Atmospheric
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and Physics

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

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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 is investigated using single-particle mass spectrometry in urban Guangzhou from 2013 to 2014. The relative abundance of NOCs is found to be strongly enhanced when they are internally mixed with photochemically produced secondary oxidized organics (i.e., formate, acetate, pyruvate, methylglyoxal, glyoxylate, oxalate, malonate, and succinate) and ammonium (NH_4^+). Moreover, both the hourly detected particle number and the relative abundance of NOCs are highly correlated with those of secondary oxidized organics and NH_4^+. Therefore, it is hypothesized that the secondary formation of NOCs is most likely linked to oxidized organics and NH_4^+. 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 oxidized organics and NH_4^+.

Interestingly, the relative abundance of NOCs is inversely correlated with NH_4^+, whereas their number fractions are positively correlated. This result suggests that although the formation of NOCs does require the involvement of NH_3/NH_4^+, the relative amount of NH_4^+ may have a negative effect. Higher humidity and NO_x likely facilitates

the conversion of oxidized organics to NOCs. Due to the relatively high oxidized organics and NH_3/NH_4^+, the relative contributions of NOCs in summer and fall were higher than 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 NH_4^+. These findings have substantial implications for the role of NH_4^+ in the atmosphere, particularly in models that predict the evolution and deposition of NOCs.

Highlights.

– NOCs were highly internally mixed with photochemically produced secondary oxidized organics

– NOCs could be well predicted by the variations of these oxidized organics and NH_4^+

– Higher relative humidity and NO_x may facilitate the conversion of these oxidized organics to NOCs

1 Introduction

Organic aerosols that strongly absorb solar radiation are referred to as brown carbon (BrC). BrC has a comparable level of light absorption in the spectral range of near-ultraviolet (UV) light to black carbon (Andreae and Gelencser, 2006; Feng et al., 2013; Yan et al., 2018). Nitrogen-containing organic compounds (NOCs) substantially contribute to the pool of BrC (Mohr et al., 2013; Li et al., 2019) and have a significant effect on atmospheric chemistry, human health, and climate forcing (Kanakidou et al., 2005; Shrivastava et al., 2017; De Gouw and Jimenez, 2009). Particulate organic nitrogen accounts for a large fraction of total airborne nitrogen ($\sim 30\%$), although the proportion exhibits a high temporal and spacial variability and, therefore, has an influence on both regional and global nitrogen (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).

NOCs are ubiquitous components in 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). Secondary NOCs, such as organic nitrates and nitroaromatic compounds, are believed to be mainly formed in the gas phase by interaction between volatile organic compounds (VOCs) and oxidants (e.g., NO$_x$, $\bullet$ OH), followed by condensation to aerosols (Ziemann and Atkinson, 2012; Seinfeld and Pandis, 2006). Recently, another group of secondary NOCs, or heterocyclic NOCs, formed by reactions involving mixtures of atmospheric aldehydes (e.g., methylglyoxal/glyoxal) and ammonium (NH$_4^+$)/amines has been of particular interest (e.g., Hawkins et al., 2016; De Haan et al., 2011, 2017). A significant portion of heterocyclic NOCs may also be derived from the heterogeneous aging of secondary organic aerosol (SOA) with ammonia (NH$_3$)/NH$_4^+$ (Liu et al., 2015; Laskin et al., 2015). Huang et al. (2017) proposed that even trace levels of NH$_3$ may be sufficient to form heterocyclic NOCs via this pathway. However, these pathways have not been confirmed with ambient data, and the relative contribution of heterocyclic NOCs is still uncertain, although they are likely to be minor (at a level of several nanograms per cubic meter, ng m^{-3}) in abundance (Teich et al., 2016).

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 establish the formation mechanisms comprehensively. 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 covariation 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 closely correlated with particle acidity in the atmosphere in Shanghai (China). In addition, real-time aerosol mass spectrometry measurements of the atmosphere in New York (US) indicated a definite 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 (Nguyen et al., 2012; Sedehi et al., 2013; Ortiz-Montalvo et al., 2014). In the present study, the mixing state of individual particles was investigated, involving NOCs, oxidized organics, and NH$_4^+$, based on online seasonal observations using a single-particle aerosol mass spectrometer (SPAMS). Our findings show that the formation of NOCs is significantly linked to oxidized organics and NH$_4^+$; this has important environmental implications regarding the assessment of the impact and fate of these compounds.

2 Methods

2.1 Field measurements

Sampling was carried out at the Guangzhou Institute of Geochemistry, a representative urban site in Guangzhou (China), a megacity in the Pearl River Delta (PRD) region. The size and chemical composition of individual particles were obtained by the SPAMS (Hexin Analytical Instrument Co., Ltd., China) in real-time (Li et al., 2011). The sampling inlet for aerosol characterization was situated 40 m above ground level. A brief description of the performance of the SPAMS and other instruments can be found in the Supplement. The sampling periods cover four seasons, including summer (13 June to 16 July 2013), fall (26 September to 19 October 2013), winter (15 to 25 December 2013), and spring (21 February to 11 April 2014). The total measured particle numbers and mean values for meteorological data and gaseous pollutants are outlined for each season in Table S1 in the Supplement and have been described in a previous publication (Zhang et al., 2019).

2.2 SPAMS data analysis

Fragments of NOCs were identified according to the detection of ion peaks at $m/z - 26$ [CN]$^-$ or $m/z - 42$ [CNO]$^-$, generally due to the presence of C–N bonds (Silva and Prather, 2000; Zawadowicz et al., 2017; Pagels et al.,
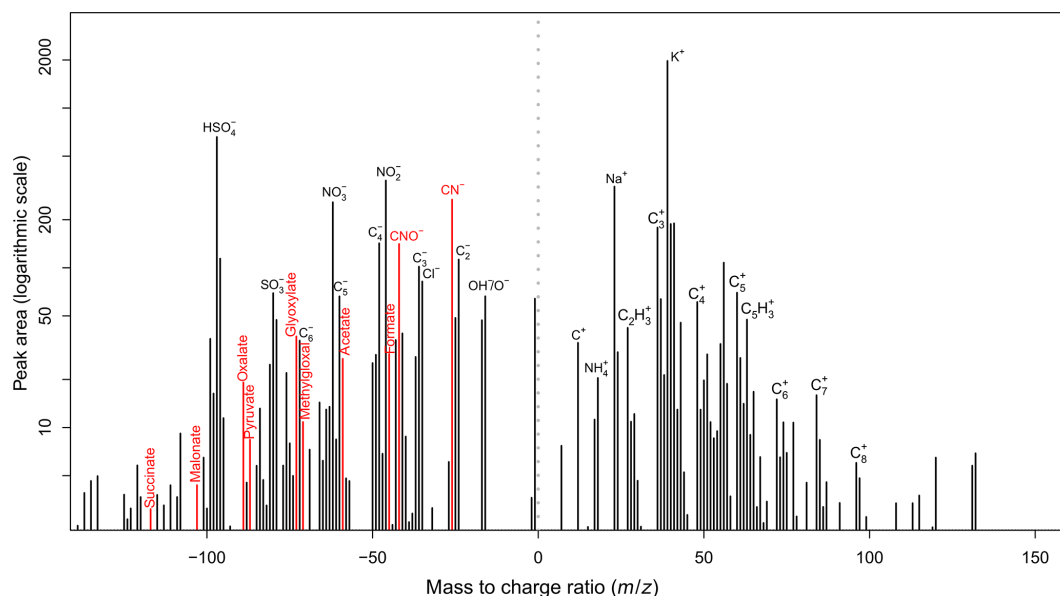
Figure 1. Representative mass spectrum for NOC-containing particles. The ion peaks corresponding to NOCs and oxidized organics are highlighted using red bars.

2013). Laboratory produced C–N bond compounds from bulk solution-phase reactions between the representative oxidized organics (i.e., methylglyoxal) and ammonium sulfate were used to confirm the generation of ion peaks at $m/z - 26$ [CN]$^-$ and/or $m/z - 42$ [CNO]$^-$ using SPAMS (Fig. S1 in the Supplement). Thus, the NOCs herein may refer to complex nitrated organics such as organic nitrates, nitroaromatics, nitrogen heterocycles, and polyphenols. Unfortunately, how well [CN]$^-$/[CNO]$^-$ ions represented NOCs could not be quantified, although they were the most commonly reported NOC 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 $C_n N^-$, $n = 1, 2, 3, \ldots$) (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% to 59% across all four seasons (Table S1). The number of detected NOC-containing particles as a function of their vacuum aerodynamic diameter (d_{va}) is shown in Fig. S2. Most of the detected NOC-containing particles had a d_{va} of between 300 and 1200 nm.

A representative mass spectrum for NOC-containing particles is shown in Fig. 1. Dominant peaks in the mass spectrum were m/z 39 [K]$^+$, m/z 23 [Na]$^+$, nitrate ($m/z - 62$ [NO$_3$]$^-$ or $m/z - 46$ [NO$_2$]$^-$), sulfate ($m/z - 97$ [HSO$_4$]$^-$), organics (m/z 27 [C$_2$H$_3$]$^+$, m/z 63 [C$_5$H$_3$]$^+$, $m/z - 42$ [CNO]$^-$,

$m/z - 26$ [CN]$^-$), NH$_4^+$ (m/z 18 [NH$_4$]$^+$), and carbon ion clusters ($C_n^{+/-}$, $n = 1, 2, 3, \ldots$). NOC-containing particles were internally mixed with various oxidized organics, represented as formate at $m/z - 45$ [HCO$_2$]$^-$, acetate at $m/z - 59$ [CH$_3$CO$_2$]$^-$, methylglyoxal at $m/z - 71$ [C$_3$H$_3$O$_2$]$^-$, glyoxylate at $m/z - 73$ [C$_2$HO$_3$]$^-$, pyruvate at $m/z - 87$ [C$_3$H$_3$O$_3$]$^-$, malonate at $m/z - 103$ [C$_3$H$_3$O$_4$]$^-$, and succinate at $m/z - 117$ [C$_4$H$_5$O$_4$]$^-$ (Zhang et al., 2017; Zauscher et al., 2013; Lee et al., 2003). These oxidized organics showed pronounced diurnal trends with an afternoon maximum and were highly correlated ($r = 0.72$–0.94, $p < 0.01$) with each other. Therefore, they were primarily attributed to secondary oxidized organics from the photochemical oxidation 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). More information on the seasonal variation range of the Nfs of oxidized organics, NH$_4^+$, 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 this, the variation of the relative peak area should be a good indicator for the investigation of atmospheric processing of various species in individual particles (Wang et
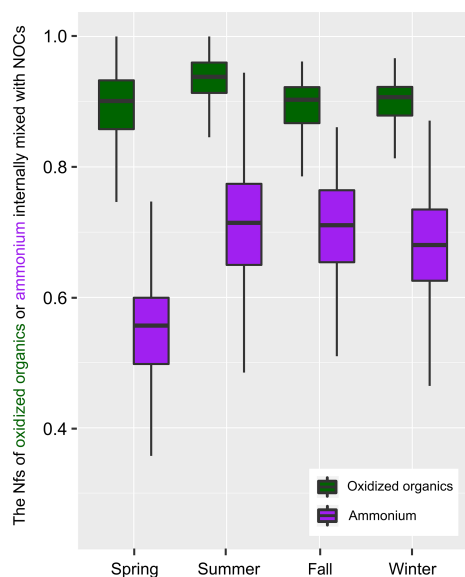
Figure 2. The variation in hourly mean Nfs of the oxidized organics and ammonium (NH_4^+) that internally mixed with NOCs. The boxes in the box and whisker plot show lower, median, and upper lines, denoting the 25th, 50th, and 75th percentiles, respectively; the whiskers denote the 10th and 90th percentiles, respectively.

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 (NH_4^+)

Figure 2 shows the seasonal variations in Nfs of the oxidized organics and NH_4^+, which were internally mixed with NOCs. On average, more than 90 % of the oxidized organics and 65 % of NH_4^+ were found to be internally mixed with NOCs, except in spring (Fig. S4). As the Nfs of NOCs relative to all of the measured particles was $\sim$ 60 %, it could be concluded that NOCs were enhanced with the presence of oxidized organics and NH_4^+, 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 their close associations, as shown in Fig. 3. Compared with the oxidized organics, the Nfs of ammonium-containing particles internally mixed with NOCs varied within a broader range ($\sim$ 40 %–90 %). However, there is still a mixing enhancement of NOCs with NH_4^+. A positive correlation ($R^2 = 0.50$, $p < 0.01$) is observed between the hourly detected number of NOCs and NH_4^+. 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 NH_4^+ (Fig. 3).

Based on both the enhancement of NOCs and the high correlations with oxidized organics and NH_4^+, it is hypothesized that interactions between oxidized organics and NH_4^+ contributed to the observed NOCs. The formation of NOCs from NH_4^+ 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 has been shown to be enhanced in an NH_3-rich environment (Chu et al., 2016). While such chemical mechanisms might be complicated, 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).

To verify this hypothesis, a multiple linear regression analysis is performed to test how well the RPAs of NOCs could be predicted by oxidized organics and NH_4^+. 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. A noticeable improvement in the R^2 value implies that a model that uses both oxidized organics and NH_4^+ to predict RPAs of NOCs is substantially better than a model that only uses a single predictor (either oxidized organics or NH_4^+ in Fig. 3). The result indicates that interactions involving oxidized organics and NH_4^+ could explain over half of the observed variations in NOCs in the atmosphere in Guangzhou. A fraction of the unaccounted for NOCs could be due to primary emissions and other formation pathways. This 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 for the NOCs. This diurnal pattern is similar to those observed in Beijing and Uintah (Yuan et al., 2016; Zhang et al., 2015). Notably, such a diurnal pattern of secondary NOCs is adequately modeled when the production of NOCs via carbonyls and NH_4^+ is included (Woo et al., 2013). In addition to possible photo-bleaching (Zhao et al., 2015), the lower contribution of NOCs during the daytime may be partly explained by the lower RH, as discussed in Sect. 3.2.

Interestingly, the relationship between NOCs and NH_4^+ is distinctly different from the relationship between NOCs and oxidized organics (Fig. 3). This implies that the controlling factors regarding the formation of NOCs from NH_4^+ are different from oxidized organics. On the one hand, the positive correlation between the detected numbers reflects that the formation of NOCs does require the participation of NH_3/NH_4^+, which is consistent with the enhancement of NOCs in ammonium-containing particles (Fig. 2) discussed above. On the other hand, the negative correlation between the RPAs signifies that the formation of NOCs is most probably influenced by the relative amount of NH_4^+ in individ-
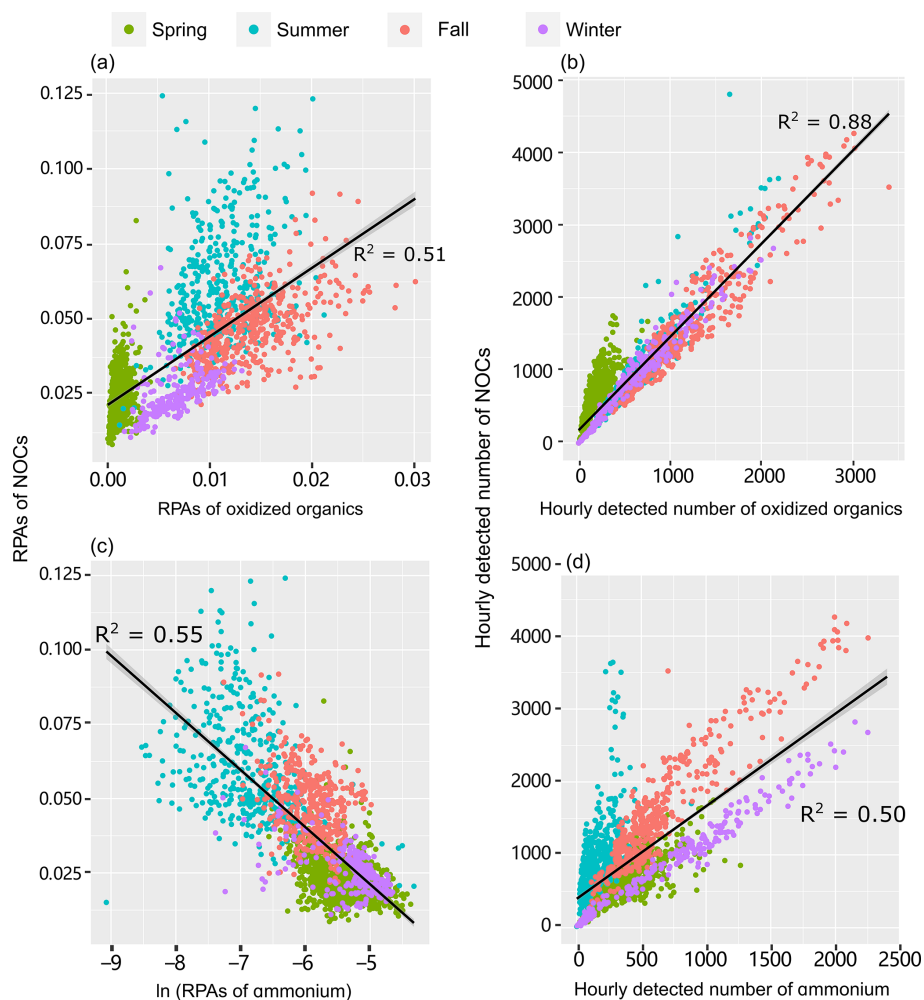
Figure 3. Correlation analysis of **(a, c)** the RPAs and **(b, d)** the number of detected NOCs with oxidized organics and ammonium (NH_4^+) in different seasons. Significant ($p < 0.01$) correlations were obtained for both the total observed data and the seasonally separated data. A RPA is defined 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).

ual particles. Such influence could also be supported by our data from both filter samples and individual particle analysis. There is a negative correlation between concentrations of water soluble organic nitrogen (WSON) and NH_4^+ for the filter samples (Fig. S6). It can also be seen from Fig. S7 that lower RPAs of NH_4^+ correspond to higher Nfs of NH_4^+ that internally mixed with NOCs. This inverse correlation could also serve as evidence to explain the influence of the relative amount of NH_4^+ on the formation of NOCs.

An influence of the relative amount of NH_4^+ on the formation of NOCs is also theoretically possible, as the formation of NOCs may be affected by particle acidity (Miyazaki et al., 2014; Nguyen et al., 2012), which is substantially affected by the abundance of NH_4^+. Higher relative acidity was consistently observed for the internally mixed NH_4^+ and NOC particles compared with ammonium-containing particles without NOCs (Fig. S6) and, thus, may influence the formation

of NOCs (Fig. S7). 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), which are precursors for the formation of oxidized organics. However, the higher relative acidity might also be a result of NOC formation. A model simulation shows that after including the chemistry of SOA aging with NH_3, an increase in aerosol acidity would be expected due to the reduction in NH_4^+ (Zhu et al., 2018). It is also noted that the particle acidity is roughly estimated by the relative abundance of NH_4^+, nitrate, and sulfate in individual particles (Denkenberger et al., 2007); thus, it may not be representative of actual aerosol acidity or pH (Guo et al., 2015; Hennigan et al., 2015; Murphy et al., 2017). In addition, NH_3 in the gas phase is also efficient at producing NOCs (Nguyen et al., 2012), which may play an intricate role in the distribution of NH_4^+ and NOCs in the particulate
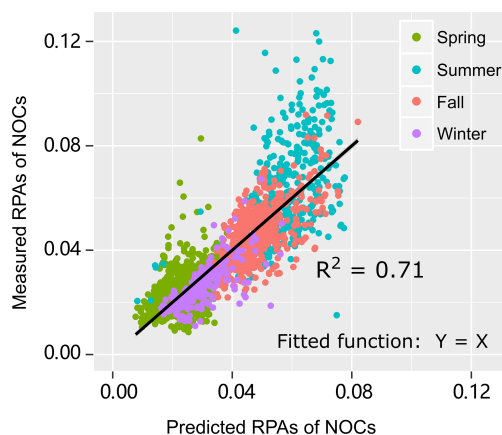
Figure 4. Comparison between the measured and predicted RPAs for NOCs.

phase. The formation of NH_4^+ and NOCs would compete for NH_3, which may also potentially result in a negative correlation between the RPAs of NOCs and NH_4^+. Unfortunately, such a role remains unclear, as the variations of NH_3 were not available in the present study.

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

Figure 5 presents the PMF factor profiles obtained from the PMF model analysis (detailed information is provided in the Supplement) (Norris et al., 2009) and their diurnal variations. Around 75 % of NOCs could be well explained by two factors, with 33 % of the PMF-resolved NOCs mainly associated with NH_4^+ and carbonaceous ion peaks (NH_4^+ factor), while 59 % were mainly associated with oxidized organics (oxidized organics factor). The fraction of NOCs explained by the NH_4^+ and oxidized organic factors is consistent with the linear regression analysis. Furthermore, PMF analysis provided information on the factor contributions and diurnal variations, which may help explain the seasonal variations and processes of NOCs. The ammonium factor showed a diurnal variation pattern that peaked during the early morning, which is consistent with the diurnal variation in RH (Zhang et al., 2019). This factor contributed to ~ 80 % (Fig. S8) of the PMF-resolved NOCs during spring (with the highest RH) (Table S1), whereas the oxidized organics factor dominated (> 80 %) in summer and fall. In winter, these two factors had similar contributions (~ 40 %). Variation of the ammonium factor may reflect a potential role of aqueous pathways in the formation of NOCs, particularly during spring. In contrast, the oxidized organics factor showed a pattern of diurnal variation, increasing from morning hours and peaking overnight, that may correspond to the photochemical production of oxidized organics and followed interactions with condensed NH_4^+. This pathway may explain the slightly late peak in NOCs compared with oxidized organics, as NH_4^+

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 NOCs in the oxalate factor, which contained ~ 80 % of the PMF-resolved oxalate. As previously discussed, these oxidized organics are also precursors for the formation of oxalate (Zhang et al., 2019). Therefore, the PMF results suggest that there are 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), whereas others interacted with NH_3/NH_4^+ 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 primary emissions, such as biomass burning (Desyaterik et al., 2013). This could be partly supported by the presence of potassium and various carbon ion clusters ($C_n^{+/-}$, $n = 1, 2, 3, \ldots$) in the mass spectrum of NOC-containing particles (Fig. 1).

3.3 Seasonal variations in the observed NOCs

There is an evident seasonal variation in NOCs, with higher relative contributions during summer and fall (Figs. 3, 4), mainly due to the variations in oxidized organics and NH_3/NH_4^+. In this region, a more considerable contribution from secondary oxidized organics is typically observed during summer and fall (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, whereas 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). This seasonal variation in NOCs 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 in winter (31 %), due to the higher NH_3 and SOA concentrations present in summer (Zhu et al., 2018). More primary NOCs may also be present during summer and fall in the present study, due to the additional biomass burning activities in these seasons (Chen et al., 2018; Zhang et al., 2013).

The seasonal variations in NOCs can be adequately explained by the variations in the concentrations of oxidized organics and NH_4^+ (Fig. 4), although the hourly variations during each season are not well explained, as indicated by the lower R^2 values (Table S2). The correlation coefficients (R^2) range from 0.24 to 0.57 for inter-seasonal variations. During spring, NOCs exhibits a limited dependence on oxidized organics (Fig. 3a, b), while during summer, the hourly detected number of NOCs shows a limited dependence on NH_4^+ (Fig. 3d). These seasonal dependences of NOCs are consis-
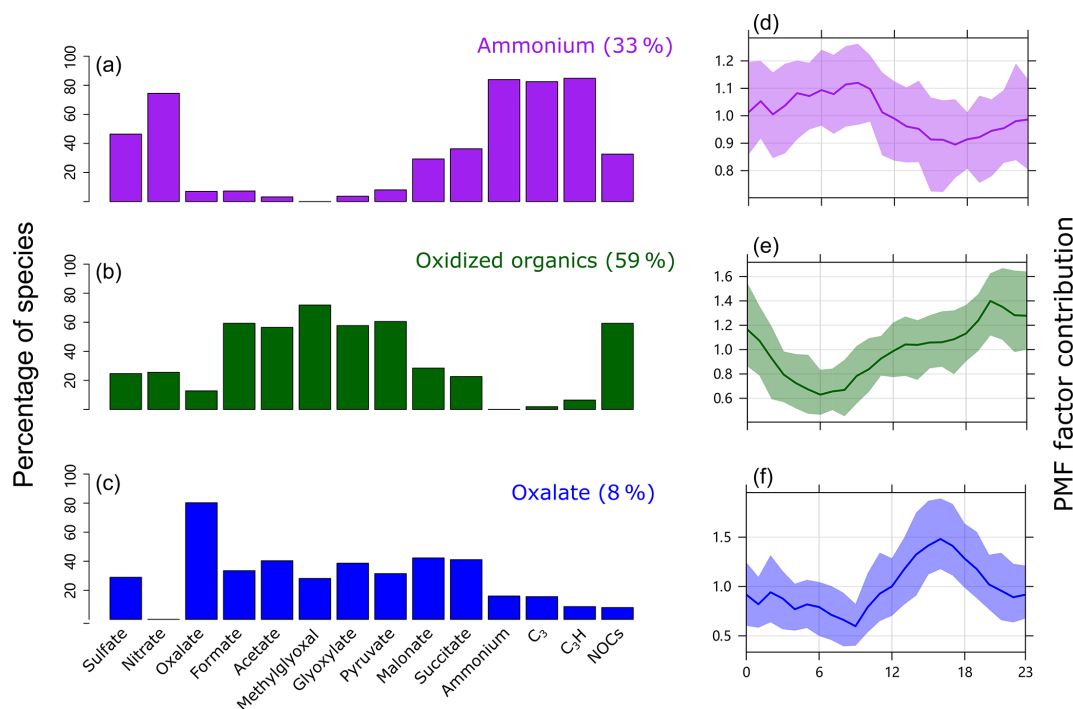
Figure 5. (a, b, c) PMF-resolved three-factor source profiles (percentage of total species) and **(d, e, f)** their diurnal variations (arbitrary unit).

tent with the PMF results, showing that the ammonium factor explained $\sim 80\%$ of the predicted NOCs during spring, whereas 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 Supplement.

3.4 Influence of RH and NO$_x$

The influence of RH on RPAs of NOCs and peak ratios of NOCs/oxidized organics are shown in Fig. 6. While NOCs do not show a clear dependence on RH, the ratio of NOCs to the oxidized organics shows an apparent increase towards higher RH. This finding is consistent with the observations reported by Xu et al. (2017), in which the N/C ratio significantly increases as a function of RH in the atmosphere of Beijing. Moreover, the diurnal variations of NOCs with peaks values around 20:00 LT (local time) are also similar to those reported by Xu et al. (2017). The peak ratios of NOCs/oxidized organics are more obviously enhanced when the RH is higher than 40 %. These findings imply that aqueous-phase processing likely plays a substantial 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 the formation of NH$_4^+$, which would also contribute to the enhancement of NOCs. However, the relatively weak correlation ($R^2 = 0.27$, $p < 0.01$) between the peak ratios and

the RH reflects the complex influence of the RH on the formation of NOCs (Xu et al., 2017; Woo et al., 2013).

One may expect that NOCs are formed through the interactions between NO$_x$ and oxidized organics in the gas phase, followed by condensation (Fry et al., 2014; Ziemann and Atkinson, 2012; Seinfeld and Pandis, 2006). Similar to the behavior observed for RH, NOCs do not show a clear dependence on NO$_x$ (Fig. 6c, $R^2 = 0.02$–0.13); however, the ratio of NOCs to the oxidized organics shows a clear increasing trend towards higher NO$_x$ (Fig. 6d, $R^2 = 0.18$, $p < 0.01$). This indicates that NO$_x$ may play a certain role in the conversion of oxidized organics to NOCs, although this cannot be quantified. It is also noted that low correlation coefficients between NO$_x$ and NOCs might not indicate a limited contribution of NO$_x$ to the formation of NOCs. NO$_x$ affects the formation of NOCs in various ways (e.g., peroxy radical chemistry in VOC oxidation mechanisms and the formation of nitrate radicals) (Xu et al., 2015; Zhang et al., 2018) and, thus, may not linearly contribute to the formation of NOCs.

3.5 Atmospheric implications and limitations

In this study, we showed that secondary NOCs were significantly contributed by the heterogeneous aging of oxidized organics with NH$_3$/NH$_4^+$ in an urban megacity area, 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 account for
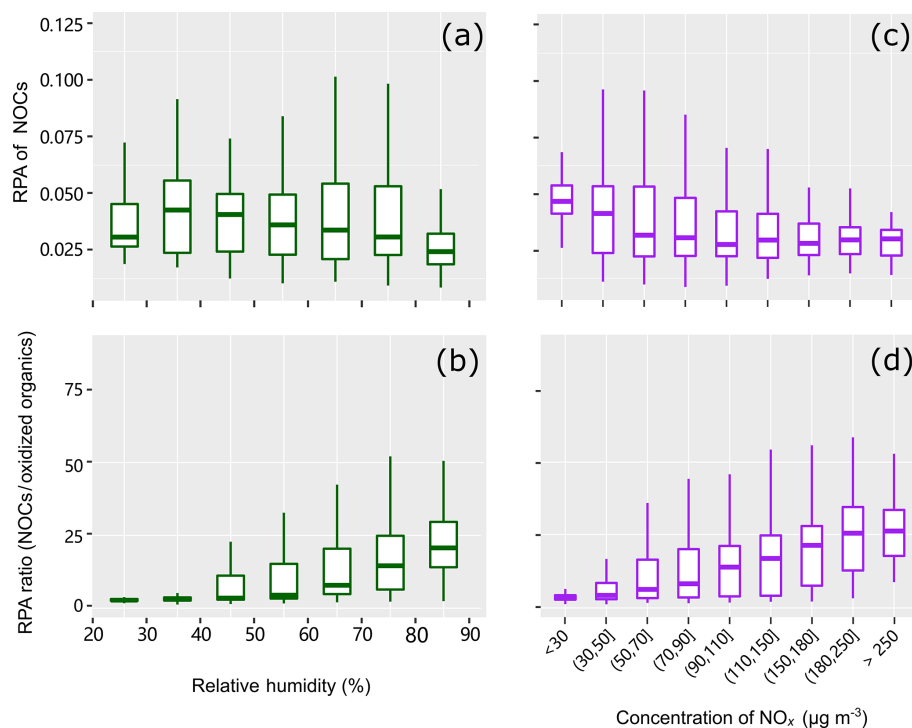
Figure 6. The dependence of NOCs and the ratio of NOCs to the oxidized organics on RH and NO_x.

more than 40 % of 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 NOC-related BrC in Nanjing, China (Chen et al., 2018). The results presented here also suggest that the production of NOCs might be adequately estimated by their correlation with secondary oxidized organics and NH_4^+. The effectiveness of correlation-based estimations needs to be examined in other regions before being generally applied in different environments. However, this approach may provide valuable insights into the investigation of NOCs using atmospheric observations. In contrast, it has previously been reported that a positive correlation exists between WSON and NH_4^+ (Li et al., 2012), indicating similar anthropogenic sources. This divergence could be mainly attributed to the varying contributions of primary sources and secondary processes to the observed NOCs. Possible future reductions in anthropogenic emissions of NH_3 may reduce particulate NOCs. Understanding the complex interplay between inorganic and organic nitrogen is an essential part of assessing 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 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 also be 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^-.

4 Conclusions

This study investigated the processes contributing to the seasonal formation of NOCs, involving NH_4^+ 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 variations in NOCs correlate well and are strongly enhanced by internal mixing with secondary oxidized organics. These findings highlight the possible formation pathway of NOCs via the aging 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 fall compared with winter and spring. This seasonal varia-

tion was well predicted by a multiple linear regression model analysis, using the relative abundance of oxidized organics and NH_4^+ as model inputs. More than 50 % of NOCs could be explained by the interaction between oxidized organics and NH_4^+. The production of NOCs via such processes is facilitated by increased humidity and NO_x. These results extend our understanding of the mixing state and the atmospheric processing of particulate NOCs as well as having substantial implications for the accuracy of models predicting the formation, fate, and impacts of NOCs in the atmosphere.

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