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.

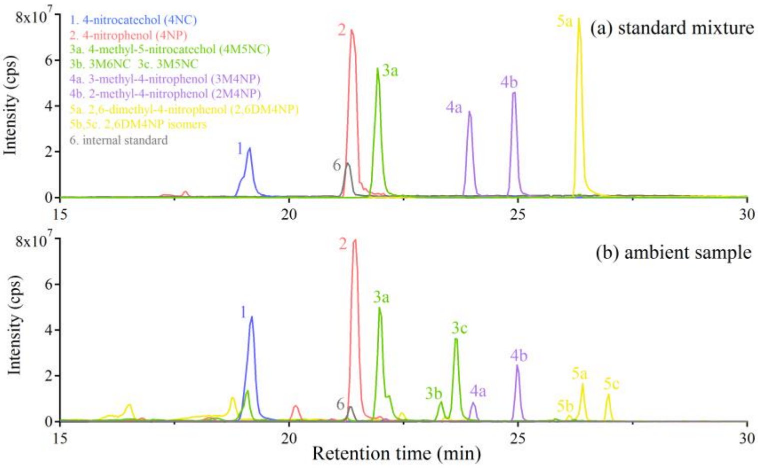

Figure S1 Extracted ion chromatograms for (a) a standard solution containing 4-nitrocatechol (4NC), 4-nitrophenol (4NP), 2-methyl-4-nitrophenol (2M4NP), 3-methyl-4-nitrophenol (3M4NP), 2,6-dimethyl-4-nitrophenol (2,6DM4NP) and internal standard and (b) an ambient sample collected during the campaign.

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.

Referee #2

General comments

This work measured two groups of nitro-aromatic compounds (NACs), including nitrophenol (NP) and nitrocatechol (NC) like species at an urban site in summer Beijing. Their diurnal variations and formation pathways were discussed thoroughly with additional data of VOCs, meteorological parameters, etc. The authors found that the secondary formation is a more dominant NAC source than biomass burning, and the two types of NACs have distinct formation mechanisms. A concentration ratio of NACs was applied to indicate the relative importance of aqueous-phase and gas-phase oxidation. The NACs are an important group of light-absorbing compounds in ambient aerosols. Their compositions and sources in the atmosphere are very complex and studied intensively in recent years. The topic of this work is very interesting, and the manuscript is very well organized and written. However, some of the conclusions might need more work with more valid evidence.

1. Page 7, lines 194-198.

As NACs were more correlated with toluene and benzene (r = 0.64 – 0.70) than potassium (r = 0.49), the authors concluded that the NACs were more likely from photo-oxidation of VOCs than biomass burning in summer Beijing.

First, please provide the significance level of the correlations.

Response: Significance levels of the correlations are added in lines 246-247 and Table S3.

Lines 246-247: 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**).

Second, the authors did regression analysis by comparing the particle-phase NACs with VOCs and potassium. In the atmosphere, NACs are mainly subject to two atmospheric processes, photolysis and gas-to-particle partitioning; toluene and benzene are in gas phase and precursors for SOA. The authors might need to consider the uncertainties in correlations due to atmospheric transformations.

Response: The gas-phase NACs were calculated based on equilibrium absorption portioning theory (section 2.4 in lines 156-187, Table S1). The following sentence has been added to consider the uncertainties in correlations between particle-phase NACs and gas-phase precursors (lines 250-254).

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.

2. Page 7, line 211 – 217

4M5NC and 3M5NC had higher nighttime concentrations than daytime, and were more correlated with RH than other NACs, which were ascribed to the aqueous-phase oxidation.

However, the authors might need to consider other possibilities.

1). Nitrocatechols are easier to be oxidized than nitrophenols. The second-order rate constant for nitrocatechol (5 × 10^9 M^{-1} s^{-1}) with OH in aqueous phase is much higher than nitrophenol (3.7 × 10^9 M^{-1} s^{-1}) (Hems and Abbatt, 2018). So the higher nighttime concentrations of 4M5NC and 3M5NC might also be associated with their shorter life time during daytime.

Response: While we agree that the aqueous-phase OH oxidation of NCs is faster than NPs, this chemical loss pathway is likely negligible during daytime due to the low RH condition (average daytime RH=26%) and therefore low aerosol liquid water content.

2) *The nitrocatechol has one more hydroxyl group and is more water soluble than the nitrophenol. Besides gas-to-particle partitioning, the nitrocatechols might also be dissolved into particle water, which could be another explanation for the higher correlations between nitrocatechols and RH%.*

Response: We have estimated the influence of NAC dissolution into particle water by Henry's law (lines 182-187). The contribution of NAC dissolution into aqueous-phase particles was estimated to be <0.02% to the total particulate NACs, indicating the dissolution pathway was negligible during our campaign. The following text is added to elaborate the contribution of the dissolution pathway.

Lines 182-187: Gas-phase NACs could also dissolve into the aqueous-phase particles. The concentrations dissolved into the aqueous phase (C_{aq}) were estimated by Henry's law (Sander, 2015). Henry constants were obtained from Sander et al. (2015) and ALWC was estimated using ISORROPIA-II (see section 2.4). The estimated $\mathrm{C_{aq}}$ of 4NP and 3M4NP were 4.4E-4 and 2.4E-5 ng/m^3, contributing <0.02% to their concentrations in particle phase. The contribution of dissolution into aqueous-phase particles for NC and MNC is expected to be lower, due to the much lower gas-phase concentrations than that of 4NP. For this reason, we will not further consider the dissolution of NACs into particle aqueous phase.

3. Page 8, lines 224- 226.
Could it be resulted from their different life times?

Response: While we cannot exclude this possibility, we have not found evidence of their different life times. Previous study (Frka et al., 2016) suggested that the aqueous formation of 3M6NC need higher activation barriers than that of 3M5NC, which could be one reason for their different variations (lines 298-301).

4. Page 9, line 250.
Why NO_X oxidation of anthropogenic VOC precursors is the dominant source of NACs? Can we estimate the relative contributions of biomass burning and NO_X oxidation?

Response: Our analysis of inter-species correlations and temporal variations detailed in section 3.2 indicates that $\mathrm{NO_x}$ oxidation of anthropogenic VOC precursors was the dominant source of NACs.

The relative contributions of $\mathrm{NO_x}$ oxidation and primary biomass burning to NAC formation were not estimated in this study, since we do not have direct field measurement data for the differentiation. Addressing this question needs modeling studies incorporating emission inventories of the relevant VOC precursors. The following text (lines 246-259) is added to the manuscript to address this review comment.

Lines 246-259: 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 $\mathrm{NO_x}$ 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. …As for the relative importance of anthropogenic VOCs and biomass burning-derived VOCs, we do not have direct field measurement data for the differentiation. 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). Modelling studies incorporating emission inventories of the relevant VOC precursors could address this issue and are suggested in future investigation of NAC sources.

5. Page 10, lines 305-306. Page 11, lines 317-319.
As mentioned in comment 2, please consider the shorter life times of nitrocatechols than nitrophenols during the daytime, and the dissolution of nitrocatechols in particulate water as RH% increases.

Response: Please see our earlier response to this issue (common 2).

Moreover (connect to Page 6, lines 181-183), the authors thought that a higher relative humidity (RH%) would increase the relative contribution of aqueous-phase oxidation. Is the aqueous-phase oxidation in ambient aerosols only dominated by RH%?

Response: The aqueous-phase oxidation in ambient aerosols is also influenced by aerosol acidity. It has been suggested that reaction pathways of nighttime formation of methyl-nitrocatechols via methylcatechol nitration are strongly pH dependent. The catechol oxidation-conjugated addition reaction mechanism can be an important pathway for dark secondary MNC formation in polluted environments with high NOx concentrations and relatively acidic particles (pH around 3) (Vidovic et al., 2018). Aerosol acidity was calculated using the ISORROPIA-II model in this study. During the campaign, particles were generally acidic with a pH range of 2.0-3.7, providing favourable conditions for the aqueous-phase oxidation formation of MNC (lines 283-289).

Specific comments

1. Page 4, line 122. Please provide the recoveries for the target compounds.

Response: The recoveries for target compounds were added in lines 129-130.

Lines 129-130: The recoveries of the target NACs were 91-106%.

References

Hems, R. F., and Abbatt, J. P. D.: Aqueous Phase Photo-oxidation of Brown Carbon Nitrophenols: Reaction Kinetics, Mechanism, and Evolution of Light Absorption, ACS Earth and Space Chemistry, 2, 225-234, 10.1021/acsearthspacechem.7b00123, 2018.

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.

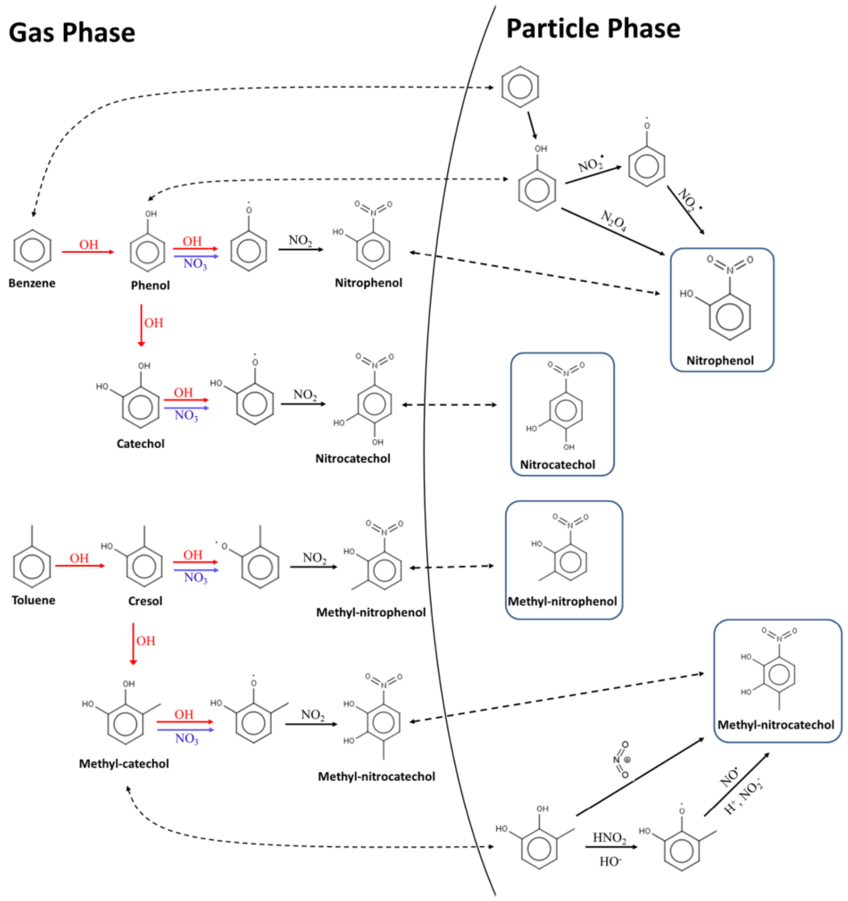

Figure 1 Formation pathways of nitrophenols, nitrocatechols, methyl-nitrophenols and methyl-nitrocatechols from the oxidation of benzene, toluene, phenol and methy-catechol in the gas phase and particle phase (Jenkin et al., 2003; Frka et al., 2016; Vione et al., 2004; Vione et al., 2001; Vidovic et 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 $\mu g/m^3$) 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

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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.

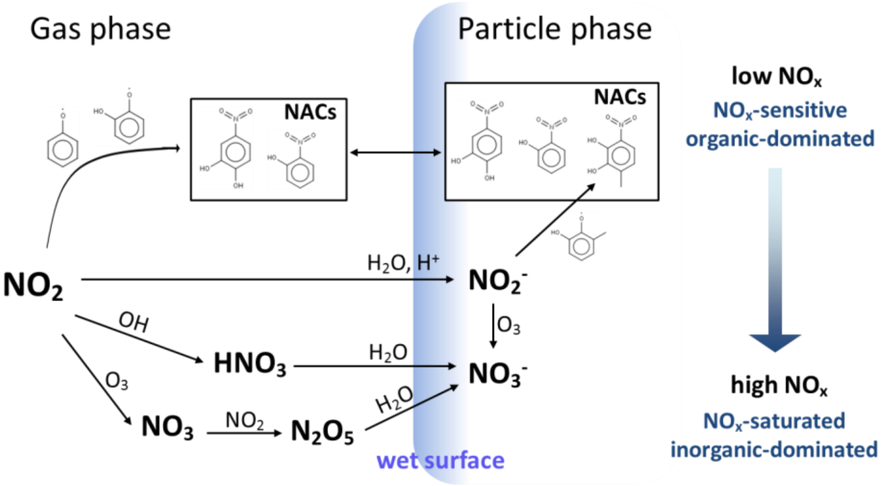

Figure S6 Schematic diagram and simplified mechanisms of the competing formation of inorganic nitrates and NACs

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.

The formation of nitro-aromatic compounds under high NO_x and anthropogenic VOC conditions in urban Beijing, China

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Abstract. Nitro-aromatic compounds (NACs), as important contributors to the light absorption by brown carbon, have been widely observed in various ambient atmospheres, however, their formation in urban atmosphere was little studied. In this work, we report an intensive field study of NACs in summer 2016 at an urban Beijing site, characterized by both high-NO_x and anthropogenic VOCs dominated conditions. We investigated the factors that influence NAC formation (e.g. NO_2, VOC precursors, RH and photolysis) through quantification of 8 NACs, along with major components in fine particulate matter, selected volatile organic compounds and gases. 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). 4-Nitrophenol (4NP, 32.4%) and 4-nitrocatechol (4NC, 28.5%) were the top two most abundant NACs, followed by methyl-nitrocatechol (MNC), methyl-nitrophenol (MNP) and dimethyl-nitrophenol (DMNP). The oxidation of toluene and benzene in the presence of NO_x were found to be more dominant sources of NACs than primary biomass burning emissions. The NO_2 concentration level was found to be an important factor influencing the secondary formation of NACs. A transition from low- to high-NO_x regimes coincided with a shift from organic- to inorganic-dominated oxidation products. The transition thresholds were NO_2~20 ppb for daytime and NO_2~25 ppb for nighttime conditions. Under low-NO_x conditions, NACs increased with NO_2, while the NO_3^- concentrations and (NO_3^-)/NACs ratios were lower, implying organic-dominated products. 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, signaling a shift from organic- to inorganic-dominated products. Nighttime enhancements were observed for 3M4NC and 4M5NC while daytime enhancements were noted for 4NP, 2M4NP and DMNP, indicating their different formation pathways for these two groups of NACs. Our analysis suggested that the aqueous-phase oxidation was likely the major formation pathways of 4M5NC and 3M5NC while photo-oxidation of toluene and benzene in the presence of NO_2 could be more important for the formation of nitrophenol and its derivatives. Using the (3M4NC+ 4M5NC)/4NP ratios as an indicator of the relative contribution of aqueous-phase and gas-phase oxidation pathways to NAC formation, we observed that the relative contribution of aqueous-phase pathways increased at elevated ambient RH and remained constant at RH> 30%. We also found that the concentrations of VOC precursors (e.g. toluene and benzene) and aerosol surface area acted as important factors in promoting NAC formation, and photolysis as an important loss pathway for nitrophenols.

1 Introduction

Organic nitrogen, including nitro-aromatic compounds (NACs), N-heterocyclic compounds, amines and other organic nitrate compounds containing (–NO_2) or (–NO_3) functional groups, represent an important fraction of ambient organic aerosols (Laskin et al., 2009;Wang et al., 2017b;Chow et al., 2016;Ge et al., 2011;Ng et al., 2017). Among organic nitrogen, NACs, with the -NO_2 and -OH functional groups attached to an aromatic ring, have gained much attention due to their light absorbing property and impacts on human health (Mohr et al., 2013; Lin et al., 2017). NACs, including nitrophenols (NPs), nitrocatechols (NCs) and their derivatives, are important contributors to the light absorption by brown carbon (BrC) (Mohr et al., 2013; Teich et al., 2017; Zhang et al., 2013; Xie et al., 2017), contributing 50-80% of the total visible light absorption by BrC emitted from biomass burning (Lin et al., 2017). Moreover, NACs also lead to mutagenesis and genotoxicity, thus posing a threat to human health (Purohit and Basu, 2000; Huang et al., 1995).

NACs have been widely observed in various ambient atmospheres, including urban, suburban, rural, as well as background environments, with the quantified concentrations varying from 0.1 ng/m^3 in rural background areas to 147.4 ng/m^3 in urban atmospheres (Iinuma et al., 2010; Teich et al., 2017; Zhang et al., 2010; Mohr et al., 2013; Chow et al., 2016; Wang et al., 2018b). Combustion processes, especially biomass burning, were the most important primary sources of NACs (Harrison et al., 2005; Wang et al., 2018b). The emission factors of NACs from biomass burning were estimated 0.8-11.1 mg/kg (Wang et al., 2017a; Hoffmann et al., 2007). Field observation studies indicated NACs are usually associated with fresh or aged biomass burning aerosols, which contributed 10- 21% of the total NACs in ambient aerosols (Chow et al., 2016; Kitanovski et al., 2012; Mohr et al., 2013; Iinuma et al., 2010; Wang et al., 2018b). Apart from primary emissions from biomass burning, NACs could also be formed via the oxidation of volatile organic compounds (VOCs) containing a benzene ring (e.g. cresol, catechol, methylcatechol) released by biomass burning in smoke plumes (Iinuma et al., 2010; Claeys et al., 2012). Methyl-nitrocatechols (MNCs) could originate from NO_x oxidation of methylated cresol or methylcatechols, which are released during biomass burning as thermal degradation products of lignin (Iinuma et al., 2010; Finewax et al., 2018; Olariu et al., 2002). 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).

In urban atmosphere, aromatic VOCs such as benzene, toluene, and xylenes are expected to be important precursors to NAC formation (Harrison et al., 2005). The main reactions leading to the secondary formation of NPs, NCs, methyl-nitrophenols (MNPs) and MNCs are shown in Figure 1 (Jenkin et al., 2003; Vione et al., 2001; Vione et al., 2004; Vidovic et al., 2018). Nitrophenols and its derivatives (e.g. MNPs) could originate through gas-phase oxidation of phenol, benzene and toluene by OH or NO_3 radicals in the presence of NO_2 (Harrison et al., 2005; Yuan et al., 2016; Sato et al., 2007; Ji et al., 2017; Olariu et al., 2002). Nitrocatechols dominated the composition of NACs formed in benzene/NO_x system (Xie et al., 2017). The NC formation could be initiated by OH or NO_3 radicals to form *β*-hydroxyphenoxy/*o*-semiquinone radicals, which then react with NO_2 to form the final products (Finewax et al., 2018). Compared with the gas-phase formation of NACs, the formation pathway via aqueous-phase aromatic nitration is less well understood (Kroflic et al., 2018). 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 (Vione et al., 2004; Vione et al., 2001). It has been suggested that nighttime aqueous-phase oxidation is an important formation pathway for methyl-nitrocatechols, especially in polluted high-NO_x environments and in presence of acidic particles (pH around 3) (Vidovic et al., 2018). The proposed aqueous-phase formation processes of MNCs include electrophilic substitution route and consecutive oxidation and conjugated addition route (Frka et al., 2016; Vidovic et al., 2018). The loss pathways for NACs is proposed to include photolysis and reactions with OH, NO_3 radicals or chlorine atoms (Atkinson et al., 1992; Bejan et al., 2007; Bejan et al., 2015; Chen et al., 2011; Yuan et al., 2016; Hems and Abbatt, 2018).

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. A group of 8 NACs (NPs, MNPs, dimethyl-nitrophenols, DMNPs, NCs and MNCs) in 19 day samples and 19 night samples were quantified using high performance liquid chromatography- mass spectrometry (HPLC-MS). Additional data of inorganic aerosol constituents, VOC precursors, inorganic gases and meteorological parameters were also obtained and analyzed to aid the investigation of the secondary formation pathways of NACs and controlling factors. This work provides insights into the secondary formation of NACs in high NO_x and anthropogenic VOCs dominated urban environments.

2 Methods

2.1 Sample collection

As part of the bilateral Sweden-China framework research program on ‘Photochemical smog in China’, an intensive field campaign was conducted in Beijing, aiming to improve the understanding on secondary chemistry during photochemical smog events in China (Hallquist et al., 2016). The campaign was conducted at Changping (40.14° N, 116.11° E), a regional site northeast of Beijing urban area, from May 15 to June 5, 2016. 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). During May 17-June 5, the daily average concentrations of benzene, toluene and NO_x were 66-922 ppt, 47-1344 ppt and 4.0-32.3 ppb, respectively.

Day and night ambient $PM_{2.5}$ (particles with aerodynamic diameter less than 2.5 μm) samples were collected on prebaked quartz fiber filters (Whatman Inc.) and Teflon filters (Whatman Inc.) using a high-volume sampler (TH-1000C, Tianhong, China) and a 4-channel sampler (TH-16A, Tianhong, China). The sampling flow rates were 1.05 m^3/min and 16.7 L/min, respectively. The daytime samples were collected from 8:30 to 17:30 LT (UTC+8) and the nighttime ones from 18:00 to 8:00 LT (UTC+8) the next morning. Field blank samples were collected by placing filters in the samplers with the pump off for 30 min.

2.2 Quantification of NACs

An aliquot of 25 cm^2 was removed from each filter sample and extracted in ultrasonic bath three times using 3, 2 and 1 mL methanol containing 30 μL saturated EDTA solution in methanol-acetic acid consecutively, each time for 30 min. The extracts were then filtered through a 0.25 μm polytetrafluoroethylene (PTFE) syringe filter (Pall Life Sciences), combined, and evaporated to dryness under a gentle stream of high-purity nitrogen. The dried samples were re-dissolved in 50 μL methanol/water (1:1) containing 100 ppb 4-nitrophenol-2,3,5,6-d_4 as internal standard. The solution was centrifuged and the supernatant was used for analysis, using Agilent 1260 LC system (Palo Alto, CA) coupled to QTRAP 4500 (AB Sciex, Toronto, Ontario, Canada) mass spectrometer. The LC-MS system was equipped with an electrospray ionization (ESI) source operated in negative mode. More details of the extraction and optimized MS parameters have been described in our previous study (Chow et al., 2016).

Chromatographic separation was performed on an Acquity UPLC HSS T3 column (2.1 mm×100 mm, 1.8 μm particle size; Waters, USA) with a guard column (HSS T3, 1.8 μm). The column temperature was kept at 45 ^{o}C and the injection volume was 5.0 μL. The mobile eluents were (A) water containing 0.1% acetic acid (v/v) and (B) methanol (v/v) containing 0.1% acetic acid at a flow rate of 0.19 mL/min. The gradient elution was set as follows: started with 1% B for 2.7 min; increased to 54% B within 12.5 min and held for 1.0 min; then increased to 90% B within 7.5 min and held for 0.2 min; and finally decreased to 1% B within 1.8 min and held for 17.3 min until the column was equilibrated. Chromatograms of NAC standards and an ambient sample are shown in Figure S1.

The quantified NAC species are listed in Table 1. The NACs were identified and quantified using the $[M-H]^-$ ions in the extracted ion chromatogram (EIC), using authentic standards or surrogates with the same molecular formula (Table 1). The standards included: 4-nitrocatechol (4NC), 4-nitrophenol (4NP), 2-methyl-4-nitrophenol (2M4NP), 3-methyl-4-nitrophenol (3M4NP) and 2,6-dimethyl-4-nitrophenol (2,6DM4NP) from Sigma–Aldrich (St. Louis, MO, USA); 4-methyl-5-nitrocatechol (4M5NC) from Santa Crutz Biotech (Dallas, TX, USA). The recoveries of the target NACs were 91-106%. 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). The concentration of dimethyl-nitrophenol (DMNP) was the sum of three isomers. 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.

2.3 Other online and offline measurements

Other online and offline instruments were also employed to obtain related database, which has been introduced in details in our previous paper (Wang et al., 2018c). In brief, a high resolution time-of-flight aerosol mass spectrometer (AMS) was used to measure the chemical composition of PM_1 (Zheng et al., 2017). 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). VOCs were measured by a proton-transfer-reaction mass spectrometer (PTR-MS). Gaseous NH_3 was measured using a NH_3 analyzer (G2103, Picarro, California, USA) (Huo et al., 2015). Meteorological parameters, including relative humidity (RH), temperature, wind direction and wind speed (WS) were continuously monitored by a weather station (Met one Instrument Inc.) during the whole campaign.

Organic carbon (OC) and element carbon (EC) were analyzed using thermal/optical carbon analyzer (Sunset Laboratory). The organic matter (OM) concentration was calculated by multiplying OC by 1.6 (Turpin and Lim, 2001). Water soluble inorganic ions were quantified by an ion chromatograph (IC, DIONEX, ICS2500/ICS2000) following procedures described in Guo et al. (2010). Aerosol acidity and liquid water content (ALWC) was then calculated using the ISORROPIA-II thermodynamic model. ISORROPIA-II was operated in forward mode, assuming the particles are "metastable" (Hennigan et al., 2015; Weber et al., 2016; Guo et al., 2015). The input parameters included: ambient RH, temperature, particle phase inorganic species (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, K^+, Na^+, Ca^{2+}, Mg^{2+}), and gaseous NH_3. More details and validation of the thermodynamic calculations have been described in our previous paper (Wang et al., 2018c).

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):

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

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:

$$C^* = \frac{M 10^6 \zeta P_V}{760RT} \qquad \text{(Eq. 2)}$$

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).

Gas-phase NACs could also dissolve into the aqueous-phase particles. The concentrations dissolved into the aqueous phase (C_{aq}) were estimated by Henry's law (Sander, 2015). Henry constants were obtained from Sander et al. (2015) and

ALWC was estimated using ISORROPIA-II (see section 2.4). The estimated C_{aq} of 4NP and 3M4NP were 4.4E-4 and 2.4E-5 ng/m^3, contributing <0.02% to their concentrations in particle phase. The contribution of dissolution into aqueous-phase particles for NC and MNC is expected to be lower, due to the much lower gas-phase concentrations than that of 4NP. For this reason, we will not further consider the dissolution of NACs into particle aqueous phase.

3 Results and Discussion

3.1 Concentration and composition of NACs

The average concentration of quantified NACs was 6.63 ng/m^3, ranging from 1.27 to 17.70 ng/m^3 in summer in Beijing. Figure 2 compares the total NAC concentrations across this and prior studies, and the individual NAC concentrations are compared in Figure S2 and Table S2. The total NAC concentration in this work was higher than those measured in other studies conducted in summer in mountain, rural or urban environments (Teich et al., 2017; Kitanovski et al., 2012; Kahnt et al., 2013; Zhang et al., 2013; Chow et al., 2016; Wang et al., 2018b), and comparable to those reported in the studies in summertime Wangdu, China (Teich et al., 2017; Wang et al., 2018b) (Figure 2). 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). Influenced by the outflow from urban Beijing air masses, the site was under typical high-NO_x conditions (Wang et al., 2018a), implying abundant potential secondary formation of NACs during the observation period. A recent study suggested that nocturnal biogenic VOCs (BVOCs) oxidation would transfer from low- to high-NO_x regimes and nearly all the BVOCs would be oxidized by NO_3 radicals, at a NO_x/BVOCs ratio higher than 1.4 (Edwards et al., 2017). If we approximate the BVOC concentrations to be the sum of isoprene, MVK+MACR (methyl vinyl ketone and methacrolein), and monoterpenes, the NO_x/BVOC ratios were higher than 8 (nighttime ratios higher than 20) (Figure S3). If we further consider the major anthropogenic VOCs (toluene, benzene), NO_x/VOCs ratios were higher than 5 (nighttime ratios higher than 10) (Figure S3). The high-NO_x conditions during the campaign were expected to facilitate the oxidation of aromatic hydrocarbons and the subsequent secondary formation of NACs. Other emissions from biomass burning and coal combustion were also observed to be contributors of organic aerosols during the campaign (Tang et al., 2018), and they could also be the precursor sources of NACs. Biomass burning episodes occurred during Wangdu campaign, indicating NAC emissions from biomass burning (Teich et al., 2017; Tham et al., 2016), which explain the high NAC levels in summer in Wangdu. 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 (Chow et al., 2016; Wang et al., 2018b; Kitanovski et al., 2012; Kahnt et al., 2013).

The NAC compositions are shown in the inserted pie chart in Figure S2. 4-Nitrophenol and 4-nitrocatechol were the most abundant ones among all the quantified NAC species, accounting for 32.4 % and 28.5 % of the total quantified NACs, followed by methyl-nitrocatechols (4M5NC, 3M5NC and 3M6NC, 16.2%), methyl-nitrophenol (2M4NP and 3M4NP, 15.6%) and dimethyl-nitrophenol (8.3%) (Table 1). 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 (Le Breton et al., 2017). Nitrophenols and nitrocatechols were generally reported among the most abundant NAC species in previous studies (Table S2 and the references therein). Nitrophenols could be formed via the oxidation of anthropogenic VOCs (e.g. benzene) in the presence of NO_2 and nitrocatechols were found to dominate the composition of NAC products formed in benzene/NO_x system in laboratory studies (Xie et al., 2017; Harrison et al., 2005; Yuan et al., 2016; Sato et al., 2007; Ji et al., 2017; Olariu et al., 2002). 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.

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). This NAC composition difference between Changping and Hong Kong may be a result of different formation pathways for NPs and MNC and different environmental conditions at two sites. The gas-phase oxidation of aromatic hydrocarbons (e.g. phenol, benzene) in the presence of NO_2 is a major source of NPs (Harrison et al., 2005; Yuan et al., 2016; Sato et al., 2007; Ji et al., 2017; Olariu et al., 2002), while aqueous-phase oxidation represents the important formation pathway for atmospheric MNC (Frka et al., 2016; Vidovic et al., 2018). 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. The influence of ambient RH on NAC formation will be further discussed in Section 3.4. In comparison, more abundant gas-phase formation of nitrophenol was expected in summer in Beijing, under higher anthropogenic VOCs, high NO_x and low RH conditions. In addition, the lower temperature in summer in Changping was more favorable for the partitioning of nitrophenols from gas phase into particle phase.

3.2 Temporal variations and sources of NACs

Temporal variations of the total quantified NAC concentrations are shown in Figure 3, along with particulate organics, nitrate, potassium ion, toluene, benzene, acetonitrile, wind speed and RH. 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. Elevated NAC concentrations were observed during pollution episodes, coinciding with the increasing of toluene, benzene, acetonitrile and potassium. The correlations between NACs and other chemical components are shown in Table S3. 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. 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. As for the relative importance of anthropogenic VOCs and biomass burning-derived VOCs, we do not have direct field measurement data for the differentiation. 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). Modelling studies incorporating emission inventories of the relevant VOC precursors could address this issue and are suggested in future investigation of NAC sources. 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.

To further investigate the formation of NACs, we examined the time series and day-night variations of individual NAC species (Figures 4, S4 and S5). Daytime enhancements of 4NP, 2M4NP and DMNP, nighttime enhancements of 3M4NC and 4M5NC were observed, and other NAC species didn’t show discernible day-night variations (Figures 4, S4 and S5), indicating different formation pathways among NAC species. 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. NC and its derivatives showed stronger correlations with toluene, benzene, acetonitrile and K^+, compared with NP and its derivatives (Table S3). 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). The oxidation degradation rates and photolysis of NC and MNC were therefore much lower. A recent laboratory study found that OH uptake by MNC particles was suppressed by a factor of 4 at RH 15-30% in comparison with dry condition, as a result of competitive co-adsorption of water molecules that occupied reactive sites (Slade and Knopf, 2014). During the campaign, the ambient RH was 37%. Such an RH condition rendered that the OH uptake by particles was suppressed and therefore heterogeneous oxidation of MNC was unlikely important.

Nighttime enhancements of 4M5NC and 3M5NC were observed during the whole observation period (Figure 4). A strong correlation between 4M5NC and 3M5NC and their similar temporal variations likely indicated shared similarity in their formation pathways. Previous studies suggested that aqueous-phase oxidation (including photooxidation and nighttime oxidation) is an important formation pathway for atmospheric MNC, especially in polluted high-NO_x environments and relatively acidic particles (pH around 3) (Vidovic et al., 2018; Frka et al., 2016). 4M5NC and 3M5NC showed relatively stronger correlations with RH compared with other NAC species (Table S3), implying the importance of water in their formation processes and the aqueous-phase pathway. During the campaign, the acidic particles (a pH in the range of 2.0-3.7) and the high-NO_x conditions (Wang et al., 2018c; Wang et al., 2018a) provided suitable environments for the aqueous-phase oxidation formation of MNC. 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. The daytime correlations between 4M5NC or 3M5NC and RH or NO_2 were stronger than the nighttime (Table S4). The aqueous-phase NO_x oxidation could be more dependent on ambient RH and NO_2 levels during the daytime, due to the lower RH and NO_2 concentrations than those at night (Figures 3, S3). MNCs also showed good correlations with acetonitrile and potassium, as MNCs could also be formed via the oxidation of biomass burning-derived VOC precursors (e.g. cresol) (Iinuma et al., 2010; Finewax et al., 2018; Olariu et al., 2002). 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. The quantum calculations have predicted the formation of 3M5NC via aqueous-phase electrophilic substitution and nitration by NO_2^+, while the formation of 3M6NC was negligible due to higher activation barriers for nitration of 3-methylcatechol to form 3M6NC (Frka et al., 2016). A dominant presence of 3M5NC in ambient aerosols was also expected according to the theoretical predictions (Frka et al., 2016). The 3M5NC concentration was higher than that of 3M6NC in summer in Beijing, consistent with the suggestion from computation study by Frka et al (2016).

Different from the nighttime enhancements of 4M5NC and 3M5NC, 4NP, 2M4NP and DMNP showed daytime enhancements during the whole campaign (Figures 4, S5). Previously, Yuan et al (2016) also suggested the daytime gas-phase oxidation of aromatics could represent the major source of NPs, while the contribution from nighttime reaction of phenol with NO_3 radicals was relatively lower(Yuan et al., 2016). 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. We did not find good correlation between 4NP and NO_2 when considering the whole campaign period (Table S3), while good correlations were observed when treating the daytime and nighttime conditions separately (Table S4). The strong correlations between 4NP and benzene, toluene or NO_2 during daytime and nighttime indicated its formation via oxidation of benzene and toluene in the presence of NO_2 (Table S4). The formation mechanisms of nitrophenol were different during daytime (OH-initiated photooxidation of aromatics in the presence of NO_2) and nighttime (NO_3-initiated oxidation of aromatics) (Harrison et al., 2005; Yuan et al., 2016; Sato et al., 2007; Ji et al., 2017; Olariu et al., 2002), thus the role and influence of NO_2 on NAC formation were different. For DMNP, 2M4NP and 3M4NP, they also showed good correlations with benzene, toluene and NO_2 during daytime, but the correlations were absent at night. Instead, their correlations with RH were higher at night, implying the possible formation via aqueous-phase pathways.

3.3 The NO_2 control of NACs formation

The analysis in section 3.2 suggests that NO_x oxidation of anthropogenic VOC precursors represented the dominant sources of NACs in summer in Beijing. To further investigate the impacts of NO_2 on NAC secondary formation, we plot the concentrations of NACs, nitrate (NO_3^-) and the NO_3^-/NAC ratios as a function of NO_2 levels (Figure 5). The variation of (NO_3^-)/NACs ratios was employed to illustrate the relative abundance of inorganic nitrate and oxidized organic nitrogen. The variation during daytime and nighttime were separately considered due to the different atmospheric conditions and oxidation mechanisms.

Generally, higher concentrations of NACs and nitrate were observed with elevated NO_2 concentration levels, in a nonlinear fashion (Figure 5). During the daytime, NACs increased with NO_2, and NO_3^- concentrations and (NO_3^-)/NACs ratios were lower at low-NO_x conditions (NO_2< 20ppb). As NO_2 increased to higher than 20 ppb, NAC concentrations did not increase with NO_2 any more, signaling the transition from NO_x-sensitive to NO_x-saturated regimes for NAC secondary formation. 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). It was likely that the daytime NO_2 was in excess for the oxidation of ambient VOCs and the NAC formation at NO_2> 20 ppb. Then the excess NO_2 would be oxidized to form inorganic nitrate, producing a shift of products from organic- to inorganic-dominated conditions. Similarly, during nighttime a transition was observed at NO_2 ~25 ppb in which oxidation products were shifted from organic- to inorganic-dominance (Figure 5d, e, f). At NO_2> 25 ppb, the nighttime NAC formation became independent of NO_2 concentrations and inorganic nitrate dominated the NO_x oxidation products. The simplified mechanisms and schematic diagram of the competing formation of inorganic nitrates and NACs are shown in Figure S6. The nighttime NO_2 transition value (~25 ppb) was higher than the daytime one (~20 ppb). The higher anthropogenic VOC precursors (Figure S3) and different oxidation mechanisms (Figure 1) were the potential reasons for elevated NO_2 transition value at night.

The compositional variation of inorganic nitrate and NACs described in this work serves as an example in illustrating that the transition from low- to high-NO_x regimes and the corresponding oxidation products shifting from organic- to inorganic-dominated conditions existed in polluted urban atmospheres that are characterized by high NO_x and anthropogenic VOCs. However, the mechanisms as well as transition thresholds were less understood compared with the well-known BVOCs/NO_x atmospheres. More comprehensive investigation in urban atmospheres is needed to develop more quantitative understanding of the NO_x regime transition. 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. The NO_x regime transition values deserve further investigation through comprehensive lab simulation and field observations to seek a more robust parameter that can be applied to various atmospheric environments.

The analysis in the previous section indicates that the formation pathways of different NAC species vary from each other, thus the role and influence of NO_2 on their formation are different. The NAC compositions under similar NO_2 concentration levels were averaged, with a bin size of 10ppb NO_2. The variation of NAC compositions as a function of NO_2 levels is shown in Figure 6 to investigate the influence of NO_2 on NAC compositions. 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. The NAC composition remained relatively constant at NO_2 >20 ppb, which was approximately the transition value from low- to high-NO_x regimes. The role of elevated NO_2 in promoting formation of NCs was more obvious than that for NPs. The oxidation of aromatics (e.g. benzene, toluene and VOCs emitted from biomass burning) in the presence of NO_2 represent the major formation pathway of NCs. The formation of NCs would increase with the increasing of ambient NO_2. 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.

3.4 Other influence factors on NACs formation

Nitration of aromatic hydrocarbons (e.g. benzene and toluene) represents the major source of NACs in summer in Beijing. NACs generally increased with the increasing of anthropogenic toluene and benzene (Figure 7). During daytime, when toluene was higher than 0.6 ppb and benzene higher than 0.4 ppb, the NACs concentrations did not increase further with VOC concentrations (Figure 7a, b). It was likely that toluene or benzene was in excess and the NAC formation became independent of these precursors. Similarly, the nighttime formation of NACs would become insensitive to these precursors when toluene was higher than 1 ppb and benzene higher than 0.6 ppb (Figure 7c, d). The transition values of toluene or benzene was higher at night than those during the daytime. This could be due to the significantly higher NO_2 levels (significant at p= 0.01 level) (Figure S3), with higher capacity to oxidize VOC precursors, and different oxidation mechanisms at night.

Though the total NACs didn't show good correlations with ambient RH, good correlations between 3M4NC, 4M5NC and RH were observed (Table S3, Figure 8). Nitrophenols and methyl-nitrophenols, dominated by gas-phase formation pathways, were less affected by ambient RH. Aqueous-phase oxidation represented the major formation pathway of 3M4NC and 4M5NC during the campaign, based on the analysis in section 3.2 and previous studies (Vidovic et al., 2018; Frka et al., 2016). Elevated ambient RH would favor the water uptake of aerosols and decrease the aerosol viscosity, which favors the uptake of organic precursors or other gas molecules into the particles, mass diffusion of reactants, and chemical reactions within the particles (Vaden et al., 2011; Booth et al., 2014; Renbaum-Wolff et al., 2013; Shrestha et al., 2015; Zhang et al., 2015), and thereby enhance the formation of 3M4NC and 4M5NC in aqueous phase.

The (3M4NC+ 4M5NC)/4NP mass concentration ratios were employed to indicate the relative contribution of aqueous-phase and gas-phase pathways to NAC formation. The variations of (3M4NC+ 4M5NC)/4NP ratios as a function of ambient RH during daytime and nighttime are shown in Figure 9. During daytime, this ratio increased with RH when RH<30%, indicating elevated contribution of aqueous-phase pathways to NAC formation with higher RH conditions. The ratio remained stable at RH>30% during both daytime and nighttime, suggesting the relative contribution of aqueous-phase and gas-phase pathways would not increase further with increasing RH beyond RH > 30% (Figures 9a and 9b). The ratio during the nighttime was obviously higher than during the daytime, indicating that the aqueous-phase oxidation played more important roles for NAC formation at night. The results implied the importance of aqueous-phase oxidation for the secondary formation of oxidized organic nitrogen at elevated ambient RH. Due to the limited sample number obtained by filter-based analysis in this study, the influence of RH or aerosol liquid water content on NAC formation needs further confirmative investigation using controlled laboratory studies.

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). Photolysis is an important loss pathway of NACs and could be the dominant sink for nitrophenols in the gas phase (Bejan et al., 2007; Yuan et al., 2016). The highest value of J(O^{1}D) of each day was used to roughly represent the photolysis intensity. The daytime NAC concentrations showed negative correlations with J(O^{1}D) (Figure 8c, Table S4), suggesting photolysis as an important sink for NACs during the daytime.

4 Conclusions

Nitroaromatic compounds (NACs) measurements from an intensive field campaign conducted in summer in Beijing were examined to investigate the abundance and formation characteristics of NACs under high-NO_x and anthropogenic VOCs dominated atmosphere. The average concentration of eight quantified NACs was 6.63 ng/m^3, generally higher than those reported in other summertime studies elsewhere. Among the eight NACs, 4-Nitrophenol (32.4%) and 4-nitrocatechol (28.5%) were the most abundant, consistent with previous studies, and followed by methyl-nitrocatechol, methyl-nitrophenol and dimethyl-nitrophenol.

Our analysis indicates that the secondary formation via oxidation of anthropogenic VOC precursors (e.g. toluene, benzene) in the presence of NO_2 represented more important sources of NACs than primary biomass burning emissions in summer in Beijing. We also observed a transition of oxidation products from organic- to inorganic-dominated conditions as NO_x shifted from low- to high-NO_x regimes. The transition occurred at NO_2 of ~20 ppb for the daytime and ~25 ppb for the nighttime atmosphere. Under low-NO_x conditions, NACs were observed to increase with NO_2, and the NO_3^- concentrations and (NO_3^-)/NACs ratios were lower. Under high-NO_x conditions, the NAC concentration did not further increase with NO_2 while the NO_3^- concentrations and (NO_3^-)/NACs ratios would show increasing trends. The shift in relative abundance of inorganic nitrate and NACs observed in this work serves as an example in illustrating the demarcation of the low- and high-NO_x regimes in the anthropogenic VOCs-NO_x interacted conditions in polluted urban atmospheres and that NO_2 plays important roles in the formation of NACs. The reaction mechanisms however are still unclear, which deserve further laboratory and field investigation in future studies.

Different day-night variations were observed between the two sub-groups of NACs (i.e, nitrophenols and nitrocatechols). Obvious nighttime enhancements of 3M4NC and 4M5NC, daytime enhancements of 4NP, 2M4NP and DMNP were noted, indicating their different formation pathways. The aqueous-phase oxidation pathways are presumed to be important for the formation of 4M5NC and 3M5NC, under the conditions with high NO_x concentrations and acidic particles during the campaign. Photo-oxidation of toluene and benzene in the presence of NO_2 were more important for the formation of nitrophenols. Subsequently, the (3M4NC+ 4M5NC)/4NP mass ratio was employed to probe the relative contribution of aqueous-phase and gas-phase pathways to NAC formation. This ratio would initially increase with RH and remain relatively consistent at RH> 30%, indicating elevated contribution of aqueous-phase pathways to NAC formation under higher RH conditions. Aqueous-phase pathways played more important roles in NAC formation at night than those during the daytime.

VOC precursors, aerosol surface area and photolysis were also important factors influencing the NAC formation. NACs generally increased with the increasing of toluene and benzene, implying nitration of aromatic hydrocarbons (e.g. benzene and toluene) may represent the major secondary source of NACs in our study location. The NAC formation would become independent of toluene and benzene, when the daytime concentrations were higher than 0.6 and 0.4 ppb, or the nighttime ones higher than 1 and 0.6 ppb. In addition, aerosol surface area was also important factor promoting the NAC formation and photolysis could be an important loss pathway of nitrophenols during the daytime.

Data availability. The data presented in this article are available from the authors upon request (minhu@pku.edu.cn).

The Supplement related to this article is available online

Author contributions. MiH, MaH, and SG organized the field campaign. YJW and YCW conducted the offline analysis and analyzed the data. YJW wrote the manuscript with input from JY. All authors contributed to the measurements, discussing results and commenting on the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

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Figures

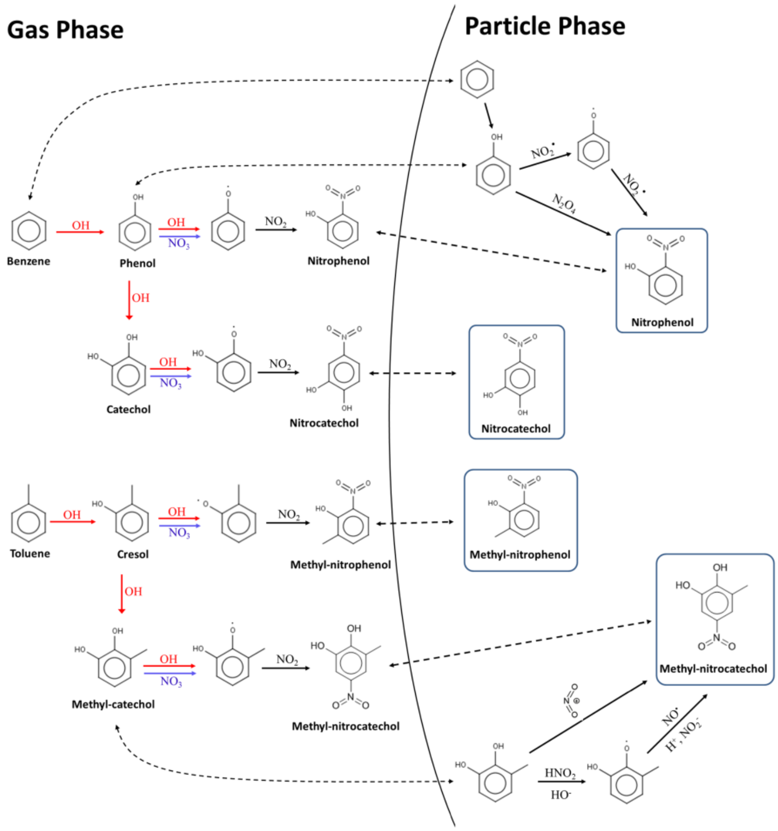


Figure 1 Schematic presentation of NAC secondary formation pathways via the oxidation of benzene, toluene, phenol and methycatechol in the gas phase and particle phase (Jenkin et al., 2003; Frka et al., 2016; Vione et al., 2004; Vione et al., 2001; Vidovic et al., 2018).

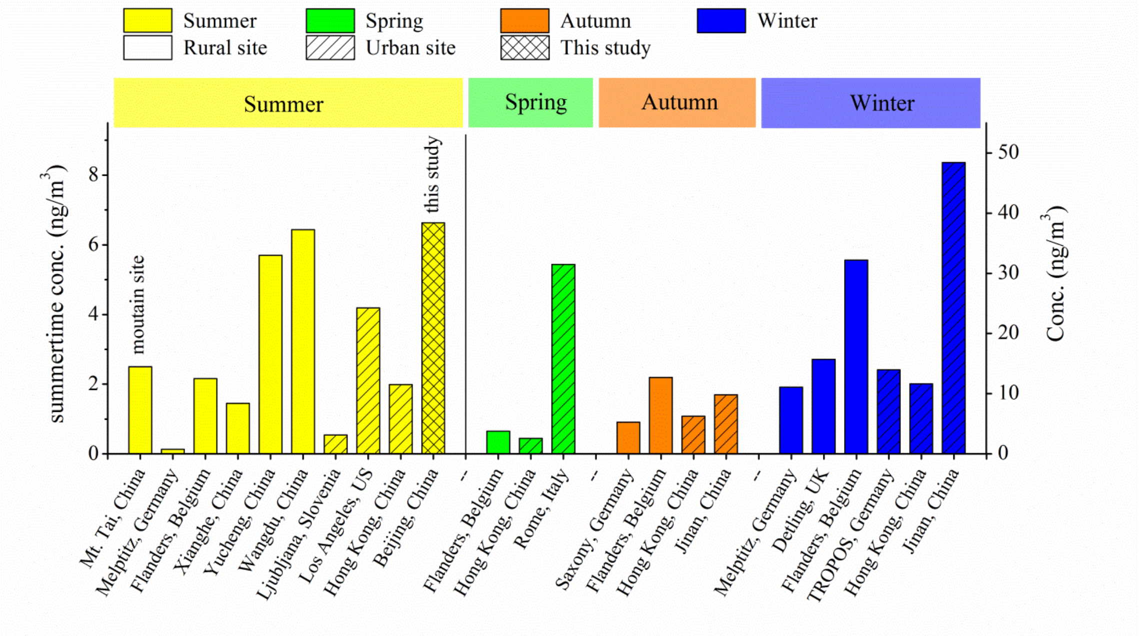


Figure 2 The summery of NAC concentrations cross this and prior studies (see Table S2 for the data and references therein). The NAC concentrations in summer correspond to the left axis and other seasons correspond to the right axis.

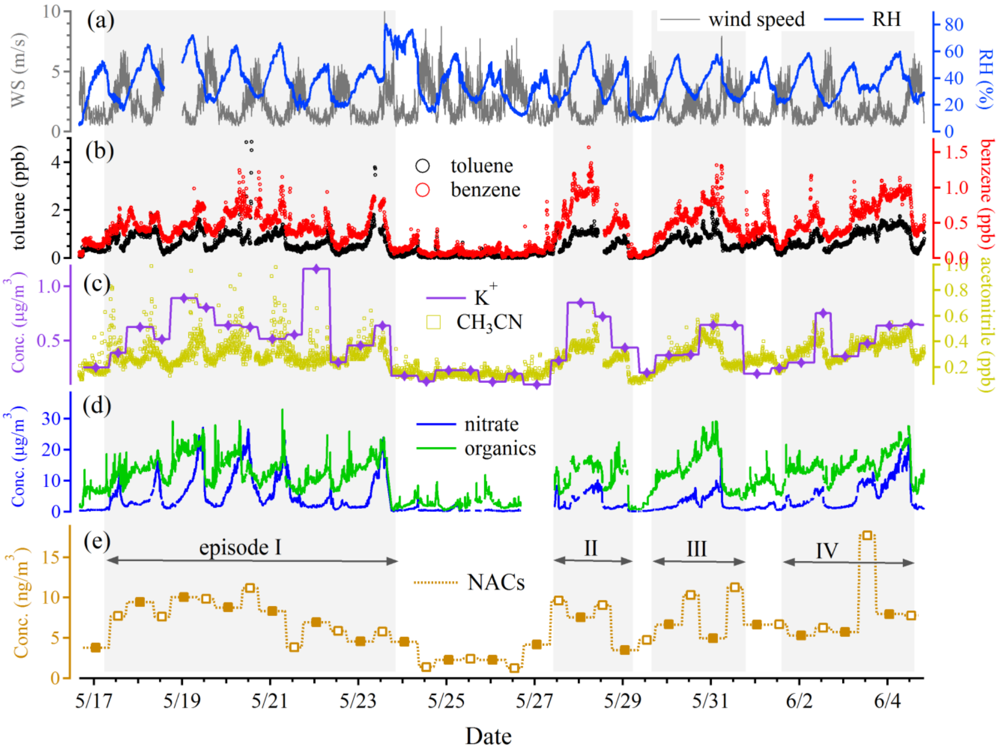


Figure 3 Time series of (a) wind speed (WS) and relative humidity (RH), (b) benzene and toluene, mass concentrations of (c) K^+, (d) organics and nitrate, and (e) NACs. The pollution episodes, with elevated organic aerosols, are marked by gray shading.

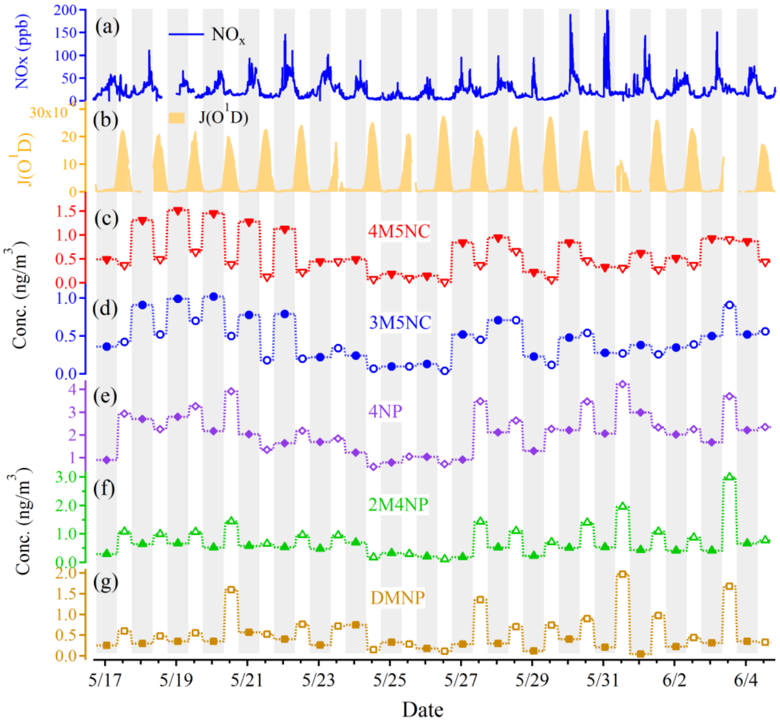


Figure 4 Time series of (a) NO_x, (b) $J(O^1D)$, (c) 4-methyl-5-nitrocatechol (4M5NC), (d) 4-methyl-5-nitrocatechol (3M5NC), (e) 4-nitrophenol (4NP), (f) 2-methyl-4-nitrophenol (2M4NP), and (g) dimethyl-nitrophenol (DMNP). The gray background denotes the nighttime and white background denotes the daytime.

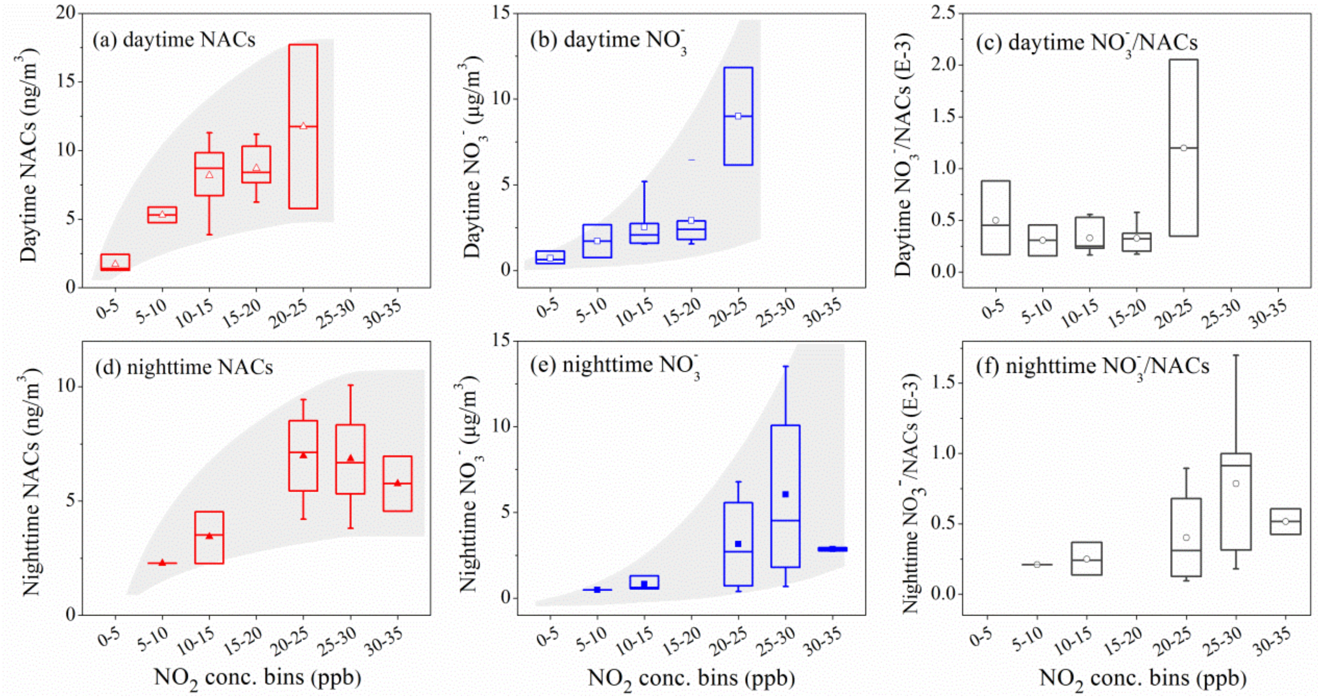


Figure 5 The concentrations of NACs, nitrate and NO$_3^-$/NAC ratios as a function of NO$_2$ concentration bins during daytime and nighttime. The markers represent the mean values and whiskers represent 25 and 75 percentiles.

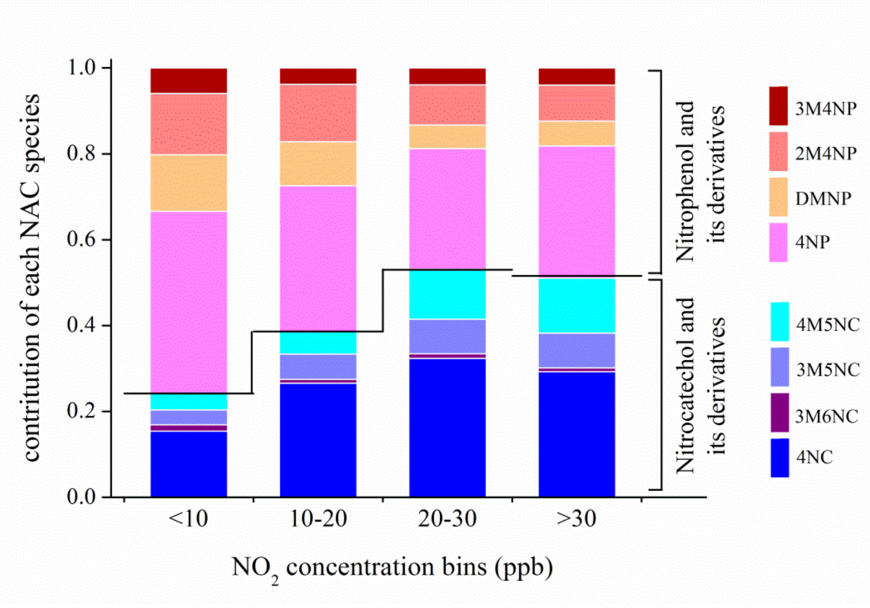


Figure 6 The variation of NAC compositions as a function of NO$_2$ concentration bins.

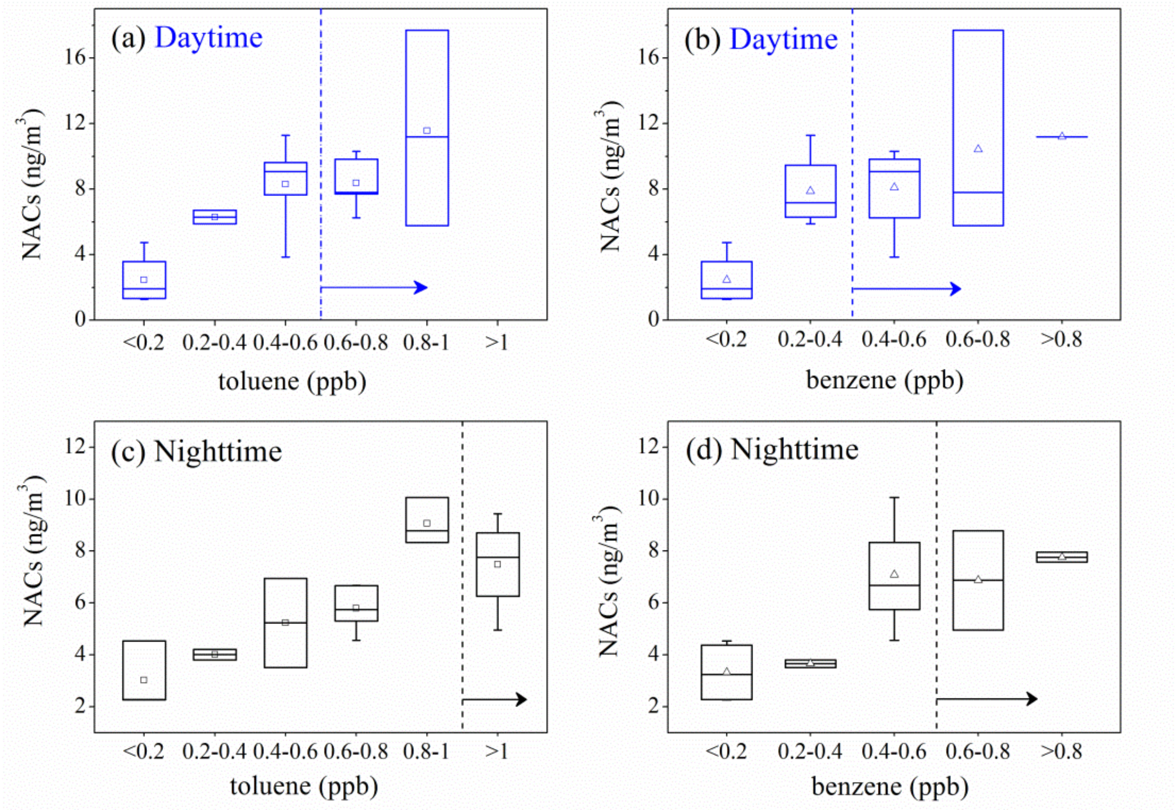


Figure 7 The concentrations of NACs as a function of toluene and benzene concentration bins during daytime and nighttime. The markers represent the mean values and whiskers represent 25 and 75 percentiles.

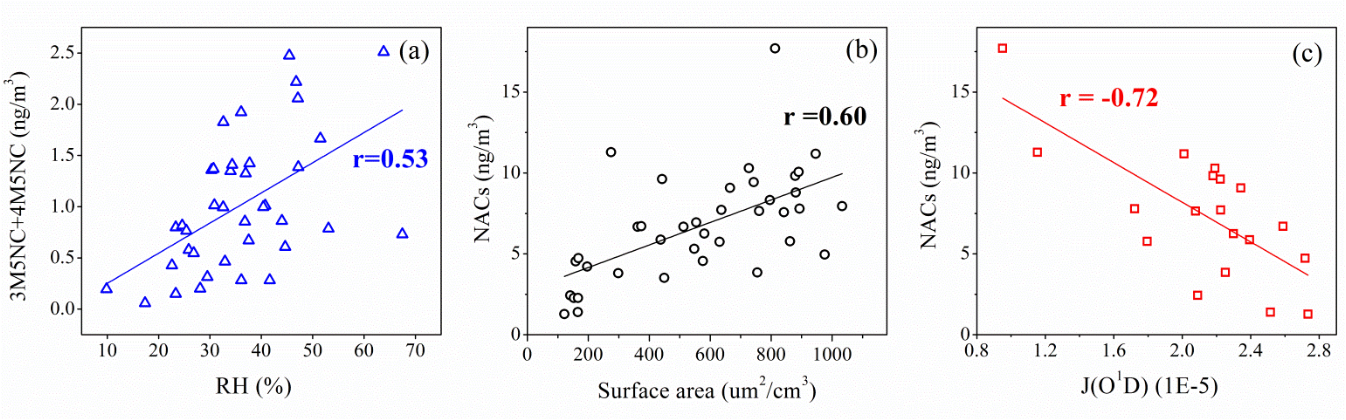


Figure 8 The correlation analysis (a) between (3M5NC+4M5NC) and RH, (b) between NACs and aerosol surface area, (c) between NACs and J(O^{1}D).

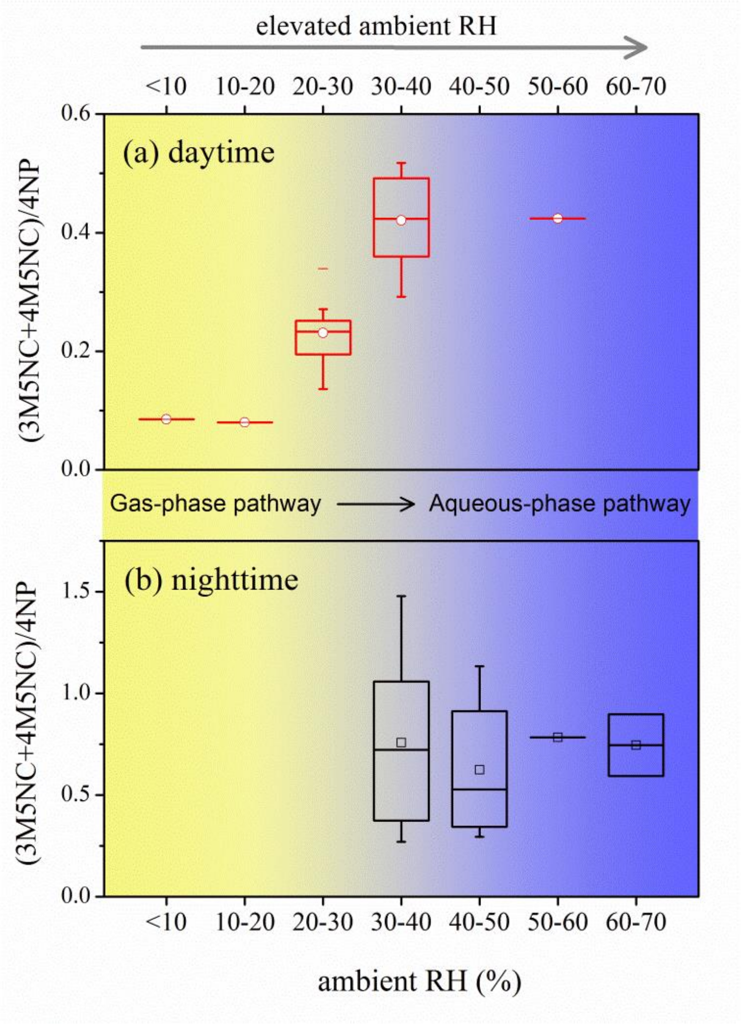
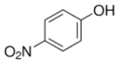
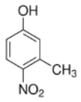
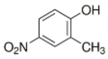
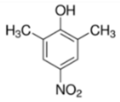
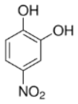
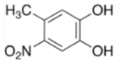
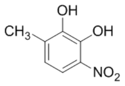
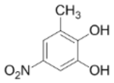


Figure 9 The (3M5NC+4M5NC)/4NP concentration ratios as a function of ambient RH during (a) daytime and (b) nighttime.

Tables

Table 1 The quantified nitro-aromatic compounds in this study

compounds	formula	[M-H]$^-$	retention time (min)	standard	structure	range	average (n=38)
4NP	$C_6H_4NO_3^-$	138.02	21.3	4NP		0.60-4.24	2.15 ± 0.93
3M4NP	$C_7H_6NO_3^-$	152.03	23.9	3M4NP		0.08-0.64	0.27 ± 0.12
2M4NP	$C_7H_6NO_3^-$	152.03	24.9	2M4NP		0.11-2.99	0.76 ± 0.55
DMNP	$C_8H_8NO_3^-$	166.05	26.0, 26.3, 26.9	2,6DM4NP		0.04-1.97	0.55 ± 0.45
Total NP							3.72
4NC	$C_6H_4NO_4^-$	154.01	18.9	4NC		0.16-6.89	1.89 ± 1.28
4M5NC	$C_7H_6NO_4^-$	168.03	21.8	4M5NC		0.02-1.52	0.56 ± 0.40
3M6NC	$C_7H_6NO_4^-$	168.03	23.2	4M5NC		0.02-0.19	0.07 ± 0.03
3M5NC	$C_7H_6NO_4^-$	168.03	23.5	4M5NC		0.04-1.02	0.44 ± 0.27
Total NC							2.96