
Response to comments 1#

Review of the manuscript revision by G. Zhang et al.

Overall, the authors have done well to address some of the referee comments, but not all. There are several major issues that remain, which prevent me from endorsing the manuscript for publication. For the comments that have not been addressed sufficiently, I have the original referee comment below in quotes, followed by my assessment of the changes and additional comments.

We would like to thank the referee again for his/her valuable comments to further improve the manuscript. We have addressed the specific comments in the sections below and made the appropriate revisions to the manuscript. The referee's comments are in the black text followed by our response in blue text.

Original comment: "For NH_3 , a positive correlation is observed between the number fraction of particles with NH_4^+ and NOC, while a negative correlation is observed between the relative peak areas of these compound classes. There is not a reasonable explanation given for this surprising and apparently contradictory behavior."

New comment: The authors' explanation for this observation still does not make sense. The authors state that ammonium is necessary for NOC formation, but that ammonium also inhibits NOC formation. Various factors contributing to this counterintuitive result are hypothesized (e.g., acidity, competition for gas-phase ammonia), but none are consistent with the results in Figure 3c and 3d. The discussion in the revised manuscript (revised manuscript with track changes lines 205 - 214) actually contradicts their finding, since ammonium does not inhibit NOC formation in any of the references cited in this added paragraph. Based on the other referee's comments, it seems there is a possibility that the results in Figures 3c and 3d stem from a measurement artifact (ionization efficiency changing with composition), rather than an actual physical/chemical process occurring in the atmosphere. The authors need to present a detailed, logical argument for this observation.

Thanks for pointing this out. Regarding the referee's concern, we also agree with

the comment that “ammonium also inhibits NOC formation” is not precise enough to pinpoint the observation results in Figure 3. It has been revised to “The formation of NOCs requires the presence of ammonium, but is most probably influenced by the relative amount of ammonium in individual particles” in the revised manuscript, which is believed to be more appropriate.

We understand that the reviewer still considered this observation as a counterintuitive result. As previously replied, we highlighted the contradictory correlation between the hourly detected number and RPAs of NOCs and ammonium as a surprising and interesting result. We think that the referee’s confusion maybe mainly due to our unclear expressions on this issue. As replied to the referee 2#, this is unlikely due to measurement artifact. To make it clearer, we attempted to provide more discussion in the revised manuscript.

First, from the observational results in Figure 3d, we stated that the formation of NOCs requires the involvement of ammonium. It is easy to understand that ammonium is important in the formation of NOCs, from the high correlations between their hourly detected number. Consistently, NOCs and ammonium showed high internal mixing state in Figure 2.

Second, we provided additional explanations on the inverse correlation between RPAs of NOCs and ammonium as shown in Figure 3c. The negative correlation between their RPAs signifies that the formation of NOCs is most probably influenced by the relative amount of ammonium in individual particles. This is supported by our data, both from filter samples and individual particle analysis. There is a negative correlation between concentrations of WSON and NH_4^+ for the filter samples (Fig. S6). It can be seen from Fig. S7 that lower RPAs of ammonium correspond to higher Nfs of ammonium that internally mixed with NOCs. Such an inverse correlation could also serve as evidence to explain the influence of the relative amount of ammonium on the formation of NOCs.

Furthermore, we discussed the theoretical possibility that the formation of NOCs is influenced by the relative amount of ammonium. We showed that this is theoretically possible since the formation of NOCs may be enhanced by particle acidity (Miyazaki

et al., 2014; Aiona et al., 2017; Nguyen et al., 2012), which is substantially affected by the amount of ammonium. This could also be supported by our data, as shown in Figure S6, that the internally mixed ammonium and NOCs particles had higher relative acidity than the ammonium-containing particles without NOCs. It is also noted that particle acidity could play a significant role in the gas-to-particle partitioning of aldehydes (Herrmann et al., 2015; Liggio et al., 2005; Gen et al., 2018; De Haan et al., 2018; Kroll et al., 2005), which are precursors for the formation of the oxidized organics.

Original comment: “NO_x is completely ruled out as a contributor to NOC formation on the basis of poor (or no) correlations between NOC and NO_x. However, this is a misinterpretation of the data. Many factors (different removal processes and lifetimes of particles vs. gasses, primary vs. secondary species, etc.) could contribute to a lack of correlation even if NO_x did contribute to NOC formation.”

New comment: First of all, the authors used the referee’s comment word-for-word in their revised manuscript (lines 460-462 in the track changes version). This is inappropriate, and constitutes plagiarism of this sentence. Clearly, this should be changed.

Thanks for pointing this out. We have changed the sentence to “A lack of correlation could probably be attributed to that NO_x affects the formation of NOCs in various ways (e.g., peroxy radical chemistry in VOCs oxidation mechanisms and formation of nitrate radicals) (Xu et al., 2015; Zhang et al., 2018), and thus may not linearly contribute to the formation of NOCs.”

The above issue aside, I still do not believe this comment was adequately addressed in the revision. There is too much emphasis on simple linear correlations, when that is not expected for the chemistry in this system. For example, NO_x controls the branching of VOC reactions, which will in turn affect product distributions, including NOCs; however, this will not (in most cases) result in a linear correlation between NO_x and NOCs. Likewise, NO_x affects nitrate radical formation, which can form NOCs, but a linear relationship between NO_x and NOCs will not necessarily occur even if this is the

predominant pathway for NOC production. Further, the references cited in lines 451-453 (track changes version) to support their position do not show linear correlations between NO_x and NOC formation in systems representative of a polluted urban atmosphere. Therefore, the possible role of NO_x in NOC formation is not accurately described in the manuscript revision.

Thanks for the referee's constructive comment. It greatly helps us to refine our discussion on the possible contribution of NO_x pathways to the formation of NOCs. We agree with the comment that simple linear correlations may not be expected for the chemistry involving NO_x and NOCs. This is because that NO_x affects the formation of NOCs in various ways (e.g., peroxy radical chemistry in VOCs oxidation mechanisms and formation of nitrate radicals) (Xu et al., 2015; Zhang et al., 2018). Besides, the related products or intermediates were not available to elucidate such complex chemical processes in the present study. Therefore in the revised manuscript, we mentioned that NO_x may play a certain role in the conversion of oxidized organics to NOCs, and yet it cannot be quantified in the present study. This is supported by the relationship between peak ratios of NOCs/oxidized organics and NO_x (Fig. 6), showing that the ratios generally increase with an increasing level of NO_x ($R^2 = 0.18$, $p < 0.01$). It is noted that low correlation coefficients ($R^2 = 0.02 - 0.13$) between NO_x and NOCs might not indicate a limited contribution of NO_x to the formation of NOCs. A lack of correlation could probably be interpreted by the fact that NO_x affects the formation of NOCs in various ways (e.g., peroxy radical chemistry in VOCs oxidation mechanisms and formation of nitrate radicals) (Xu et al., 2015; Zhang et al., 2018), and thus may not linearly contribute to the formation of NOCs.

Finally, the revised manuscript needs editing for grammar and language.

Thanks for the comment. We have carefully examined and corrected possible technical errors.

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

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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-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 were~~ investigated by ~~single-single-~~particle mass spectrometry in urban
31 Guangzhou from 2013-2014. The relative abundance of NOCs is found to be strongly enhanced
32 when internally mixed with the photochemically produced secondary oxidized organics (i.e.,
33 formate, acetate, pyruvate, methylglyoxal, glyoxylate, oxalate, malonate, and succinate) and
34 ammonium. ~~In addition~~ Besides, both the hourly detected particle number and relative
35 abundance of NOCs are highly correlated with those of secondary oxidized organics and
36 ammonium. It is therefore hypothesized that secondary formation of NOCs most likely links to
37 the oxidized organics and ammonium. Results from both multiple linear regression analysis and
38 positive matrix factorization analysis further show that the relative abundance of NOCs could
39 be well predicted ($R^2 > 0.7$, $p < 0.01$) 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 NOx likely facilitate t~~The~~
44 conversion of oxidized organics to NOCs ~~is likely facilitated by higher humidity and NOx~~. Due
45 to the relatively high oxidized organics and $\text{NH}_3/\text{NH}_4^+$, the relative contributions of NOCs in
46 summer and autumn were higher than those in spring and winter. To the best of our knowledge,

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

51

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

54

55 **1 Introduction**

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

69 NOCs are ubiquitous components of atmospheric aerosols, cloud water and rainwater
70 (Altieri et al., 2009; Desyaterik et al., 2013; Laskin et al., 2015), spanning a wide range of
71 molecular weights, structures and light absorption properties (Lin et al., 2016). Emissions of
72 primary NOCs have been attributed to biomass burning, coal combustion, vehicle emissions,
73 biogenic production and soil dust (Laskin et al., 2009; Desyaterik et al., 2013; Sun et al.,
74 2017; Mace et al., 2003; Rastogi et al., 2011; Wang et al., 2017). A growing body of evidence

75 from laboratory studies suggests that secondary NOCs may be produced in gas phase,
76 aerosol, and clouds. Maillard reactions involving mixtures of atmospheric aldehydes (e.g.,
77 methylglyoxal/glyoxal) and ammonium/amines are of particular interests (e.g., Hawkins et
78 al., 2016; De Haan et al., 2017; De Haan et al., 2011). A significant portion of NOCs may
79 also be derived from the heterogeneous ageing of secondary organic aerosol (SOA) with
80 $\text{NH}_3 / \text{NH}_4^+$ (Liu et al., 2015; Laskin et al., 2015). Mang et al. (2008) proposed that even
81 trace levels of ammonia may be sufficient to form NOCs via this pathway. In addition, ~~gas~~
82 gas-phase formation of NOCs through interaction between volatile organic hydrocarbons
83 and NO_x and other oxidations, followed by condensation, may have a potential contribution
84 (Fry et al., 2014; ~~Stefaneli et al., 2019~~; Lehtipalo et al., 2018).

85 The secondary formation of NOCs is especially prevalent in environments experiencing
86 high anthropogenic emissions (Yu et al., 2017; Ho et al., 2015), although further studies are
87 required to ~~comprehensively~~ establish the formation mechanisms comprehensively. A major
88 obstacle is that organic and inorganic matrix effects have a profound impact on the chemistry
89 of organic compounds in bulk aqueous particles and particles undergoing drying (El-Sayed
90 et al., 2015; Lee et al., 2013). While real-time characterization studies remain a challenge
91 due to the extremely complex chemical nature of NOCs, establishing this data along with
92 the co-variation of NOCs with other chemical components would help to identify the sources
93 and evolution of NOCs. Using single-particle aerosol time-of-flight mass spectrometry,
94 Wang et al. (2010) observed that the widespread occurrence of NOCs ~~was~~ closely correlated
95 with particle acidity in the atmosphere of Shanghai (China). In addition, real-time

96 measurements of the atmosphere in New York (US) by aerosol mass spectrometry indicated
97 a ~~positive-definite~~ link between the age of organic species and the N/C ratio (Sun et al., 2011).
98 Further in-depth studies are required to identify the role of formation conditions (e.g.,
99 relative humidity (RH) and pH) for secondary NOCs (Aiona et al., 2017; Nguyen et al.,
100 2012). In the present study, the mixing state of individual particles ~~were~~-was investigated,
101 involving NOCs, oxidized organics, and ammonium, based on on-line seasonal observations
102 using a single particle aerosol mass spectrometry (SPAMS). Our findings show that the
103 formation of NOCs is significantly linked to oxidized organics and NH_4^+ , which has
104 important environmental implications for assessing the impact and fate of these compounds.

105

106 2 Methods

107 2.1 Field measurements

108 Sampling was ~~performed-constructed~~ at the Guangzhou Institute of Geochemistry, a
109 representative urban site in Guangzhou (China), a megacity in the Pearl River Delta (PRD)
110 region. The size and chemical composition of individual particles were obtained by the
111 SPAMS (Hexin Analytical Instrument Co., Ltd., China) in real-time analysis was performed
112 ~~(Hexin Analytical Instrument Co., Ltd., China) to establish the size and chemical~~
113 ~~composition of individual particles in real time~~ (Li et al., 2011). The sampling inlet for
114 aerosol characterization was situated 40 meters above the ground level. A brief description
115 of the performance of the SPAMS and other instruments can be found in the Supporting
116 Information. The sampling periods covered four seasons, including spring (21/02 to 11/04

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117 2014), summer (13/06 to 16/07 2013), autumn (26/09 to 19/10 2013), and winter (15/12 to
118 25/12 2013). The total measured particle numbers and mean values for meteorological data
119 and gaseous pollutants, are outlined for each season in Table S1 and were described in a
120 previous publication (Zhang et al., 2019).

121

122 2.2 SPAMS data analysis

123 Fragments of NOCs were identified according to the detection of ion peaks at m/z -26
124 $[\text{CN}]^-$ or -42 $[\text{CNO}]^-$, generally due to the presence of C-N bonds (Silva and Prather, 2000;
125 Zawadowicz et al., 2017; Pagels et al., 2013). Laboratory produced C-N bonds compounds
126 from bulk solution-phase reactions between the representative oxidized organics (i.e.,
127 methylglyoxal) and ammonium sulfate was used to confirm the generation of ion peaks at
128 m/z -26 $[\text{CN}]^-$ and/or -42 $[\text{CNO}]^-$ using SPAMS (Fig. S1). Thus, the NOCs herein may refer
129 to complex nitrated organics such as organic nitrates, nitro-aromatics, nitrogen heterocycles,
130 and polyphenols. Unfortunately, how well $[\text{CN}]^- / [\text{CNO}]^-$ ions could represent NOCs cannot
131 be quantified, although they were the most commonly reported NOCs peaks by single-single-
132 particle mass spectrometry (Silva and Prather, 2000; Zawadowicz et al., 2017; Pagels et al.,
133 2013). In the present study, $[\text{CN}]^- / [\text{CNO}]^-$ ions are among the major peaks detected by the
134 SPAMS (Fig. 1). A rough estimate from the peak area ratio of $[\text{CN}]^- / [\text{CNO}]^-$ ions and the
135 most likely NOCs fragments (i.e., various amines, and an entire series of nitrogen-containing
136 cluster ions C_nN^- , $n = 1, 2, 3, \dots$) (Silva and Prather, 2000) shows that $[\text{CN}]^- / [\text{CNO}]^-$ ions
137 may represent more than 90% of these NOCs peaks. The number fractions (Nfs) of particles

138 that contained NOCs ranged from 56-59% across all four seasons (Table S1). The number
139 of detected NOCs-containing particles distributing along their vacuum aerodynamic
140 diameter (d_{va}) is shown in Fig. S2. Most of the detected NOC-containing particles had a d_{va}
141 in a range of 300-1200 nm.

142 A representative mass spectrum for NOCs-containing particles is shown in Fig. 1.
143 Dominant peaks in the mass spectrum were 39 [K]⁺, 23 [Na]⁺, nitrate (-62 [NO₃]⁻ or -46
144 [NO₂]⁻), sulfate (-97 [HSO₄]⁻), organics (27 [C₂H₃]⁺, 63 [C₅H₃]⁺, -42 [CNO]⁻, -26 [CN]⁻),
145 ammonium (18 [NH₄]⁺) and carbon ion clusters (C_n^{+/·}, n = 1, 2, 3,...). NOCs-containing
146 particles were internally mixed with various oxidized organics, represented as formate at m/z
147 -45 [HCO₂]⁻, acetate at m/z -59 [CH₃CO₂]⁻, methylglyoxal at m/z -71 [C₃H₃O₂]⁻, glyoxylate
148 at m/z -73 [C₂HO₃]⁻, pyruvate at m/z -87 [C₃H₃O₃]⁻, malonate at m/z -103 [C₃H₃O₄]⁻ and
149 succinate at m/z -117 [C₄H₅O₄]⁻ (Zhang et al., 2017; Zauscher et al., 2013; Lee et al., 2003).

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

157 Hourly mean Nfs and relative peak areas were applied herein to indicate the variations
158 of aerosol compositions in individual particles. Even though advances have been made in

159 the quantification of specific chemical species for individual particles based on their
160 respective peak area information, it is still quite a challenge for SPAMS to provide
161 quantitative information on aerosol components mainly due to matrix effects, incomplete
162 ionization and so forth (Qin et al., 2006; Jeong et al., 2011; Healy et al., 2013; Zhou et al.,
163 2016). Despite ~~of~~ this, the variation of relative peak area should be a good indicator for the
164 investigation of atmospheric processing of various species in individual particles (Wang et
165 al., 2010; Zauscher et al., 2013; Sullivan and Prather, 2007; Zhang et al., 2014).

166

167 **3 Results and Discussion**

168 **3.1 Evidence for the formation of NOCs from oxidized organics and ammonium**

169 Figure 2 shows the seasonal variations in Nfs of the oxidized organics and ammonium,
170 which were internally mixed with NOCs. On average, more than 90% of the oxidized
171 organics and 65% of ammonium (except spring) were found to be internally mixed with
172 NOCs (Fig. S4). Regarding that the Nfs of NOCs relative to all the measured particles was
173 ~60%, it could be concluded that NOCs were enhanced with the presence of oxidized
174 organics and ammonium, with the enhancement associated with oxidized organics being the
175 most pronounced.

176 A strong correlation between both the Nfs and relative peak areas (RPAs) of NOCs and
177 oxidized organics further demonstrates their close associations, as shown in Fig. 3.
178 Compared with the oxidized organics, the Nfs of ammonium-containing particles internally
179 mixed with NOCs varied within a ~~wider~~ broader range (~40-90%). However, there is still an

180 enhancement mixing of NOCs with ammonium. A positive correlation ($R^2 = 0.50, p < 0.01$)
181 is observed between the hourly detected number of NOCs and ammonium. It is worth noting
182 that a negative correlation ($R^2 = 0.55, p < 0.01$) is obtained between the hourly average RPAs
183 of NOCs and ammonium (Fig. 3).

184 Based on both the enhancement of NOCs and the high correlations with oxidized
185 organics and ammonium, it is hypothesized that interactions between oxidized organics and
186 ammonium contributed to the observed NOCs. ~~Actually, The~~ formation of NOCs from
187 ammonium and carbonyls has been confirmed in several laboratory studies (Sareen et al.,
188 2010; Shapiro et al., 2009; Noziere et al., 2009; Kampf et al., 2016; Galloway et al., 2009).
189 Secondary organic aerosols (SOA) produced from a large group of biogenic and
190 anthropogenic VOCs can be further aged by $\text{NH}_3/\text{NH}_4^+$ to generate NOCs (Nguyen et al.,
191 2012; Bones et al., 2010; Updyke et al., 2012; Liu et al., 2015; Huang et al., 2017). In a
192 chamber study, the formation of NOCs is enhanced in an NH_3 -rich environment (Chu et al.,
193 2016). While such chemical mechanisms might be ~~complex~~complicated, the initial steps
194 generally involve reactions forming imines and amines, which can further react with
195 carbonyl SOA compounds to form more complex products (e.g., oligomers/BrC) (Laskin et
196 al., 2015).

197 To verify this hypothesis, multiple linear regression analysis is performed to test how
198 well the RPAs of NOCs could be predicted by the oxidized organics and ammonium. As
199 expected, there is a close association ($R^2 = 0.71, p < 0.01$) between the predicted RPAs and
200 the observed values of NOCs (Fig. 4), which supports this hypothesis. ~~An obvious~~ noticeable

201 improvement in R^2 implies that a model that uses both oxidized organics and ammonium to
202 predict RPAs of NOCs is substantially better than one that uses only one predictor (either
203 oxidized organics or ammonium in Fig. 3). The result indicates that interactions involving
204 oxidized organics and ammonium could explain over half of the observed variations in
205 NOCs in the atmosphere of Guangzhou. A fraction of the unaccounted NOCs could be due
206 to primary emissions and other formation pathways. This hypothesis could also be supported
207 by ~~the~~a similar pattern of diurnal variation observed for NOCs and oxidized organics (Fig.
208 S5), although there is a slight lag for the NOCs. Such a diurnal pattern is similar to those
209 observed in Beijing and Uintah (Yuan et al., 2016; Zhang et al., 2015). Notably, such a
210 diurnal pattern of secondary NOCs is ~~effectively-adequately~~ modelled when the production
211 of NOCs via carbonyls and ammonium is included (Woo et al., 2013). In addition to possible
212 photo-bleaching (Zhao et al., 2015), the lower contribution of NOCs during the daytime may
213 be partly explained by the lower RH, as discussed in section 3.2.

214 Interestingly, the relationship between NOCs and ammonium is distinctly different from
215 the relationship between NOCs and oxidized organics (Fig. 3). This implies that the
216 controlling factors on the formation of NOCs from ammonium are different from oxidized
217 organics. On the one hand, the positive correlation between the detected numbers reflects
218 that the formation of NOCs does require the participant of $\text{NH}_3/\text{NH}_4^+$, consistent with the
219 enhancement of NOCs in ammonium-containing particles (Fig. 2) discussed above. On the
220 other hand, the negative correlation between the RPAs signifies that ~~particles with higher~~
221 ~~relative ammonium content may inhibit the formation of NOCs~~the formation of NOCs is

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222 most probably influenced by the relative amount of ammonium in individual particles. Such
223 influence could also be supported by our data, both from filter samples and individual
224 particle analysis. There is a negative correlation between concentrations of WSON and NH
225 $\frac{+}{4}$ for the filter samples (Fig. S6). It can be seen from Fig. S7 that lower RPAs of ammonium
226 correspond to higher Nfs of ammonium that internally mixed with NOCs. Such an inverse
227 correlation could also serve as evidence to explain the influence of the relative amount of
228 ammonium on the formation of NOCs. Consistently, there is a negative correlation between
229 concentrations of WSON and NH₄⁺ in filter samples (Fig. S6).

230 The influence of relative ammonium amount on the formation of NOCs. This is
231 supported by the inverse correlation between that Nfs of ammonium that internally mixed
232 with NOCs and the RPAs of ammonium (Fig. S7). This is also theoretically possible since
233 the formation of NOCs may be ~~influenced~~ enhanced by particle acidity (Miyazaki et al.,
234 2014; Aiona et al., 2017; Nguyen et al., 2012), which is substantially affected by the
235 abundance of ammonium. Consistently, higher relative acidity was observed for the
236 internally mixed ammonium and NOCs particles, compared to ammonium-containing
237 particles without NOCs (Fig. S6) and thus may influence the formation of NOCs (Fig. S7).

238 Particle acidity could also play a significant role in the gas-to-particle partitioning of
239 aldehydes (Herrmann et al., 2015; Liggio et al., 2005; Gen et al., 2018; De Haan et al., 2018;
240 Kroll et al., 2005), precursors for the formation of oxidized organics. ~~Consistently, higher~~
241 ~~relative acidity was observed for the internally mixed ammonium and NOCs particles,~~
242 ~~compared to ammonium-containing particles without NOCs (Fig. S6), and thus may~~

243 ~~influence the formation of NOCs (Fig. S7)~~. However, the higher relative acidity might also
244 be a result of NOCs formation. A model simulation shows that after including the chemistry
245 of SOA ageing with NH₃, an increase in aerosol acidity would be expected due to the
246 reduction in ammonium (Zhu et al., 2018). It is also noted that the particle acidity is roughly
247 estimated by the relative abundance of ammonium, nitrate, and sulfate in individual particles
248 (Denkenberger et al., 2007), and thus may not be representative of actual aerosol acidity or
249 pH (Guo et al., 2015; Hennigan et al., 2015; Murphy et al., 2017). In addition, ammonia in
250 ~~the~~ gas phase is also efficient at producing NOCs (Nguyen et al., 2012), which may play ~~a~~
251 ~~an intricate complex~~ role in the distribution of ammonium and NOCs in ~~the~~ particulate phase.
252 The formation of ammonium and NOCs would compete for ammonia, which may also
253 potentially result in the negative correlation between the RPAs of NOCs and ammonium.
254 Unfortunately, such a role remains unclear since the variations of ammonia were not
255 available in the present study.

256

257 **3.2 Factors contributing to the NOCs resolved by positive matrix factorization (PMF)** 258 **analysis**

259 Figure 5 presents the PMF factor profiles obtained from the PMF model analysis
260 (detailed information is provided in the SI) (Norris et al., 2009) and their diurnal variations.
261 Around 75% of NOCs could be well explained by two factors, with 33% of the PMF resolved
262 NOCs mainly associated with ammonium and carbonaceous ion peaks (ammonium factor),
263 while 59% were mainly associated with oxidized organics (oxidized organics factor). The

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

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

292

293 3.3 Seasonal variations in the observed NOCs

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

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

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

319

320 3.4 Influence of RH and NO_x

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

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

336 One may expect that NOCs ~~were-are~~ formed through the interactions between NOx and
337 oxidized organics in the gas phase, followed by condensation (Fry et al., 2014; Lehtipalo et
338 al., 2018). Similar to that observed for RH, while NOCs do not show a clear dependence on
339 NOx (Fig. 6c, $R^2 = 0.02-0.13$), the ratio of NOCs to the oxidized organics shows a clear
340 increasing trend towards higher NOx (Fig. 6d, $R^2 = 0.18, p < 0.01$). Low correlation
341 coefficients ($R^2 = 0.02-0.13$) between NOCs and NOx likely indicates limited contribution
342 of this pathways to the observed NOCs. We have also included an analysis on the
343 relationship between peak ratios of NOCs/oxidized organics and NOx. This indicates that
344 NOx may play a certain role in the conversion of oxidized organics to NOCs, and yet it
345 cannot be quantified in the present study. It is also noted that low correlation coefficients
346 between NOx and NOCs might not indicate a limited contribution of NOx to the formation
347 of NOCs. NOx affects the formation of NOCs in various ways (e.g., peroxy radical chemistry

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348 ~~in VOCs oxidation mechanisms and formation of nitrate radicals) {Xu, 2015~~
349 ~~#20234}{Zhang, 2018 #22855}, and thus may not linearly contribute to the formation of~~
350 ~~NOCs. Peak area ratios of NOCs/oxidized organics generally increases with increasing level~~
351 ~~of NOx (Fig. 6), but still with relatively weak correlation ($R^2=0.18, p<0.01$). An inclusion~~
352 ~~of both NOx and RH in the above linear regression model (NOCs versus the oxidized~~
353 ~~organics and ammonium) does not improve the prediction of NOCs ($R^2=0.71, p<0.01$).~~
354 ~~However, it is also noted that many factors (e.g., different removal processes and lifetimes~~
355 ~~of particles vs. gasses, primary vs. secondary species, etc.) could contribute to a lack of~~
356 ~~strong correlation even if NOx did contribute to NOC formation. (Xu et al., 2015)~~

357

358 3.5 Atmospheric implications and limitation

359 In this study₂ we showed that in an urban megacity area, secondary NOCs were
360 significantly contributed by the heterogeneous ageing of oxidized organics with $\text{NH}_3/\text{NH}_4^+$,
361 providing valuable insight into SOA aging mechanisms. In particular, the effects of NH_3/NH
362 $^+$ on SOA or BrC formation remain relatively poorly understood. In the PRD region, it has
363 been shown that oxygenated organic aerosols (OOA) account for more than 40% of the total
364 organic mass (He et al., 2011), with high concentrations of available gaseous carbonyls (Li
365 et al., 2014). Therefore, it is expected that over half of all water₂-soluble NOCs in this region
366 might link to secondary processing (Yu et al., 2017). Furthermore, secondary sources have
367 been found to contribute significantly to NOCs related BrC in Nanjing, China (Chen et al.,
368 2018). The results presented herein also suggest that the production of NOCs might be

369 ~~effectively~~adequately estimated by their correlation with secondary oxidized organics and
370 ammonium. The effectiveness of correlation-based estimations needs to be examined in
371 other regions before being generally applied in other environments. However, this approach
372 may provide valuable insights into investigations ~~into~~of NOCs using atmospheric
373 observations. In contrast, it has previously been reported that a positive correlation exists
374 between WSON and ammonium (Li et al., 2012), indicating similar anthropogenic sources.
375 This divergence could be mainly attributed to varying contributions of primary sources and
376 secondary processes to the observed NOCs. Possible future reductions in anthropogenic
377 emissions of ammonia may reduce particle NOCs. Understanding the complex interplay
378 between inorganic and organic nitrogen is an ~~important~~essential part of assessing ~~the~~ global
379 nitrogen cycling.

380 Moise et al. (2015) proposed that with high concentrations of reduced nitrogen
381 compounds, high photochemical activity, and frequent changes in humidity, BrC formed via
382 $\text{NH}_3/\text{NH}_4^+$ and SOA may become a dominant contributor to aerosol absorption, specifically
383 in agricultural and forested areas. However, this study suggests that even in typical urban
384 areas, BrC formation via $\text{NH}_3/\text{NH}_4^+$ and SOA should not be neglected. In particular, SOA
385 was found to account for 44 – 71% of the organic mass in megacities across China (Huang
386 et al., 2014), with NH_3 concentrations in urban areas comparable with those from
387 agricultural sites and 2- or 3-fold those of forested areas in China (Pan et al., 2018).
388 Additionally, the acidic nature of particles in these regions would also be ~~also~~-favorable for
389 the formation of NOCs (Guo et al., 2017; Jia et al., 2018). Considering the formation of

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390 NOCs from the uptake of NH₃ onto SOA particles, Zhu et al. (2018) suggested that this
391 mechanism could have a significant impact on the atmospheric concentrations of NH₃/NH₄⁺
392 and NO₃.

393

394 5 Conclusions

395 This study investigated the processes contributing to the seasonal formation of NOCs,
396 involving ammonium and oxidized organics in urban Guangzhou, using ~~single-single-~~
397 particle mass spectrometry. This is the first study to provide direct field observation results
398 to confirm that the variation of NOCs correlate well and are strongly enhanced internal
399 mixing with secondary oxidized organics. These findings highlight the possible formation
400 pathway of NOCs through the ageing of secondary oxidized organics by NH₃/NH₄⁺ in
401 ambient urban environments. A clear pattern of seasonal variation in NOCs was observed,
402 with higher relative contributions in summer and autumn as compared to spring and winter.
403 This seasonal variation was well predicted by multiple linear regression model analysis,
404 using the relative abundance of oxidized organics and ammonium as model inputs. More
405 than 50% of NOCs could be explained by the interaction between oxidized organics and
406 ammonium. The production of NOCs through such processes ~~were-was~~ facilitated by
407 increased humidity and NO_x. These results extend our understanding of the mixing state and
408 atmospheric processing of particulate NOCs, as well as having ~~important-substantial~~
409 implications for the accuracy of models predicting the formation, fate, and impacts of NOCs
410 in the atmosphere.

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411

412 **Author contribution**

413 GHZ and XHB designed the research (with input from WS, LL, ZYW, DHC, MJT, XMW
414 and GYS), analyzed the data, and wrote the manuscript. XFL, YZF, and QHL conducted air
415 sampling work and laboratory experiments under the guidance of GHZ, XHB and XMW.

416 All authors contributed to the refinement of the submitted manuscript.

417

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784

785 **Figure captions**

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

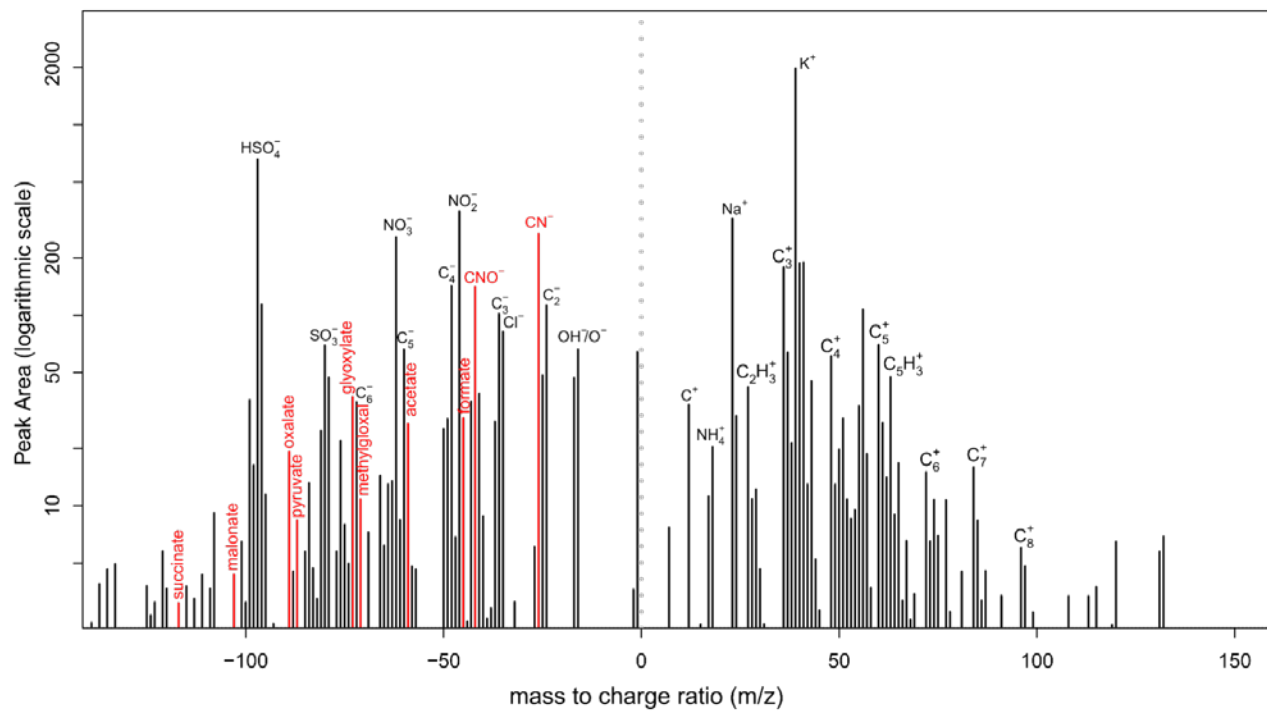
788 Figure 2. The variation in hourly mean Nfs of the oxidized organics and
789 ammonium that internally mixed with NOCs. Box and whisker plot shows lower,
790 median, and upper lines, denoting the 25th, 50th, and 75th percentiles, respectively; the
791 lower and upper edges denote the 10th and 90th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

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

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

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

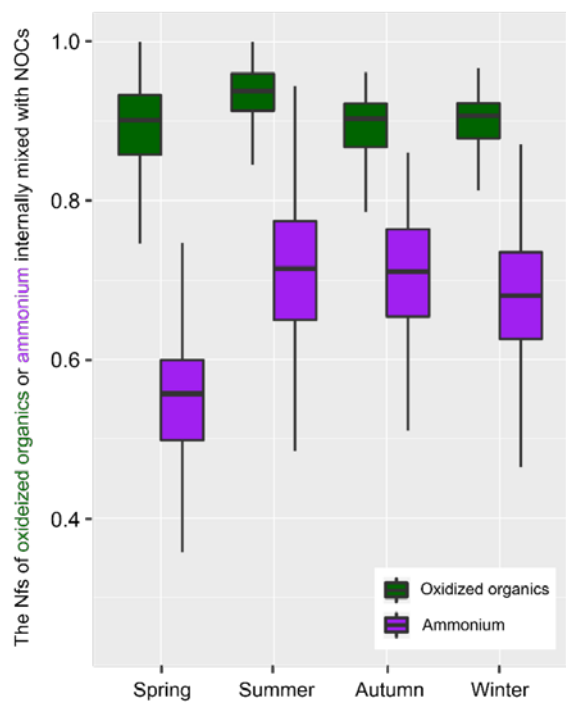
801 Figure 6. The dependence of NOCs and the ratio of NOCs to the oxidized organics
802 on RH.



803

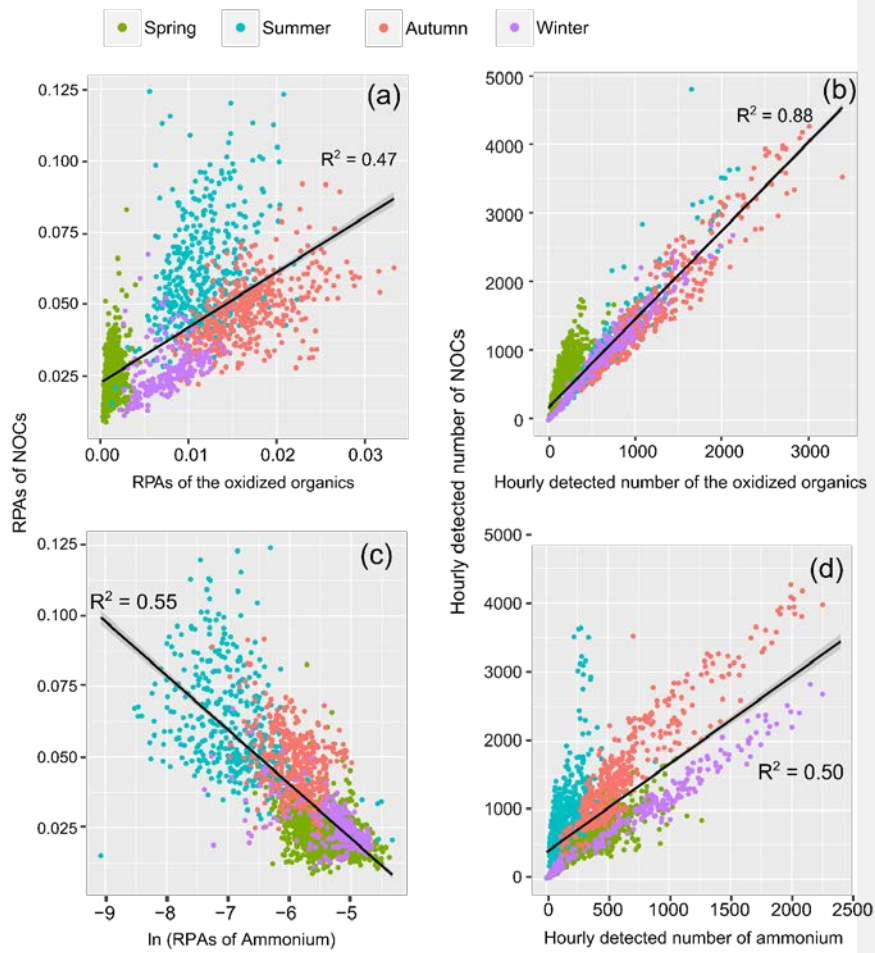
804

Fig. 1.



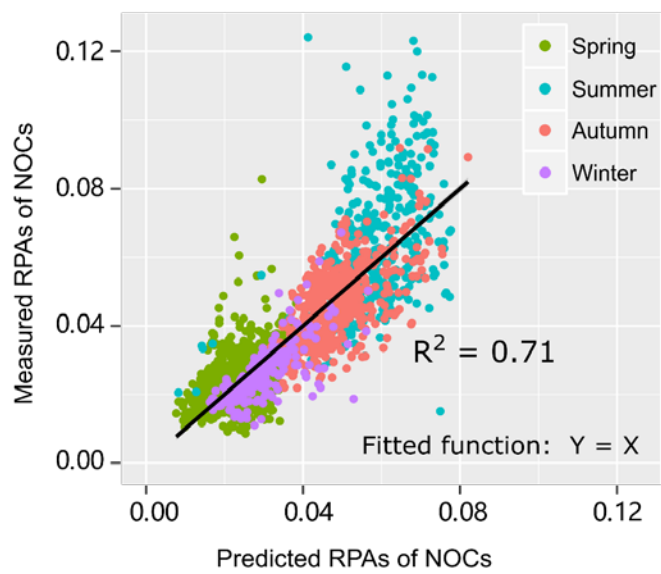
805

806 Fig. 2.



807

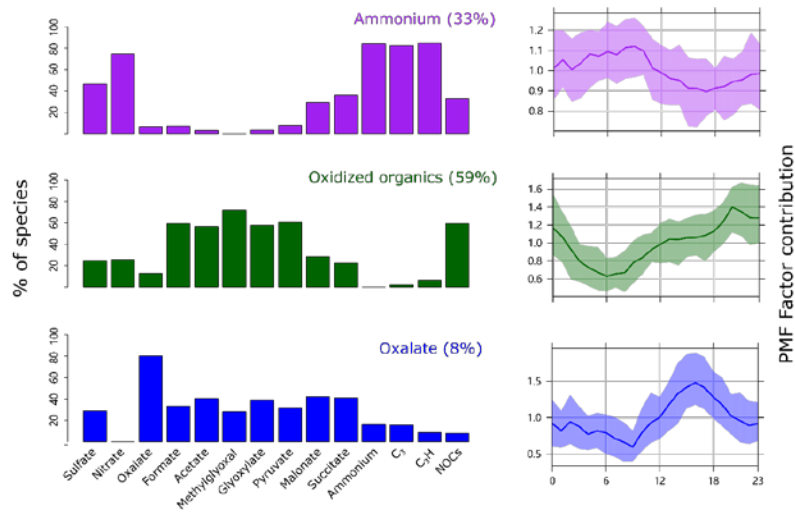
808 Fig. 3.



809

810 **Fig. 4.**

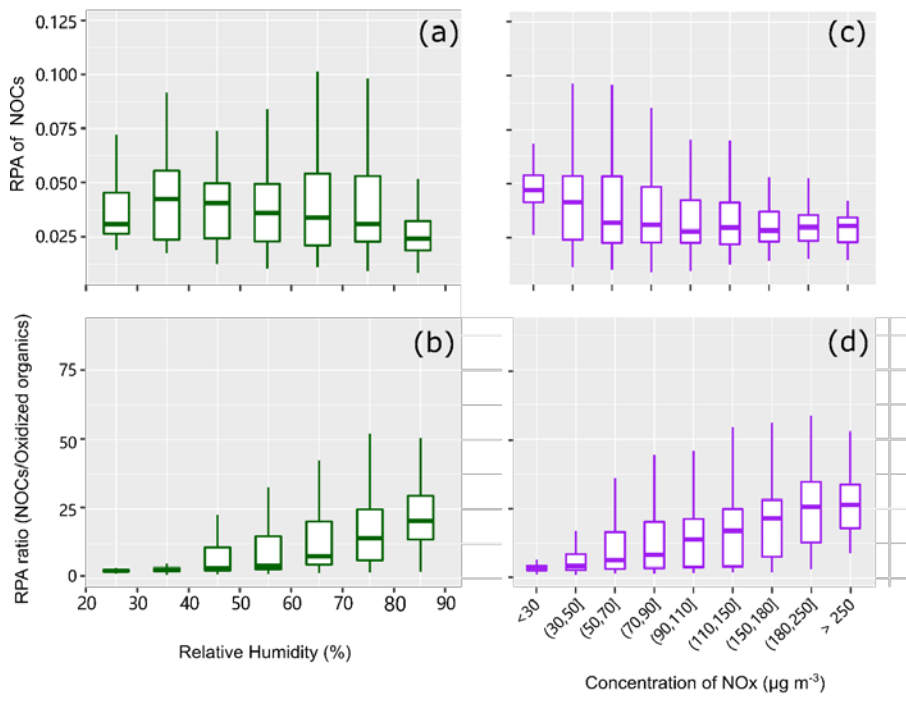
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812

813

Fig. 5.



814

815 **Fig. 6.**