Dear co-editor and referees,

We appreciate all your detailed and valuable comments on our manuscript of "acp-2018-1256". Please see the point-by-point response below and changes are marked blue in the revised manuscript.

Referee #3

General comments

Based on the extensive data from the field collected during the summertime campaign in Beijing, the manuscript discusses formation mechanisms of the most abundant groups of atmospheric nitroaromatic compounds, nitrophenols and nitrocatechols. The represented dataset is very valuable and the manuscript is well structured, however the conclusions made by the authors are sometimes vague and require more justification.

The authors distinguish between biomass-burning and anthropogenic emissions. As BB emissions are often of an anthropogenic origin, please make it clear that you mean traffic emissions when referring to anthropogenic emissions

Response: In addition to vehicular exhaust, solvent evaporation could also be an anthropogenic precursor source for NACs. We have added the following text to clarify:

Lines 256-261: However, previous studies suggested that the sources of anthropogenic VOCs in summer in Beijing were dominated by vehicle emissions (>50%), with minor contributions from solvent evaporation and biomass burning (Wang et al., 2014; Liu et al., 2008). … We note that biomass burning could often be of an anthropogenic origin. Within this work, the term "anthropogenic VOCs" does not include VOCs from human-caused biomass burning activities.

References

Liu, Y., Shao, M., Fu, L., Lu, S., Zeng, L., and Tang, D.: Source profiles of volatile organic compounds (VOCs) measured in China: Part I, Atmos. Environ., 42, 6247-6260, 10.1016/j.atmosenv.2008.01.070, 2008.

Wang, M., Shao, M., Chen, W., Yuan, B., Lu, S., Zhang, Q., Zeng, L., and Wang, Q.: A temporally and spatially resolved validation of emission inventories by measurements of ambient volatile organic compounds in Beijing, China, Atmos. Chem. Phys., 14, 5871-5891, 10.5194/acp-14-5871-2014, 2014.

In the introduction, much space is devoted to biomass burning as a possible source of NP and NC, however the characteristic methoxyphenols (substituted guaiacols and syringols) and their nitrated analogues are not even mentioned.

Response: The NACs formation via the oxidation of methoxyphenols was added in the introduction (lines 62-65).

Lines 62-65: 4-Nitrocatechol could be formed via the OH-initiated oxidation of guaiacol, an abundant methoxyphenol emitted from biomass burning, in the presence of NO_2 (Lauraguais et al., 2014). However, under high-NO_x conditions, this pathway seems to be of minor importance to nitrocatechol formation, instead, nitroguaiacols were formed as the major products (Lauraguais et al., 2014).

Why don't you report the concentrations of (nitro)guaiacols and (nitro)syringols (maybe you didn't detect them?). This could help support the statement that anthropogenic (traffic?) emissions prevailed *over biomass burning emissions during the campaign. To my opinion, this assumption is not justified enough in the manuscript (although it is very likely to be true). Also, explain why primary emissions are not likely the important source of measured NAC.*

Response: (Nitro)guaiacols or (nitro)syringols were not detected in this study. Previous studies suggested that the sources of anthropogenic VOCs in summer in Beijing were dominated by vehicle emissions (>50%), with minor contributions from solvent evaporation and biomass burning (Wang et al., 2014; Liu et al., 2008). Modelling studies incorporating emission inventories of the relevant VOC precursors could address this issue and are suggested in future investigation of NAC sources (lines 256-259).

The explanation for why primary emissions are unlikely an important source of the measured NACs is provided in lines 246-250 and copied below for easy reference.

Lines 246-250: It was noticed that NACs showed stronger correlations with toluene (r=0.70**), benzene (r=0.64**) or acetonitrile (r=0.61**) than those with potassium (r=0.49**). This appeared to suggest that the NO_x oxidation of anthropogenic VOCs and precursor VOCs from biomass burning was a more important source of NACs than primary biomass burning emission in summer in Beijing. A lower correlation between particulate NACs and EC (Table S3, r=0.39**) was also in agreement with the suggestion of the less importance of primary emissions to NACs during the campaign.

In the cited paper of Frka et al. it is nicely demonstrated that the usage of surrogate molecules for the quantification of aromatic isomers by LC-MS can result in the over- or underestimation of the concentration of analyte, even for the factor of 10. The case of 3M4NC and 3M6NC is specifically exposed, as well as their misidentification in the past studies. Make it clear that you considered this issues during the analysis (if not, 3M6NC is more likely to be 3M4NC) and comment on the determined concentration of 3M6NC by use of 4M5NC standard. Reconsider also the conclusion in L224-226. Moreover, how do you know that DMNP peaks are truly dimethylnitrophenols and not ethylnitrophenols or their methoxylated isomers?

Response: The over- or underestimation of 3M6NC and the possibility of misidentification 3M4NC as 3M6NC were described in lines 130-134. The conclusion in lines 224-226 was revised (lines 296-298). 2,6DM4NP was identified based on its retention time matching with that of authentic standards (Figure S1), while we cannot exclude the possibility of the other two DMNP peaks as ethylnitrophenols or methoxylated isomers (lines 135-137).

Lines 130-134: 4M5NC was employed as a surrogate standard to quantify 3M5NC and 3M6NC. However, a recent study suggested that no 3M6NC could be detected in ambient aerosols and the MNC isomer could be an incorrect assignment of 3M4NC as 3M6NC (Frka et al., 2016). We cannot exclude the possibility of MNC isomer as 3M4NC due to a lack of authentic standards. Employing 4M5NC as a surrogate standard, the concentrations of 3M6NC could be obviously underestimated due to its poor ionization under ESI condition compared with that of 4M5NC (Frka et al., 2016).

Lines 296-298: 3M6NC (or 3M4NC isomer) showed different temporal variations from 4M5NC or 3M5NC (Figures 4, S4) and their correlations were lower than that between 4M5NC and 3M5NC (Tables S3, S4), possibly suggesting different formation pathway for 3M6NC (or 3M4NC isomer) from those of 4M5NC or 3M5NC.

Lines 135-137: 2,6DM4NP was identified based on its retention time matching that of the authentic standard (Figure S1), while we cannot exclude the possibility of the other two DMNP isomers as ethylnitrophenols or methoxylated isomers.

The language should be edited before the manuscript is published in ACP.

Response: We have the manuscript edited and proofread by co-authors with extensive publishing experience in scientific journals.

Specific comments

L60-62: how can MNC form by the oxidation of catechol? Did you mean methylcatechol?

Response: Thanks for pointing out this mistake. Yes, we mean methylcatechols. The sentence is revised as below:

Line 60: Methyl-nitrocatechols (MNCs) could originate from NO_x oxidation of methylated cresol or methylcatechols…

L64-65: the sentence is misleading. In Fig. 1 you only show the most generally accepted pathways of gas-phase NAC formation. Revise the sentence for clarity and/or show also the aqueous-phase chemistry which you are referring to later in this paragraph. I strongly suggest extending the figure to at least the aqueous-phase formation of NC, which you show to be dominant in the atmosphere. Include also the relevant references in the figure caption.

Response: Thanks for your suggestion. The figure has been extended to include the aqueous-phase formation of NCs and relevant references are included in the figure caption.

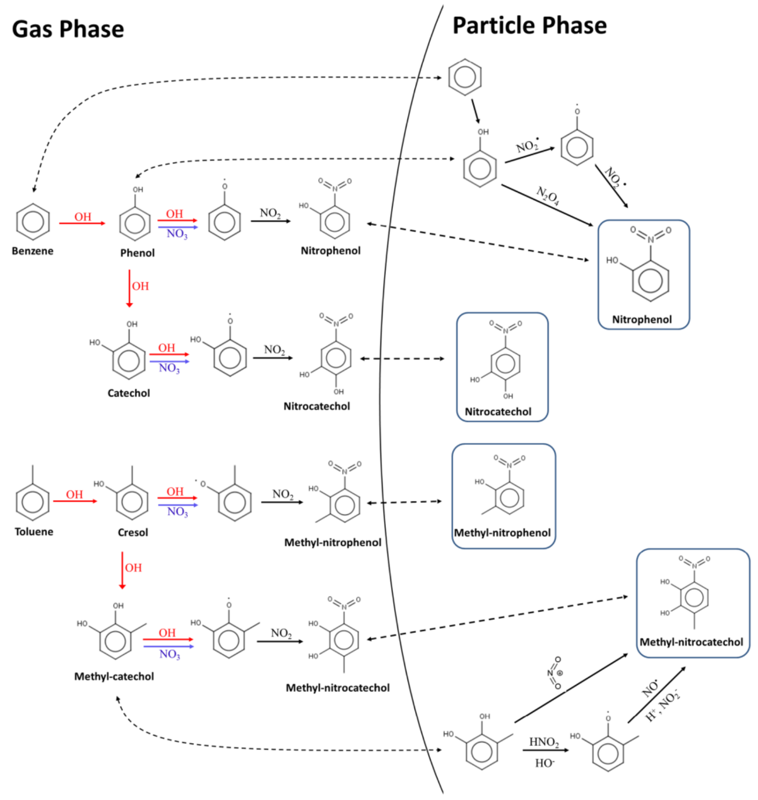

Figure 1 Formation pathways of nitrophenols, nitrocatechols, methyl-nitrophenols and methyl-nitrocatechols from the oxidation of benzene, toluene, phenol and methy-catechol in the gas phase and particle phase (Jenkin et al., 2003; Frka et al., 2016; Vione et al., 2004; Vione et al., 2001; Vidovic et al., 2018).

L71-72: refer here to the very recent and comprehensive study on the possible nitration mechanisms of activated methoxyphenols in the atmospheric aqueous phase by Kroflič et al.: https://pubs.acs.org/doi/10.1021/acs.est.8b01903

Response: This study has been referred in line 74.

L72: 'Nitrophenols could form through the nitration and hydroxylation of benzene…' note that NO_2 group deactivates the aromate, whereas OH makes it more reactive. Therefore, oxidation-first and nitration-second is more likely to occur. Change the order accordingly.

Response: Revised accordingly (lines 75-76).

Lines 75-76: Nitrophenols could be formed through the hydroxylation and nitration of benzene in the presence of nitrite/nitrous acid or photo-nitration of phenol upon UV irradiation of nitrite in aqueous solutions.

L93-94:I cannot see it obvious that anthropogenic emissions dominated during the campaign.

Response: The obvious influence of anthropogenic pollutants was suggested in another study conducted during the campaign (Tang et al., 2018), which is referred here (lines 99). The sentence is re-phrased below to improve clarity:

Lines 97-99: During this period, the site was influenced by anthropogenic pollutants from Beijing urban areas and under high-NO_x conditions, as suggested by field measurement evidence reported in previous publications related to this campaign (Tang et al., 2018; Wang et al., 2018a).

L149-150: check again, NP is also not always higher than in other studies.

Response: This sentence was revised (lines 195-197).

Lines 195-197: Most NAC species (NC, MNP and MNC), except for DMNP and NP, also showed elevated concentrations in Changping, compared with those reported in other summertime studies (Figure S2).

L192 (and Fig. 3 caption): what kind of pollution episodes?

Response: The pollution episodes were characterized by elevated organic concentrations. This sentence (lines 240-241) and Fig. 3 caption were revised for clarity.

Lines 240-241: During the field campaign, four pollution episodes (episodes I, II, III, IV), marked by grey shading in Figure 3, were identified through observation of elevated organic aerosols.

Fig. 3 caption: "…The pollution episodes, with elevated organic aerosols, are marked by gray shading."

L210, L290, L326-327: It seems like photolysis is not important for the aqueous-phase products (NC)?

Response: Yes, we think the photolysis of aqueous-phase products (methyl-nitrocatechols) is of minor importance under low RH conditions during the campaign (average daytime RH=26%), compared with that of gas-phase products (nitrophenols). The gas-phase photolysis has been widely proved an important loss pathway of nitrophenols and methyl-nitrophenols (Yuan et al., 2016; Sangwan and Zhu, 2018; Bejan et al., 2007), with high fractions in gas phase. The aqueous-phase products (methyl-nitrocatechols) have been suggested to be dominated in particle phase. Under the low RH conditions (average daytime RH=26%) and low aerosols liquid water content (average daytime ALWC=2.9 μg/m^3) during daytime, the particles were at a solid to semisolid state (Liu et al., 2017) and photochemical reactions in aqueous phase were largely suppressed. Thus, we think the photolysis of aqueous-phase products is of minor importance under our field campaign condition, which need more evidences to be validated in our future studies.

References

Bejan, I., Barnes, I., Olariu, R., Zhou, S., Wiesen, P., and Benter, T.: Investigations on the gas-phase photolysis and OH radical kinetics of methyl-2-nitrophenols, Phys. Chem. Chem. Phys., 9, 5686-5692, 10.1039/b709464g, 2007.

Liu, Y., Wu, Z., Wang, Y., Xiao, Y., Gu, F., Zheng, J., Tan, T., Shang, D., Wu, Y., Zeng, L., Hu, M., Bateman, A. P., and Martin, S. T.: Submicrometer Particles Are in the Liquid State during Heavy Haze Episodes in the Urban Atmosphere of Beijing, China, Environmental Science & Technology Letters, 4, 427-432, 10.1021/acs.estlett.7b00352, 2017.

Sangwan, M.and Zhu, L.: Role of Methyl-2-nitrophenol Photolysis as a Potential Source of OH Radicals in the Polluted Atmosphere: Implications from Laboratory Investigation, J. Phys. Chem. A, 122, 1861-1872, 10.1021/acs.jpca.7b11235, 2018.

Slade, J. H.and Knopf, D. A.: Multiphase OH oxidation kinetics of organic aerosol: The role of particle phase state and relative humidity, Geophys. Res. Lett., 41, 5297-5306, 10.1002/2014gl060582, 2014.

Yuan, B., Liggio, J., Wentzell, J., Li, S.-M., Stark, H., Roberts, J. M., Gilman, J., Lerner, B., Warneke, C., Li, R., Leithead, A., Osthoff, H. D., Wild, R., Brown, S. S., and de Gouw, J. A.: Secondary formation of nitrated phenols: insights from observations during the Uintah Basin Winter Ozone Study (UBWOS) 2014, Atmos. Chem. Phys., 16, 2139-2153, 10.5194/acp-16-2139-2016, 2016.

L219-222: refer also to Fig. 9 – at the nightime RH levels, daytime ratios are also not dependent on RH anymore.

Response: Yes. The daytime ratios are not dependent on RH anymore at the nighttime RH levels, which means the relative contribution of aqueous-phase and gas-phase pathways remain constant under higher RH conditions (the nighttime RH levels). While the concentrations of 3M4NC, 4M5NC and 4NP also increased at higher RH, the (3M4NC+ 4M5NC)/4NP ratio remained nearly constant. The aqueous-phase formation could be more dependent on ambient RH under lower RH levels during daytime.

L259-260: ‘NO_3^- concentrations and (NO_3^-)/NACs ratios showed significant increasing trends (Figure 5a, b, c).’ Not sure if I can see this, especially for the ratio. Please correct.

Response: ‘Significant’ was deleted in the revised version. The NO_3^- concentrations and (NO_3^-)/NACs ratios at NO_2 20-25 ppb were higher than those under low-NOx conditions (NO_2<20 ppb) (lines 330-331).

Lines 330-331: At the same time, the NO_3^- concentrations and (NO_3^-)/NACs ratios showed increasing trends compared with those under low-NO_x conditions (NO_2< 20ppb) (Figure 5a, b, c).

L325: Use here the original research of Frka et al. to avoid misunderstanding: https://pubs.acs.org/doi/abs/10.1021/acs.est.5b01811

Response: The reference has been changed in the revised version (lines 393).

Fig. 7: cannot find r value referred to in the caption.

Response: This sentence was not supposed to be part of Figure 7 caption. We forget to delete this sentence in figure caption during the paper revision. This has been deleted in the revised version.

Fig. S5: this is again only gas-phase chemistry presented. Make this crystal clear or add also heterogeneous/aqueous-phase pathways.

Response: Figure S6 has been extended to include the aqueous-phase pathways.

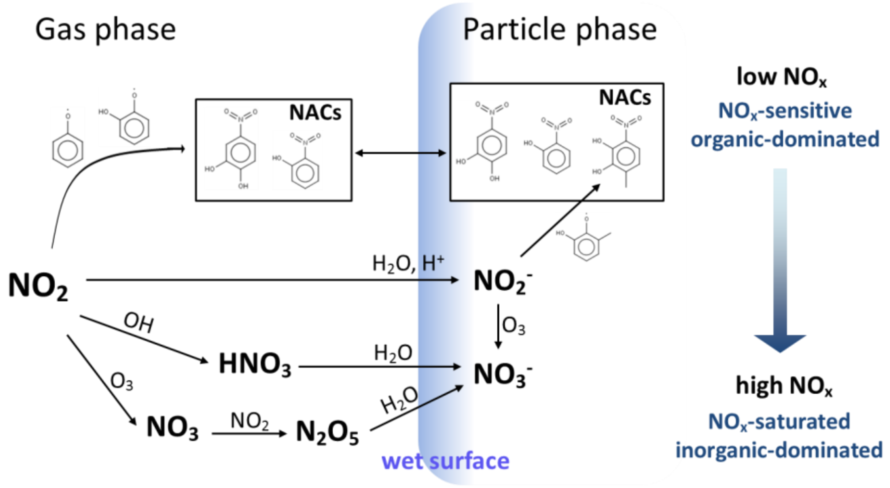

Figure S6 Schematic diagram and simplified mechanisms of the competing formation of inorganic nitrates and NACs

TECHNICAL CORRECTIONS

The usage of word 'obvious' is excessive. You should avoid it throughout the text.

Response: The word 'obvious' were deleted where it's not clear or not necessary.

It is not clear to me why you used Results and Discussion section 3 and later on again a Discussion section 4. I would use only section 3 – Results and Discussion.

Response: Only section 3– Results and Discussion is now used in the revised version.

L16 and L47: the phrase 'ultraviolet light absorption by brown carbon' is incorrect, the characteristics of BrC is visible light absorption. Please correct accordingly.

Response: Revised accordingly (lines 46).

Lines 46: "…important contributors to the light absorption by brown carbon (BrC),…"

L162-165: the sentence needs revision.

Response: Revised accordingly (lines 209-211).

Lines 209-211: The NAC concentrations during summer (including this study) are generally lower than those during spring, autumn or winter, which could be due to stronger contributions from combustion sources (e.g. biomass burning and coal combustion) during spring, autumn or winter than those during summer.

In general, the language, especially the grammar, requires editing.

Response: Suggestion taken. We have edited the text to improve the language and grammar uses.