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 #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 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 NO_x oxidation of anthropogenic VOC precursors was the dominant source of NACs.

The relative contributions of 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 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.