

EDITORIAL SUGGESTIONS:

1. I would suggest mentioning in the introduction that there are several types of NOC in particulate matter: primary NOC formed by direct emissions from various sources such as biomass burning; organic nitrates and nitroaromatic compounds formed by the traditional gas-phase oxidation of VOCs, and believed to represent the major part of NOC; heterocyclic NOC compounds formed by reactions of carbonyls with ammonia and amines. The contribution of the last group to NOC is still uncertain but as described in some of the reviews cited in this paper they are likely to be minor in abundance. Right now, the most important type of NOC is mentioned in passing on lines 80-83, which is not ideal. I think distinguishing various types of NOC more clearly in the introduction will make it easier to discuss the results.

We would like to thank the editor for the valuable comments to further improve our manuscript. We have revised the *Introduction* according to the suggestion. To distinguish various types of NOCs makes the discussion on the origin and formation pathways clearer. We also note that secondary NOCs, such as organic nitrates and nitroaromatic compounds, are believed to be mainly formed in the gas-phase by interaction between volatile organic compounds and oxidations. However, reactions involving mixtures of atmospheric aldehydes (e.g., methylglyoxal/glyoxal) and ammonium/amines have not been confirmed with ambient data and the relative contribution of heterocyclic NOCs is still uncertain, although they are likely to be minor (at a level of several ng m^{-3}) in abundance.

2. I find the references do not always directly support the statements. I encourage the authors to go through the reference list one more time carefully and update them as needed.

Thanks for the comment. We have carefully examined and updated the references.

Examples of references that do not correlate well with the statements:

Line 59 and line 67: Feng et al. (2013) does not mention any nitrogen containing organic compounds in their paper, so this reference does not support the statements on these lines. Feng paper is about the importance of BrC in general, not about NOC in BrC.

Thanks for the comment. The reference has been removed.

Line 60: Reference to Noziere et al. (2015) is the only one in this list that is not a review. It could be a better reference for supporting the previous statement about NOC in BrC.

Thanks for the comment. The reference has been removed.

Line 79: Mang et al. (2008) paper did not conclude that NH₃ reactions lead to the formation of NOC. The authors may instead refer to Bones et al. (2010) paper, which they already cite.

Thanks for the comment. The reference has been revised to (Huang et al., 2017) :

Huang, M., Xu, J., Cai, S., Liu, X., Zhao, W., Hu, C., Gu, X., Fang, L., and Zhang, W.: Characterization of brown carbon constituents of benzene secondary organic aerosol aged with ammonia, J. Atmos. Chem., 75, 205-218, doi:10.1007/s10874-017-9372-x, 2017.

Line 83 and 324: Paper by Lehtipalo et al. (2018) is not the best choice to support the importance of NOC formation through gas-phase mechanisms. The classic organonitrate formation in photooxidation of hydrocarbons is described in many old papers and books

Thanks for the comment. This reference has been removed accordingly. We think the

following two references may be more appropriate.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, edited by: John Wiley&Sons, I., John Wiley&Sons, Inc., New Jersey, 2006.

Ziemann, P. J., and Atkinson, R.: Kinetics, products, and mechanisms of secondary organic aerosol formation, Chem. Soc. Rev., 41, 6582-6605, doi:10.1039/c2cs35122f, 2012.

Lin 98 and 226: Aiona et al. (2017) paper did not study effects of pH or RH on NOC formation. It looked the photodegradation of NOC once they formed. Perhaps a different paper should be cited here.

Thanks for the comment. This reference has been removed accordingly.

Line 239: Pure gas-phase formation of NOC was also demonstrated, for example, in [Duporte et al. 2017, Chemical Characterization of Gas- and Particle-Phase Products from the Ozonolysis of alpha-Pinene in the Presence of Dimethylamine. Environ. Sci. Technol. 2017, 51, (10), 5602-5610.]

Thanks for the comment. We think that this reference is not related to our discussion on the distribution of ammonium and NOCs in the particulate phase, and thus it is not included.

TECHNICAL CORRECTIONS:

Line 56: (BrC), capable of a comparable level of light absorption-> (BrC). BrC has a comparable level of light absorption

Line 107: Sampling was constructed -> Sampling was done

Line 120: here and below "m/z" should be italicized

Line 136: distributing along their vacuum -> as a function of their vacuum

Line 140: 39 -> m/z 39

Line 136, 139, 142, 279, 760: NOCs-containing -> NOC-containing

Line 149: photochemical oxidation products of -> photochemical oxidation of

Line 225: enhanced -> affected

Line 332: unformatted citations

Line 409, 451, 607, 742: sub and superscripts in chemical formulas

Line 417: missing volume and page

Line 551: verify page number

Line 576: missing page number

Figure 3 may benefit from a higher resolution

Figure 6 contains faint gridlines in the PDF version that should be removed. Figure 6 caption only mentions dependence on RH but dependence of NO_x is shown also. The caption needs to be amended.

[Thanks for pointing these out. We have corrected them accordingly.](#)

SUPPORTING INFORMATION:

I would recommend placing figures and table immediately next to whether they are mentioned and not at the end of the document.

Line 44: 14 -> Fourteen

Line 44: -97[HSO₄]- -> m/z -97 [HSO₄]- and similar edits in this paragraph

Line 64, 66: dependent -> dependence

Line 89: missing space before the Pratt reference

Line 113: there are earlier reports of making BrC by methyl glyoxal + AS reaction, I would use the original report.

Line 159: Acs -> ACS

Figure S1 has low image quality

Figure S2: In my opinion, this figure should be split into 4 panels, one for each season

Figure S5: the traces in the left panels are very hard to see

Thanks for pointing these out. We have addressed these issues accordingly.

1 **High secondary formation of nitrogen-containing organics (NOCs) and its**
2 **possible link to oxidized organics and ammonium**

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19

20 **Highlights**

- 21 ● Nitrogen-containing organics (NOCs) were highly internally mixed with photochemically
22 produced secondary oxidized organics
- 23 ● NOCs could be well predicted by the variations of these oxidized organics and ammonium
- 24 ● Higher relative humidity and NO_x may facilitate the conversion of these oxidized organics
25 to NOCs

26 **Abstract**

27 Nitrogen-containing organic compounds (NOCs) substantially contribute to light-
28 absorbing organic aerosols, although the atmospheric processes responsible for the secondary
29 formation of these compounds are poorly understood. In this study, seasonal atmospheric
30 processing of NOCs was investigated by single-particle mass spectrometry in urban Guangzhou
31 from 2013-2014. The relative abundance of NOCs is found to be strongly enhanced when
32 internally mixed with the photochemically produced secondary oxidized organics (i.e., formate,
33 acetate, pyruvate, methylglyoxal, glyoxylate, oxalate, malonate, and succinate) and ammonium.
34 Besides, both the hourly detected particle number and relative abundance of NOCs are highly
35 correlated with those of secondary oxidized organics and ammonium. It is therefore
36 hypothesized that secondary formation of NOCs most likely links to the oxidized organics and
37 ammonium. Results from both multiple linear regression analysis and positive matrix
38 factorization analysis further show that the relative abundance of NOCs could be well predicted
39 ($R^2 > 0.7$, $p < 0.01$) by the oxidized organics and ammonium.

40 Interestingly, the relative abundance of NOCs is inversely correlated with ammonium,
41 whereas their number fractions are positively correlated. This result suggests that although the
42 formation of NOCs does require the involvement of $\text{NH}_3/\text{NH}_4^+$, the relative amount of
43 ammonium may have a negative effect. Higher humidity and NO_x likely facilitate the
44 conversion of oxidized organics to NOCs. Due to the relatively high oxidized organics and
45 $\text{NH}_3/\text{NH}_4^+$, the relative contributions of NOCs in summer and autumn were higher than those in
46 spring and winter. To the best of our knowledge, this is the first direct field observation study

47 reporting a close association between NOCs and both oxidized organics and ammonium. These
48 findings have substantial implications for the role of ammonium in the atmosphere, particularly
49 in models that predict the evolution and deposition of NOCs.

50

51 **Keywords:** nitrogen-containing organic compounds, individual particles, oxidized organics,
52 ammonium, mixing state, single-particle mass spectrometry

53

54 **1 Introduction**

55 Organic aerosols that strongly absorb solar radiation are referred to as brown carbon
56 (BrC). ~~BrC has ,capable of~~ a comparable level of light absorption in the spectral range of
57 near-ultraviolet (UV) light as black carbon (Andreae and Gelencser, 2006; Feng et al., 2013;
58 Yan et al., 2018). Nitrogen-containing organic compounds (NOCs) substantially contribute
59 to the pool of BrC (Mohr et al., 2013; Li et al., 2019), and have a significant effect on
60 atmospheric chemistry, human health and climate forcing (Kanakidou et al., 2005;
61 Shrivastava et al., 2017; De Gouw and Jimenez, 2009). The particulate organic nitrogen
62 accounts for a large fraction of total airborne nitrogen (~30%), although the proportion
63 exhibits a high variability temporally and spatially, and therefore has an influence on both
64 regional and global N deposition (Neff et al., 2002; Shi et al., 2010; Cape et al., 2011).
65 However, the sources, evolution, and optical properties of NOCs remain unclear and
66 contribute significantly to uncertainties in the estimation of their impacts on the environment
67 and climate (Laskin et al., 2015).

68 NOCs are ubiquitous components of atmospheric aerosols, cloud water and rainwater
69 (Altieri et al., 2009; Desyaterik et al., 2013; Laskin et al., 2015), spanning a wide range of
70 molecular weights, structures and light absorption properties (Lin et al., 2016). Emissions of
71 primary NOCs have been attributed to biomass burning, coal combustion, vehicle emissions,
72 biogenic production and soil dust (Laskin et al., 2009; Desyaterik et al., 2013; Sun et al.,
73 2017; Mace et al., 2003; Rastogi et al., 2011; Wang et al., 2017). Secondary NOCs, such as

74 ~~organic nitrates and nitroaromatic compounds, are believed to be mainly formed in the gas-~~
75 ~~phase by interaction between volatile organic compounds and oxidations (e.g., NO_x, ·OH).~~
76 ~~In addition, gas phase formation of NOCs through interaction between volatile organic~~
77 ~~hydrocarbons and NO_x and other oxidations, followed by condensation to aerosols (Fry et~~
78 ~~al., 2014), may have a potential contribution (Fry et al., 2014; Lehtipalo et al.,~~
79 ~~2018)(Ziemann and Atkinson, 2012; Seinfeld and Pandis, 2006). Recently, another type of~~
80 ~~secondary NOCs, or heterocyclic NOCs, formed by reactions. A growing body of evidence~~
81 ~~from laboratory studies suggests that secondary NOCs may be produced in gas phase,~~
82 ~~aerosol, and clouds. Maillard reactions~~ involving mixtures of atmospheric aldehydes (e.g.,
83 methylglyoxal/glyoxal) and ammonium/amines are of particular interest (e.g., Hawkins et
84 al., 2016; De Haan et al., 2017; De Haan et al., 2011). A significant portion of heterocyclic
85 NOCs may also be derived from the heterogeneous ageing of secondary organic aerosol
86 (SOA) with NH₃/NH₄⁺ (Liu et al., 2015; Laskin et al., 2015).- Huang et al. (2017) proposed
87 that even trace levels of ammonia may be sufficient to form heterocyclic NOCs via this
88 pathway. However, these pathways have not been confirmed with ambient data and the
89 relative contribution of heterocyclic NOCs is still uncertain, although they are likely to be
90 minor (at a level of several ng m⁻³) in abundance (Teich et al., 2016){Teich, 2016 #21856}.
91 ~~In addition, gas phase formation of NOCs through interaction between volatile organic~~
92 ~~hydrocarbons and NO_x and other oxidations, followed by condensation, may have a potential~~
93 ~~contribution (Fry et al., 2014; Lehtipalo et al., 2018).~~

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94 The secondary formation of NOCs is especially prevalent in environments experiencing
95 high anthropogenic emissions (Yu et al., 2017; Ho et al., 2015), although further studies are
96 required to establish the formation mechanisms comprehensively. A major obstacle is that
97 organic and inorganic matrix effects have a profound impact on the chemistry of organic
98 compounds in bulk aqueous particles and particles undergoing drying (El-Sayed et al., 2015;
99 Lee et al., 2013). While real-time characterization studies remain a challenge due to the
100 extremely complex chemical nature of NOCs, establishing this data along with the co-
101 variation of NOCs with other chemical components would help to identify the sources and
102 evolution of NOCs. Using single-particle aerosol time-of-flight mass spectrometry, Wang et
103 al. (2010) observed that the widespread occurrence of NOCs closely correlated with particle
104 acidity in the atmosphere of Shanghai (China). In addition, real-time measurements of the
105 atmosphere in New York (US) by aerosol mass spectrometry indicated a definite link
106 between the age of organic species and the N/C ratio (Sun et al., 2011). Further in-depth
107 studies are required to identify the role of formation conditions (e.g., relative humidity (RH)
108 and pH) for secondary NOCs (Nguyen et al., 2012; [Sedehi et al., 2013](#); Ortiz-Montalvo et
109 al., 2014). In the present study, the mixing state of individual particles was investigated,
110 involving NOCs, oxidized organics, and ammonium, based on on-line seasonal observations
111 using a single particle aerosol mass spectrometry (SPAMS). Our findings show that the
112 formation of NOCs is significantly linked to oxidized organics and NH_4^+ , which has
113 important environmental implications for assessing the impact and fate of these compounds.
114

115 2 Methods

116 2.1 Field measurements

117 Sampling was ~~constructed~~done at the Guangzhou Institute of Geochemistry, a
118 representative urban site in Guangzhou (China), a megacity in the Pearl River Delta (PRD)
119 region. The size and chemical composition of individual particles were obtained by the
120 SPAMS (Hexin Analytical Instrument Co., Ltd., China) in real-time (Li et al., 2011). The
121 sampling inlet for aerosol characterization was situated 40 meters above the ground level. A
122 brief description of the performance of the SPAMS and other instruments can be found in
123 the Supporting Information. The sampling periods covered four seasons, including spring
124 (21/02 to 11/04 2014), summer (13/06 to 16/07 2013), autumn (26/09 to 19/10 2013), and
125 winter (15/12 to 25/12 2013). The total measured particle numbers and mean values for
126 meteorological data and gaseous pollutants, are outlined for each season in Table S1 and
127 were described in a previous publication (Zhang et al., 2019).

128

129 2.2 SPAMS data analysis

130 Fragments of NOCs were identified according to the detection of ion peaks at m/z -26
131 $[\text{CN}]^-$ or m/z -42 $[\text{CNO}]^-$, generally due to the presence of C-N bonds (Silva and Prather,
132 2000; Zawadowicz et al., 2017; Pagels et al., 2013). Laboratory produced C-N bonds
133 compounds from bulk solution-phase reactions between the representative oxidized organics
134 (i.e., methylglyoxal) and ammonium sulfate was used to confirm the generation of ion peaks
135 at m/z -26 $[\text{CN}]^-$ and/or m/z -42 $[\text{CNO}]^-$ using SPAMS (Fig. S1). Thus, the NOCs herein may

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136 refer to complex nitrated organics such as organic nitrates, nitro-aromatics, nitrogen
137 heterocycles, and polyphenols. Unfortunately, how well $[\text{CN}]^- / [\text{CNO}]^-$ ions could represent
138 NOCs cannot be quantified, although they were the most commonly reported NOCs peaks
139 by single-particle mass spectrometry (Silva and Prather, 2000; Zawadowicz et al., 2017;
140 Pagels et al., 2013). In the present study, $[\text{CN}]^- / [\text{CNO}]^-$ ions are among the major peaks
141 detected by the SPAMS (Fig. 1). A rough estimate from the peak area ratio of $[\text{CN}]^- / [\text{CNO}]^-$
142 ions and the most likely NOCs fragments (i.e., various amines, and an entire series of
143 nitrogen-containing cluster ions C_nN^+ , $n = 1, 2, 3, \dots$) (Silva and Prather, 2000) shows that
144 $[\text{CN}]^- / [\text{CNO}]^-$ ions may represent more than 90% of these NOCs peaks. The number
145 fractions (Nfs) of particles that contained NOCs ranged from 56-59% across all four seasons
146 (Table S1). The number of detected NOCs-containing particles ~~distributing along as a~~
147 function of their vacuum aerodynamic diameter (d_{va}) is shown in Fig. S2. Most of the
148 detected NOC-containing particles had a d_{va} in a range of 300-1200 nm.

149 A representative mass spectrum for NOCs-containing particles is shown in Fig. 1.
150 Dominant peaks in the mass spectrum were m/z 39 $[\text{K}]^+$, m/z 23 $[\text{Na}]^+$, nitrate (m/z -62 $[\text{NO}_3]^-$
151 or m/z -46 $[\text{NO}_2]^-$), sulfate (m/z -97 $[\text{HSO}_4]^-$), organics (m/z 27 $[\text{C}_2\text{H}_3]^+$, m/z 63 $[\text{C}_5\text{H}_3]^+$, m/z
152 -42 $[\text{CNO}]^-$, m/z -26 $[\text{CN}]^-$), ammonium (m/z 18 $[\text{NH}_4]^+$) and carbon ion clusters (C_n^{+} , $n = 1,$
153 2, 3, ...). NOCs-containing particles were internally mixed with various oxidized organics,
154 represented as formate at m/z -45 $[\text{HCO}_2]^-$, acetate at m/z -59 $[\text{CH}_3\text{CO}_2]^-$, methylglyoxal at
155 m/z -71 $[\text{C}_3\text{H}_3\text{O}_2]^-$, glyoxylate at m/z -73 $[\text{C}_2\text{HO}_3]^-$, pyruvate at m/z -87 $[\text{C}_3\text{H}_3\text{O}_3]^-$, malonate
156 at m/z -103 $[\text{C}_3\text{H}_3\text{O}_4]^-$ and succinate at m/z -117 $[\text{C}_4\text{H}_5\text{O}_4]^-$ (Zhang et al., 2017; Zauscher et

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157 al., 2013; Lee et al., 2003). These oxidized organics showed their pronounced diurnal trends
158 with afternoon maximum and were highly correlated ($r = 0.72 - 0.94$, $p < 0.01$) with each
159 other. Therefore, they were primarily attributed to secondary oxidized organics from
160 photochemical oxidation products of various volatile organic compounds (VOCs) (Paulot et
161 al., 2011; Zhao et al., 2012; Ho et al., 2011), and the details can be found in our previous
162 publication (Zhang et al., 2019). More information on the seasonal variation range of the Nfs
163 of oxidized organics, ammonium and NOCs is presented in Fig. S3.

164 Hourly mean Nfs and relative peak areas were applied herein to indicate the variations
165 of aerosol compositions in individual particles. Even though advances have been made in
166 the quantification of specific chemical species for individual particles based on their
167 respective peak area information, it is still quite a challenge for SPAMS to provide
168 quantitative information on aerosol components mainly due to matrix effects, incomplete
169 ionization and so forth (Qin et al., 2006; Jeong et al., 2011; Healy et al., 2013; Zhou et al.,
170 2016). Despite this, the variation of relative peak area should be a good indicator for the
171 investigation of atmospheric processing of various species in individual particles (Wang et
172 al., 2010; Zauscher et al., 2013; Sullivan and Prather, 2007; Zhang et al., 2014).

173

174 **3 Results and Discussion**

175 **3.1 Evidence for the formation of NOCs from oxidized organics and ammonium**

176 Figure 2 shows the seasonal variations in Nfs of the oxidized organics and ammonium,
177 which were internally mixed with NOCs. On average, more than 90% of the oxidized

178 organics and 65% of ammonium (except spring) were found to be internally mixed with
179 NOCs (Fig. S4). Regarding that the Nfs of NOCs relative to all the measured particles was
180 ~60%, it could be concluded that NOCs were enhanced with the presence of oxidized
181 organics and ammonium, with the enhancement associated with oxidized organics being the
182 most pronounced.

183 A strong correlation between both the Nfs and relative peak areas (RPAs) of NOCs and
184 oxidized organics further demonstrates their close associations, as shown in Fig. 3.
185 Compared with the oxidized organics, the Nfs of ammonium-containing particles internally
186 mixed with NOCs varied within a broader range (~40-90%). However, there is still an
187 enhancement mixing of NOCs with ammonium. A positive correlation ($R^2 = 0.50, p < 0.01$)
188 is observed between the hourly detected number of NOCs and ammonium. It is worth noting
189 that a negative correlation ($R^2 = 0.55, p < 0.01$) is obtained between the hourly average RPAs
190 of NOCs and ammonium (Fig. 3).

191 Based on both the enhancement of NOCs and the high correlations with oxidized
192 organics and ammonium, it is hypothesized that interactions between oxidized organics and
193 ammonium contributed to the observed NOCs. The formation of NOCs from ammonium
194 and carbonyls has been confirmed in several laboratory studies (Sareen et al., 2010; Shapiro
195 et al., 2009; Noziere et al., 2009; Kampf et al., 2016; Galloway et al., 2009). Secondary
196 organic aerosols (SOA) produced from a large group of biogenic and anthropogenic VOCs
197 can be further aged by $\text{NH}_3/\text{NH}_4^+$ to generate NOCs (Nguyen et al., 2012; Bones et al., 2010;
198 Updyke et al., 2012; Liu et al., 2015; Huang et al., 2017). In a chamber study, the formation

199 of NOCs is enhanced in an NH₃-rich environment (Chu et al., 2016). While such chemical
200 mechanisms might be complicated, the initial steps generally involve reactions forming
201 imines and amines, which can further react with carbonyl SOA compounds to form more
202 complex products (e.g., oligomers/BrC) (Laskin et al., 2015).

203 To verify this hypothesis, multiple linear regression analysis is performed to test how
204 well the RPAs of NOCs could be predicted by the oxidized organics and ammonium. As
205 expected, there is a close association ($R^2 = 0.71$, $p < 0.01$) between the predicted RPAs and
206 the observed values of NOCs (Fig. 4), which supports this hypothesis. A noticeable
207 improvement in R^2 implies that a model that uses both oxidized organics and ammonium to
208 predict RPAs of NOCs is substantially better than one that uses only one predictor (either
209 oxidized organics or ammonium in Fig. 3). The result indicates that interactions involving
210 oxidized organics and ammonium could explain over half of the observed variations in
211 NOCs in the atmosphere of Guangzhou. A fraction of the unaccounted NOCs could be due
212 to primary emissions and other formation pathways. This hypothesis could also be supported
213 by a similar pattern of diurnal variation observed for NOCs and oxidized organics (Fig. S5),
214 although there is a slight lag for the NOCs. Such a diurnal pattern is similar to those observed
215 in Beijing and Uintah (Yuan et al., 2016; Zhang et al., 2015). Notably, such a diurnal pattern
216 of secondary NOCs is adequately modelled when the production of NOCs via carbonyls and
217 ammonium is included (Woo et al., 2013). In addition to possible photo-bleaching (Zhao et
218 al., 2015), the lower contribution of NOCs during the daytime may be partly explained by
219 the lower RH, as discussed in section 3.2.

220 Interestingly, the relationship between NOCs and ammonium is distinctly different from
221 the relationship between NOCs and oxidized organics (Fig. 3). This implies that the
222 controlling factors on the formation of NOCs from ammonium are different from oxidized
223 organics. On the one hand, the positive correlation between the detected numbers reflects
224 that the formation of NOCs does require the participant of $\text{NH}_3/\text{NH}_4^+$, consistent with the
225 enhancement of NOCs in ammonium-containing particles (Fig. 2) discussed above. On the
226 other hand, the negative correlation between the RPAs signifies that the formation of NOCs
227 is most probably influenced by the relative amount of ammonium in individual particles.
228 Such influence could also be supported by our data, both from filter samples and individual
229 particle analysis. There is a negative correlation between concentrations of WSON and NH_4^+
230 for the filter samples (Fig. S6). It can be seen from Fig. S7 that lower RPAs of ammonium
231 correspond to higher Nfs of ammonium that internally mixed with NOCs. Such an inverse
232 correlation could also serve as evidence to explain the influence of the relative amount of
233 ammonium on the formation of NOCs.

234 The influence of relative ammonium amount on the formation of NOCs is also
235 theoretically possible since the formation of NOCs may be ~~enhanced~~-affected by particle
236 acidity (Miyazaki et al., 2014; Nguyen et al., 2012), which is substantially affected by the
237 abundance of ammonium. Consistently, higher relative acidity was observed for the
238 internally mixed ammonium and NOCs particles, compared to ammonium-containing
239 particles without NOCs (Fig. S6) and thus may influence the formation of NOCs (Fig. S7).
240 Particle acidity could also play a significant role in the gas-to-particle partitioning of

241 aldehydes (Herrmann et al., 2015; Liggio et al., 2005; Gen et al., 2018; De Haan et al., 2018;
242 Kroll et al., 2005), precursors for the formation of oxidized organics. However, the higher
243 relative acidity might also be a result of NOCs formation. A model simulation shows that
244 after including the chemistry of SOA ageing with NH₃, an increase in aerosol acidity would
245 be expected due to the reduction in ammonium (Zhu et al., 2018). It is also noted that the
246 particle acidity is roughly estimated by the relative abundance of ammonium, nitrate, and
247 sulfate in individual particles (Denkenberger et al., 2007), and thus may not be representative
248 of actual aerosol acidity or pH (Guo et al., 2015; Hennigan et al., 2015; Murphy et al., 2017).
249 In addition, ammonia in the gas phase is also efficient at producing NOCs (Nguyen et al.,
250 2012), which may play an intricate role in the distribution of ammonium and NOCs in the
251 particulate phase. The formation of ammonium and NOCs would compete for ammonia,
252 which may also potentially result in the negative correlation between the RPAs of NOCs and
253 ammonium. Unfortunately, such a role remains unclear since the variations of ammonia were
254 not available in the present study.

255

256 **3.2 Factors contributing to the NOCs resolved by positive matrix factorization (PMF)** 257 **analysis**

258 Figure 5 presents the PMF factor profiles obtained from the PMF model analysis
259 (detailed information is provided in the SI) (Norris et al., 2009) and their diurnal variations.
260 Around 75% of NOCs could be well explained by two factors, with 33% of the PMF resolved
261 NOCs mainly associated with ammonium and carbonaceous ion peaks (ammonium factor),

262 while 59% were mainly associated with oxidized organics (oxidized organics factor). The
263 explained fraction of NOCs by the ammonium and oxidized organic factors is consistent
264 with the linear regression analysis. Furthermore, PMF analysis provided information on the
265 factor contribution and diurnal variations, which may help explain the seasonal variations
266 and processes of NOCs. The ammonium factor showed a diurnal variation pattern peaking
267 during the early morning, which is consistent with the diurnal variation in RH (Zhang et al.,
268 2019). This factor contributed to ~80% (Fig. S8) of the PMF resolved NOCs during spring
269 with the highest RH (Table S1), whereas the oxidized organics factor dominated (> 80%) in
270 summer and fall. In winter, these two factors similarly contributed (~40%). Variation of the
271 ammonium factor may reflect a potential role of aqueous pathways in the formation of NOCs,
272 particularly during spring. Differently, the oxidized organics factor showed a pattern of
273 diurnal variation, increasing from morning hours and peaking overnight, which may
274 correspond to the photochemical production of oxidized organics and followed interactions
275 with condensed ammonium. This pathway may explain the slightly late peaking of NOCs
276 compared to oxidized organics, as ammonium condensation is favorable overnight (Hu et al.,
277 2008). While there were similarities in the fractions of oxidized organics in the oxalate factor
278 and the oxidized organics factor, they only contributed to 8% of the PMF resolved NOCs in
279 the oxalate factor, which contained ~80% of the PMF resolved oxalate. As previously
280 discussed, these oxidized organics are also precursors for the formation of oxalate (Zhang et
281 al., 2019). Therefore, the PMF results suggest that there are two competitive pathways for
282 the evolution of these oxidized organics. Some oxidized organics formed from

283 photochemical activities were further oxidized to oxalate, resulting in a diurnal pattern of
284 variation with concentration peaks during the afternoon (Fig. 5), while others interact with
285 $\text{NH}_3/\text{NH}_4^+$ to form NOCs, peaking during the nighttime. However, the controlling factors for
286 these pathways could not be determined in the present study. The unexplained NOCs (~25%)
287 might be linked to the primary emissions, such as biomass burning (Desyaterik et al., 2013).
288 It could be partly supported by the presence of potassium and various carbon ion clusters (C
289 $\frac{+/-}{n}$, $n = 1, 2, 3, \dots$) in the mass spectrum of NOCs-containing particles (Fig. 1).

291 3.3 Seasonal variations in the observed NOCs

292 There is an evident seasonal variation of NOCs, with higher relative contributions
293 during summer and autumn (Figs. 3 and 4), mainly due to the variations in oxidized organics
294 and $\text{NH}_3/\text{NH}_4^+$. In this region, a more considerable contribution from secondary oxidized
295 organics is typically observed during summer and autumn (Zhou et al., 2014; Yuan et al.,
296 2018). The seasonal maximum NH_3 concentrations have also been reported during the
297 warmer seasons, corresponding to the peak emissions from agricultural activities and high
298 temperatures, while the low NH_3 concentrations observed in colder seasons may be
299 attributed to gas-to-particle conversion (Pan et al., 2018; Zheng et al., 2012). Such seasonal
300 variation in NOCs is also obtained in a model simulation, showing that the conversion of
301 NH_3 into NOCs would result in a significantly higher reduction of gas-phase NH_3 during
302 summer (67%) than winter (31%), due to the higher NH_3 and SOA concentrations present in
303 the summer (Zhu et al., 2018). More primary NOCs may also be present during summer and

304 autumn in the present study, due to the additional biomass burning activities in these seasons
305 (Chen et al., 2018; Zhang et al., 2013).

306 The seasonal variations of NOCs can be adequately explained by the variations in
307 concentrations of oxidized organics and ammonium (Fig. 4), although the hourly variations
308 during each season are not well explained, as indicated by the lower R^2 values (Table S2).
309 The correlation coefficients (R^2) range from 0.24 to 0.57 for inter-seasonal variations.
310 During spring, NOCs exhibits a limited dependence on oxidized organics (Figs. 3a and 3b),
311 while during summer, the hourly detected number of NOCs shows a limited dependence on
312 ammonium (Fig. 3d). These seasonal dependences of NOCs are consistent with the PMF
313 results, showing that the ammonium factor explained ~80% of the predicted NOCs during
314 spring, while the oxidized organics factor dominantly contributed to the predicted NOCs
315 during warmer seasons (Fig. S8). A detailed discussion of this issue is provided in the SI.

316

317 **3.4 Influence of RH and NO_x**

318 The influence of RH on RPAs of NOCs and peak ratios of NOCs/oxidized organics are
319 shown in Fig. 6. While NOCs do not show a clear dependence on RH, the ratio of NOCs to
320 the oxidized organics shows an apparent increase towards higher RH. This finding is
321 consistent with the observations reported by Xu et al. (2017), in which the N/C ratio
322 significantly increases as a function of RH in the atmosphere of Beijing. Besides, the diurnal
323 variations of NOCs with peaks values around 20:00 are also similar to those reported by Xu
324 et al. (2017). The peak ratios of NOCs/oxidized organics are more obviously enhanced when

325 RH is higher than 40%. These findings imply that aqueous-phase processing likely plays a
326 substantial role in the formation of NOCs. Significant changes in RH, such as during the
327 evaporation of water droplets, have been reported to facilitate the formation of NOCs via
328 $\text{NH}_3/\text{NH}_4^+$ and SOA (Nguyen et al., 2012). In addition, an increase in RH would improve
329 the uptake of NH_3 and the formation of NH_4^+ , which also contributes to the enhancement of
330 NOCs. However, the relatively weak correlation ($R^2 = 0.27$, $p < 0.01$) between the peak
331 ratios and RH, reflect the complex influence of RH on the formation of NOCs (Xu et al.,
332 2017; Woo et al., 2013).

333 One may expect that NOCs are formed through the interactions between NO_x and
334 oxidized organics in the gas phase, followed by condensation (Fry et al., 2014; Ziemann and
335 Atkinson, 2012; Seinfeld and Pandis, 2006). Similar to that observed for RH, while NOCs
336 do not show a clear dependence on NO_x (Fig. 6c, $R^2 = 0.02\text{--}0.13$), the ratio of NOCs to the
337 oxidized organics shows a clear increasing trend towards higher NO_x (Fig. 6d, $R^2 = 0.18$, p
338 < 0.01). This indicates that NO_x may play a certain role in the conversion of oxidized
339 organics to NOCs, and yet it cannot be quantified in the present study. It is also noted that
340 low correlation coefficients between NO_x and NOCs might not indicate a limited
341 contribution of NO_x to the formation of NOCs. NO_x affects the formation of NOCs in
342 various ways (e.g., peroxy radical chemistry in VOCs oxidation mechanisms and formation
343 of nitrate radicals) (Xu et al., 2015; Zhang et al., 2018), and thus may not linearly contribute
344 to the formation of NOCs.

345

346 3.5 Atmospheric implications and limitation

347 In this study, we showed that in an urban megacity area, secondary NOCs were
348 significantly contributed by the heterogeneous ageing of oxidized organics with $\text{NH}_3/\text{NH}_4^+$,
349 providing valuable insight into SOA aging mechanisms. In particular, the effects of $\text{NH}_3/\text{NH}_4^+$
350 on SOA or BrC formation remain relatively poorly understood. In the PRD region, it has
351 been shown that oxygenated organic aerosols (OOA) account for more than 40% of the total
352 organic mass (He et al., 2011), with high concentrations of available gaseous carbonyls (Li
353 et al., 2014). Therefore, it is expected that over half of all water-soluble NOCs in this region
354 might link to secondary processing (Yu et al., 2017). Furthermore, secondary sources have
355 been found to contribute significantly to NOCs related BrC in Nanjing, China (Chen et al.,
356 2018). The results presented herein also suggest that the production of NOCs might be
357 adequately estimated by their correlation with secondary oxidized organics and ammonium.
358 The effectiveness of correlation-based estimations needs to be examined in other regions
359 before being generally applied in other environments. However, this approach may provide
360 valuable insights into investigations of NOCs using atmospheric observations. In contrast, it
361 has previously been reported that a positive correlation exists between WSON and
362 ammonium (Li et al., 2012), indicating similar anthropogenic sources. This divergence could
363 be mainly attributed to varying contributions of primary sources and secondary processes to
364 the observed NOCs. Possible future reductions in anthropogenic emissions of ammonia may
365 reduce particle NOCs. Understanding the complex interplay between inorganic and organic
366 nitrogen is an essential part of assessing global nitrogen cycling.

367 Moise et al. (2015) proposed that with high concentrations of reduced nitrogen
368 compounds, high photochemical activity, and frequent changes in humidity, BrC formed via
369 $\text{NH}_3/\text{NH}_4^+$ and SOA may become a dominant contributor to aerosol absorption, specifically
370 in agricultural and forested areas. However, this study suggests that even in typical urban
371 areas, BrC formation via $\text{NH}_3/\text{NH}_4^+$ and SOA should not be neglected. In particular, SOA
372 was found to account for 44 – 71% of the organic mass in megacities across China (Huang
373 et al., 2014), with NH_3 concentrations in urban areas comparable with those from agricultural
374 sites and 2- or 3-fold those of forested areas in China (Pan et al., 2018). Additionally, the
375 acidic nature of particles in these regions would also be favorable for the formation of NOCs
376 (Guo et al., 2017; Jia et al., 2018). Considering the formation of NOCs from the uptake of
377 NH_3 onto SOA particles, Zhu et al. (2018) suggested that this mechanism could have a
378 significant impact on the atmospheric concentrations of $\text{NH}_3/\text{NH}_4^+$ and NO_3^- .

379

380 **5 Conclusions**

381 This study investigated the processes contributing to the seasonal formation of NOCs,
382 involving ammonium and oxidized organics in urban Guangzhou, using single-particle mass
383 spectrometry. This is the first study to provide direct field observation results to confirm that
384 the variation of NOCs correlate well and are strongly enhanced internal mixing with
385 secondary oxidized organics. These findings highlight the possible formation pathway of
386 NOCs through the ageing of secondary oxidized organics by $\text{NH}_3/\text{NH}_4^+$ in ambient urban
387 environments. A clear pattern of seasonal variation in NOCs was observed, with higher

388 relative contributions in summer and autumn as compared to spring and winter. This
389 seasonal variation was well predicted by multiple linear regression model analysis, using the
390 relative abundance of oxidized organics and ammonium as model inputs. More than 50% of
391 NOCs could be explained by the interaction between oxidized organics and ammonium. The
392 production of NOCs through such processes was facilitated by increased humidity and NOx.
393 These results extend our understanding of the mixing state and atmospheric processing of
394 particulate NOCs, as well as having substantial implications for the accuracy of models
395 predicting the formation, fate, and impacts of NOCs in the atmosphere.

396

397 **Author contribution**

398 GHZ and XHB designed the research (with input from WS, LL, ZYW, DHC, MJT, XMW
399 and GYS), analyzed the data, and wrote the manuscript. XFL, YZF, and QHL conducted air
400 sampling work and laboratory experiments under the guidance of GHZ, XHB and XMW.
401 All authors contributed to the refinement of the submitted manuscript.

402

403 **Acknowledgement**

404 This work was supported by the National Nature Science Foundation of China (No.
405 41775124 and 41877307), the National Key Research and Development Program of China
406 (2017YFC0210104 and 2016YFC0202204), the Science and Technology Project of
407 Guangzhou, China (No. 201803030032), and the Guangdong Foundation for Program of
408 Science and Technology Research (No. 2017B030314057).

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763 **Figure captions**

764 Figure 1. Representative mass spectrum for NOCs-containing particles. The ion
765 peaks corresponding to NOCs and oxidized organics are highlighted with red bars.

766 Figure 2. The variation in hourly mean Nfs of the oxidized organics and
767 ammonium that internally mixed with NOCs. Box and whisker plot shows lower,
768 median, and upper lines, denoting the 25th, 50th, and 75th percentiles, respectively; the
769 lower and upper edges denote the 10th and 90th percentiles, respectively.

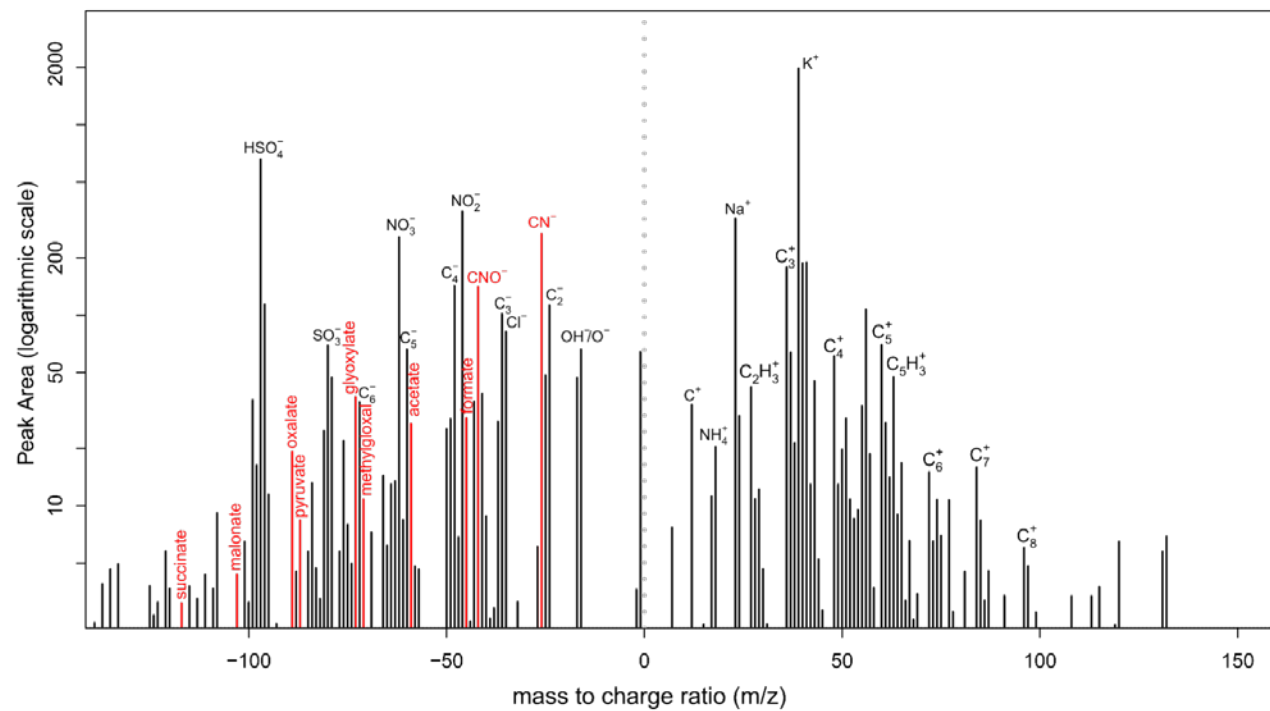
770 Figure 3. Correlation analysis of (a, c) the RPAs and (b, d) the number of
771 detected NOCs, with the oxidized organics and ammonium in different seasons.
772 Significant ($p < 0.01$) correlations were obtained for both the total observed data and
773 the seasonally separated data. RPA is defined as the fractional peak area of each m/z
774 relative to the sum of peak areas in the mass spectrum and is applied to represent the
775 relative amount of a species on a particle (Jeong et al., 2011; Healy et al., 2013).

776 Figure 4. Comparison between the measured and predicted RPAs for NOCs.

777 Figure 5. (left) PMF-resolved 3-factor source profiles (percentage of total species)
778 and (right) their diurnal variations (arbitrary unit).

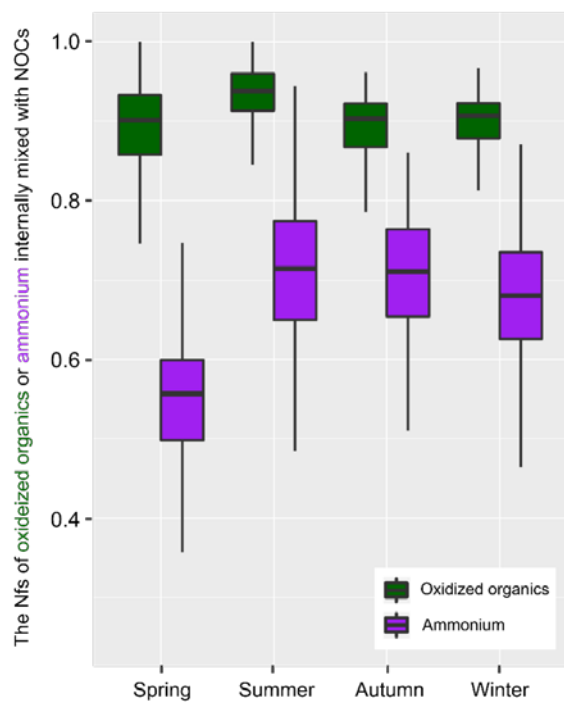
779 Figure 6. The dependence of NOCs and the ratio of NOCs to the oxidized organics
780 on RH and NOx.

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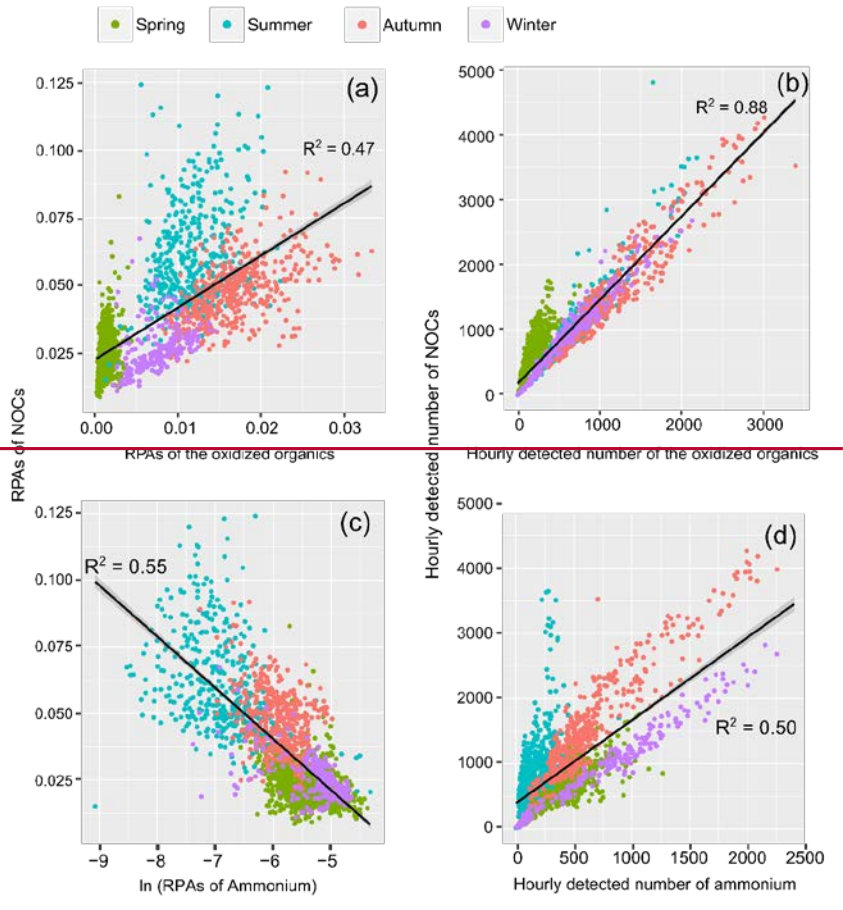
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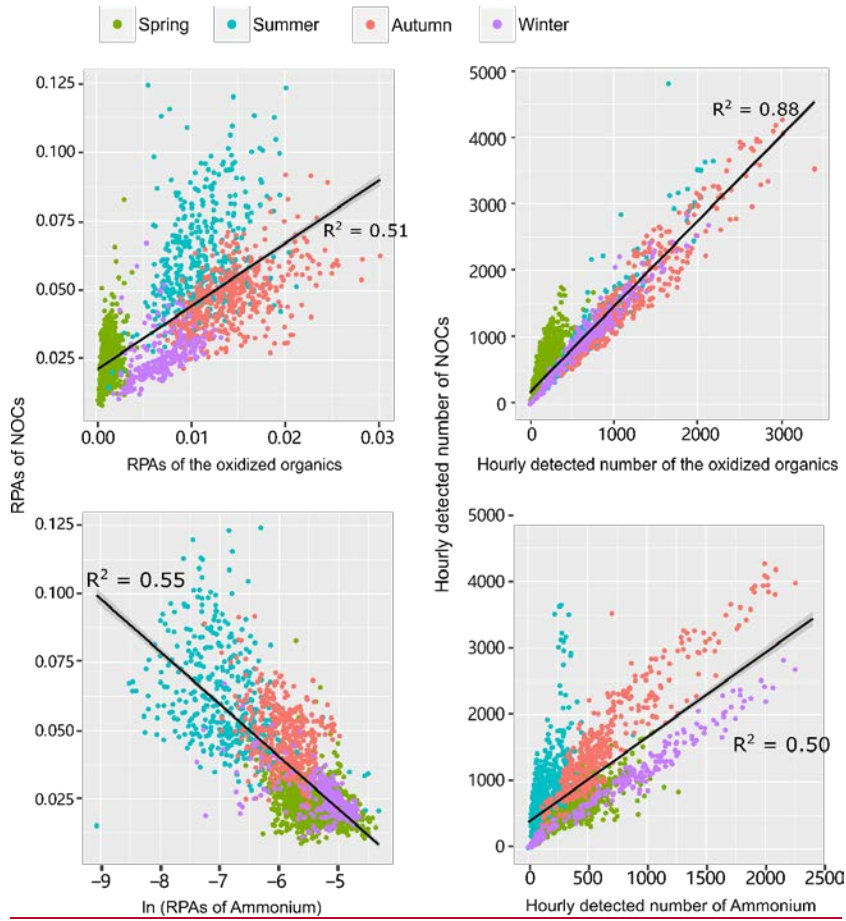
782 Fig. 1.



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784 Fig. 2.

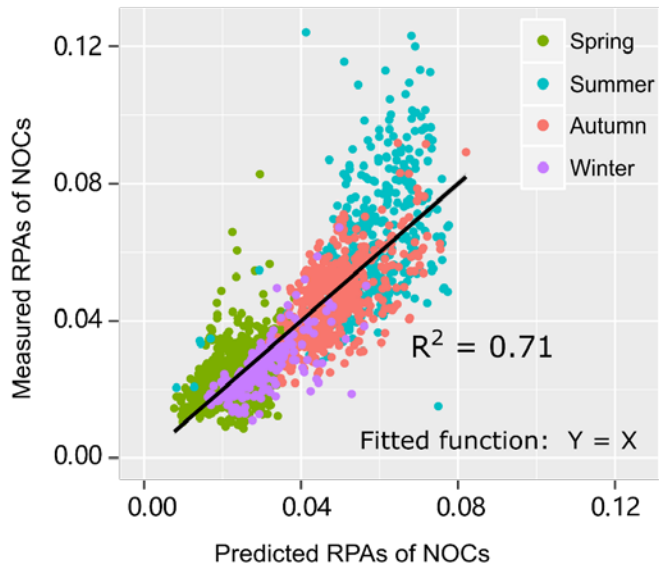




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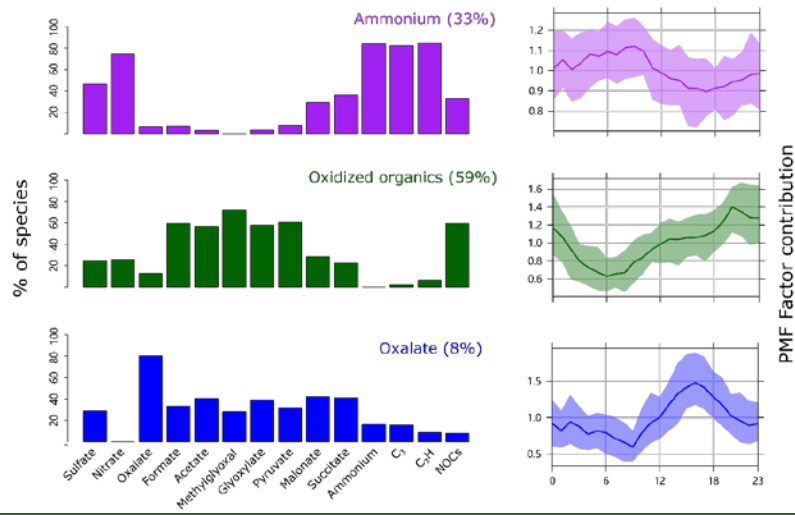


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~~Fig. 4.~~

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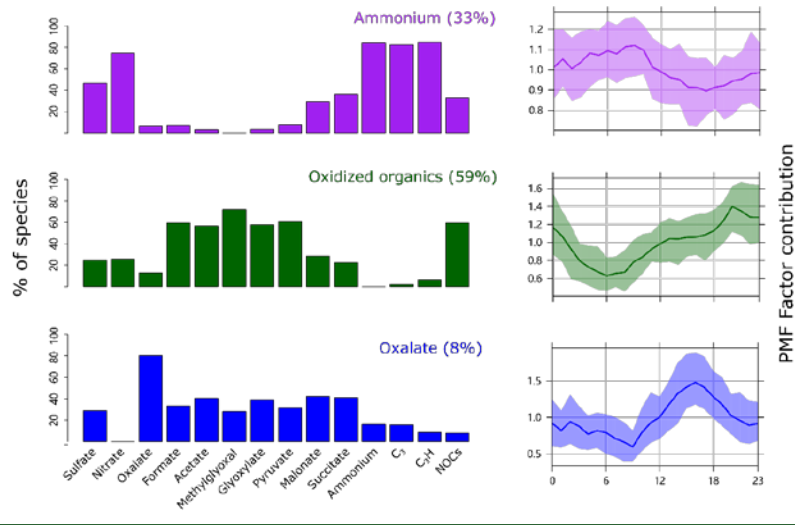


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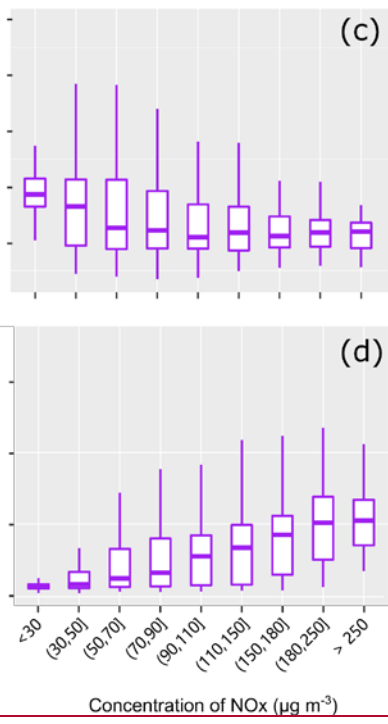
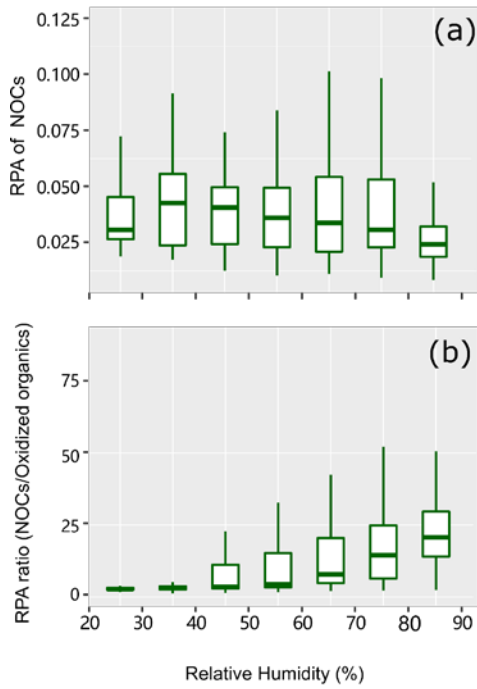


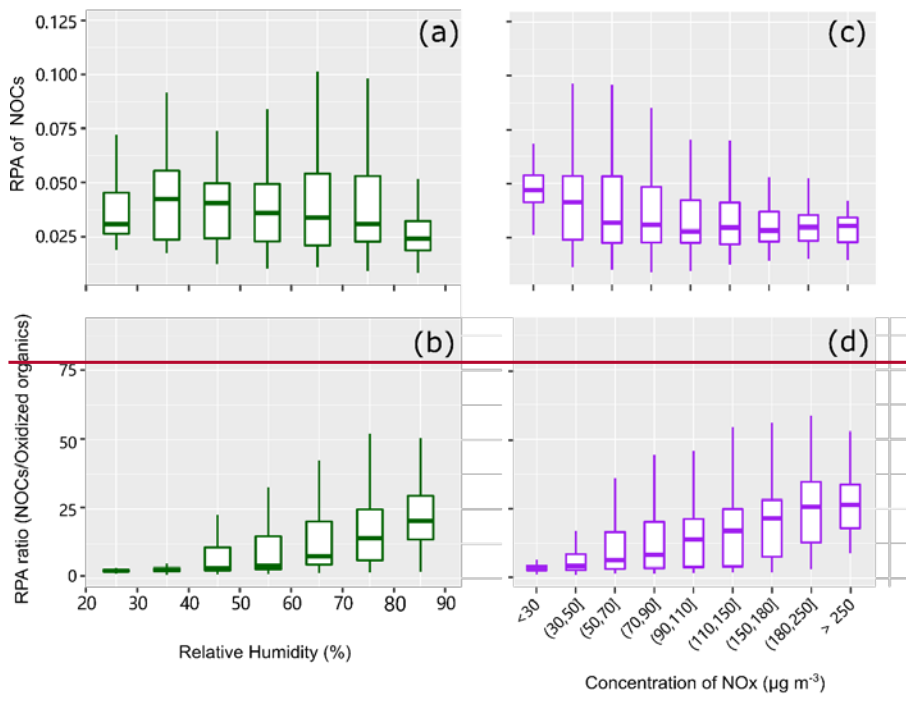
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Fig. 5.

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Fig. 6.