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 #1

1 General Comments

This paper examines the formation of nitro-aromatic compounds (NACs) in the Beijing summer under high NOx and high anthropogenic VOC conditions. NAC formation is of interest owing to their light- absorbing and toxicological properties. Formation properties of both the nitro-phenols (NPs) and the nitro-catechols (NC) are diurnal with the latter forming at night and the former forming predominantly during the day time. Excess NOx and VOC concentration thresholds were reported. Higher NOx generally favored formation of the NCs. Generally, VOC concentration thresholds of < 1 ppb were observed. It was concluded that aqueous phase oxidation was more important at night than daytime.

The study's subject matter is of interest to the ACP audience, and the paper is well written. NACs in biomass burning and in the atmosphere are becoming well investigated, and while fewer studies may examine NACs in the urban environment, a clearer statement about the novelty of the current research is due. For example, Figure 1 shows that NACs have been measured throughout the world, including at several urban sites in China. So, this paper should explicitly state why another study is needed on this topic now. Additionally, the study would benefit from showing the NC and NP compound peaks and their resolution in the LC-MS chromatograms. Next, the pollution events and K+ need to clearly connect to the main story of the paper (e.g. Figure 3). The discussion suggests that biomass burning is mainly a non-factor despite the K+ possibly showing otherwise, and the diurnal profile seems much more robust than any of the four so-called `pollution events'. In other words, the importance of the individual pollution events and the source of the events is just isn't clear enough. These points should be better addressed during revision. Finally, the paper would also benefit from further analysis of the potential gas-phase concentrations of some of these compounds and quantification of the likelihood of volatilization losses. Use of vapor pressures or partitioning coefficients should help with this issue. Once addressing these concerns and the additional comments below, the paper should be publishable.

Response: Thanks for your suggestions.

1) *NACs in biomass burning and in the atmosphere are becoming well investigated, and while fewer studies may examine NACs in the urban environment, a clearer statement about the novelty of the current research is due. For example, Figure 1 shows that NACs have been measured throughout the world, including at several urban sites in China. So, this paper should explicitly state why another study is needed on this topic now.*

Responses: Though NACs were investigated throughout the world, including several sites (two rural sites in Hebei Province and an urban site in Hong Kong) in China. Few studies in China has been as comprehensive in supporting measurements as this study. In this work, with the additional field data of inorganic aerosols, VOC precursors, gases and meteorological parameters, we are able to gain more comprehensive understanding of the characteristics, secondary formation and influence factors of NACs in urban atmospheres characteristic of high NO_x and high anthropogenic VOC concentrations, which was not done in the past studies conducted in urban environment. A statement about the novelty of the current research has been added in lines 83-86.

Lines 83-86: However, few observational field studies have been conducted to investigate the formation of NACs in urban atmospheres. In this work, we report results from an intensive field campaign conducted in summertime Beijing, aiming to gain understanding of ambient concentration variation characteristics of NAC, relative importance of various proposed formation pathways and major influence factors in high NO_x and anthropogenic VOCs dominated urban atmospheres.

2) *the study would benefit from showing the NC and NP compound peaks and their resolution in the LC-MS chromatograms.*

Responses: The chromatograms of NAC standards and an ambient sample are added in Figure S1.

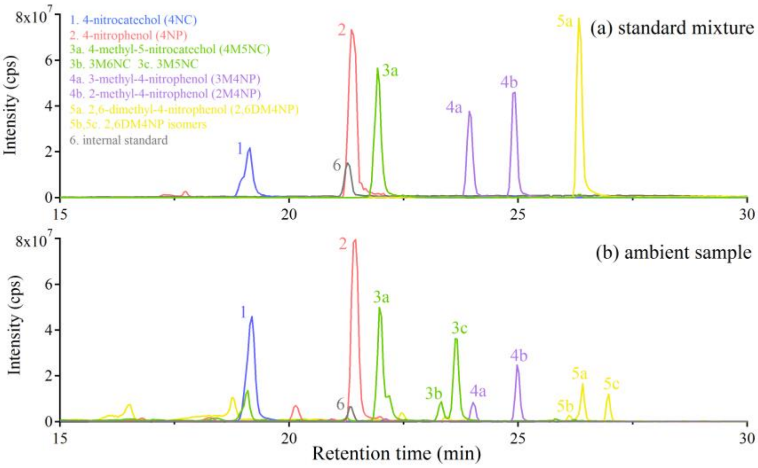

Figure S1 Extracted ion chromatograms for (a) a standard solution containing 4-nitrocatechol (4NC), 4-nitrophenol (4NP), 2-methyl-4-nitrophenol (2M4NP), 3-methyl-4-nitrophenol (3M4NP), 2,6-dimethyl-4-nitrophenol (2,6DM4NP) and internal standard and (b) an ambient sample collected during the campaign.

3) *the pollution events and K^+ need to clearly connect to the main story of the paper (e.g. Figure 3). The discussion suggests that biomass burning is mainly a non-factor despite the K^+ possibly showing otherwise, and the diurnal profile seems much more robust than any of the four so-called `pollution events'. In other words, the importance of the individual pollution events and the source of the events is just isn't clear enough. These points should be better addressed during revision.*

Responses:

(1) In this study, the potassium ion was employed to indicate the particles (particulate NACs) primarily emitted from biomass burning. Gas-phase acetonitrile was employed to indicate the variations of gases (VOC precursors) released by biomass burning. The correlation analysis between NACs and acetonitrile could indicate the secondary formation of NACs via the oxidation of VOCs (e.g. cresol) emitted from biomass burning. Lower correlation between NACs and K^+ (r=0.49) than that between NACs and acetonitrile (r=0.61) suggested that primary biomass burning emissions were less important source of NACs than oxidation of VOCs released by biomass burning. The revised text now provides a clearer explanation (lines 243-250).

Lines 243-250: The potassium ion was employed to indicate particulate emissions from biomass burning. As the biomass burning-derived immediate VOC precursors to NACs were not detected in this study, acetonitrile was used to track the variations of VOCs released by biomass burning. 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.

(2) The nighttime aqueous-phase formation pathways played more important roles during episode I, and the daytime gas-phase photooxidation pathways could be more important during episodes II-IV. Description of the differences of pollution episodes in relation to sources/formation mechanisms was revised to provide more clarity (lines 289-291, 307-310).

Lines 289-291: The nighttime enhancements of 4M5NC and 3M5NC were more obvious during episode I than those during episodes II-IV (nighttime/daytime concentrations at 1.9-3.1 vs. 0.9-1.5) (Figure 4), which suggested that nighttime aqueous-phase formation pathways played more important roles during the first episode.

Lines 307-310: The daytime enhancements of NP and its derivatives (2M4NP, DMNP) were more prominent during episodes II-IV than episode I (daytime/nighttime concentrations at 3.1-4.5 vs. 1.8-2.0) (Figure 4), which indicated that gas-phase photochemical oxidation play more important roles during the later period of campaign.

4) *the paper would also benefit from further analysis of the potential gas-phase concentrations of some of these compounds and quantification of the likelihood of volatilization losses. Use of vapor pressures or partitioning coefficients should help with this issue.*

Responses: Thanks for the suggestion. We now have added analysis to provide a semi-quantitative estimate of the gas-phase presence of the NACs. The information of the different gas-particle distributions between two sub-groups of NACs (i.e., nitrophenols and nitrocatechols) is used to better explain their distinct formation mechanisms.

The methodology of estimating gas-phase concentrations of NACs is described in Section 2.4 and copied below for easy reference. New discussions arising from this added information are added (lines 216-219, 250-254, 271-275, 359-361).

Section 2.4 Estimation of the gas-phase NACs

The concentrations of gas-phase NACs were not measured in this study. They were calculated based on the measured particle-phase NAC concentrations and equilibrium absorption portioning theory (Pankow, 1994a, b; Pankow et al., 2001) (Eqs. 1, 2):

$$F_p = (1 + \frac{C^*}{C_{OA}})^{-1} = \frac{c_p}{c_g + c_p} \qquad \text{(Eq. 1)}$$

where F_p is the fraction of NACs in the particle-phase. C_{OA} is the concentrations of organic aerosols (OA), calculated to be OC multiplying by 1.6. c_g and c_p are the concentrations of NACs in gas phase and particle phase, respectively. C^* is the effective saturation mass concentration (μg/m^3), and is calculated using Eq. 2:

$$C^* = \frac{M10^6 \zeta P_V}{760RT} \qquad \text{(Eq. 2)}$$

where M is the molecular weight of NACs (g/mol). ζ is the activity coefficient of the species (assumed =1). R is the gas constant (8.314 J/(mol K)), T is the temperature (K), and P_v (Pa) is the saturated pressure. P_v at the average temperature during the campaign (296 K) is calculated using the multiphase system online property prediction tool developed by University of Manchester (UManSysProp, http://umansysprop.seaes.manchester.ac.uk). The vapor pressures were estimated using Nannoolal approach, and the boiling points were estimated using the Joback and Reid approach.

The estimated P_v, F_p and gas-phase concentrations of NACs are listed in Table S1. 4NP and methyl-nitrophenols (2M4NP and 3M4NP) were predicted to be mainly in the gas phase (F_p<10%) while DMNP, 4NC and MNC (3M6NC, 3M5NC and 4M5NC) were mainly in the particle phase (F_p>60%). The gas-phase DMNP and MNC (F_p>95%) would not be further discussed in this study. While the equilibrium model gives reasonable estimation of F_p and gas-phase concentrations for nitrocacatechols, it overestimates the vapor pressure of NPs by several orders of magnitude (Bannan et al., 2017). The estimated F_p (0.83%) was obviously lower than the measured values for 4NP. For example, Cecinato et al. (2005) measured F_p of 4NP and 3M4NP to be 82% and 78%, respectively in downtown Rome; Le Breton et al. (2018) reported F_p of nitrophenol at ~17% using Chemical-Ionization Mass Spectrometer (CIMS) coupled with the Filter Inlet for Gases and AEROsols (FIGAERO) during this campaign. We note that CIMS could not distinguish the isomers (e.g. 2NP) of 4NP, however, the measured F_p values showed us the range of particulate fraction of 4NP during the campaign. The equilibrium absorption portioning model could underestimate the F_p of 4NP by ~20 times. Thus, the gas-phase 4NP concentration was roughly calculated using the measured F_p (17%) by FIGAERO-CIMS (Le Breton et al., 2017).

Table S1 The saturated pressure (P_v), NAC fraction in particles (F_p) and NAC concentrations in gas-phase

compounds	*Pv* (Pa)	F_p (%)		conc. in gas phase (ng/m^3)	
		range	average	range	average
4NP	3.0E-02	0.25-1.3	0.83	143-566	268
2M4NP	4.2E-03	1.2-7.6	5.1	5.2-42	15
3M4NP	4.2E-03	1.2-7.6	5.1	1.9-20	5.8
DMNP	5.3E-04	99-100	100	0.000-0.007	0.002
4NC	3.4E-05	67-91	85	0.06-0.79	0.27
3M6NC	3.1E-06	95-99	98	0.000-0.003	0.001
3M5NC	3.1E-06	95-99	99	0.002-0.017	0.007
4M5NC	3.1E-06	95-99	98	0.001-0.028	0.009

Lines 216-219: The contribution of NP and NC could be larger when considering both gas- and particle-phases. The average concentration of 4NC in both gas- and particle-phases was estimated 2.2 ng/m^3 using equilibrium absorption portioning model. The total concentration of 4NP (13 ng/m^3) in both gas- and particle-phases was approximated using the measured F_p (17%) by FIGAERO-CIMS.

Lines 250-254: We note that only particulate NAC concentrations were used to do the correlation analysis. Two atmospheric processes, namely photolysis and gas-to-particle partitioning, could influence the abundance of particle-phase NACs, especially for NP and MNPs, since majority of them was expected to be in the gas phase (Table S1). As such, correlations of particle-phase NP and MNPs with other species may less reliably reflect the underlying associations with the correlation species.

Lines 271-275: This was more likely associated with the fact that particle-phase NPs only account for a minor part of the atmospheric NP abundance due to the high vapor pressure of NPs (Table S1). The abundance of particulate NP could largely depend on gas-to-particle partitioning, which is strongly affected by temperature, as well as their gas-phase loss pathways (e.g. photolysis) (Bejan et al., 2007; Yuan et al., 2016; Sangwan and Zhu, 2018). NC and MNC were mainly present in the particle phase (Table S1).

Lines 359-361: As particle-phase NP and MNP were strongly dependent on the gas-to-particle partitioning and gas-phase loss (e.g. photolysis), their increasing trends as a function of NO_2 were not as obvious as those of NC and MNC.

2 Specific comments

1. *lines 19-21: This sentence should be revised for clarity. `high NOx anthropogenic VOCs' is this one or two concepts? Also, not certain what `influence factors' are. Please fix.*

Response:

(1) We now revise 'High NO_x anthropogenic VOCs' to "High NO_x and anthropogenic VOCs" throughout the manuscript.

(2) "Influence factors" means "factors that influence NAC formation, including NO_2, VOC precursors, RH and photolysis". The relevant text in the abstract has been re-worded to improve clarity (lines 18-19).

Lines 18-19: We investigated the factors that influence NAC formation (e.g. NO_2, VOC precursors, RH and photolysis)…

2. *line 21: Is this total concentration an average? Or the top end of the range? Be specific.*

Response: It's the average concentration of all the quantified NACs. It has been revised to be specific (lines 20-21).

Lines 20-21: The average total concentration of the quantified NACs was 6.63 ng/m^3, higher than those reported in other summertime studies (0.14- 6.44 ng/m^3).

3. *line 29: just state that there was excess NOx for VOC oxidation. As written the sentence is awkward.*

Response: We revised the text to be the following:

Lines 28-29: Under high-NO_x conditions, NAC concentrations did not further increase with NO_2, while the NO_3^- concentrations and (NO_3^-)/NACs ratios showed increasing trends…"

4. *line 38: Where are the aerosol surface area data?*

Response: The aerosol surface area data was described and analyzed in lines 141-143, 391-393 and Fig. 8(b).

Lines 141-143: The aerosol surface area was calculated based on the measurements of particle number and size distribution by a scanning mobility particle sizer (SMPS, TSI 3936) and an aerosol particle sizer (APS, TSI 3321) (Yue et al., 2009; Wang et al., 2018a).

Lines 391-393: The NAC concentrations also showed good correlations with aerosol surface area (Figure 8b). Higher aerosol surface area would facilitate the partitioning of gas-phase NAC products or precursors into particle phase and the aqueous-phase or heterogeneous oxidation processes (Kroflic et al., 2015; Bauer et al., 2004; Fenter et al., 1996; Vidovic et al., 2018).

5. *lines 112-117: Please provide a chromatogram that shows the separation. Many of these compounds are isomers, and it is important to see evidence of sound chromatographic resolution. Evidence of peak quality for this study is warranted.*

Responses: The chromatograms of NAC standards and an ambient sample are added in Figure S1 (see general comments 2)). The NACs were identified and quantified based on the retention time of reference standards.

6. *Figure 1: these reaction schematics are not chemically balanced. If -H_2O is removed than it should be indicated in the reaction scheme. What happens to the NO_3? This reaction scheme should show the reader exactly what happens chemically. Are these compounds also present in the gas-phase?*

Response: Only the major intermediate products related to NAC formation are shown in the schematic, and other intermediate products are omitted for clarity. The NO_3 radical would transform to HNO_3 in the reactions.

Yes. These compounds are present in both gas-phase and particle-phase, and both gas-phase and particle-phase pathways are included in Figure 1.

7. *line 162-165: This last sentence should be revised for clarity. Can't tell which conditions go with which season.*

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.

8. *lines 173-174: So, it's a high NOx and a high anthropogenic VOC environment?*

Response: Yes. It’s the environment characterized by both high-NO_x and anthropogenic VOCs dominated conditions. This sentence has been revised to be clear (lines 223-225).

Lines 223-225: Thus, it is not a surprise to observe the high concentrations of nitrophenol and nitrocatechol in the typical high-NO_x and anthropogenic VOCs dominated environments in summer in Beijing.

9. *lines 179-181: Please clarify the sentence about `Different NAC compositions'. How much higher is the RH in Hong Kong compared with Beijing in summer?*

Response: “Different NAC compositions” were described in lines 226-227: The contribution of NP among the total NACs at Changping was higher than that in summer in Hong Kong, while that of MNC was lower (Table S2 and the inserted pie charts in Figure S2).

The ambient RH in Hong Kong and Beijing were added in lines 232-234: The ambient RH in Hong Kong (>70%) was significantly higher than that in summer in Beijing (5-81%, 37% on average), thus the relative contribution of aqueous-phase pathways could be more dominant in Hong Kong, promoting the aqueous-phase formation of MNC.

10. *lines 205-209: It is unclear what is being discussed here with regard to the pathway, loss mechanisms, and groups. Please be specific and quantitative if possible.*

Response: The sentences have been revised (lines 265-270). The specific formation and loss pathways were analyzed in the following two paragraphs (lines 281-318).

Lines 265-270: Good inter-species correlations were observed among nitrophenol and its derivatives (2M4NP, 3M4NP, DMNP, r=0.56-0.88), as well as among nitrocatechol and its derivatives (3M6NC, 3M5NC, 4M5NC, r=0.49-0.84). This signaled that the formation and loss pathways as well as the influence factors were likely similar within NP and NC groups. In comparison, the correlations of NACs across the two groups, i.e., between nitrophenol derivatives (MNP, DMNP) and nitrocatechol derivatives (MNC, r=0.05-0.45), were lower (Table S3), suggesting different formation pathways and influence factors.

11. *lines 209-210: Why was the gas-phase not sampled for this study? It would have brought more clarity and we could have learned if the mass was simply distributed in the gas-phase as opposed to being 'lost'. It may be a good idea to use individual NAC concentrations, vapor pressures and day and night time temperature to estimate the total mass in both the gas- and particle-phase.*

Response: The gas-phase NACs were not measured due to the limitation of the samplers in this study. We have taken the reviewer's suggestion and estimated the gas-phase concentrations of NACs based on the equilibrium absorption partitioning theory. This new information indeed helps to explain the different behaviors of nitrophenols and nitrcatecols. The details have been provided in our response to the earlier comment (general comments 4)).

12. *line 271: please clarify `interacted conditions'*

Response: The interaction and reactions between anthropogenic VOCs and NO_x are important pathways for the secondary formation of NACs in polluted urban atmospheres. This sentence was revised for clarity (lines 342-343).

Lines 342-343:…in polluted urban atmospheres that are characterized by high NO_x and anthropogenic VOCs.

13. *lines 275-277: Please rewrite this sentence for clarity.*

Response: Revised accordingly (lines 345-347).

Lines 345-347: As only a limited number of VOC species were measured in this study, the NO_x regime transition value was expressed by NO_2 concentrations rather than NO_2/VOC or NO_x/VOC ratios. We also note that the NO_x regime transition values in other atmospheres could be quite different.

14. *Figure 6: While this figure is meant to indicate a general trend, it is unclear where the values in this figure came from. Are these averages? How much error are in these values? Please be specific.*

Response: Yes, these are the averages in each NO_2 concentration bin. The NAC compositions under similar NO_2 concentration levels were averaged, with a bin size of 10ppb NO_2 (lines 351-352). Figure 6 shows NAC compositions as a function of NO_2 levels. The standard deviations of the percentages (nitrocatechols among the total NACs or nitrophenols among the total NACs) were lower than 12% within each NO_2 bin (lines 353-355).

Lines 353-355: The contributions of NCs (standard deviation< 12% within each NO_2 bin) increased and those of NPs (standard deviation< 12% within each NO_2 bin) decreased at elevated NO_2 concentrations.

15. *lines 289-291: Again, a table containing the vapor pressures for these NAC compounds may help*

explain some of these observations. Try the CHEMSPIDER web site.

Response: The estimated vapor pressures of NACs are now added in Table S1.

16. *line 301: is this statistically `significant'?*

Response: Yes, this is statistically ‘significant’ at the 0.01 level. This is added in lines 370.

17. *347-348: The last sentence in this paragraph is unclear.*

Response: Revised accordingly (lines 415-416)

Lines 415-416: The reaction mechanisms however are still unclear, which deserve further laboratory and field investigation in future studies.