well done the former has some room for improvements. Actually, the
9 manuscript is in these parts difficult to follow. I think there are two reasons for that. There may be
10 some weaknesses in the language (however, I am not a native speaker myself) and possibly some
11 errors and un-preciseness in relation of the figures and their description in the text. Both together
12 made it difficult to really judge the quality of the scientific content.

13 Still, in my opinion, the manuscript has valuable information and potentially good science in it. I
14 suggest, to consider the manuscript for publication in ACP after some major revisions and formal
15 improvements along the comments below.

16 We thank the referee for the careful review and valuable suggestions. We have asked a native speaker
17 to help us to go through the manuscript.

18

19 **Formal:**

20 I suggest the authors a) check use of present time / past tense; b) check use singular / plural for
21 predicates / verbs; c) check use of single words and notations (in a thesaurus), if they really express
22 what they wanted to say. In addition, it seems that names are mixed up, which makes it difficult and
23 time consuming to understand the results. I indicated some examples below, but not all.

24 We thank the reviewer for the comments. We go through the text to check the expressions and
25 grammar. In addition, We have asked a native speaker to help us to edit the manuscript.

26

27

28 **Major comments:**

29 line 126 – 131: The authors notate missing “mechanism” for NP formation. But NP from phenol
30 oxidation is in their chemical mechanism, so I would call it missing “sources of phenol”. And that is
31 actually, how they treat the problem, by testing phenol sources with two different source strength.

32 We agree with the reviewer that "source of phenol" is more appropriate here.

33 The manuscript has been revised as follows (line 128-130): "However, less than 1% of the total
34 nitrophenol (NP) concentration could be explained (Figure S3) which was inconsistent with the
35 estimation from NP/CO ratio in other studies, implying there are probably missing sources of
36 phenol."

37

38 At the same time, I am wondering what is to be learned from the use of the two suggested emission
39 factors of phenol. The emission ratios phenol/NO_y and phenol/CO look similar, but de facto they
40 lead to an order of magnitude different phenol concentrations, because of the different concentrations
41 of NO_y and CO. Do the authors want to say that linking phenol to CO leads to more realistic phenol
42 concentrations? However, the use of the CO related phenol source leads indeed to about the right
43 level NP concentrations, but the model time series does not really match the time series of
44 observations.

45 Thank you for your comment. The concentrations of NO_y and CO play an important role in phenol
46 estimation. However, the atmospheric behaviors of NO_y and CO are more important. VOCs to CO
47 ratio is widely used to quantify anthropogenic emissions because the atmospheric CO is inert (Li et
48 al., 2019). In this study, we linked the phenol to CO in order to identify a more reliable estimation for
49 phenol concentrations. We agree that the time series of the model estimation by phenol/CO ratio
50 showed discrepancies in some days when nitrophenol concentration is low. Nevertheless, the trend
51 and concentration level of NP and DNP (Figure S3) showed good agreement in polluted days when
52 using phenol to CO. However, when using phenol/NO_y ratio, there shows large discrepancies. NMF
53 and CWT analysis revealed the importance of primary emissions during the heavy pollution period
54 and estimation from freshly emitted CO could be more reasonable. We add some detailed
55 explanation in the main text to show why we use phenol to CO ratio to estimate phenol concentration
56 as follows (line 133 - 139):

57 As the concentration of primary phenol was not determined in this study, we used the ratio of
 58 phenol/NO_y (0.3 ppt/ppb) and phenol/CO (0.4 ppt/ppb) from fresh emitted vehicle exhaust (Inomata
 59 et al., 2013; Sekimoto et al., 2013). Atmospheric CO is inert so that VOCs to CO ratio is widely used
 60 to quantify anthropogenic emissions (Li et al., 2019). The estimation of phenol from phenol/CO
 61 ratio showed good agreement in trend and concentration level (Figure S3). The estimated phenol
 62 concentration in this approach was comparable to the measured concentration from other sites (Table
 63 1). As a result, the budget analysis and the source apportionment were composed based on the
 64 constrained results of estimated phenol concentration by the ratio of phenol/CO.

65

66 In addition, unfortunately, the most important last lines in Table 1 are messed up. What is the
 67 meaning of the number in brackets? I would also suggest, to replace the different references in the
 68 last column of Table 1 by numbers or symbols and list them in the captions under the table.

69 Thank you for your comment. The meaning of the number in brackets are the standard deviations of
 70 the concentrations in Table 1 which was demonstrated in the table caption. We revised the table
 71 caption to make it more clear to readers. The revision is as follows in line 513, "The estimated
 72 concentrations were displayed in the italic script. Standard variations were displayed in brackets."
 73 The references are replaced by numbers in the manuscript (line 545 - 547).

74

75 **Table 1. The concentration of phenol and nitrated phenols (NPs) in different sampling sites and**
 76 **their site categories, sampling time and analytical methods (ng m⁻³).**

Sampling site	Site category	Sampling time	Method	phenol	NP	DNP	MNP	DM	NC	MDN	MN	References
Strasbourg area, France	urban and rural sites	annual mean	GC-MS	0.4-58.7	0.01-2.2	5.6	2.6			0.1-0.3 ^a		1
Rome, Italy	downtown	winter-spring	GC-MS		14.3		13.9	2.0		(1.0)		2
Great Dun	remote site	spring	GC-MS	14-70	2-41 ^c	0.1-8.5				0.2-6.		3

Fell, England			S							6	
Beijing, China	regional site	spring	LC-M	143-56		7.1-62 ^e		0.06-	0.017	4	
			S	6 ^d				0.79 ^f	g		
Milan, Italy	polluted urban site	summer	HPLC	400	300					5	
northern	dairy farms	autumn-	TD-G	3000-						6	
Sweden		winter	C	50000							
Manchester,	with Bonfire	autumn-	ToF-C		780		630			7	
UK	Plume Removed	winter	IMS								
Ottawa,	selected dwellings	winter	TD-G	10-14						8	
Canada	sites		C-MS	10							
Santa Catarina,	near a coal-fired	winter	GC-FI	980-1						9	
Brazil	power station		D	600							
Switzerland	urban site	winter	GC-M	40	350 ^h		250 ⁱ		50 ^j	10	
			S								
Manchester,	measured during	winter	ToF-C		3700		3600			7	
UK	the bonfire night		IMS								
Detling,	rural site	winter	MOVI-HR	0.02	3	5		2.5	8.2	11	
United			ToF-CIMS								
Kingdom											
Beijing, China	urban site	winter	ToF-C	63 ^k	606.3	243.5	203.5	46.2	22.1	26.0	10.4
(this study)			IMS	1013 ^l	(511.1)	(339.6)	(156.6)	(32.6)	(12.4)	(25.8)	(6.3)

77

78 The estimated concentrations were displayed in the *italic* script. Standard variations were displayed
79 in brackets. Nitrated phenols investigated in this study referred to nitrophenol (NP), dinitrophenol
80 (DNP), methyl-nitrophenol (MNP), dimethyl-nitrophenol (DMNP), nitrocatechol (NC),
81 methyl-dinitrophenol (MDNP) and methyl-nitrocatechol (MNC).

82 **Symbols:** ^a gas+particle phase; ^b 2,6-Dimethyl-4-nitrophenol; ^c 2/4-Nitrophenol; ^d 4NP, estimated; ^e

83 2M4NP+3M4NP, estimated; ^f 4NC, estimated; ^g 3M6NC+3M5NC+4M5NC, estimated; ^h
84 2-Nitrophenol; ⁱ 3M2NP+4M2NP; ^j 2,4-Dinitro-6-methyl phenol; ^k estimated by 0.3NO_y; ^l estimated
85 by 0.4CO

86 **References:** ¹ (Delhomme et al., 2010); ² (Cecinato et al., 2005); ³ (Lüttke et al., 1997); ⁴ (Wang et
87 al., 2019); ⁵ (Belloli et al., 1999); ⁶ (Sunesson et al., 2001); ⁷ (Priestley et al., 2018); ⁸ (Zhu et al.,
88 2005); ⁹ (Moreira Dos Santos et al., 2004); ¹⁰ (Leuenberger et al., 1988); ¹¹ (Mohr et al., 2013).

89

90

91 line 195-199: I am sorry, I am not able to recognize the features described in the manuscript for the
92 Figure b and c. E.g. NC and MNC have a different diurnal cycle but are treated together. I can also
93 not identify gentle peaks at 5 pm. To me it looks as if either the descriptions do not express what is
94 intended to say or the explanations and plots maybe mixed up.

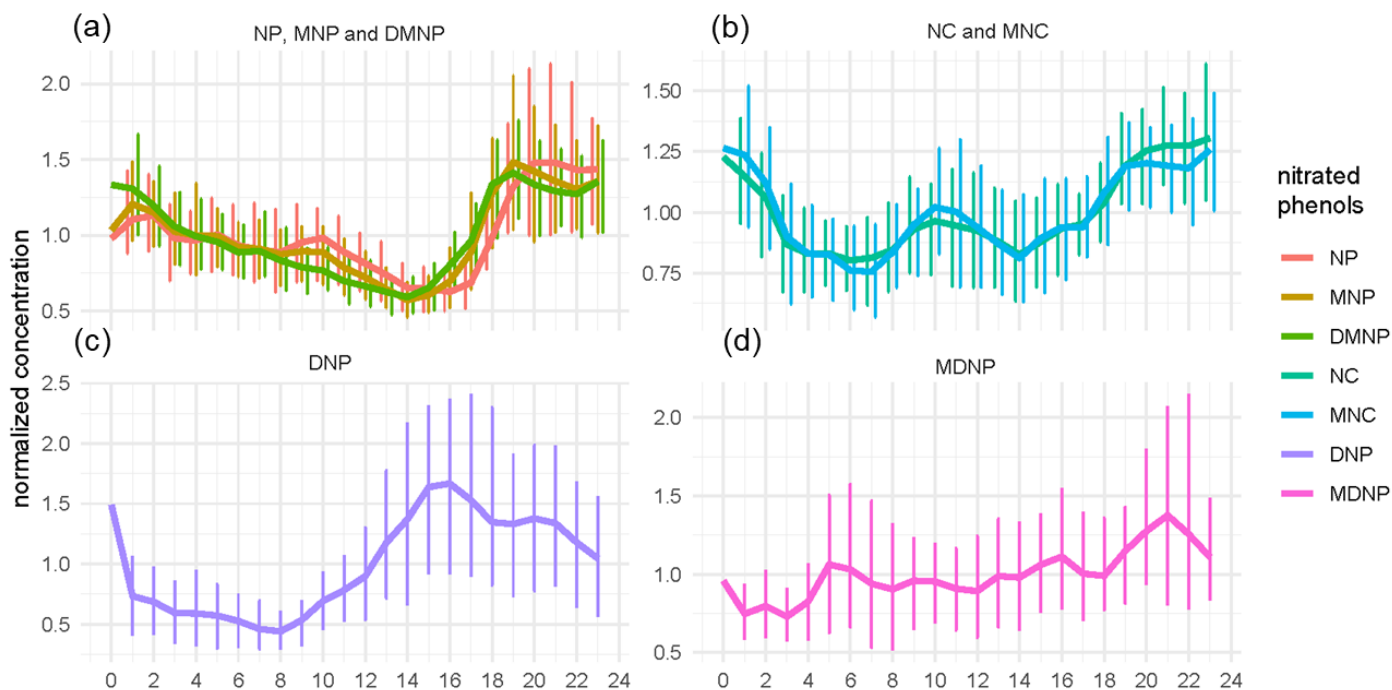
95 It would be also helpful if the time notations in the manuscripts and at the axis of the Figure would
96 be the same and to have minor ticks at the time axis or a grid in the diagram.

97 Because of all this I cannot really judge conclusions drawn from diurnal cycles.

98 Thank you for your comment. The revised diurnal profiles of nitrated phenols were displayed in
99 Figure 3 in the manuscript, with clear axes, ticks, and grids. The different diurnal cycles of DNP and
100 MDNP are also separated. The revised sentences are as follows,

101 "Nonetheless, NC and MNC (NPs with two -OH groups and one -NO₂ group) displayed a small peak
102 at about 10:00 am, and revealed high concentrations at night. DNP and MDNP (NPs with one -OH
103 groups and two -NO₂ groups) displayed distinct patterns from either NP or NC. DNP accumulated
104 during the afternoon and began to decline after 5:00 p.m., suggesting that NO₃ oxidation of DNP
105 might be a non-negligible sink. The diurnal profile of MDNP did not vary much during the whole
106 day with a slight increase at night" (line 200 - 204).

107



108

109 **Figure 3.** Diurnal profiles of nitrated phenols (NPs) with 95% confidence interval in error bars. The
 110 concentration of NPs was normalized by their mean values. (a) Diurnal profiles of nitrophenol (NP),
 111 methyl-nitrophenol (MNP) and dimethyl-nitrophenol (DMNP). These are NPs with one -OH group
 112 and one -NO₂ group. (b) Diurnal profiles of nitrocatechol (NC) and methyl-nitrocatechol (MNC).
 113 These are NPs with two -OH groups and one -NO₂ group). Diurnal profiles of (c) dinitrophenol
 114 (DNP) and (d) methyl-dinitrophenol (MDNP). These are NPs with one -OH groups and two -NO₂
 115 groups.

116 line 205 – 214: Again, I have difficulties to follow the text along the Figure S3. If DMNP is
 117 explained by the xylene emissions the red symbols should indicate that, because this should be
 118 covered by the base case, right? I don't see them. On the other hand, MDNP is according Figure 1 a
 119 product of toluene, not of xylene, as I think, is claimed in line 213. In any case, if MDNP can be
 120 understood from the VOC then there should be again red symbols showing that? Why do you show
 121 the effect of phenol constraints in the lower panels when phenol is not expected to contribute to the
 122 formation of DMNP and MDNP? In addition, the symbol style is chosen such, that overlapped
 123 curves cannot be seen very well.

124 And as already mentioned above, even if the model predicts the levels of the observations quite well,

125 the time behavior does not really match.

126 Thank you for your comment. The revised Figure S3 is displayed in the supplementary information.

127 The previous overlapped model estimations are displayed in different panels to make it clear to

128 readers. Besides, the reason why we showed the effect of phenol constraints to DMNP and MDNP

129 was that there were non-linear effects of oxidation capacities and radical concentration when phenol

130 was constrained (line 216 - 218). As a result, there were indeed slight differences in estimating

131 DMNP and MDNP between these model scenarios (Figure S3). We agree that time behaviors showed

132 discrepancies in some days. However, on the one hand, the trend of nitrated phenols agreed with the

133 observations during heavy pollution episodes. On the other hand, the discrepancies between the

134 model simulations and observations were regarded as primary emissions in this study. According to

135 NMF, NPs were also derived from primary emissions like biomass burning.



136

137 **Figure S3. The measured concentration of nitrated phenols and their secondary formation simulation**

138 **by the box model in different model scenarios.**

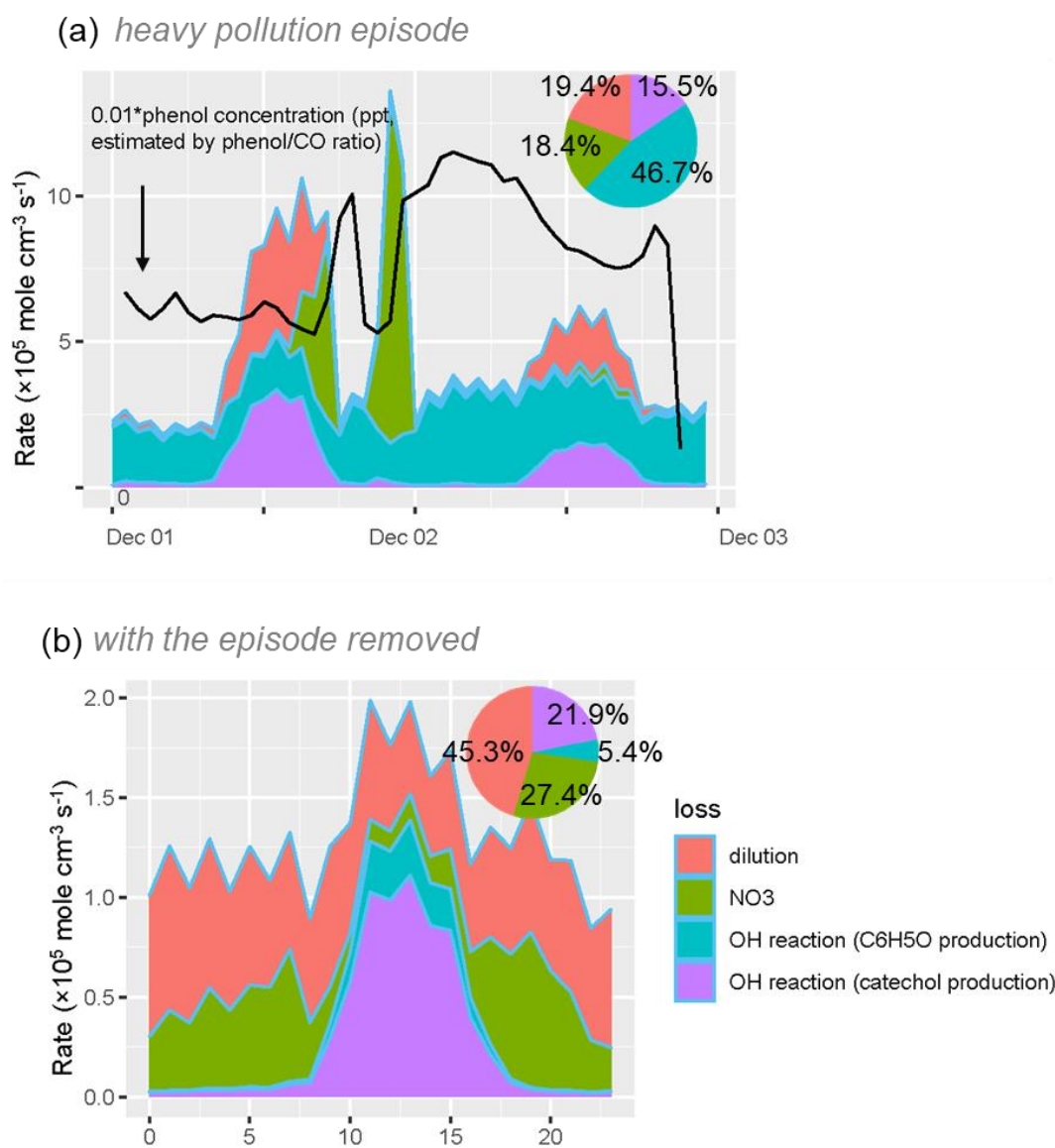
139 Line 220-227: NO₃ and OH contribute to C₆H₅O production. In the model phenol + NO₃ and
140 phenol + O have fixed branching ratios into C₆H₅O of 75% and 6%, respectively, and others of
141 which about 80% lead to catechol in the OH case. Now I am wondering, does the green NO₃ section
142 comprise NO₃-produced C₆H₅O or is it subsumed under the turquoise C₆H₅O part? For first case,
143 how can the ratio of C₆H₅O path to catechol path vary since the phenol + OH reaction has a fix
144 branching ratio? For the second case, assuming that NO₃ will dominate C₆H₅O production the path
145 to the other NO₃ products seems to large. Please add a more detailed explanation what you used in
146 detail to achieve the results in Figure 4 and Figure 5.

147 Thank you for your comment. The legend in Figure 4 caused misunderstanding and we have revised
148 it accordingly. Neither NO₃ section comprised NO₃-produced C₆H₅O nor it was subsumed under the
149 turquoise C₆H₅O part. The turquoise C₆H₅O part was the **OH-phenol** reaction part which eventually
150 formed C₆H₅O. We also revise the manuscript accordingly (line 221 - 231).

151 "Time series and diurnal profile of the loss of phenol during and without the heavy pollution episode
152 were shown in Figure 4. It was obvious that the OH loss mainly took place during the day while NO₃
153 loss mainly happened at night. However, the fraction of these two pathways diverged dramatically
154 taking the episode into account. During the heavy pollution episode, 46.7% of phenol lost from the
155 pathway of OH-reaction which caused the production of phenoxy radical (C₆H₅O). We noticed that
156 the C₆H₅O-NO₂ reaction was the only formation pathway of nitrophenol (Berndt and Böge, 2003).
157 With the heavy pollution episode removed, the proportion of the C₆H₅O production pathway of
158 OH-reaction was only 5.4%. The phenol-OH reaction which produced catechol (then reacted with
159 OH/NO₃, NO₂ to produce NC) was the predominant OH reaction (21.9%). The distinct pattern of the
160 phenol-OH pathway which formed C₆H₅O indicated a probable source of the nitrophenol
161 accumulation during the heavy pollution episode. The high atmospheric reactivity and oxidation
162 capacity in Beijing (Lu et al., 2019c; Yang et al., 2020) might be the foundation of high potential
163 reactivity between phenol and OH radical".

164

165 The revised Figure 4 is displayed in the manuscript with clear descriptions in the legend. In addition,
166 the branching ratios and rate constants of the box model were added to Figure 1.



168

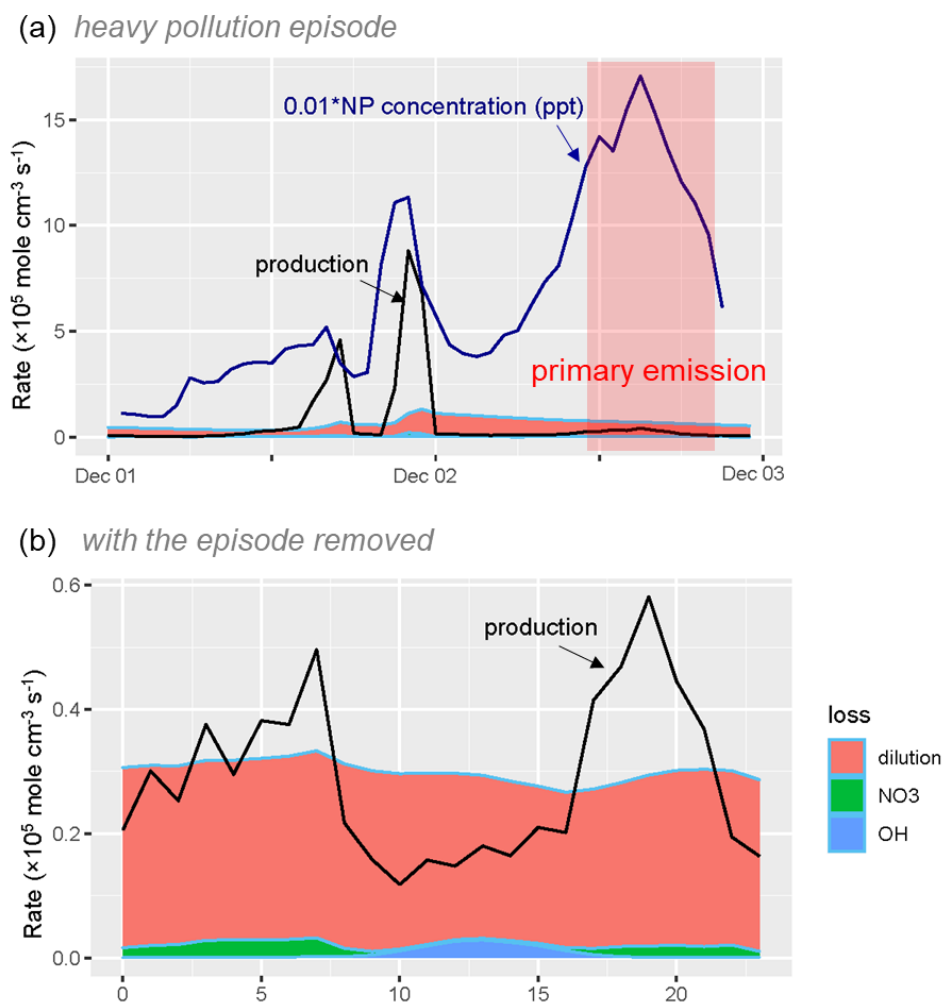
169 **Figure 4.** Time series and the loss rate of phenol during the heavy pollution episode (a) and diurnal

170 profile of the loss of phenol with the heavy pollution removed (b).

171

172

173 Line 228-234: I do understand what you wanted to say, but it is somewhat difficult to grab. It might
174 be helpful to show the NP concentrations in Figure 5, too.
175 Thank you for your comment. The revised Figure 5 is displayed in the manuscript.
176

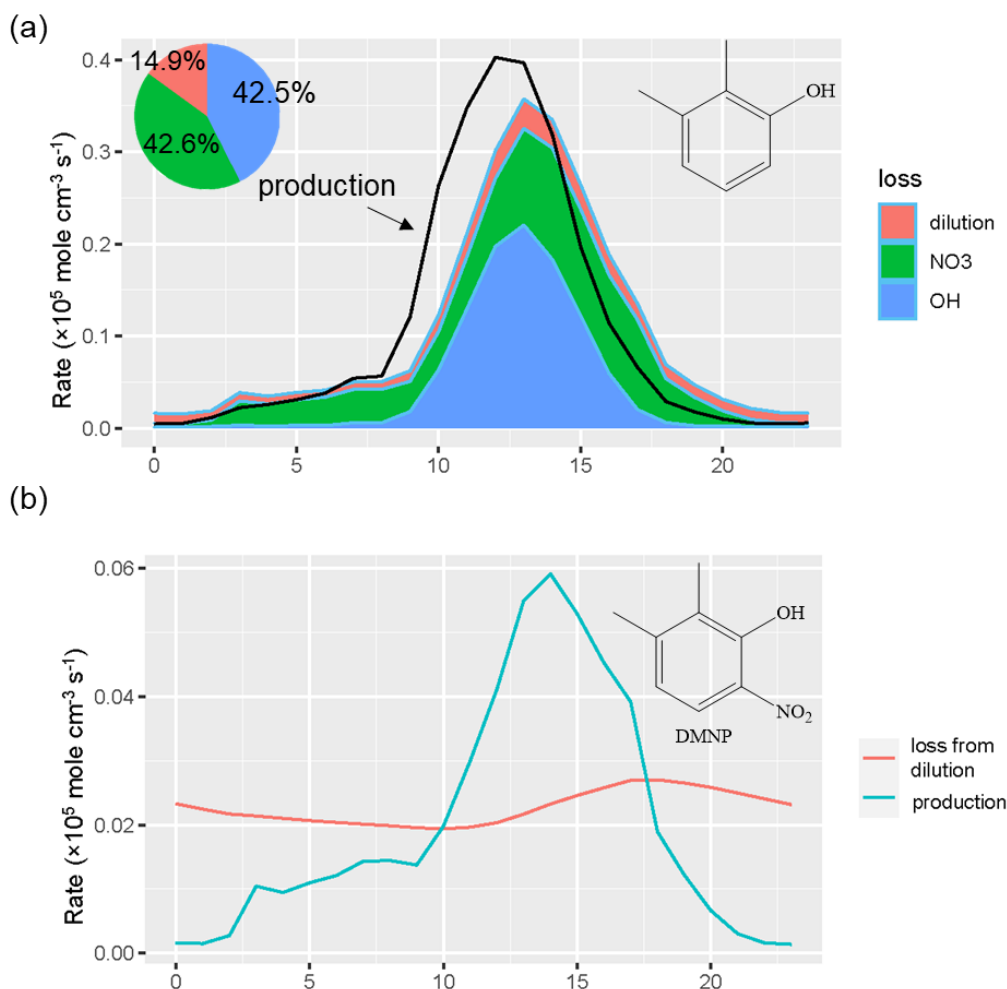


177
178 **Figure 5.** Time series of production and loss of nitrophenol (NP) during the heavy pollution episode
179 (a) and diurnal profiles of production and loss of NP with the heavy pollution removed (b).
180

181 Line 241 – 244: What exactly is the Xylenol+NO₂ reaction? The sentence starting with “As for
182 DMNP, the production ...” is unclear. Please rephrase it. Where can I see the loss of DMNP in Figure
183 6?

184 Thank you for your comment. The revised sentence is "The production of DMNP increased rapidly
185 from the xylenol-NO₂ reaction during the daytime and decreased from noon" in line 244 - 245. The
186 loss of DMNP (dilution) is displayed in Figure 6 in the revised version.

187



188

189 **Figure 6.** Production and loss of xylenol (a) and DMNP (b) during the sampling period.

190

191 In general, I would suggest, to modify the Figures remove overlap of elements. E.g., pie charts are
192 partially in the Figure, partially outside. Formulas are crossing the frame of the diagrams, or in
193 Figure S1 the formulas are too large and overlap the MS peaks.

194 Thank you for your comment. We have double-checked the figures.

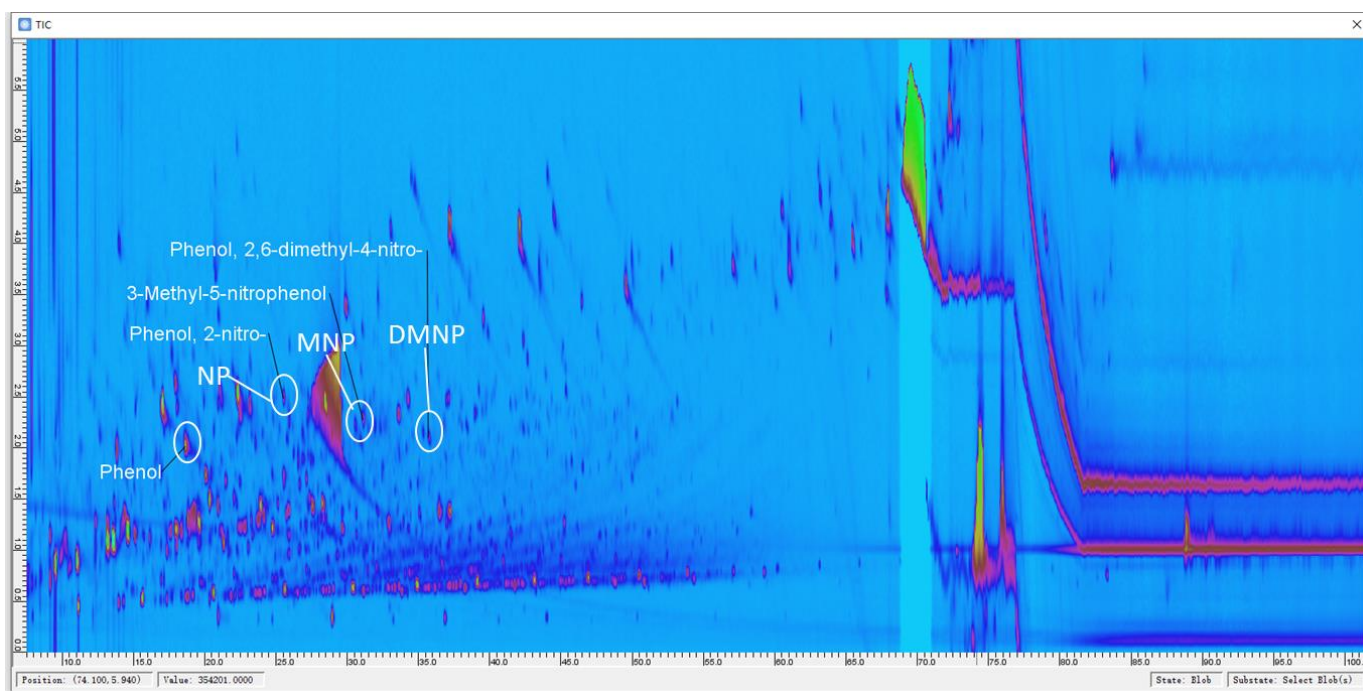
195

196 **Minor comments:**

197 line 94f: how can you be sure about the suggested structures? You used MS.

198 Thank you for your comment. The revised sentence is "The chemical structures of these NPs were
199 identified by ToF-MS. The results of high-resolution peak fits of reagent ions and NPs could be
200 found in Figure S1" in line 93-95.

201 We use several approaches to determine the molecular structure. First, the data processing procedures
202 were conducted following previous studies (Priestley et al., 2018; Yuan et al., 2016). Second, we
203 compare the structure with GC×GC-qMS data to further determine the structure and make sure the
204 identification more reliable. For instance, the number of chemical structures of C₆H₅NO₃ in National
205 Institute of Standards and Technology (NIST) library is 15, nevertheless, only nitrophenol (NP) is
206 probable in gas-phase samples in Beijing. This was guaranteed by non-targeted measurement of >50
207 gas-phase samples in autumn of Beijing utilizing thermal desorption comprehensive two-dimensional
208 gas chromatography-quadruple mass spectrometer (TD-GC×GC-qMS). The campaign was
209 conducted from Sep. 1 to Oct. 31 in 2020. More than 3600 blobs were detected, including phenol,
210 and isomers of NP, MNP, DMNP (Figure R1). The molecular weight of C₆H₅NO₃ (identified as NP in
211 CIMS), C₇H₇NO₃ (identified as MNP in CIMS), C₈H₉NO₃ (identified as MNP in CIMS) was 139,
212 153, and 167, respectively. The select ion chromatograms (SIC) of 139, 153, and 167 were displayed
213 in Figure R2, R3 and R4. Despite NP, MNP, and DMNP, the molecular ion peaks of other compounds
214 including these select ions were not 139, 153, and 167. This demonstrated that other structures of
215 these molecular ion peaks occurred in the library of mass spectrums, however, they were not
216 abundant in ambient air of Beijing. As a result, we identified seven peaks as nitrophenols in our
217 study.

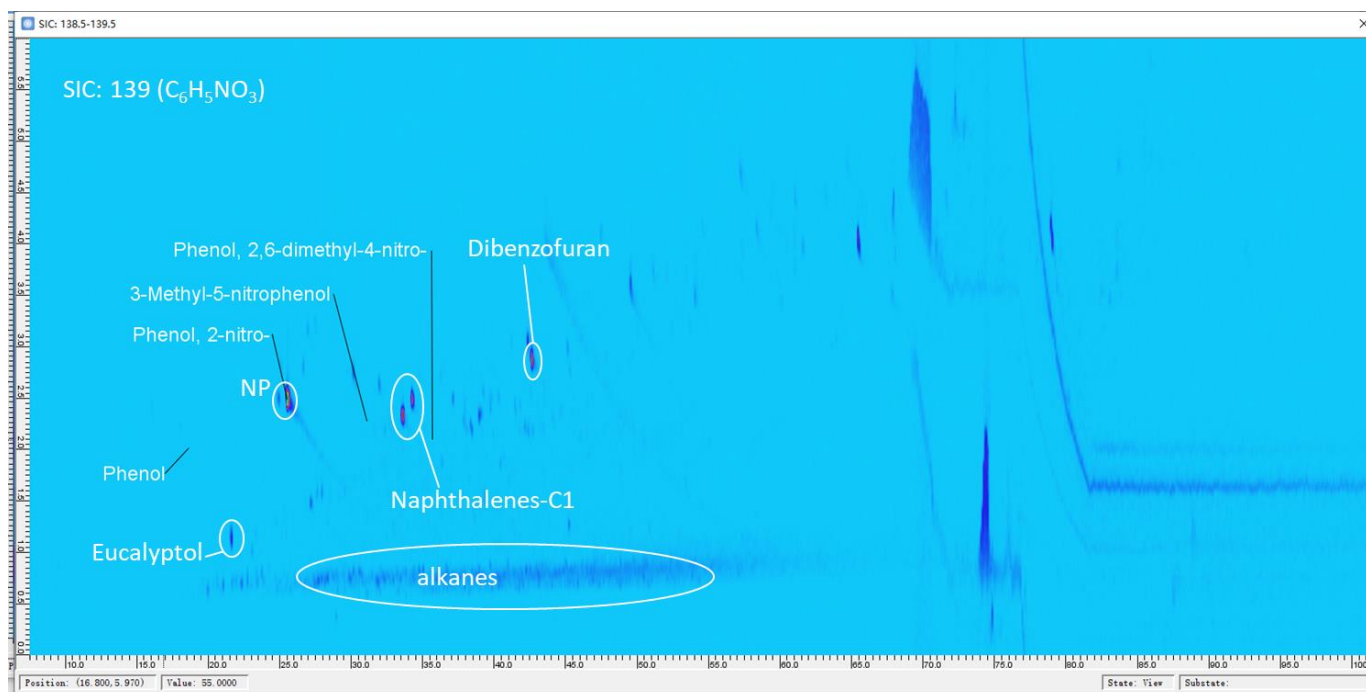


218

219

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

220



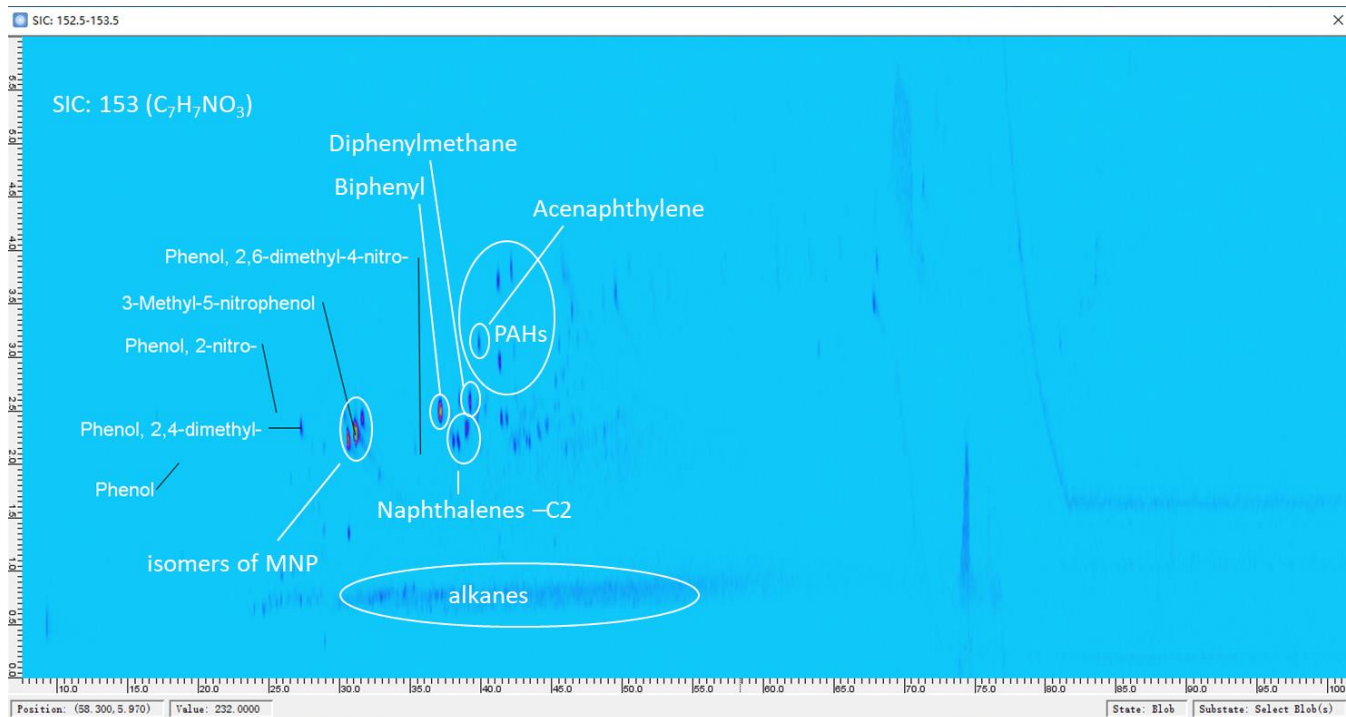
221

222

Figure R2. Select ion chromatogram (C₆H₅NO₃) of 139. Despite NP, the molecular ion peaks of eucalyptol, naphthalenes, alkanes, and dibenzofuran were not 139.

223

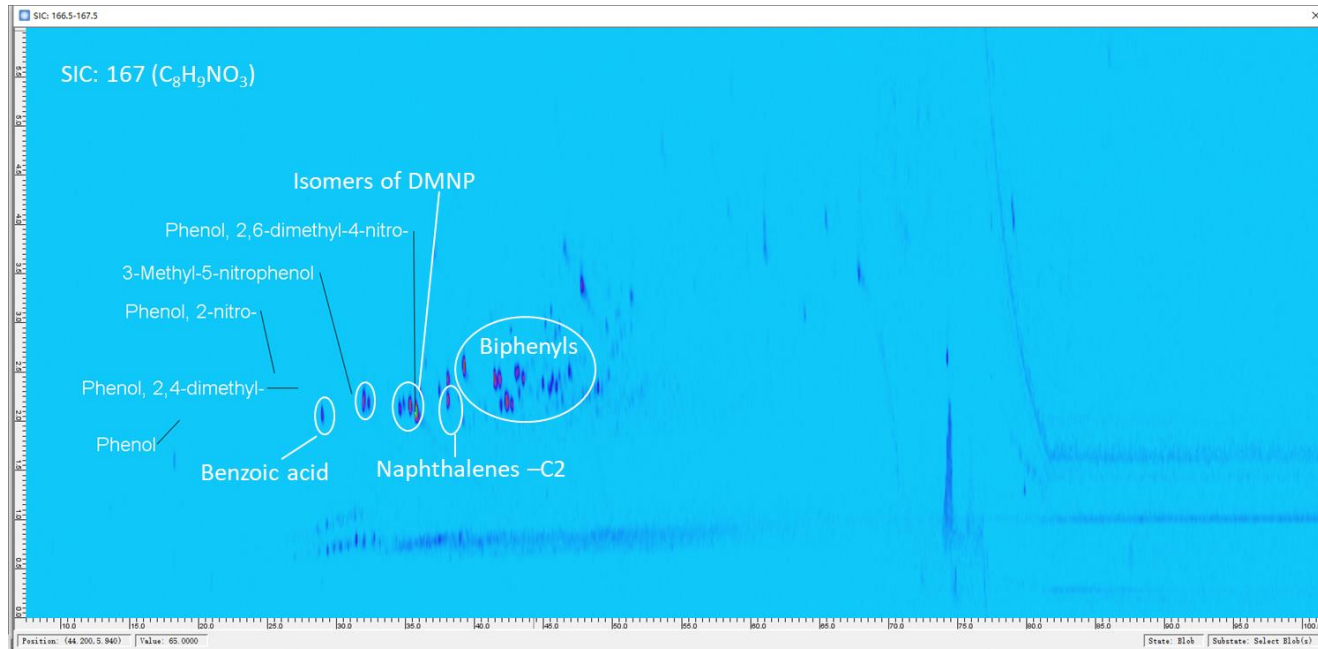
224



225

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

228



229

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

232

233

234 line 100f: you calibrated with only one compound. Can you add something on the range of
235 sensitivity expected for measurement of the addressed compounds by NO₃-CIMS?

236 Thank you for your comment. Only one nitrophenol was used for calibration in this study, which
237 could lead to uncertainty in quantifying other nitrophenols. We added uncertainty analysis in the SI
238 to make the reader more clear about how much the uncertainty is. Yuan et al. calibrated nitrophenol
239 (NP), methylnitrophenol (MNP) and dinitrophenol (DNP) in the previous study utilizing
240 nitrate-CIMS. The sensitivity of NP, MNP and DNP were 13.2, 16.6, 10.3 npcs ppt⁻¹, respectively
241 (Yuan et al., 2016). The sensitivities of MNP and DNP ranged -26% and 22% from NP. Rebecca H.
242 Schwantes et al. estimated sensitivity factors for CIMS operated in both negative and positive mode
243 using CF₃O⁻ and H₃O (H₂O)⁺. The estimated sensitivities of *o*-nitrophenol, 3-nitrocatechol,
244 4-methyl-2-nitrophenol were 1.48, 1.16 and 1.69, respectively. The sensitivities of NC and MNP
245 ranged 22% and -14% from NP (Schwantes et al., 2017). Even though uncertainties remain, we tend
246 to believe that the addressed NPs calibrated by NP were correct in concentration levels and
247 magnitudes. Besides, the secondary formation process simulated by the box model is constrained
248 only by precursors of NPs measured by online GC-MS rather than the actual concentrations of NPs.
249 NMF model might be influenced by the uncertainties in the quantification. However, the high time
250 resolution of CIMS increased sample inputs of the NMF model and reduced the uncertainties for this
251 statistical approach. Even though the actual contribution of sources faces uncertainties, the proportion
252 of source profiles is still reliable in this approach.

253 The text above was added to the drawing statement of Figure S2. In addition, we add uncertainty
254 analysis in the manuscript (line 101 – 105) as follows, "The calibration curve was made by plotting
255 the actual gas-phase NP concentration as the function of ion signals detected. The uncertainty in
256 quantifying other NPs from the sensitivity of NP ranged from -26% to 22% (Schwantes et al., 2017;
257 Yuan et al., 2016). The addressed NPs calibrated by NP were correct in concentration levels and
258 magnitudes. See more detail in Figure S2".

259

260 line 117: "other necessary packages", if the packages were necessary/important, you should name it
261 otherwise I would skip that phrase.

262 Thank you for your comment. The revised sentence is "The data were analyzed by R 3.6.3 (R Core
263 Team, 2020), including packages of openair (Ropkins and Carslaw, 2012), Biobase (Huber et al.,
264 2015), NMF (Gaujoux and Seoighe, 2010), and ggplot2 (Wickham, 2016)" in line 120 – 121.

265

266 Figure S2: Why do you observe larger noise/fluctuations for the higher signals?

267 Thank you for your comment. The intensity of noise varies with the signal. The higher
268 concentration/signal will increase the noise intensity accordingly. The signals were all normalized by
269 reagent ions (NO_3^- (HNO_3)₀₋₂). The impact of fluctuations on calibration was reduced in this way.

270

271 **Typos etc:**

272 line 19f: contribution to production or concentration?

273 Thank you for your comment. We have modified the relevant content in the manuscript. The revised
274 sentence is "Our results showed that secondary formation contributed 38%, 9%, 5%, 17% and almost
275 100% of the nitrophenol (NP), methyl-nitrophenol (MNP), dinitrophenol (DNP),
276 methyl-dinitrophenol (MDNP or DNOC), and dimethyl-nitrophenol (DMNP) concentrations" in line
277 19 – 21.

278 line 34: "gained much concern", I would formulate that differently

279 Thank you for your comment. The revised sentence is "They are crucial species in forest decline" in
280 line 34.

281 line 39: I believe that Beijing is still the capital ...?

282 Thank you for your comment. We have modified the relevant content in the manuscript. The revised
283 sentence is "Beijing is the capital city of China which retains a population of more than 20 million
284 and more than 5 million private cars" in line 39 – 40.

285 line 40: "preserves ... cars", I would formulate that differently

286 Thank you for your comment. The revised sentence is "Beijing is the capital city of China which
287 retains a population of more than 20 million and more than 5 million private cars" in line 39 – 40.

288 line 42: NAC is not defined

289 Thank you for your comment. The revised sentence is "Most of the studies in Beijing focus on

290 particle-phase NPs (or so-called nitro-aromatic compounds, NACs)" in line 41 – 42.

291 line 45: either “spectrometry” or “spectrometers” (2x)

292 Thank you for your comment. We have modified the relevant content in the manuscript. The revised
293 sentence is "Gas chromatography-mass spectrometers (GC-MS) and high-performance liquid
294 chromatography-mass spectrometers (HPLC-MS) were commonly used to quantify the ambient
295 concentration of NPs with accurate molecular information (Belloli et al., 1999; Harrison et al., 2005;
296 Lüttke et al., 1997)" in line 45 - 47.

297

298 line 91: “...time resolution of the measurement...”? and ‘The CIMS data processing was “conducted”
299 by...’?

300 Thank you for your comment. We have modified the relevant content in the manuscript in line 91 -93,
301 as followed, "The original time resolution of the concentration of NPs was 1s. The CIMS data was
302 processed by Tofware 3.0.3 (Tofwerk AG, Aerodyne Research) in Igor Pro 7.08 (WaveMetrics
303 Inc)".

304

305 line 112f: something is wrong with this sentence

306 Thank you for your comment. We have modified the relevant content in the manuscript. The revised
307 sentence is "Totally 98 kinds of VOCs were measured, including alkanes, alkenes, aromatics,
308 acetylene and oxygenated volatile organic compounds (OVOCs). The detailed information of these
309 VOCs can be found elsewhere (Yu et al., 2021; Yuan et al., 2013)" in line 111 – 113.

310

311 line 119: I believe “functioned” is not the right word here.

312 Thank you for your comment. We have modified the relevant content in the manuscript. The revised
313 sentence is "A zero-dimensional box model equipped with Master Chemical Mechanism
314 (MCMv3.3.1) was utilized to simulate the secondary formation process of NPs" in line 115 – 116;
315 and "The secondary formation process of NPs was simulated by a zero-dimensional box model
316 equipped with Master Chemical Mechanism (MCMv3.3.1, <http://mcm.leeds.ac.uk/MCM/home>)" in
317 line 123 – 125.

318 line 121: I would use present time (you should check the whole manuscript, there are more of these)
319 Thank you for your comment. We have revised the sentence into the present tense. The revised
320 sentence "The related mechanism is presented in Figure 1" in line 124.

321

322 line 132: budget

323 Thank you for your comment. The revised sentence is "The budget analysis and the source
324 apportionment were composed based on the constrained results of estimated phenol concentration by
325 the ratio of phenol/CO" in line 138.

326

327 line 137: "total primary NPs 'were' calculated by subtracting", plural (you should check the whole
328 manuscript, there are more like these)

329 Thank you for your comment. We have changed the word into "were". The revised sentence is "The
330 total primary NPs were calculated by subtracting the secondary NPs from box model by the total
331 NPs" in line 141 - 142. We have gone through the whole manuscript to check the words.

332

333 line 188: explanation for what exactly?

334 Thank you for your comment. The revised sentence is "The non-negligible secondary formation of
335 nitrophenol from phenol oxidation was a plausible explanation for the higher concentration of DNP
336 in Beijing" in line 193 - 194.

337

338 line 201f: something is wrong with this sentence

339 Thank you for your comment. We did not make this sentence clear. The revised sentences are as
340 follows, "Nonetheless, NC and MNC (NPs with two -OH groups and one -NO₂ group) displayed a
341 small peak at about 10:00 am, and revealed high concentrations at night. DNP and MDNP (NPs with
342 one -OH groups and two -NO₂ groups) displayed distinct patterns from either NP or NC. DNP
343 accumulated during the afternoon and began to decline after 5:00 p.m., suggesting that NO₃
344 oxidation of DNP might be a non-negligible sink. The diurnal profile of MDNP did not vary much
345 during the whole day with a slight increase at night" (line 200 - 204).

346 line 244: is hailed the right word?

347 Thank you for your comment. The revised sentence is " DMNP mainly originated from the secondary
348 formation process and its accumulation mainly took place in the afternoon while nitrophenol mainly
349 occurred at night which were mainly derived from primary emission" in line 246 - 248.

350

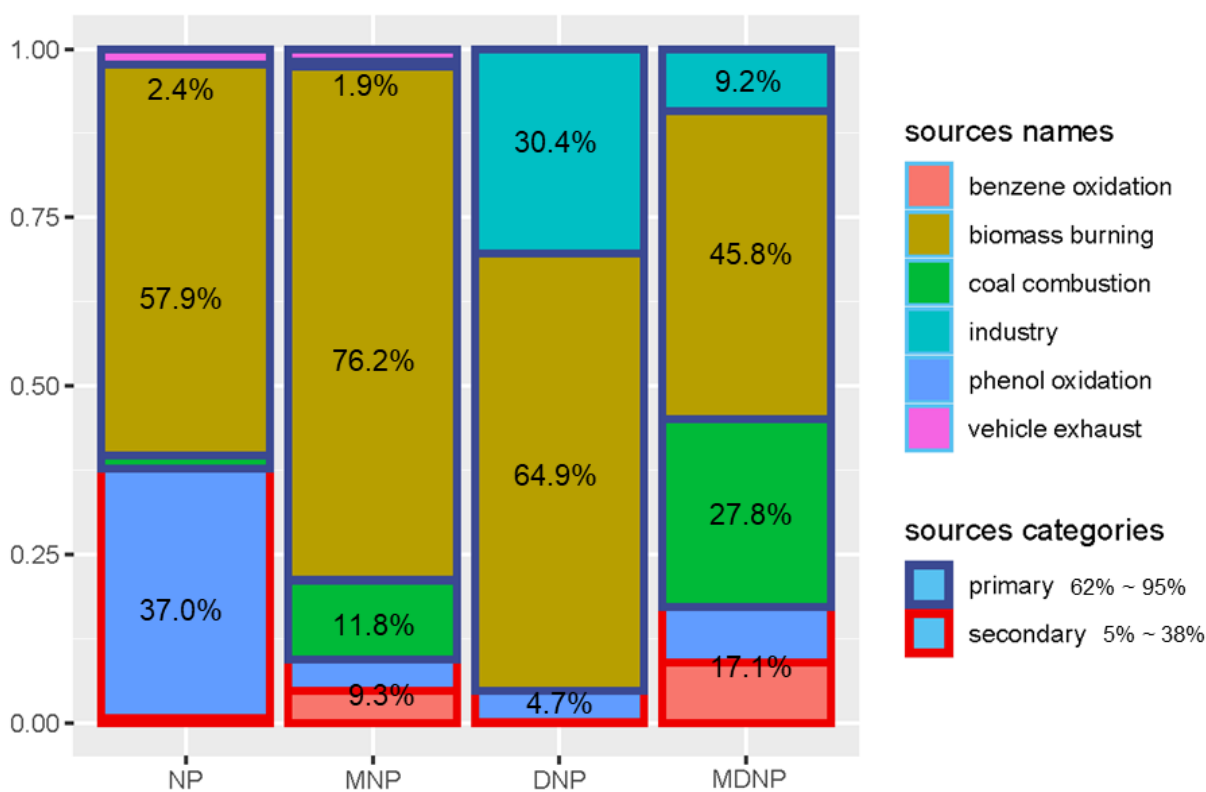
351 Figure 1: scenarios (bold red)

352 Thank you for your comment. We have changed the word into "scenarios".

353

354 Figure 8: I suggest, to use different colors for the grouping boxes

355 Thank you for your comment. We have revised Figure 8 accordingly.



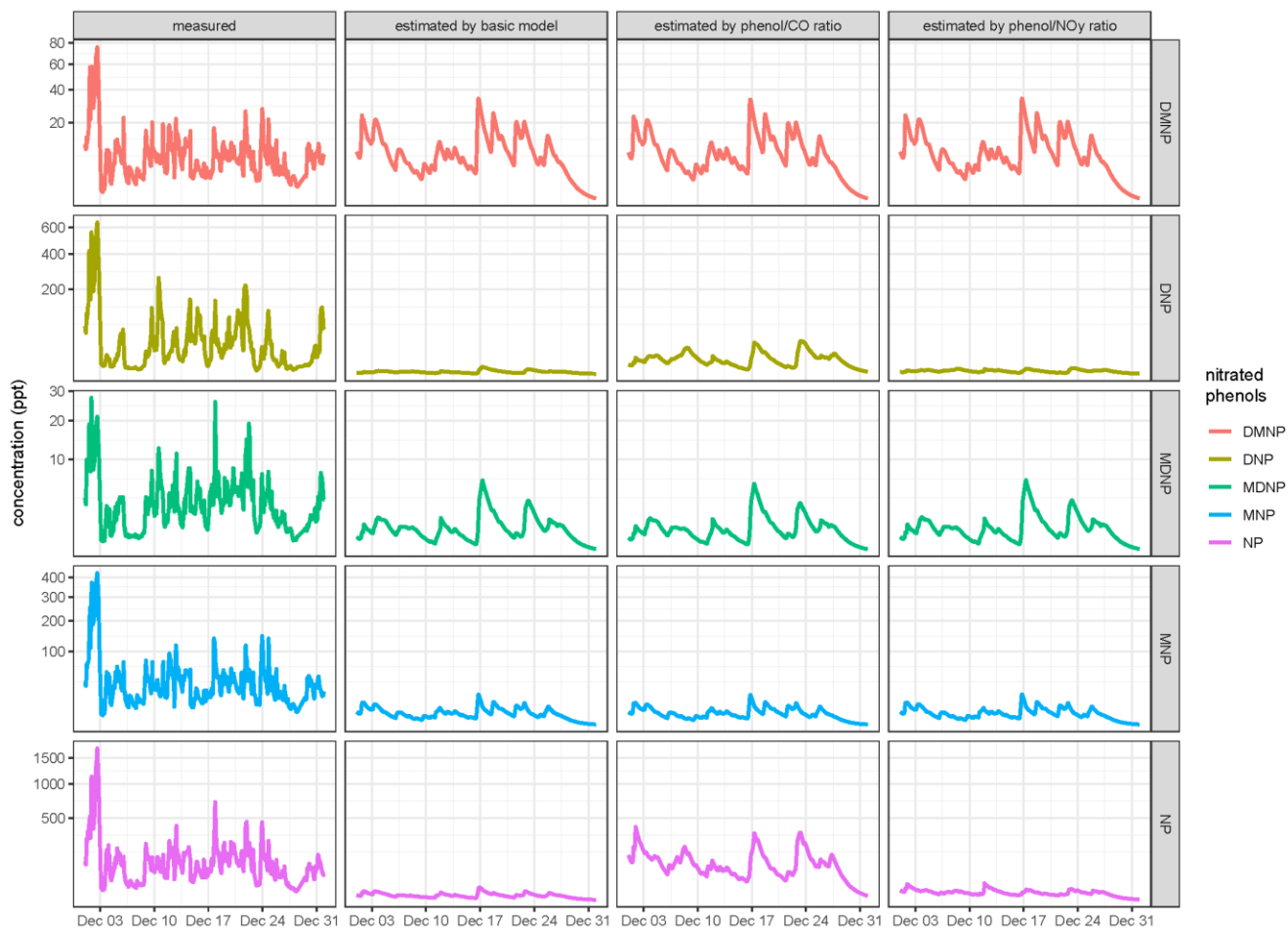
356

357 **Figure 8.** Contribution of primary emission (in dark blue borderline) and second formation (in red
358 borderline) of nitrated phenols. Primary emission was classified as biomass burning, coal combustion
359 industry and vehicle exhaust which were resolved by non-negative matrix factorization (NMF). NPs
360 in the legend referred to dinitrophenol (DNP), methyl-dinitrophenol (MDNP), methyl-nitrophenol
361 (MNP), and nitrophenol (NP). Secondary formation of nitrophenol was categorized as benzene
362 oxidation (<1%) and the oxidation of primarily emitted phenol (phenol oxidation, 37%). It was
363 noticeable that nitrophenol derived from the primary phenol oxidation was much more important
364 than the pathway from the traditional benzene oxidation in winter of Beijing.

365

366 Figure S3: see my major comments, I suggest, to improve the figure such that you can better separate
367 the different cases.

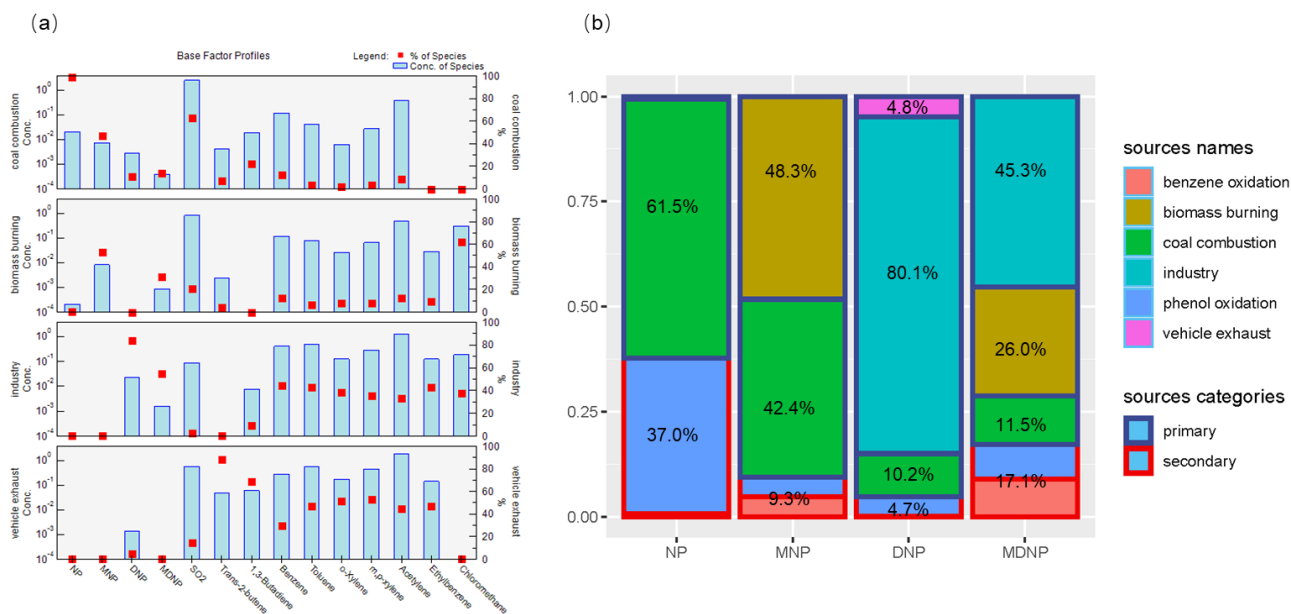
368 Thank you for your comment. We have revised Figure S3 accordingly.



369
370 Figure S3. The measured concentration of nitrated phenols and their secondary formation simulation
371 by the box model in different model scenarios.
372

373 Figure S8: I suggest, to use different colors for the grouping boxes

374 Thank you for your comment. We have revised Figure S8 accordingly.



375

376 Figure S8. Source profile from the PMF model. (a) Source profile of PMF results. SO₂,

377 chloromethane, aromatics and 1,3-butadiene as the markers of coal combustion, biomass burning,

378 industry and vehicle exhaust sources. (b) Contribution of primary emission (in dark blue borderline)

379 and second formation (in red borderline) of NPs.

380

381 **References**

- 382 Aljawhary, D., Lee, A. K. Y. and Abbatt, J. P. D.: High-resolution chemical ionization mass
383 spectrometry (ToF-CIMS): Application to study SOA composition and processing, *Atmos. Meas.*
384 *Tech.*, 6(11), doi:10.5194/amt-6-3211-2013, 2013.
- 385 Belloli, R., Barletta, B., Bolzacchini, E., Meinardi, S., Orlandi, M. and Rindone, B.: Determination
386 of toxic nitrophenols in the atmosphere by high-performance liquid chromatography, *J. Chromatogr.*
387 *A*, 846(1–2), 277–281, doi:10.1016/S0021-9673(99)00030-8, 1999.
- 388 Cecinato, A., Di Palo, V., Pomata, D., Tomasi Scianò, M. C. and Possanzini, M.: Measurement of
389 phase-distributed nitrophenols in Rome ambient air, Elsevier Ltd., 2005.
- 390 Delhomme, O., Morville, S. and Millet, M.: Seasonal and diurnal variations of atmospheric
391 concentrations of phenols and nitrophenols measured in the Strasbourg area, France, *Dokuz Eylul*
392 *Universitesi.*, 2010.
- 393 Duncianu, M., David, M., Kartigeyane, S., Cirtog, M., Doussin, J. F. and Picquet-Varrault, B.:
394 Measurement of alkyl and multifunctional organic nitrates by proton-transfer-reaction mass
395 spectrometry, *Atmos. Meas. Tech.*, 10(4), 1445–1463, doi:10.5194/amt-10-1445-2017, 2017.
- 396 Harrison, M. A. J., Barra, S., Borghesi, D., Vione, D., Arsene, C. and Iulian Olariu, R.: Nitrated
397 phenols in the atmosphere: A review, *Atmos. Environ.*, 39(2), 231–248,
398 doi:10.1016/j.atmosenv.2004.09.044, 2005.
- 399 Inomata, S., Tanimoto, H., Fujitani, Y., Sekimoto, K., Sato, K., Fushimi, A., Yamada, H., Hori, S.,
400 Kumazawa, Y., Shimono, A. and Hikida, T.: On-line measurements of gaseous nitro-organic
401 compounds in diesel vehicle exhaust by proton-transfer-reaction mass spectrometry, *Atmos. Environ.*,
402 73, 195–203, doi:10.1016/j.atmosenv.2013.03.035, 2013.
- 403 Leuenberger, C., Czuczwa, J., Tresp, J. and Giger, W.: Nitrated phenols in rain: Atmospheric
404 occurrence of phytotoxic pollutants, Pergamon., 1988.
- 405 Li, K., Li, J., Tong, S., Wang, W., Huang, R. J. and Ge, M.: Characteristics of wintertime VOCs in
406 suburban and urban Beijing: Concentrations, emission ratios, and festival effects, *Atmos. Chem.*
407 *Phys.*, 19(12), 8021–8036, doi:10.5194/acp-19-8021-2019, 2019.
- 408 Lüttke, J., Scheer, V., Levsen, K., Wünsch, G., Cape, J. N., Hargreaves, K. J., Storeton-West, R. L.,

409 Acker, K., Wieprecht, W. and Jones, B.: Occurrence and formation of nitrated phenols in and out of
410 cloud, Pergamon., 1997.

411 Mohr, C., Lopez-Hilfiker, F. D., Zotter, P., Prévôt, A. S. H., Xu, L., Ng, N. L., Herndon, S. C.,
412 Williams, L. R., Franklin, J. P., Zahniser, M. S., Worsnop, D. R., Knighton, W. B., Aiken, A. C.,
413 Gorkowski, K. J., Dubey, M. K., Allan, J. D. and Thornton, J. A.: Contribution of nitrated phenols to
414 wood burning brown carbon light absorption in detling, united kingdom during winter time, *Environ.*
415 *Sci. Technol.*, 47(12), 6316–6324, doi:10.1021/es400683v, 2013.

416 Moreira Dos Santos, C. Y., De Almeida Azevedo, D. and De Aquino Neto, F. R.: Atmospheric
417 distribution of organic compounds from urban areas near a coal-fired power station, *Atmos. Environ.*,
418 38(9), 1247–1257, doi:10.1016/j.atmosenv.2003.11.026, 2004.

419 Priestley, M., Le Breton, M., Bannan, T. J., Leather, K. E., Bacak, A., Reyes-Villegas, E., De Vocht,
420 F., Shallcross, B. M. A., Brazier, T., Anwar Khan, M., Allan, J., Shallcross, D. E., Coe, H. and
421 Percival, C. J.: Observations of Isocyanate, Amide, Nitrate, and Nitro Compounds From an
422 Anthropogenic Biomass Burning Event Using a ToF-CIMS, *J. Geophys. Res. Atmos.*, 123(14),
423 7687–7704, doi:10.1002/2017JD027316, 2018.

424 Schwantes, R. H., Schilling, K. A., McVay, R. C., Lignell, H., Coggon, M. M., Zhang, X., Wennberg,
425 P. O. and Seinfeld, J. H.: Formation of highly oxygenated low-volatility products from cresol
426 oxidation, *Atmos. Chem. Phys.*, 17(5), 3453–3474, doi:10.5194/acp-17-3453-2017, 2017.

427 Sekimoto, K., Inomata, S., Tanimoto, H., Fushimi, A., Fujitani, Y., Sato, K. and Yamada, H.:
428 Characterization of nitromethane emission from automotive exhaust, *Atmos. Environ.*, 81, 523–531,
429 doi:10.1016/j.atmosenv.2013.09.031, 2013.

430 Sunesson, A. L., Gullberg, J. and Blomquist, G.: Airborne chemical compounds on dairy farms, *J.*
431 *Environ. Monit.*, 3(2), 210–216, doi:10.1039/b008873k, 2001.

432 Wang, Y. Y., Hu, M., Wang, Y. Y., Zheng, J., Shang, D., Yang, Y., Liu, Y., Li, X., Tang, R., Zhu,
433 W., Du, Z., Wu, Y., Guo, S., Wu, Z., Lou, S., Hallquist, M. and Yu, J. Z.: The formation of
434 nitro-aromatic compounds under high NO_x and anthropogenic VOC conditions in urban Beijing,
435 China, Copernicus GmbH., 2019.

436 Yu, Y., Wang, H. H., Wang, T., Song, K., Tan, T., Wan, Z., Gao, Y., Dong, H., Chen, S., Zeng, L.,

437 Hu, M., Wang, H. H., Lou, S., Zhu, W. and Guo, S.: Elucidating the importance of semi-volatile
438 organic compounds to secondary organic aerosol formation at a regional site during the
439 EXPLORE-YRD campaign, *Atmos. Environ.*, 246, 118043, doi:10.1016/j.atmosenv.2020.118043,
440 2021.

441 Yuan, B., Hu, W. W., Shao, M., Wang, M., Chen, W. T., Lu, S. H., Zeng, L. M. and Hu, M.: VOC
442 emissions, evolutions and contributions to SOA formation at a receptor site in eastern China, *Atmos.*
443 *Chem. Phys.*, 13(17), 8815–8832, doi:10.5194/acp-13-8815-2013, 2013.

444 Yuan, B., Liggió, J., Wentzell, J., Li, S. M., Stark, H., Roberts, J. M., Gilman, J., Lerner, B.,
445 Warneke, C., Li, R., Leithead, A., Osthoff, H. D., Wild, R., Brown, S. S. and De Gouw, J. A.:
446 Secondary formation of nitrated phenols: Insights from observations during the Uintah Basin Winter
447 Ozone Study (UBWOS) 2014, *Atmos. Chem. Phys.*, 16(4), 2139–2153,
448 doi:10.5194/acp-16-2139-2016, 2016.

449 Zhu, J., Newhook, R., Marro, L. and Chan, C. C.: Selected volatile organic compounds in residential
450 air in the city of Ottawa, Canada, *Environ. Sci. Technol.*, 39(11), 3964–3971,
451 doi:10.1021/es050173u, 2005.

452