Response to comments 1#

Review of “High secondary formation of nitrogen-containing organics (NOCs) and its possible link to oxidized organics and ammonium” by G. Zhang et al.

General Comments:

This study presents the results of single-particle measurements in Guangzhou, China. The focus is on nitrogen-containing organic compounds (NOC) and the role of ammonium in NOC formation. The highly time resolved measurements span four seasons, and thus could offer new insight into NOC chemistry. While the data set is unique and the topic is certainly appropriate for Atmospheric Chemistry and Physics, there are quite a few major issues with the study – including analysis methods, assumptions, data interpretations, and conclusions – that prevent me from recommending it for publication at this time. It is possible that these issues could be addressed with a major revision, but not guaranteed. My specific concerns are addressed below.

We would like to thank the reviewer for his/her useful comments and recommendations to improve the manuscript. We have addressed the specific comments in the sections below and made the appropriate revisions to the manuscript. Reviewer comments are in black text followed by our response in blue text.

Specific Comments:

1. The authors come to the conclusion that NOC formation during their study is not likely from gas-phase reactions, but is predominantly from heterogeneous/particle-phase reactions. Their logic for this argument is quite confusing. I do not believe this conclusion is at all supported by the data presented in the manuscript.

Thanks for the constructive comment. The reviewer thought our hypothesis that NOCs formation from oxidized organics and ammonium was confusing, which is largely because the supporting evidence was not separately discussed and emphasized. In the revised manuscript, therefore, we reorganized the text and emphasized the evidence to make the argument more clear. Based on both the enhancement of NOCs and the high correlations with oxidized organics and ammonium, a hypothesis is put forward: interactions between oxidized organics and ammonium contribute to the observed NOCs. To support such hypothesis, further evidence such as diurnal variations of NOCs, filter measurements and multiple linear regression analysis are provided and discussed. Supporting evidence from previous laboratory and modeling studies is also discussed. Please refer to section 3.1 for more details.

2. Similarly, I think the explanations for the role of NOx and NH3 in particle NOC formation are extremely muddled. For NH3, a positive correlation is observed between the number fraction of particles with NH4 + 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. Further, the manuscript mostly discounts the negative correlation in the relative peak areas, instead assuming that NH3 drives (or is prominently involved in) NOC formation. NOx is completely ruled out as a contributor to NOC formation on the basis of poor (or no) correlations between NOC and NOx. 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 NOx did contribute to NOC formation. As the data are currently presented and explained, it is completely unclear how NH3 or NOx play a role in NOC formation in the present study, although such analyses should be possible with their data set.

Thanks for the comment. We also think that it is a surprising and interesting results for the contradictory correlation between NOCs and ammonium. We have highlighted it as “Interestingly, the relationship between NOCs and ammonium was distinctly different from the relationship between NOCs and oxidized organics.” and “A positive correlation (R^2 = 0.50, $p < 0.01$) is observed between the hourly detected number of NOCs and ammonium. It is worth noting that a negative correlation (R^2 = 0.55, $p < 0.01$) is obtained between the hourly average RPAs of NOCs and ammonium (Fig. 3)." in Lines 176-179 and 201-202.

To make the statement clearer, we highlighted the reasoning in two parts in the revised manuscript as "Interestingly, the relationship between NOCs and ammonium is distinctly different from the relationship between NOCs and oxidized organics (Fig. 3). This implies that the controlling factors on the formation of NOCs from ammonium are different from oxidized organics. On one hand, the positive correlation between the detected numbers reflects that the formation of NOCs does require the participant of NH_3/NH_4^+ , consistent with the enhancement of NOCs in ammonium-containing particles discussed above. On the other hand, the negative correlation between the RPAs signifies that particles with higher relative ammonium content may inhibit the formation of NOCs.". Please refer to Lines 209–216.

For the role of NOx on the formation of NOCs, we agree with the comment that 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 NOx did contribute to NOC formation. In the Lines 319-328 of the revised manuscript, we have added this probability in our discussion, as "Low correlation coefficients (R^2 = 0.02–0.13) between NOCs and NOx likely indicates limited contribution of this pathways to the observed NOCs. We have also included an analysis on the relationship between peak ratios of NOCs/oxidized organics and NOx. Peak area ratios of NOCs/oxidized organics generally increases with increasing level of NOx (Fig. 6), but still with relatively weak correlation (R^2 = 0.18, $p < 0.01$). An inclusion of both NOx and RH in the above linear regression model (NOCs versus the oxidized organics and ammonium) does not improve the prediction of NOCs (R^2 = 0.71, $p < 0.01$). However, it is also noted that many factors (e.g., different removal processes and lifetimes of particles vs. gasses, primary vs. secondary species, etc.) could contribute to a lack of strong correlation even if NOx did contribute to NOC formation.”.

3. The assumptions and discussion related to particle acidity (lines 307 – 337, Figure 7) are not correct. Recent studies have shown that ratios of aerosol inorganics (including variations involving NH4-SO4-NO3) are not suitable proxies for particle acidity (Guo et al., 2015; Hennigan et al., 2015; Murphy et al., 2017). Also, the discussion of acid-catalyzed SOA (lines 375-381) is not correct, so the implications of the present study are misstated.

Thanks for pointing out the deficiency. We agree with the comment that ratios of aerosol inorganics are not suitable proxies for particle acidity. Therefore, we have shorten our discussion on this issue, and included these references to show that the estimated particle acidity may not be representative of actual aerosol acidity or pH. In the revised manuscript, we only intend to show that the variation of ammonium may affect the particle acidity in the following sentence: “…particles with higher relative ammonium content may inhibit the formation of NOCs. This is supported by the inverse correlation between that Nfs of ammonium that internally mixed with NOCs and the RPAs of ammonium (Fig. S7). This is also theoretically possible since the formation of NOCs may be influenced by particle acidity (Miyazaki et al., 2014; Aiona et al., 2017; Nguyen et al., 2012), which is substantially affected by the abundance of ammonium. Particle acidity could also 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), precursors for the formation of oxidized organics. Consistently, higher relative acidity was observed for the internally mixed ammonium and NOCs particles, compared to ammonium-containing particles without NOCs (Fig. S6), and thus may influence the formation of NOCs (Fig. S7). However, the higher relative acidity might also be a result of NOCs formation. A model simulation shows that after including the chemistry of SOA ageing with NH_3, an increase in aerosol acidity would be expected due to the reduction in ammonium

(Zhu et al., 2018). It is also noted that the particle acidity is roughly estimated by the relative abundance of ammonium, nitrate, and sulfate in individual particles (Denkenberger et al., 2007), and thus may not be representative of actual aerosol acidity or pH (Guo et al., 2015; Hennigan et al., 2015; Murphy et al., 2017).", please refer to Line 217-233.

4. Finally, the application, interpretation, and discussion of PMF and multiple linear regression methods need substantial revision. The explanation of the PMF approach is quite confusing, and as it is written, does not add anything substantive beyond the general correlations presented before it. The multiple linear regression also does not support any of the stated conclusions, beyond what was already presented for the individual correlations to NH4 + and oxygenated organics. The discussion of "modelled NOCs" (e.g., lines 291, 374, Fig. 4) is misleading, especially compared to how this is typically used in atmospheric studies.

Thanks for the comment. We think the reviewer's confusion about the explanation of PMF and linear regression analysis is largely because the additional information provided by PMF and linear regression analysis was not emphasized in the original manuscript. In the revised manuscript (section 3.2), we have highlighted the additional information provided by the PMF approach in a new section 3.2: Three PMF factors were resolved to explain the formation of NOCs. Around 75% of NOCs could be well explained by two factors, with 33% of the PMF resolved NOCs mainly associated with ammonium and carbonaceous ion peaks (ammonium factor), while 59% were mainly associated with oxidized organics (oxidized organics factor). The explained fraction of NOCs by the ammonium and oxidized organic factors is consistent with the linear regression analysis. In addition, PMF analysis provided information on the factor contribution and diurnal variations, which may help explain the seasonal variations and processes of NOCs. Profiles and their diurnal variations of these factors (Fig. 5) suggest that there were two competitive pathways for the evolution of these oxidized organics. Some oxidized organics formed from photochemical activities were further oxidized to oxalate, resulting in a diurnal pattern of variation with concentration peaks during the afternoon (Fig. 5), while others interact with NH_3/NH_4^+ to form NOCs, peaking during the nighttime.

The multiple linear regression applied herein is to show how well the observed NOCs could be reconstructed by the observed oxidized organics and ammonium. As expected, there is a close association ($R^2 = 0.71$, $p < 0.01$) between the predicted RPAs and the observed values of NOCs (Fig. 4), which supports this hypothesis. An obvious improvement in R^2 implies that a model that uses both oxidized organics and ammonium to predict RPAs of NOCs is substantially better than one that uses only one predictor (either oxidized organics or ammonium in Fig. 3). We understand that the use of "modelled NOCs" for the regression analysis may be misleading. In the revised manuscript, we revised the "modelled NOCs" to "PMF resolved NOCs" to avoid the misunderstanding.

Technical Corrections:

The above issues are substantial enough that any technical corrections can be addressed on review of the revised manuscript.

Thanks for the comment. We have carefully examined possible technical errors, including those raised by Refree 2#.

References:

Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite Jr., J. R., Carlton, A. G., Lee, S.-H., Bergin, M. H., Ng, N. L., Nenes, A., and Weber, R. J.: Fine-particle water and pH in the southeastern United States, Atmos. Chem. Phys., 15, 5211-5228, https://doi.org/10.5194/acp-15- 5211-2015, 2015.

Hennigan, C. J., Izumi, J., Sullivan, A. P., Weber, R. J., and Nenes, A.: A critical evaluation of proxy methods used to estimate the acidity of atmospheric particles, Atmos. Chem. Phys., 15, 2775–2790, https://doi.org/10.5194/acp-15-2775-2015, 2015.

Murphy, J. G., Gregoire, P. K., Tevlin, A. G., Wentworth, G. R., Ellis, R. A., Markovic, M. Z., and VandenBoer, T. C.: Observational constraints on particle acidity using measurements and modelling of particles and gases, Faraday Discuss., 200, 379-395, https://doi.org/10.1039/c7fd00086c, 2017.

Response to comments 2#

This paper analyzed single particle aerosol mass spectrometer (SPAMS) data for ambient aerosols and found there are relations between CN-/CNO- ion intensities and some other species, such as oxidized organic ions and ammonium. It is an interesting report. But there are some concerns which need to be addressed before publication.

We would like to thank the reviewer for his/her useful comments and recommendations to improve the manuscript. We have addressed the specific comments in the sections below and made the appropriate revisions to the manuscript. Reviewer comments are in black text followed by our response in blue text.

One of the major problems is that this paper attribute oxidized organics to secondary formation. However, it may not be the case. Biomass burning or coal combustion can also produce oxidized organics including large amounts of NOCs. Actually, in many previous single particle mass spectrometry studies, CN- and CNO- were taken as ion markers for combustion sources. The authors need to provide more evidences either to rule out the possibility of primary oxygenated organics and primary NOCs or to distinguish the secondary organics from the primary ones.

Thanks for the suggestion. In our manuscript, oxidized organics, represented as formate at m/z -45 $[HCO_2]^-$, acetate at m/z -59 $[CH_3CO_2]^-$, methylglyoxal at m/z -71 $[C_3H_3O_2]^-$, glyoxylate at m/z -73 $[C_2HO_3]^-$, pyruvate at m/z -87 $[C_3H_3O_3]^-$, malonate at m/z -103 $[C_3H_3O_4]^-$ and succinate at m/z -117 $[C_4H_5O_4]^-$, which are generally regarded as secondary compositions (Zhang et al., 2017; Zauscher et al., 2013; Lee et al., 2003). To make it clear, we revised the original description to "These oxidized organics showed their pronounced diurnal trends with afternoon maximum, and were highly correlated ($r = 0.72 - 0.94$, $p < 0.01$) with each other. Therefore, they were primarily attributed to the secondary oxidized organics from photochemical oxidation products of various volatile organic compounds (VOCs) (Paulot et al., 2011; Zhao et al., 2012; Ho et al., 2011), and the details can be found in our previous publication (Zhang et al., 2019).”. Please refer to Lines 136-141 of the revised manuscript.

We strongly agree with the reviewer that biomass burning or coal combustion can also produce oxidized organics and NOCs. As discussed above, these oxidized organics most probably formed from secondary process. In the original manuscript, we provided evidence for the secondary formation of NOCs. However, the primary NOCs cannot be ruled out. In the revised manuscript (line 271-274), we have included the following sentence to mention this: “The unexplained NOCs (~25%) might be linked to the primary emissions, such as biomass burning (Desyaterik et al., 2013). It could be partly supported by the presence of potassium and various carbon ion clusters ($C_n^{+/-}$, n = 1, 2, 3, …) in the mass spectrum of NOCs-containing particles (Fig. 1).”.

Another major concern is that how well CN-/CNO- ions can represent total NOCs. Can they represent 25%, 50% or 75% of total NOCs? The paper needs to provide more discussion on this issue.

Thanks for the comment. We understand that it would be better if the exact fraction of NOCs represented by CN^-/CNO^- can be obtained. Unfortunately, how well $[CN]^-$ / $[CNO]^-$ ions could represent NOCs cannot be quantified, although they were the most commonly reported NOCs peaks by single particle mass spectrometry (Silva and Prather, 2000; Zawadowicz et al., 2017; Pagels et al., 2013). In the present study, $[CN]^-$ / $[CNO]^-$ ions are among the major peaks detected by the SPAMS (Fig. 1). A rough estimate from the peak area ratio of $[CN]^-$ / $[CNO]^-$ ions and the most likely NOCs fragments (i.e., various amines, and an entire series of nitrogen-containing cluster ions C_nN^-, n = 1, 2, 3, …) (Silva and Prather, 2000) shows that $[CN]^-$ / $[CNO]^-$ ions may represent more than 90% of these NOCs peaks. It has been added in section 2.2.

Pagels, J., Dutcher, D. D., Stolzenburg, M. R., McMurry, P. H., Galli, M. E., and Gross, D. S.: Fine-particle emissions from solid biofuel combustion studied with single-particle mass spectrometry: Identification of markers for organics, soot, and ash components, J. Geophys. Res.-Atmos., 118, 859-870, doi:10.1029/2012jd018389, 2013.

Silva, P. J., and Prather, K. A.: Interpretation of mass spectra from organic compounds in aerosol time-of-flight mass spectrometry, Anal. Chem., 72, 3553-3562, 2000.

Zawadowicz, M. A., Froyd, K. D., Murphy, D. M., and Cziczo, D. J.: Improved identification of primary biological aerosol particles using single-particle mass spectrometry, Atmos. Chem. Phys., 17, 7193-7212, doi:10.5194/acp-17-7193-2017, 2017.

The third concern is that ammonium sulfate is very difficult to be ionized under 266 nm UV laser. Thus, it is likely that some mass spectra of particles do not contain NH4+ peak but these particles may still contain ammonium sulfate. The authors also need to provide some discussions on this possibility.

Thanks for the comment. It is true that pure ammonium sulfate is very difficult to be ionized under 266 nm UV laser used in our study. In the present study, this may not be the case since we focused on the NOCs-containing particles, in which the Nfs of ammonium varied in a wide range (~40-90%) (Fig. 2). Such possibility has been added in Lines 27-28 of the revised *Supplements*.

Specific comments:

Line 54: how much is “large”? It would be always better to provide a number or range.

Thanks for the comment. We have revised the sentence to “Nitrogen-containing organic compounds (NOCs) substantially contribute to the pool of BrC”. And we have also stated that “The particulate organic nitrogen accounts for a large fraction of total airborne nitrogen (~30%)”. Please refer to Lines 57-61 of the revised manuscript.

Line 149: “so on” is a bit informal. I would change “so on” to “so forth”

It has been revised as suggested.

Line 220: How do you come up with this statement: “: : :explain over half of the observed variations in NOCs in the atmosphere of Guangzhou.”? Please elaborate and provide more details.

Thanks for the comment. Multiple linear regression analysis was performed to predict the RPAs of NOCs generated from oxidized organics and ammonium, showing a close association ($R^2 = 0.71$, $p < 0.01$) between the predicted RPAs and the observed values of NOCs (Fig. 4). Based on this result, we infer that over half of the observed variations of NOCs can be explained by the interactions involving oxidized organics and ammonium. This is also supported by the PMF analysis provided in Fig. 5. The sentence has been revised to “The result indicates that interactions involving oxidized organics and ammonium could explain over half of the observed variations in NOCs in the atmosphere of Guangzhou.”, and the discussion can be found in Lines 192-200 of the revised manuscript.

Line 224: Please report if the PMF analysis reaches convergence or not. How much is the error of the PMF modelling in the paper?

Thanks for the comment. Such information has been added in the *Supplements*. It can be found in section “Positive matrix factorization analysis”, as “PMF solutions with 2−5 factors were tested and showed convergence results. The relevant Q values and Q_{robust} / Q_{theory} for these solutions are shown in Table S3.”, and “An uncertainty of 50% in RPA was used due to the shot-to-shot fluctuations of desorption laser and complex particle matrix (Zauscher et al., 2013).”

Line 387: Check English

Thanks for the comment. We have carefully checked and corrected the syntax errors.

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

Guohua Zhang[1], Xiufeng Lian[1,2], Yuzhen Fu[1,2], Qinhao Lin[1], Lei Li[3], Wei Song[1], Zhanyong Wang[4], Mingjin Tang[1], Duohong Chen[5], Xinhui Bi[1,*], Xinming Wang[1], Guoying Sheng[1]

[1] State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Resources Utilization and Protection, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China

[2] University of Chinese Academy of Sciences, Beijing 100039, PR China

[3] Institute of Mass Spectrometer and Atmospheric Environment, Jinan University, Guangzhou 510632, PR China

[4] School of Intelligent Systems Engineering, Sun Yat-sen University, Shenzhen 518107, PR China

[5] State Environmental Protection Key Laboratory of Regional Air Quality Monitoring, Guangdong Environmental Monitoring Center, Guangzhou 510308, PR China

Correspondence to: Xinhui Bi (bixh@gig.ac.cn)

Highlights

- Nitrogen-containing organics (NOCs) were highly internally mixed with photochemically produced secondary oxidized organics
- ~~More than 50% of~~ NOCs ~~were~~ could be well predicted by ~~secondary formation from~~ the variations of these~~–~~ oxidized organics and ammonium
- Higher relative humidity and ~~particle acidity~~ NOx may facilitate~~d~~ the ~~formation~~ conversion of these oxidized organics to NOCs

Abstract

Nitrogen-containing organic compounds (NOCs) substantially contribute to light absorbing organic aerosols, although the atmospheric processes responsible for the secondary formation of these compounds are poorly understood. In this study, seasonal atmospheric processing of NOCs were investigated by single particle mass spectrometry in urban Guangzhou from 2013-2014. The relative abundance of NOCs is found to be strongly enhanced ~~by~~ when internal mixed~~ing~~ with the photochemically produced secondary oxidized organics (~~such as~~i.e., formate, acetate, pyruvate, methylglyoxal, glyoxylate, oxalate, malonate and succinate) and ~~. Furthermore, the co-occurrence of NOCs with~~ ammonium ~~was also observed~~. In addition, both the hourly detected particle number and relative abundance of NOCs are highly correlated with those of secondary oxidized organics and ammonium. It is therefore hypothesized that secondary formation of NOCs most likely links to the oxidized organics and ammonium. Results from both multiple linear regression analysis and positive matrix factorization analysis further show that the relative abundance of NOCs could be well predicted ($R^2 > 0.7$, $p < 0.01$) by the oxidized organics and ammonium. Interestingly, the relative abundance of NOCs is inversely correlated with ammonium, ~~while~~ whereas their number fractions are positively correlated. This result suggests~~s~~ that although the formation of NOCs does require the involvement of NH_3/NH_4^+, the relative amount of ammonium may have a negative effect~~does involvement NH_3/NH_4^+~~. ~~Multiple linear regression analysis and positive matrix factorization analysis were performed to predict the relative abundance of NOCs generated from oxidized organics and ammonium.~~The conversion of oxidized organics to

NOCs is likely facilitated by higher ~~Both results showed close associations ($R^2 > 0.7$, $p < 0.01$) between the predicted NOCs and the observed values. Increased~~ humidity and ~~higher particle acidity~~NOx~~ may promote the production of NOCs~~. Due to the relatively high ~~contribution of~~ oxidized organics and NH_3/NH_4^+, the relative contributions of NOCs in summer and autumn ~~is~~were higher than ~~that~~ those in spring and winter. To the best of our knowledge, this is the first direct field observation study reporting a close association between NOCs and both oxidized organics and ammonium. These findings have substantial implications for the role of ammonium in the atmosphere, particularly in models that predict the evolution and deposition of NOCs.

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

1 Introduction

Organic aerosols that strongly absorb solar radiation are referred to as brown carbon (BrC), capable of a comparable level of light absorption in the spectral range of near-ultraviolet (UV) light as black carbon (Andreae and Gelencser, 2006; Feng et al., 2013; Yan et al., 2018). Nitrogen-containing organic compounds (NOCs) substantially ~~represent a large and complicate fraction of atmospheric aerosols{Nehir, 2018 #21993;Zhang, 2012 #9722;Cape, 2012 #22004}, significantly~~ contribute~~ting~~ to the pool of BrC (Feng et al., 2013; Mohr et al., 2013; Li et al., 2019), and ~~. Furthermore, NOCs~~ have a major effect on atmospheric chemistry, human health and climate forcing (Noziere et al., 2015; Kanakidou et al., 2005; Shrivastava et al., 2017; De Gouw and Jimenez, 2009). The particulate organic nitrogen ~~component of NOCs~~ accounts for a large fraction of total airborne nitrogen (~30%), although the proportion exhibits a high variability temporally and spatially, and therefore has an influence on both regional and global N deposition (Neff et al., 2002; Shi et al., 2010; Cape et al., 2011). However, the sources, evolution and optical properties of NOCs remain unclear and contribute significantly to uncertainties in the estimation of their impacts on the environment and climate (Laskin et al., 2015; Feng et al., 2013).

NOCs are ubiquitous components of atmospheric aerosols, cloud water and rainwater (Altieri et al., 2009; Desyaterik et al., 2013; Laskin et al., 2015), spanning a wide range of molecular weights, structures and light absorption properties (Lin et al., 2016). Emissions of primary NOCs have been attributed to biomass burning, coal combustion, vehicle emissions, biogenic production and soil dust (Laskin et al., 2009; Desyaterik et al., 2013; Sun et al., 2017; Mace et al., 2003; Rastogi et al., 2011; Wang et al., 2017). A ~~G~~growing body of evidence from laboratory studies suggests that secondary NOCs may be produced in gas phase, aerosol, and clouds. Maillard reactions involving mixtures of atmospheric aldehydes (e.g., methylglyoxal/glyoxal) and ammonium/amines are of particular interests (e.g., Hawkins et al., 2016; De Haan et al., 2017; De Haan et al., 2011). ~~Similarly, a~~A significant portion of NOCs may also be derived from the heterogeneous ageing of secondary organic aerosol (SOA) with NH_3 / NH_4^+ (Liu et al., 2015; Laskin et al., 2015). Mang et al. (2008) proposed that even trace levels of ammonia may be sufficient to form NOCs via this pathway. In addition, gas phase formation of NOCs through interaction between volatile organic hydrocarbons and NO_x and other oxidations, followed by condensation may ~~also~~ have potential contribution (Fry et al., 2014; Stefenelli et al., 2019; Lehtipalo et al., 2018).

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

2 Methods

2.1 Field measurements

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

2.2 SPAMS data analysis

Fragments of NOCs were identified according to detection of ion peaks at m/z -26 [CN]$^-$ or -42 [CNO]$^-$, generally due to the presence of C-N bonds (Silva and Prather, 2000; Zawadowicz et al., 2017; Pagels et al., 2013). Laboratory produced C-N bonds compounds from bulk solution-phase reactions between the representative oxidized organics (i.e., methylglyoxal) and ammonium sulfate was used to confirm the generation of ion peaks at m/z -26 [CN]$^-$ and/or -42 [CNO]$^-$ using SPAMS (Fig. S1). Thus, the NOCs herein may refer to complex nitrated organics such as organic nitrates, nitro-aromatics, nitrogen heterocycles and polyphenols. Unfortunately, how well [CN]$^-$/ [CNO]$^-$ ions could represent NOCs cannot be quantified, although they were the most commonly reported NOCs peaks by single particle mass spectrometry (Silva and Prather, 2000; Zawadowicz et al., 2017; Pagels et al., 2013). In the present study, [CN]$^-$/ [CNO]$^-$ ions are among the major peaks detected by the SPAMS (Fig. 1). A rough estimate from the peak area ratio of [CN]$^-$/ [CNO]$^-$ ions and the most likely NOCs fragments (i.e., various amines, and an entire series of nitrogen-containing cluster ions C_nN^-, n = 1, 2, 3, …) (Silva and Prather, 2000) shows that [CN]$^-$/ [CNO]$^-$ ions may represent more than 90% of these NOCs peaks. The number fractions (Nfs) of particles that contained NOCs ranged from 56-59% across all four seasons (Table S1). The number of detected NOCs-containing particles distributing along their vacuum aerodynamic diameter (d_{va}) is shown in Fig. S2. Most of the detected NOC-containing particles had a d_{va} in a range of 300-1200 nm.

A representative mass spectrum for NOCs-containing particles is shown in Fig. 1. Dominant peaks in the mass spectrum were 39 $[K]^+$, 23 $[Na]^+$, nitrate (-62 $[NO_3]^-$ or -46 $[NO_2]^-$), sulfate (-97 $[HSO_4]^-$), organics (27 $[C_2H_3]^+$, 63 $[C_5H_3]^+$, -42 $[CNO]^-$, -26 $[CN]^-$), ammonium (18 $[NH_4]^+$) and carbon ion clusters ($C_n^{+/-}$, n = 1, 2, 3,…). NOCs-containing particles were internally mixed with various oxidized organics, represented as formate at m/z -45 $[HCO_2]^-$, acetate at m/z -59 $[CH_3CO_2]^-$, methylglyoxal at m/z -71 $[C_3H_3O_2]^-$, glyoxylate at m/z -73 $[C_2HO_3]^-$, pyruvate at m/z -87 $[C_3H_3O_3]^-$, malonate at m/z -103 $[C_3H_3O_4]^-$ and succinate at m/z -117 $[C_4H_5O_4]^-$ (Zhang et al., 2017; Zauscher et al., 2013; Lee et al., 2003). These oxidized organics showed their pronounced diurnal trends with afternoon maximum, and were highly correlated (r = 0.72 - 0.94, p < 0.01) with each other. Therefore, they were primarily attributed to ~~The contribution of these ion peaks to the formation of~~ secondary oxidized organics from photochemical oxidation products of various volatile organic compounds (VOCs) (Paulot et al., 2011; Zhao et al., 2012; Ho et al., 2011), and the details can be found in our previous publication ~~has been previously confirmed based on their pronounced diurnal trends, with maximum concentrations observed in the afternoon~~ (Zhang et al., 2019). ~~Furthermore, these oxidized organics have been reported to be highly correlated (r = 0.72 - 0.94,~~ ~~p < 0.01) with each other (Zhang et al., 2019), consistent with the assumption~~

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that they are~~ photochemical oxidation products of various volatile organic compounds (VOCs) (Paulot et al., 2011; Zhao et al., 2012; Ho et al., 2011).~~ More information on the seasonal variation range of the Nfs of oxidized organics, ammonium and NOCs is presented in Fig. S3.

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

3 Results and Discussion

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

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

A strong correlation between both the Nfs and relative peak areas (RPAs) of NOCs and oxidized organics further demonstrates ~~a~~ their close associations~~ between these factors~~, as shown in Fig. 3. Compared with the ~~variation in~~ oxidized organics, the Nfs of ammonium-containing particles internally mixed with NOCs varied within a wider range (~40-90%). However, there ~~was~~ is still an enhancement mixing of NOCs with ammonium. ~~In addition,~~ ~~a~~A positive correlation (R^2 = 0.50, $p < 0.01$) is observed between the hourly detected number of NOCs and ammonium. ~~In contrast,~~It is worth noting that a negative correlation (R^2 = 0.55, $p < 0.01$) is obtained between the hourly average RPAs of NOCs and ammonium (Fig. 3). ~~Interestingly, the relationship between NOCs and ammonium was distinctly different from the relationship between NOCs and oxidized organics. A positive correlation (R^2 = 0.50, p < 0.01) was observed between the hourly detected number of NOCs and ammonium. In contrast, a negative correlation (R^2 = 0.55, p < 0.01) was observed between the hourly average relative peak areas (RPAs) of NOCs and ammonium (Fig. 3).~~

Based on both the enhancement of NOCs and the high correlations with oxidized organics and ammonium, it is hypothesized that interactions between oxidized organics and ammonium contributed to the observed NOCs~~the dominant association between oxidized organics and NOCs (Fig. 2) indicates that NOCs may be formed from the processing of secondary oxidized organics in particle phase, rather than gas phase reactions followed by condensation~~. Actually, formation of NOCs from ammonium and carbonyls has been confirmed in several laboratory studies (Sareen et al., 2010; Shapiro et al., 2009; Noziere et al., 2009; Kampf et al., 2016; Galloway et al., 2009). Secondary organic aerosols (SOA) produced from a large group of biogenic and anthropogenic VOCs can be further aged by NH_3/NH_4^+ to generate NOCs (Nguyen et al., 2012; Bones et al., 2010; Updyke et al., 2012; Liu et al., 2015; Huang et al., 2017). In a chamber study, the formation of NOCs ~~were found to be~~is enhanced in a NH_3-rich environment (Chu et al., 2016). While such chemical mechanisms might be complex, the initial steps generally involve reactions forming imines and amines, which can further react with carbonyl SOA compounds to form more complex products (e.g., oligomers/BrC) (Laskin et al., 2015).

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To verify this hypothesis, multiple linear regression analysis ~~was~~ is performed to test how well ~~could~~ the RPAs of NOCs could be predicted by the oxidized organics and ammonium. As expected, there is a close association (R^2 = 0.71, p < 0.01) between the predicted RPAs and the observed values of NOCs (Fig. 4), which supports this hypothesis. An obvious ~~substantial~~ improvement in R^2 implies that a model that uses both oxidized organics and ammonium to predict RPAs of NOCs is substantially better than one that uses only one predictor (either oxidized organics or ammonium in Fig. 3). The result indicates that interactions involving oxidized organics and ammonium could explain over half of the observed variations in NOCs in the atmosphere of Guangzhou. A fraction of the unaccounted NOCs could be due to primary emissions and other formation pathways.

~~Actually, formation of NOCs from ammonium and carbonyls have been confirmed in several laboratory studies (Sareen et al., 2010; Shapiro et al., 2009; Noziere et al., 2009;~~

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~~Kampf et al., 2016; Galloway et al., 2009). Secondary organic aerosols (SOA) produced from a large group of biogenic and anthropogenic VOCs can be further aged by NH_3/NH_4^+ to generate NOCs (Nguyen et al., 2012; Bones et al., 2010; Updyke et al., 2012; Liu et al., 2015; Huang et al., 2017). In a chamber study, the formation of NOCs were found to be enhanced in a NH_3-rich environment (Chu et al., 2016). While such chemical mechanisms might be complex, the initial steps generally involve reactions forming imines and amines, which can further react with carbonyl SOA compounds to form more complex products (e.g., oligomers/BrC) (Laskin et al., 2015).~~

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Theis hypothesis could also be supported by the similar pattern of diurnal variation observed for NOCs and oxidized organics (Fig. S5), although there is a slight lag ~~period was observed in~~for the ~~the overnight peaks of~~ NOCs. Such diurnal pattern is similar to those observed in Beijing and Uintah (Yuan et al., 2016; Zhang et al., 2015). Notably, such diurnal pattern of secondary NOCs is effectively modelled when the production of NOCs via carbonyls and ammonium is included (Woo et al., 2013). In addition to possible photo-bleaching (Zhao et al., 2015), the lower contribution of NOCs during daytime may be partly explained by the lower RH, as discussed in section 3.2.

Interestingly, the relationship between NOCs and ammonium is distinctly different from the relationship between NOCs and oxidized organics (Fig. 3). ~~Water soluble organic nitrogen (WSON) was reported to be positively correlated with some oxidation products in~~

~~a forest in northern Japan (Miyazaki et al., 2014). This is further supported by the similar pattern of diurnal variation observed for NOCs and oxidized organics (Fig. S6). However, a slight lag period was observed in the overnight peaks of NOCs, as compared to those of the oxidized organics. This finding was consistent with previously reported results, showing NOCs to have concentration maxima overnight in Beijing and Uintah (Yuan et al., 2016; Zhang et al., 2015). The lower contribution of NOCs during daytime may be partly explained by the lower RH, as discussed in section 3.2, in addition to photo-bleaching which occurs during daytime (Zhao et al., 2015).~~

~~Interestingly, the relationship between NOCs and ammonium was distinctly different from the relationship between NOCs and oxidized organics. A positive correlation ($R^2 = 0.50$, $p < 0.01$) was observed between the hourly detected number of NOCs and ammonium. In contrast, a negative correlation ($R^2 = 0.55$, $p < 0.01$) was observed between the hourly average relative peak areas (RPAs) of NOCs and ammonium (Fig. 3).~~ This implies that the controlling factors on the formation of NOCs from ammonium are different from ~~those controlling~~ oxidized organics. On one hand, the positive correlation between the detected numbers reflects that the formation of NOCs does require the participant of NH_3/NH_4^+, consistent with the enhancement of NOCs in ammonium-containing particles discussed above. On the other hand, the negative correlation between the RPAs signifies that particles with higher relative ammonium content may inhibit the formation of NOCs. ~~the relative amount of ammonium may influences the formation of NOCs.~~ Consistently, there is a negative correlation between concentrations of WSON and NH_4^+ in filter samples (Fig. S6).

This is supported by the inverse correlation between that Nfs of ammonium that internally mixed with NOCs and the RPAs of ammonium (Fig. S7). This is also theoretically possible since the formation of NOCs may be influenced by particle acidity (Miyazaki et al., 2014; Aiona et al., 2017; Nguyen et al., 2012), which is substantially affected by the abundance of ammonium. Particle acidity could also 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), precursors for the formation of oxidized organics. Consistently, higher relative acidity was observed for the internally mixed ammonium and NOCs particles, compared to ammonium-containing particles without NOCs (Fig. S6), and thus may influence the formation of NOCs (Fig. S7). However, the higher relative acidity might also be a result of NOCs formation. A model simulation shows that after including the chemistry of SOA ageing with NH_3, an increase in aerosol acidity would be expected due to the reduction in ammonium (Zhu et al., 2018). It is also noted that the particle acidity is roughly estimated by the relative abundance of ammonium, nitrate, and sulfate in individual particles (Denkenberger et al., 2007), and thus may not be representative of actual aerosol acidity or pH (Guo et al., 2015; Hennigan et al., 2015; Murphy et al., 2017). In addition, ammonia in gas phase is also efficient at producing NOCs (Nguyen et al., 2012), which may play a complex role in the distribution of ammonium and NOCs in particulate phase. The formation of ammonium and NOCs would compete for ammonia, which may also potentially result in the negative correlation between the RPAs of NOCs and ammonium. Unfortunately, such a role remains unclear since the variations of ammonia were not available in the present study.~~This finding was consistent with the results discussed in section 3.1, indicating that particles containing a higher abundance of ammonium may not facilitate the formation of NOCs.~~

~~Similarly, ambient observations reported from a forest site in Japan indicate that aerosol acidity likely plays an important role in the formation of WSON via acid-catalyzed reactions in summer (Miyazaki et al., 2014). Enhanced organic aerosol yields from gas-phase carbonyls in the acidic seed aerosol have been attributed to the occurrence of acid-catalyzed reactions (Jang et al., 2002). Furthermore, acidity could also 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), although some studies have indicated that browning of some SOA occurs independently within a pH range of 4–10 (Nguyen et al., 2012). Consistently higher relative acidity was observed for the internally mixed ammonium and NOCs particles, as compared to ammonium-containing particles without NOCs (Fig. S7).This may be due to the fact that the ammonium available to react with secondary oxidized organics was from the uptake of ammonia, regarding that NOCs were mainly supplied by heterogeneous reactions of oxidized organics, as discussed above. In this case, the formation of ammonium and NOCs would compete for ammonia, potentially resulting in a negative correlation between the RPAs of NOCs and ammonium as observed (Fig. 3). A study shows that ammonia is more efficient at producing NOC than ammonium (Nguyen et al., 2012). The negative correlation between concentrations of WSON and~~ ~~NH_4^+~~ ~~in filter samples (Fig. S7), may serve as quantitative support for the close association between~~

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~~WSON formation and NH_4^+. Furthermore, the negative correlation between the RPA of NOCs and ammonium, may indicate that the formation of NOCs is influenced by particle acidity,~~ ~~Consistently, the Nfs of ammonium that internally mixed with NOCs were inversely correlated with the RPAs of ammonium (Fig. S8).~~~~{Guo, 2015 #22779;Hennigan, 2015 #22780;Murphy, 2017 #22781}which is directly affected by the abundance of ammonium (as discussed in section 3.3).~~ ~~Consistently, the Nfs of ammonium that internally mixed with NOCs were inversely correlated with the RPAs of ammonium (Fig. S8).~~

~~One may expect that NOCs were formed through the interactions between NOx and oxidized organics in gas phase followed by condensation (Fry et al., 2014; Stefenelli et al., 2019; Lehtipalo et al., 2018). However, low correlation coefficients (R^2 = 0.02-0.13) between NOCs and NOx indicates limited contribution of this pathways to the observed NOCs. Also, NOCs formed through NOx and oxidized organics followed by partitioning would not be dependent on the amount of ammonium, which is incompatible with our results.~~

~~Multiple linear regression analysis was performed to predict the RPAs of NOCs generated from oxidized organics and ammonium, showing a close association (R^2 = 0.71, $p < 0.01$) between the predicted RPAs and the observed values of NOCs (Fig. 4). Therefore, the interactions involving oxidized organics and ammonium may explain over half of the observed variations in NOCs in the atmosphere of Guangzhou. A fraction of the unaccounted NOCs could be due to primary emissions and other formation pathways.~~

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

~~Consistent results were also obtained from the PMF model analysis (Norris et al., 2009) (detailed information is provided in the SI).~~ Figure~~.~~ 5 presents the PMF factor profiles obtained from the PMF model analysis (detailed information is provided in the SI) (Norris et al., 2009) and their diurnal variations. Around 75% of NOCs could be well explained by two factors, with 33% of the ~~modelled~~PMF resolved NOCs mainly associated with ammonium and carbonaceous ion peaks (ammonium factor), while 59% were mainly associated with oxidized organics (oxidized organics factor). The explained fraction of NOCs by the ammonium and oxidized organic factors is consistent with the linear regression analysis. In addition, PMF analysis provided information on the factor contribution and diurnal variations, which may help explain the seasonal variations and processes of NOCs. The ammonium factor showed a diurnal variation pattern peaking during early morning, which is consistent with the diurnal variation in RH (Zhang et al., 2019). ~~In addition, t~~This factor contributed to ~80% (Fig. S8) of the PMF resolved ~~modelled~~ NOCs during spring with ~~when~~ the highest RH ~~was observed~~ (Table S1), whereas ~~, while~~ the oxidized organics factor dominated (> 80%) in ~~all~~ summer and fall~~other seasons~~. In winter, these two factors similarly contributed (~40%). This may indicate a potential role of aqueous pathways in the formation of NOCs, particularly during spring. Differently, the oxidized organics factor showed a pattern of diurnal variation, increasing from morning hours and peaking overnight, which may correspond to the photochemical production of oxidized organics and follow~~-up~~ed interactions with condensed ammonium. This pathway may explain the slightly late peaking of NOCs compared to oxidized organics, as ~~condensation of~~ ammonium condensation is favorable overnight (Hu et al., 2008). While there were similarities in the fractions of oxidized organics in the oxalate factor and the oxidized organics factor, they only contributed to 8% of the PMF resolved ~~modelled~~ NOCs in the oxalate factor, which contained ~80% of the PMF resolved~~modelled~~ oxalate. As previously discussed, these oxidized organics are also precursors for the formation of oxalate (Zhang et al., 2019). Therefore, the PMF results ~~, and therefore, these results~~ suggest that there ~~were~~ are two competitive pathways for the evolution of these oxidized organics. Some oxidized organics formed from photochemical activities were further oxidized to oxalate, result~~ed~~ing in a diurnal pattern of variation ~~and~~ with concentration peaks during the afternoon (Fig. 5), while others interact with NH_3/NH_4^+ ~~ammonium~~ to form NOCs, peaking during the nighttime. However, the controlling factors for these pathways could not be determined in the present study. The unexplained NOCs (~25%) might be linked to the primary emissions, such as biomass burning (Desyaterik et al., 2013). It could be partly supported by the presence of potassium and various carbon ion clusters ($C_n^{+/-}$, n = 1, 2, 3, …) in the mass spectrum of NOCs-containing particles (Fig. 1).

3.~~2~~ 3 Seasonal variations in the observed NOCs

There is a~~A~~ clear seasonal variation ~~in~~ of NOCs ~~were also observed~~, with higher relative contributions during summer and autumn (Figs. 3 and 4), mainly due to the variations in oxidized organics and NH_3/NH_4^+. ~~As discussed in section 3.3, particle acidity was lower~~

~~during spring and winter than during summer and autumn, which may contribute to the observed seasonal variations.~~ In this region, a larger contribution from secondary oxidized organics is typically observed during summer and autumn (Zhou et al., 2014; Yuan et al., 2018). The seasonal maximum NH_3 concentrations have also been reported during the warmer seasons, corresponding to the peak emissions from agricultural activities and high temperatures, while the low NH_3 concentrations observed in colder seasons may be attributed to gas-to-particle conversion (Pan et al., 2018; Zheng et al., 2012). Such seasonal variation in NOCs ~~were~~ is also obtained in a model simulation, showing that the conversion of NH_3 into NOCs would result in a significantly higher reduction of gas-phase NH_3 during summer (67%) than winter (31%), due to the higher NH_3 and SOA concentrations present in the summer (Zhu et al., 2018). More primary NOCs may also be present during summer and autumn in the present study, due to the additional biomass burning activities in these seasons (Chen et al., 2018; Zhang et al., 2013).

~~While t~~The seasonal variations ~~in~~ of NOCs can be adequately explained by the variations in concentrations of oxidized organics and ammonium (Fig. 4), although the hourly variations during each season ~~were~~ are not well explained, as indicated by the lower R^2 values (Table S2). The correlation coefficients (R^2) range~~d~~ from 0.24 to 0.57 for inter-seasonal variations~~, although all the regressions were found to be significant~~. ~~As shown in Fig. 3, the seasonal dependencevariation of NOCs on oxidized organics and ammonium varieswas dependent on seasons, despite the correlations between NOCs and oxidized organics / ammonium being significant ($p < 0.01$) over different seasons.~~ During spring, NOCs exhibits~~ed~~ a limited dependence on oxidized organics (Figs. 3a and 3b), while during summer, the hourly detected number of NOCs shows~~ed~~ a limited dependence on ammonium (Fig. 3d). These ~~findings~~ results can be explained by ~~were consistent with~~ the PMF results, showing that the ammonium factor explained ~80% of the predicted NOCs during spring, while the oxidized organics factor dominantly contributed to the predicted NOCs during warmer seasons (Fig. S8). A detailed discussion of this issue is provided in the SI.

3.~~3~~ 4 Influence of RH and ~~particle acidity~~NOx

The ~~importance~~ influence of RH on ~~NOC~~ RPAs of NOCs and peak ratios of NOCs ~~and~~ /oxidized organics, are shown in Fig. 6. While NOCs ~~did~~ do not show a clear dependence on RH, the ratio of NOCs to oxidized organics shows~~ed~~ a clear increase ~~with~~ towards higher RH. This finding is consistent with the observations reported by Xu et al. (2017), in which the N/C ratio significantly increases~~d~~ as a function of RH in the atmosphere of Beijing. In addition, the diurnal variations of NOCs with peaks values around 20:00 ~~were~~ are also similar to those reported by Xu et al. (2017). ~~It is~~ The peak ratios of ~~noted that the formation of~~ NOCs~~ ~~/~~from~~ oxidized organics ~~was~~ are more obviously ~~not~~ enhanced when RH is higher ~~conditions were lower~~ than 40%. These findings imply that aqueous-phase processing likely plays an important role in the formation of NOCs. Significant changes in RH, such as during the evaporation of water droplets, have been reported to facilitate the formation of NOCs via NH_3/NH_4^+ and SOA (Nguyen et al., 2012). In addition, an increase in RH would improve the uptake of NH_3 and formation of NH_4^+, which also contributes to the enhancement of

NOCs. However, the relatively weak correlation (R^2 = 0.27, $p < 0.01$) between the peak ratios and RH, reflect the complex influence of RH on the formation of NOCs (Xu et al., 2017; Woo et al., 2013). ~~It is noted that the formation of NOCs from oxidized organics was not enhanced when RH conditions were lower than 40%.~~

~~While particulate organics with a high N/C ratio were formed in the presence of ammonium salts (Lee et al., 2013), the influence of particle acidity on the formation of NOCs has not previously been thoroughly evaluated. We further analyzed the influence of particle acidity on the formation of NOCs, with particle acidity represented by the relative acidity ratio, defined as the sum of absolute average peak areas of nitrate (m/z -62) and sulfate (m/z -97) divided by those of ammonium (m/z 18) (Denkenberger et al., 2007). Fig. 7 clearly shows the dependence of NOCs on particle acidity. Similarly, ambient observations reported from a forest site in Japan indicate that aerosol acidity likely plays an important role in the formation of WSON via acid-catalyzed reactions in summer (Miyazaki et al., 2014). Enhanced organic aerosol yields from gas-phase carbonyls in the acidic seed aerosol have been attributed to the occurrence of acid-catalyzed reactions (Jang et al., 2002). Furthermore, acidity could also 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), although some studies have indicated that browning of some SOA occurs independently within a pH range of 4–10 (Nguyen et al., 2012). Consistently higher relative acidity was observed for the internally mixed ammonium and NOCs particles, as compared to ammonium-containing particles without NOCs (Fig. S7). This finding was consistent with~~

~~the results discussed in section 3.1, indicating that particles containing a higher abundance of ammonium may not facilitate the formation of NOCs. A previously reported modelled simulation showed that after including the chemistry of SOA ageing with NH_3, an increase in aerosol acidity would be expected due to the reduction in NH_4, resulting in more SOA generated from acid-catalyzed reactions (Zhu et al., 2018). Consequently, the relative acidity ratio was also included in the multiple linear regression model applied in the present study, as previously discussed. However, the inclusion of relative acidity did not improve the degree of fit between the observed and modeled RPAs of NOCs. This suggests that the selection of the RPAs of ammonium or the relative acidity ratio in regression analysis resulted in similar outcomes for the formation of NOCs as the present study, due to the overlap between these variables. Sulfate might also play a role in the enhancement of formation kinetics for NOCs ($R^2 = 0.13$, $p < 0.01$), as previously demonstrated in laboratory simulations showing that sulfate can enhance the partitioning of some carbonyls (Lee et al., 2013).~~

One may expect that NOCs were formed through the interactions between NOx and oxidized organics in gas phase followed by condensation (Fry et al., 2014; Stefenelli et al., 2019; Lehtipalo et al., 2018). Low correlation coefficients (R^2 = 0.02–0.13) between NOCs and NOx likely indicates limited contribution of this pathways to the observed NOCs. We have also included an analysis on the relationship between peak ratios of NOCs/oxidized organics and NOx. Peak area ratios of NOCs/oxidized organics generally increases with increasing level of NOx (Fig. 6), but still with relatively weak correlation (R^2 = 0.18, $p <$

0.01). An inclusion of both NOx and RH in the above linear regression model (NOCs versus the oxidized organics and ammonium) does not improve the prediction of NOCs ($R^2 = 0.71$, $p < 0.01$). However, it is also noted that many factors (e.g., different removal processes and lifetimes of particles vs. gasses, primary vs. secondary species, etc.) could contribute to a lack of strong correlation even if NOx did contribute to NOC formation.

3.~~4~~ 5 Atmospheric implications and limitation

In this study we showed that in an urban megacity area, secondary NOCs were significantly contributed by the heterogeneous ageing of oxidized organics ~~photochemical products~~ with NH_3/NH_4^+, providing valuable insight into SOA aging mechanisms. In particular, the effects of NH_3/NH_4^+ on SOA or BrC formation remain relatively poorly understood. In the PRD region, it has been shown that oxygenated organic aerosols (OOA) account for more than 40% the total organic mass (He et al., 2011), with high concentrations of available gaseous carbonyls (Li et al., 2014). Therefore, it is expected that over half of all water soluble NOCs in this region ~~,~~ might link to secondary processing (Yu et al., 2017). Furthermore, secondary sources have been found to contribute significantly to NOCs related BrC in Nanjing, China (Chen et al., 2018). The results presented herein also suggest that the production of NOCs might be effectively estimated by their correlation with secondary oxidized organics and ammonium. The effectiveness of correlation-~~-~~based estimations needs to be examined in other regions before being generally applied in other environments. However, this approach may provide valuable insights in investigations into NOCs using atmospheric observations. In contrast, it has previously been reported that a positive correlation exists between WSON and ammonium (Li et al., 2012), indicating similar anthropogenic sources. This divergence could be mainly attributed to varying contributions of primary sources and secondary processes to the observed NOCs. Possible future reductions in anthropogenic emissions of ammonia may reduce particle NOCs. Understanding the complex interplay between inorganic and organic nitrogen is an important part of assessing the global nitrogen cycling.

Moise et al. (2015) proposed that with high concentrations of reduced nitrogen compounds, high photochemical activity and frequent changes in humidity, BrC formed via NH_3/NH_4^+ and SOA may become a dominant contributor to aerosol absorption, specifically in agricultural and forested areas. However, this study suggests that even in typical urban areas, BrC formation via NH_3/NH_4^+ and SOA should not be ~~considered~~neglected. In particular, SOA was found to account for 44 – 71% of the organic mass in megacities across China (Huang et al., 2014), with NH_3 concentrations in urban areas comparable with those from agricultural sites and 2- or 3-fold those of forested areas in China (Pan et al., 2018). Additionally, the acidic nature of particles in these regions would be also favorable for the formation of NOCs (Guo et al., 2017; Jia et al., 2018).

Considering the formation of NOCs from the uptake of NH_3 onto SOA particles, Zhu et al. (2018) suggested that this mechanism could have a significant impact on the atmospheric concentrations of NH_3/NH_4^+ and NO_3^-.~~ However, the uptake of carbonyl onto the ammonium-containing particles was not considered. As discussed above, 33% of the~~

~~modelled NOCs on average could be explained by the ammonium factor, with this effect most pronounced during spring (Fig. 5 and Fig. S9). Such chemistry may also result in an increase in aerosol acidity due to the reduction in NH_4^+, resulting in the formation of more SOA from acid-catalyzed reactions of gas-phase carbonyls (Jang et al., 2002). Given that RH and particle acidity play an important role in the aqueous formation of SOA and uptake of NH_3, such models should be developed to include these factors, in order to improve our understanding of the impact of the discussed chemical mechanisms in atmospheric chemistry and the global nitrogen cycle.~~

5 Conclusions

This study investigated the processes contributing to the seasonal formation of NOCs, involving ammonium and oxidized organics in urban Guangzhou, using single particle mass spectrometry. This is the first study to provide direct field observation results to confirm that the variation ~~in~~ of NOCs correlate~~d~~ well and are strongly enhanced internal mixing with secondary oxidized organics. These findings highlight the possible formation pathway of NOCs through ageing of secondary oxidized organics by NH_3/NH_4^+ in ambient urban environments. A clear pattern of seasonal variation in NOCs was observed, with higher relative contributions in summer and autumn as compared to spring and winter. This seasonal variation was well predicted by multiple linear regression model analysis, using the relative abundance of oxidized organics and ammonium as model inputs. More than 50% of NOCs could be explained by the interaction between oxidized organics and ammonium. The production of NOCs through such processes were facilitated by increased humidity and NOx ~~and higher particle acidity~~. These results extend our understanding of the mixing state and atmospheric processing of particulate NOCs, as well as having important implications for the accuracy of models predicting the formation, fate and impacts of NOCs in the atmosphere.

Author contribution

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

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Figure captions

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

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

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

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

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

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

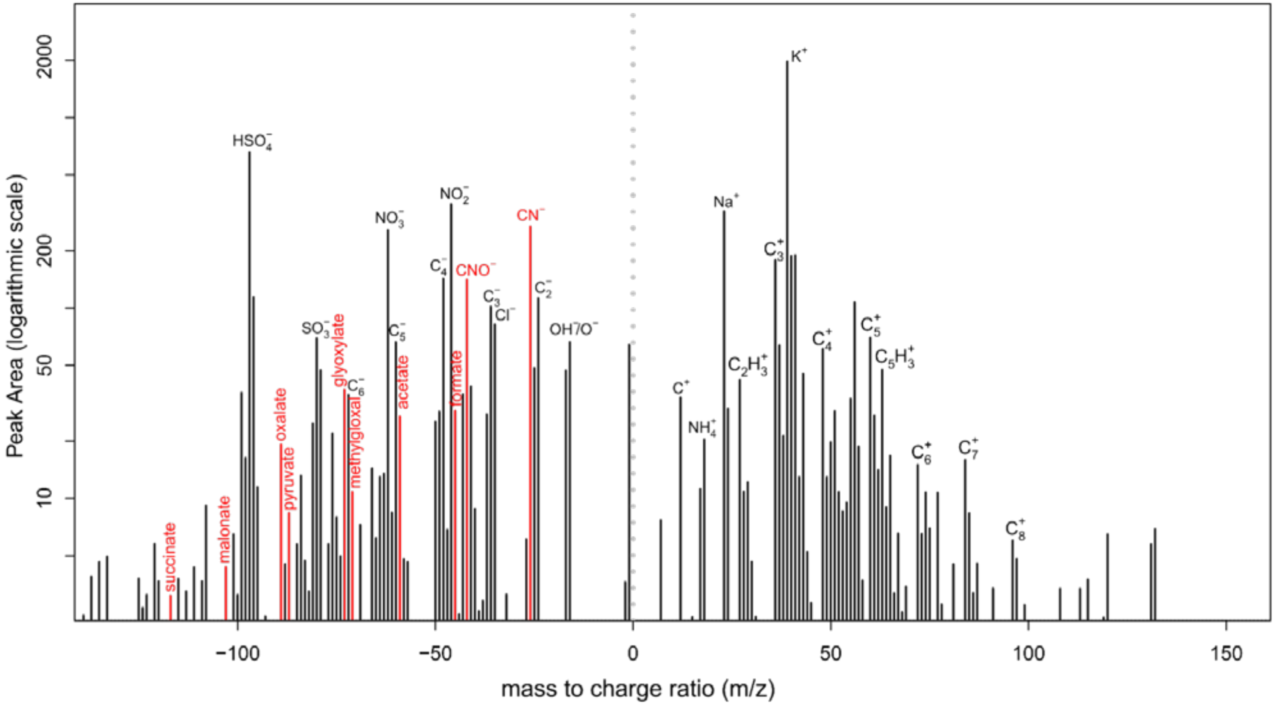

Peak Area (logarithmic scale)
2000
200
50
10
mass to charge ratio (m/z)
−100
−50
0
50
100
150
HSO_4^-
NO_3^-
NO_2^-
C_4^-
CNO^-
CN^-
C_3^-
Cl^-
C_2^-
SO_3^-
C_5^-
C_6^-
OH^-/O^-
succinate
malonate
oxalate
pyruvate
glyoxylate
methylglyoxal
acetate
formate
K^+
Na^+
C_3^+
$C_2H_3^+$
C^+
NH_4^+
C_4^+
C_5^+
$C_5H_3^+$
C_6^+
C_7^+
C_8^+

Fig. 1.

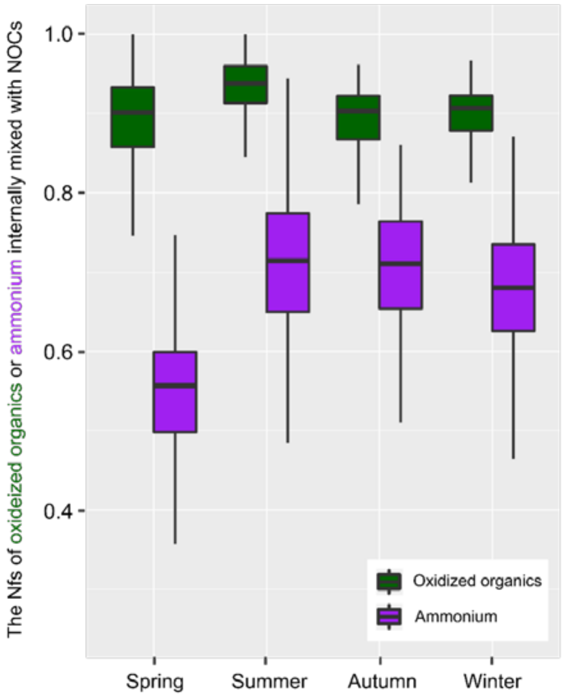

The Nfs of oxideized organics or ammonium internally mixed with NOCs
1.0
0.8
0.6
0.4
Spring
Summer
Autumn
Winter
🟩 Oxidized organics
🟪 Ammonium

Fig. 2.

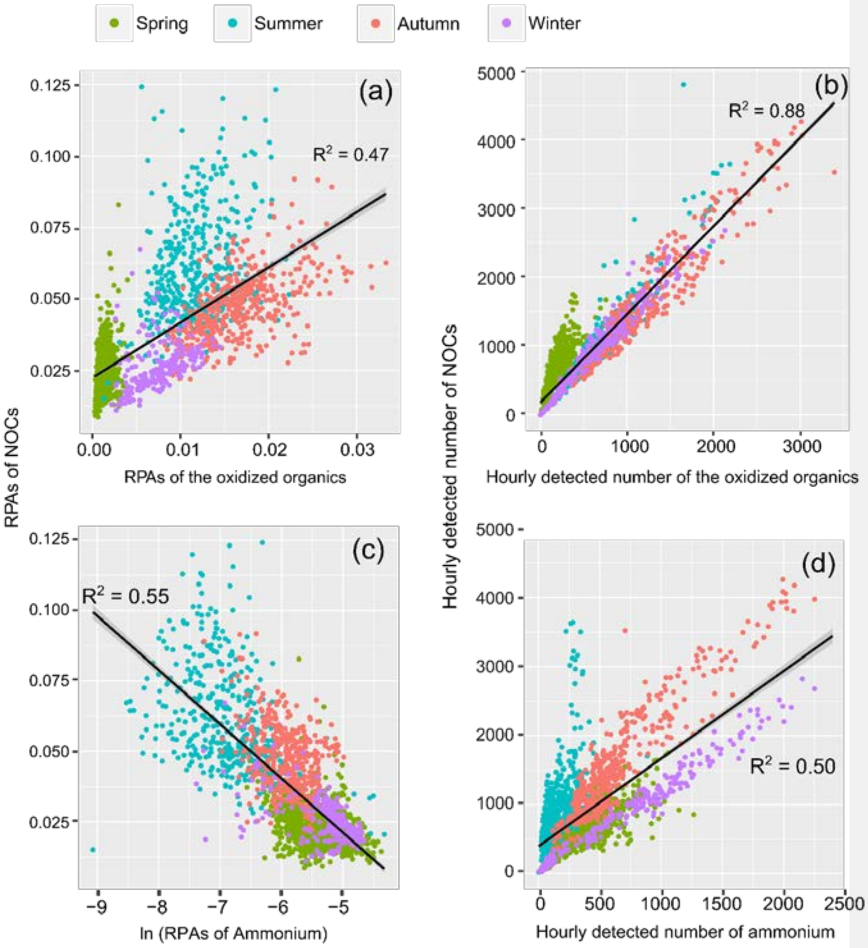

Spring
Summer
Autumn
Winter
(a)
R² = 0.47
RPAs of NOCs
RPAs of the oxidized organics
0.125
0.100
0.075
0.050
0.025
0.00
0.01
0.02
0.03
(b)
R² = 0.88
Hourly detected number of NOCs
Hourly detected number of the oxidized organics
5000
4000
3000
2000
1000
0
1000
2000
3000
(c)
R² = 0.55
ln (RPAs of Ammonium)
-9
-8
-7
-6
-5
(d)
R² = 0.50
Hourly detected number of ammonium
0
500
1000
1500
2000
2500

Fig. 3.

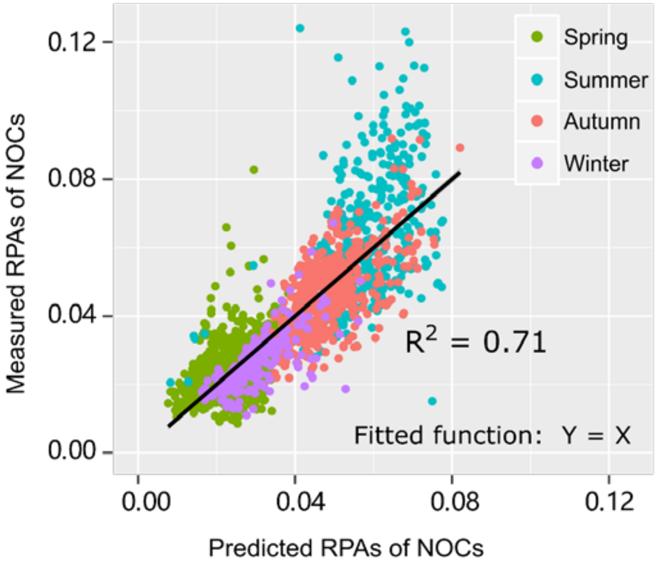

0.12
0.08
0.04
0.00
Measured RPAs of NOCs
0.00
0.04
0.08
0.12
Predicted RPAs of NOCs
● Spring
● Summer
● Autumn
● Winter
R² = 0.71
Fitted function: Y = X

Fig. 4.

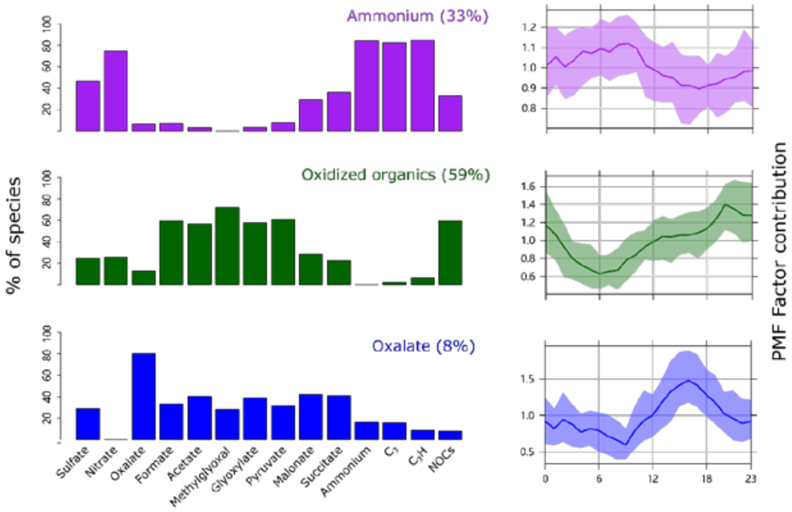
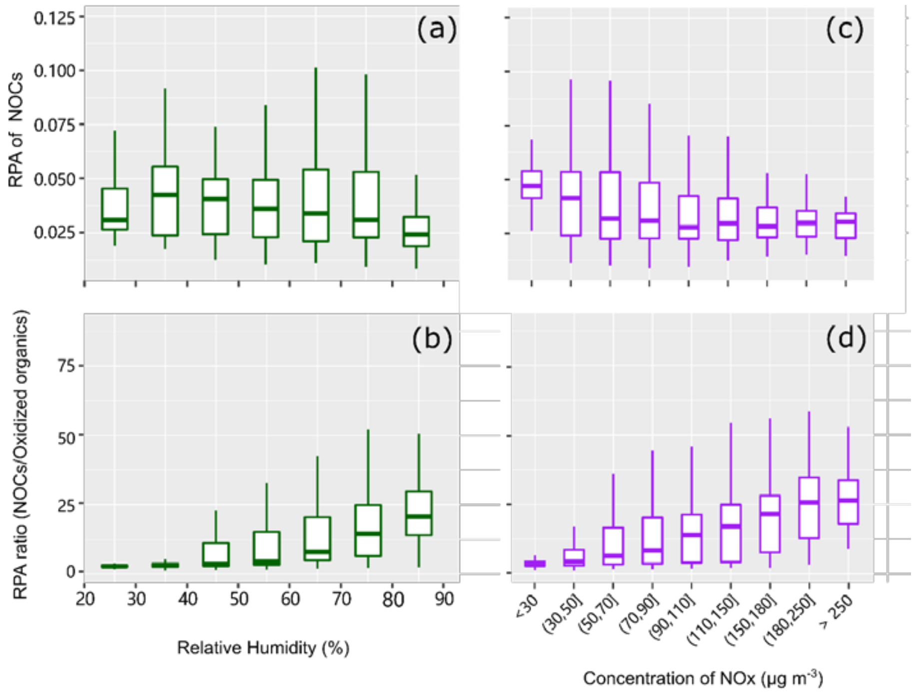

Ammonium (33%)
Oxidized organics (59%)
Oxalate (8%)
% of species
PMF Factor contribution
20
40
60
80
100
1.2
1.1
1.0
0.9
0.8
1.6
1.4
1.2
1.0
0.8
0.6
1.5
1.0
0.5
0
6
12
18
23
Sulfate
Nitrate
Oxalate
Formate
Acetate
Methylglyoxal
Glyoxylate
Pyruvate
Malonate
Succitate
Ammonium
C_3
C_3H
NOCs

Fig. 5.


(a)
(b)
(c)
(d)
RPA of NOCs
0.125
0.100
0.075
0.050
0.025
RPA ratio (NOCs/Oxidized organics)
75
50
25
0
20
30
40
50
60
70
80
90
Relative Humidity (%)
<30
(30,50]
(50,70]
(70,90]
(90,110]
(110,150]
(150,180]
(180,250]
> 250
Concentration of NOx (µg m-3)

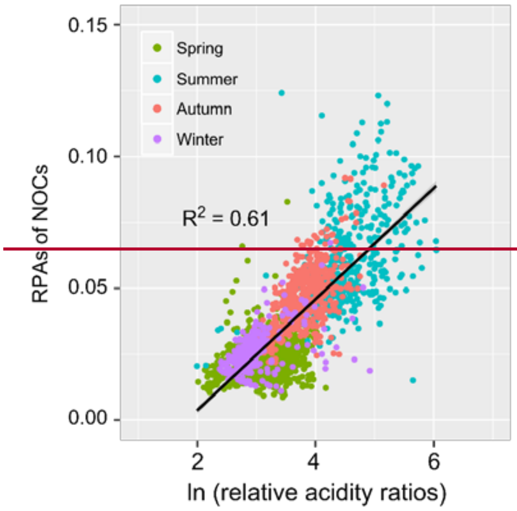

Spring
Summer
Autumn
Winter
R2 = 0.61
RPAs of NOCs
0.15
0.10
0.05
0.00
2
4
6
ln (relative acidity ratios)

Fig. 6. ~~**Fig. 7.**~~

Supporting Information for

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

Guohua Zhang[1], Xiufeng Lian[1,2], Yuzhen Fu[1,2], Qinhao Lin[1], Lei Li[3], Wei Song[1], Zhanyong Wang[4], Mingjin Tang[1], Duohong Chen[5], Xinhui Bi[1,*], Xinming Wang[1], Guoying Sheng[1]

[1] State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Resources Utilization and Protection, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China

[2] University of Chinese Academy of Sciences, Beijing 100039, PR China

[3] Institute of Mass Spectrometer and Atmospheric Environment, Jinan University, Guangzhou 510632, China

[4] School of Intelligent Systems Engineering, Sun Yat-sen University, Shenzhen 518107, PR China

[5] State Environmental Protection Key Laboratory of Regional Air Quality Monitoring, Guangdong Environmental Monitoring Center, Guangzhou 510308, PR China

Instrumentation

Individual particles are introduced into SPAMS through a critical orifice. They are focused and accelerated to specific velocities, which are determined by two continuous diode Nd:YAG laser beams (532 nm). Based on the measured velocities, a pulsed laser (266 nm) downstream is trigger to desorp/ionize the particles. The produced positive and negative molecular fragments are recorded. In summary, a velocity, a detection moment, and an ion mass spectrum are recorded for each ionized particle, while there is no mass spectrum for not ionized particles. The velocity could be converted to d_{va} based on a calibration using polystyrene latex spheres (PSL, Duke Scientific Corp., Palo Alto) with predefined sizes. It is noted that pure ammonium sulfate is difficult to be ionized under 266 nm UV laser used in the SPAMS, although this may not be the case since we focused on the NOCs-containing particles.

The concentrations of NO_x, and O_3 were measured by Model 42i (NO-NO_2-NO_x) Analyzer, and Model 49i O_3 Analyzer (Thermo Fisher Scientific Inc.), respectively. The concentrations of $PM_{2.5}$ were continuously measured using a tapered element oscillating microbalance (TEOM 1405, Thermo Fisher Scientific Inc.), respectively.

Positive matrix factorization

PMF is a multivariate receptor model used to determine source factors, and it has been used extensively with temporal variation data. In order to complement single particle data analysis, we used USEPA PMF 5.0 (Norris et al., 2009) to group chemical markers from all the detected particles. In such analysis, RPAs for ion markers were typically used as input in the PMF model. An uncertainty of 50% in RPA was used due to the shot-to-shot fluctuations of desorption laser and complex particle matrix (Zauscher et al., 2013). 14 marker ions with were used, including sulfate (-97$[HSO_4]^-$), nitrate (-62$[NO_3]^-$), ammonium (18$[NH_4]^+$), oxalate (89$[HC_2O_4]^-$), oxidized organics markers (at m/z -45$[HCO_2]^-$, m/z -59$[CH_3CO_2]^-$, m/z -71$[C_3H_3O_2]^-$, m/z -73$[C_2HO_3]^-$, m/z -87$[C_3H_3O_3]^-$, m/z -103$[C_3H_3O_4]^-$, and m/z -117$[C_4H_5O_4]^-$), organic nitrogen markers (NOCs, sum of -42$[CNO]^-$ and -26$[CN]^-$), and other carbonaceous fragments (i.e., 36$[C_3]^+$, 37$[C_3H]^+$).

PMF solutions with 2−5 factors were tested and showed convergence results. The relevant Q values and Q_{robust} / Q_{theory} for these solutions are shown in Table S3. In these solutions explored Q_{robust} / Q_{theory} < 1, although it is recommended that $Q_{robust} \approx Q_{theory}$. The 3-factor solution was chosen as the best because the measured versus predicted RPA of more relevant chemical species (i.e., NOCs, the oxidized organics and ammonium) in the PMF model had strong correlations ($R^2 = 0.56 - 0.95$), and also has the most physically meaningful factors. The residuals of this solution were between -2 and 2. In the 4 and 5-factor solution, with slightly stronger R^2 values than the 3-factor solution for NOCs and ammonium, but had two similar oxalate factors or an additional methylglyoxal factor, respectively, which seemed less physically meaningful. Bootstrapping on the 3-factor solution shows stable results, with > 90 out of 100 bootstrap factors mapped with those in the based run. Fpeak value from −0.5 to 0.5 was examined, and an examination of Q values showed the application of Fpeak of 0 giving the best result.

Limited dependent of NOCs on the oxidized organics during spring and ammonium during summer

During summer, the hourly detected number of NOCs showed a limited dependent on ammonium (Fig. 3d). As shown in Fig. S4, the detected number of ammonium is obviously lower than NOCs. In contrast, there were prevalent oxidized organics that were associated with NOCs. Due to the volatility of ammonium nitrate, there is less particulate ammonium in summer. Higher level of NH_3 during summer (Pan et al., 2018) may have potential influence on the formation of NOCs. Less dependence of NOCs on ammonium could be due to the more predominant formation of secondary NOCs through the uptake of NH_3 and the following interactions with secondary oxidized organics. As shown by Nguyen et al. (2012), ammonia is more efficient for the formation of NOCs in this pathway than ammonium. As also supported with PMF results shown in Fig. 5, the oxidized organics factor dominant contributed to the predicted NOCs during warmer seasons. Limited ammonium in this factor may also indicate that abundance of oxidized organics during warmer season consumed the available ammonium. As discussed, such chemistry would even lead to a reduction in the concentrations of NH_3 and NH_4^+ through a model simulation (Zhu et al., 2018). However, NOCs showed a limited dependent on the oxidized organics during spring (Fig. 3a and 3b). Consistently, the lowest fraction of NOCs that contained the oxidized organics was observed (Fig. S4), and ammonium factor explained ~80% of the predicted NOCs (Fig. 5) during spring. It is likely attributed to the higher conversion of oxidized organics to the observed NOCs in humid air during spring (Fig. 6 and Table S1). In addition, possible reasons might also include more primary NOCs and unidentified oxidized organics.

Table S1. The number and Nfs of NOCs-containing particles in the all the detected particles during four seasons, respectively. Standard errors for the Nfs of particles were estimated assuming Poisson distribution(Pratt et al., 2010). Temperature (T), relative humidity (RH), O_3, and $PM_{2.5}$ were provided by Guangdong Environmental Monitoring Center. The arriving air masses in Guangzhou, have been described previously: prevalence of marine air masses in spring and summer, whereas northern air masses from inland China in autumn and winter.

	Spring	Summer	Autumn	Winter
Num. of all the detected particles	933934	719371	1202604	397637
Nfs of NOCs-containing particles	58.7 ± 0.08%	59.4 ± 0.09%	59.0 ± 0.07%	55.6 ± 0.1%
Temperature (°C)	18.8 ± 4.2	29.0 ± 2.7	24.9 ± 2.6	11.3 ± 2.3
Relative Humidity (%)	68.0 ± 13.4	66.0 ± 11.4	47.0 ± 10.1	43.0 ± 19.1
O_x (µg m^{-3})	100.4 ± 43.7	114.5 ± 70.6	136.3 ± 35.4	113.1 ± 34.0
$PM_{2.5}$ (µg m^{-3})	51.2 ± 26.0	31.9 ± 21.0	44.3 ± 18.1	55.3 ± 28.9

Table S2. Coefficients calculated with a multiple linear regression analysis of the RPAs of NOCs and those of the oxidized organics and ammonium. All the regressions show significant correlation, with the fitting coefficients shown with a standard error.

	The oxidized organics	Ln (Ammonium)	R^2
Spring	4.24 ± 0.36	-0.0064 ± 0.00057	0.24
Summer	1.69 ± 0.22	-0.012 ± 0.0013	0.24
Autumn	1.27 ± 0.09	-0.0086 ± 0.0011	0.38
Winter	1.57 ± 0.14	-0.0010 ± 0.00069	0.57
Autumn 2014	1.18 ± 0.11	-0.013 ± 0.0042	0.35

Table S3. Q values for PMF Analysis with different number of factors.

Num. of factors	$R^{2\#}$ for all the input species	R^2 for NOCs	R^2 for the oxidized organics	R^2 for ammonium	Q_{robust} *	Q_{robust} /Q_{theory}
2	0.28-0.95	0.28	0.44-0.95	0.46	12110	0.76
3	0.25-0.95	0.74	0.59-0.95	0.56	8278	0.59
4	0.49-0.92	0.78	0.59-0.92	0.64	6485	0.53
5	0.41-0.94	0.83	0.58-0.94	0.66	4944	0.47

[#] R^2 between the observed and predicted species

* Q_{robust} with $F_{peak} = 0$.

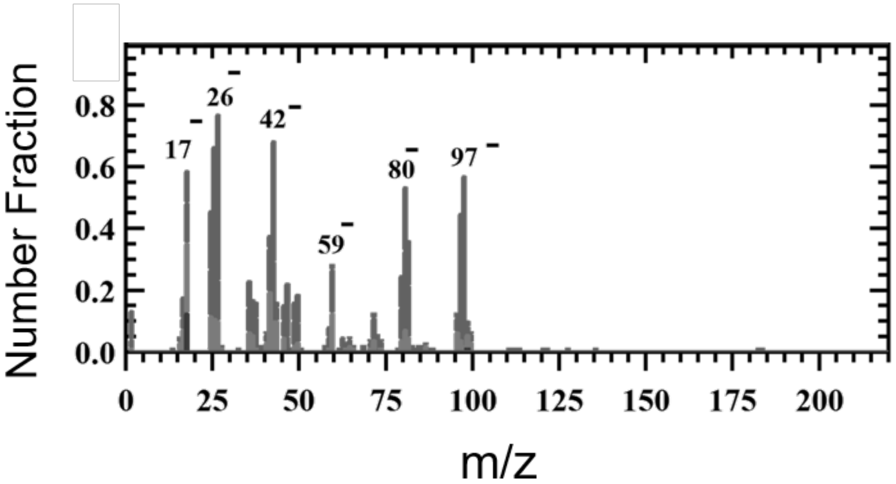


Figure S1. The number fraction of ion peaks versus m/z from the bulk solution-phase reaction of ammonium sulfate and methylglyoxal. The bulk solution-phase reaction was prepared with 1M ammonium sulfate and 1M methylglyoxal solution, and aged in sealed bottles under dark conditions and at room temperature for several days. BrC SOA formed from such reaction has been previously reported to be significantly contributed from NOCs (Aiona et al., 2017).

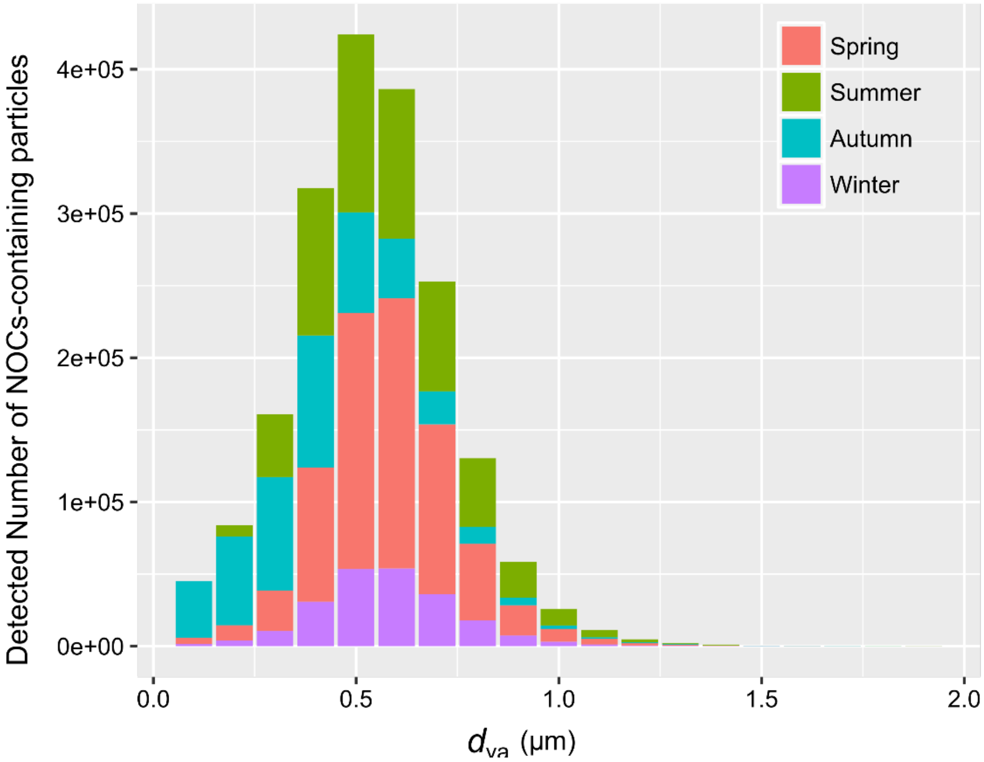


Figure S2. The detected number of NOC-containing particles along d_{va}.

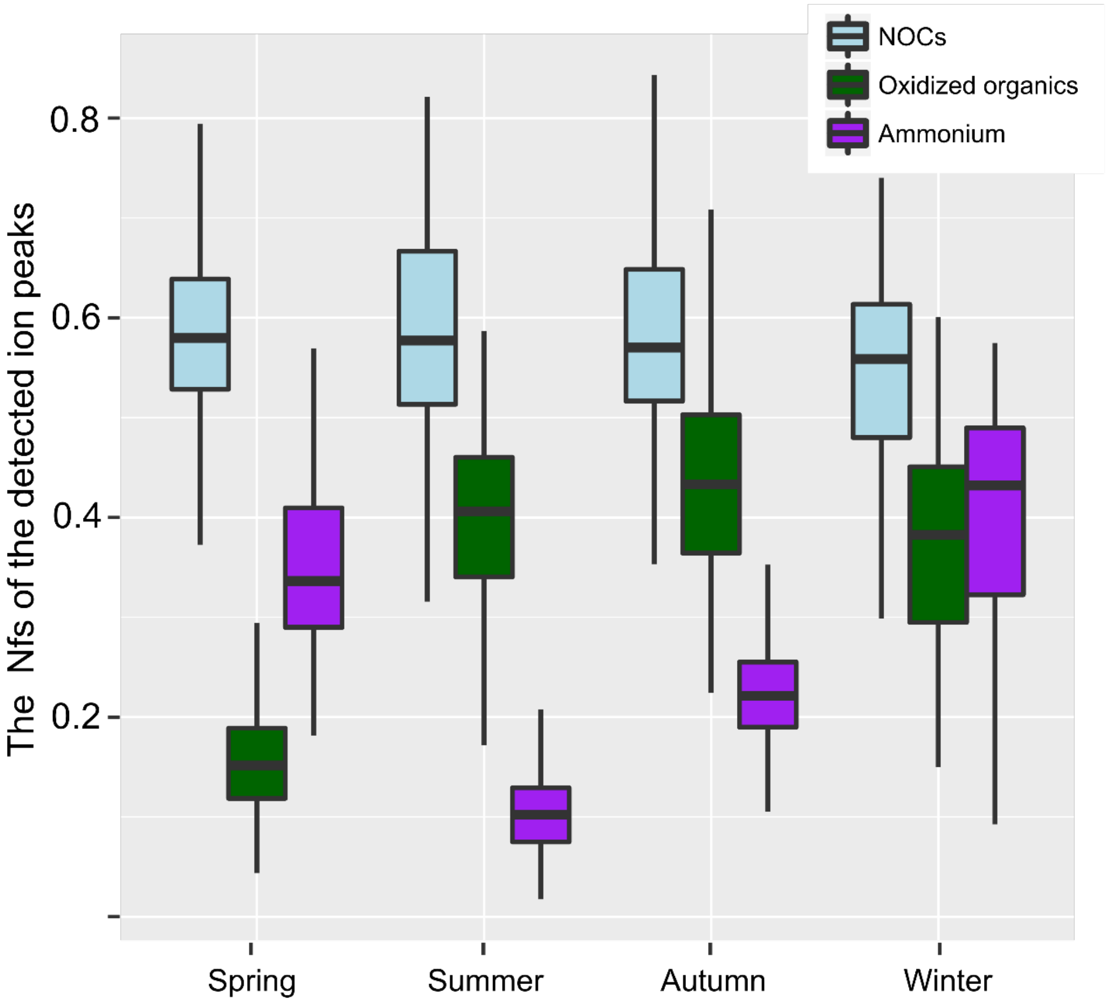


Figure S3. The distribution of the Nfs of the detected ion peaks over four seasons.

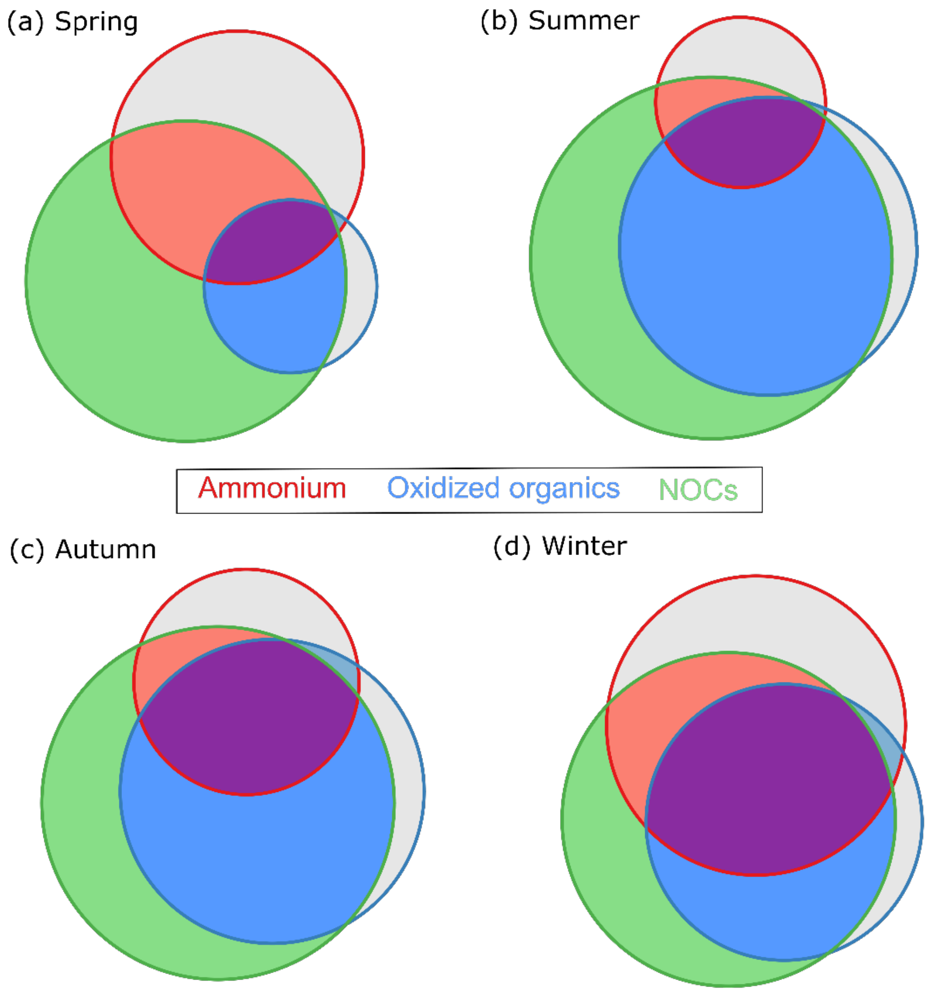
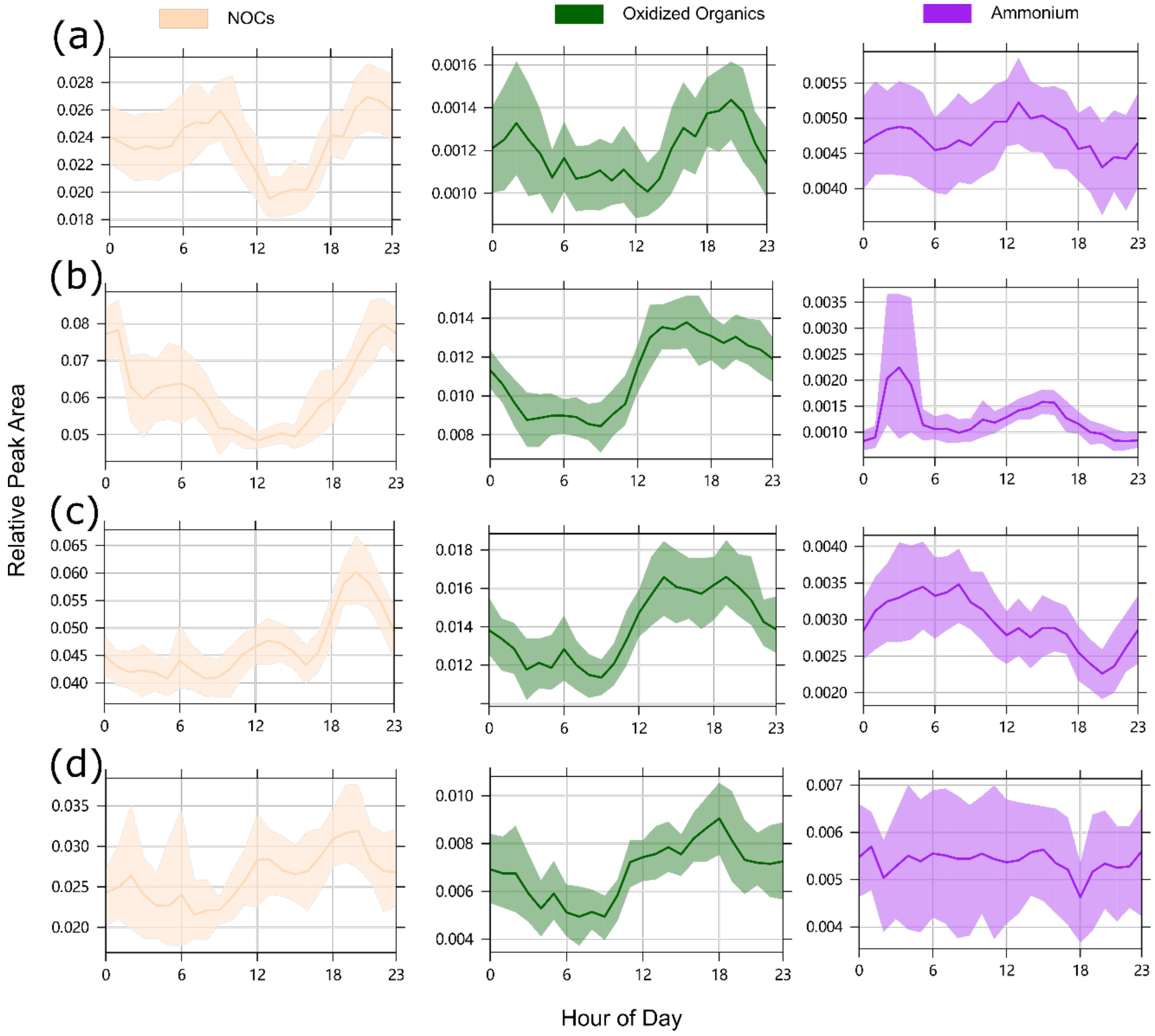


Figure S4. Venn plot of number based mixing state involving NOCs (green circle), the oxidized organics (blue circle), and ammonium (red circle).

122 

123

124 Figure S5. Diurnal variations of RPAs of NOCs, oxidized organics, and ammonium from

125 spring to winter (a-d).

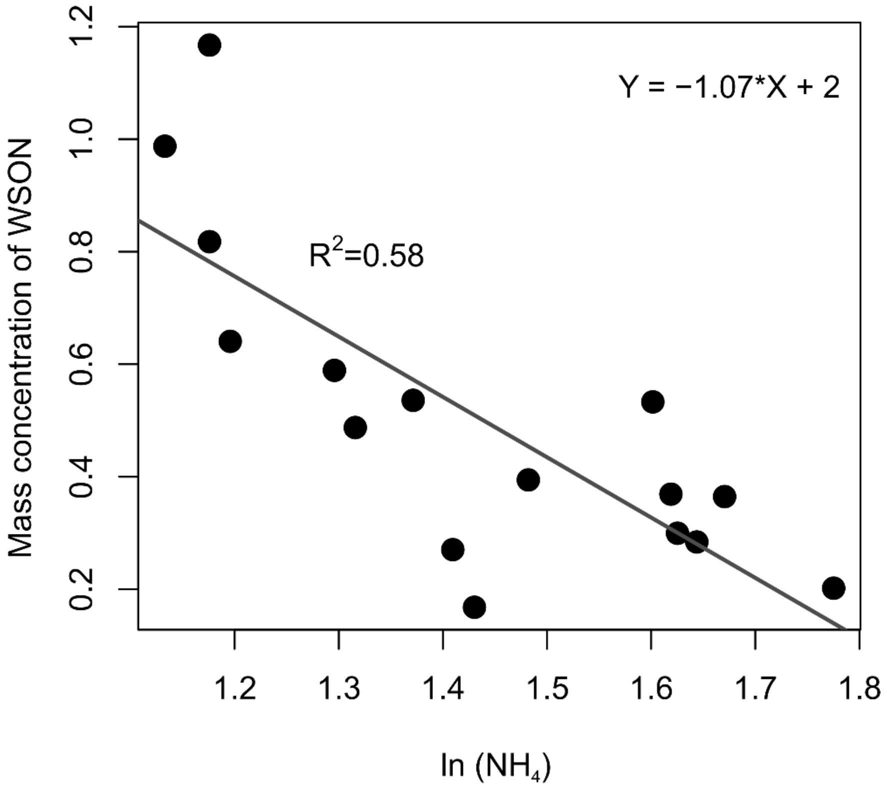


Figure S6. Relationship between the mass concentration of WSON and ammonium (logarithmic transformed) in submicron particles during autumn of 2014. It is noted that WSON (represented as the mass concentration of organic N) might not be properly regarded as NOCs, as no significant correlation between daily mean mass concentrations/fraction of WSON and the RPAs of NOCs. This is probably because the daily mean values calculated for the RPAs of NOCs miss the temporal variation information. Also, a part of NOCs might not be water-soluble (Cape et al., 2011).

During the autumn of 2014, daily size-resolved quartz fiber filter samples were collected using an Andersen PM_{10} sampler equipped with a size-selective inlet high volume cascade impactor (Model SA235, Andersen Instruments Inc.). The filters were baked for 4 h in a muffle furnace at 500 °C before use. Water-soluble inorganic ions were analyzed by ion chromatography (Metrohm 883, Switzerland). In addition, water soluble organic carbon (WSOC) and nitrogen (WSON) were analyzed by a Total Organic Carbon Analysis Instrument (TOC, Germany). It is noted that NOCs, the oxidized organics, and ammonium during this period also showed a similar relationship with that during autumn of 2013.

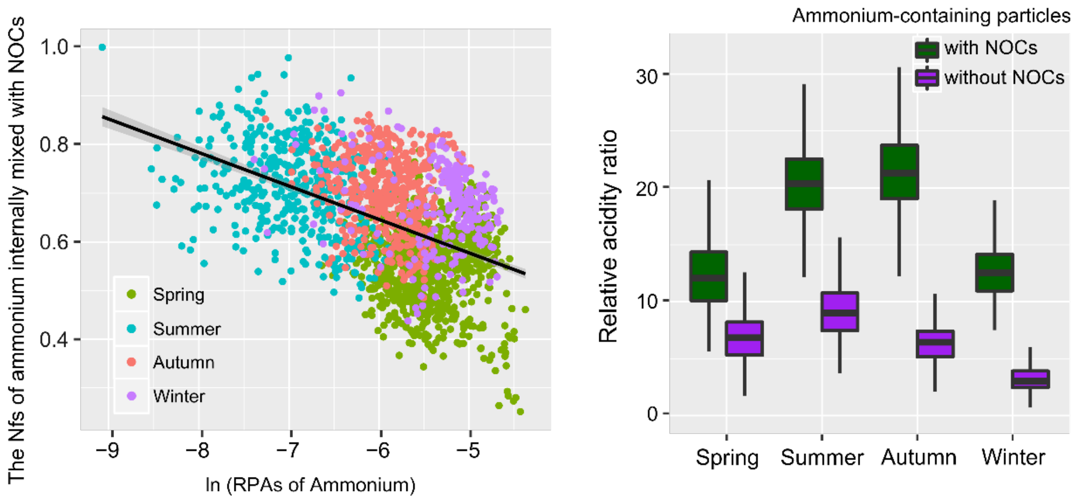


Figure S7. Relationship between the Nfs of ammonium that was internally mixed with NOCs and RPAs of ammonium (left), and comparison of the relative acidity ratio between ammonium-containing particles internally and externally mixed with NOCs (right).

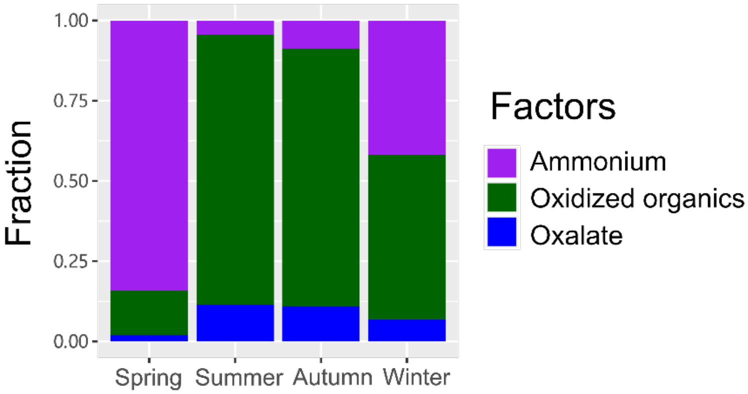


Figure S8. The relative contributions of the PMF-resolved 3-factor to the modelled NOCs over the seasons.

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