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

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19 Highlights

20 ● Nitrogen-containing organics (NOCs) were highly internally mixed with photochemically
    produced secondary oxidized organics

22 ● More than 50% of NOCs were well predicted by secondary formation from these
    oxidized organics and ammonium

24 ● Higher relative humidity and particle acidity facilitated the formation of 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 was found to be strongly enhanced by internal mixing with the photochemically produced secondary oxidized organics (such as formate, acetate, pyruvate, methylglyoxal, glyoxylate, oxalate, malonate and succinate). Furthermore, the co-occurrence of NOCs with ammonium was also observed. Interestingly, the relative abundance of NOCs was inversely correlated with ammonium, while their number fractions were positively correlated. Multiple linear regression analysis and positive matrix factorization analysis were performed to predict the relative abundance of NOCs generated from oxidized organics and ammonium. 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 were found to promote the production of NOCs. Higher relative contributions of NOCs were observed in summer and autumn, in comparison to spring and winter, due to the relatively higher contribution of oxidized organics and NH$_3$/NH$_4^+$ in summer and autumn periods. To the best of our knowledge, this is the first direct field observation study establishing a close association between NOCs and both oxidized organics and ammonium. These findings have substantial implications on the role of ammonium in the atmosphere, particularly in models predicting the evolution and deposition of NOCs.
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47 **Keywords:** nitrogen-containing organic compounds, individual particles, oxidized organics,

48 ammonium, mixing state, single particle mass spectrometry
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) represent a large and complicate fraction of atmospheric aerosols, significantly contributing to the pool of BrC (Feng et al., 2013; Mohr et al., 2013; Li et al., 2019). 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 nitrogen component of NOCs accounts for a large fraction of total airborne nitrogen (~30%), although the proportion exhibits a high level of 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.,...
Growing evidence from laboratory studies suggest that the production pathways for secondary NOCs 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 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 in-line seasonal observations using single particle aerosol mass spectrometry (SPAMS). These findings show that the formation of NOCs was significantly linked to oxidized organics and NH$_4^+$, which ought to have important environmental implications for 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...
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). Thus, the NOCs herein may refer to complex nitrated organics such as organic nitrates, nitro-aromatics, nitrogen heterocycles and polyphenols. The bulk solution-phase reaction between the representative oxidized organics (i.e., methylglyoxal) and ammonium sulfate was also performed in the laboratory to confirm that the formation of C-N bonds would generate ion peaks at m/z -26 [CN]⁻ and/or -42 [CNO]⁻ using SPAMS (Fig. S1). 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 and their vacuum aerodynamic diameter ($d_{va}$) are 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 [NO₃]⁻ or -46 [NO₂]⁻), sulfate (-97 [HSO₄]⁻), organics (27 [C₂H₃]⁺, 63 [C₃H₃]⁺, -42 [CNO]⁻, -26 [CN]⁻), ammonium (18 [NH₄]⁺) and carbon ion clusters (Cⁿ⁻, n = 1, 2, 3,…). NOCs-containing particles were internally mixed with various oxidized organics, represented as formate at m/z
-45 \([\text{HCO}_2^-]\), acetate at m/z -59 \([\text{CH}_3\text{CO}_2^-]\), methylglyoxal at m/z -71 \([\text{C}_3\text{H}_3\text{O}_2^-]\); glyoxylate at m/z -73 \([\text{C}_2\text{HO}_3^-]\), pyruvate at m/z -87 \([\text{C}_3\text{H}_3\text{O}_3^-]\), malonate at m/z -103 \([\text{C}_3\text{H}_3\text{O}_4^-]\) and succinate at m/z -117 \([\text{C}_4\text{H}_5\text{O}_4^-]\) (Zhang et al., 2017; Zauscher et al., 2013; Lee et al., 2003).

The contribution of these ion peaks to the formation of secondary oxidized organics 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 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 can be found 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 due to matrix effects, incomplete ionization and so on (Qin et al., 2006; Jeong et al., 2011; Healy et al., 2013; Zhou et al., 2016). Despite 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). Based on the comparison of the Nfs of NOCs (~60%) relative to all the measured particles, it may be concluded that NOCs were enhanced with the presence of oxidized organics and ammonium, with the increase associated with oxidized organics being most pronounced. A strong correlation between NOCs and oxidized organics further demonstrates a close association between these factors, as shown in Fig. 3. Thus, 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. 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). A close correlation observed ($R^2 = 0.55$, $p < 0.01$) between the temporal variation of NOCs internally and externally mixed with oxidized organics, further indicates that NOCs-containing particles free of oxidized organics may also be associated with the processing of these compounds (Fig. S5). 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).

A previously reported study effectively modelled predictions of the diurnal variation in secondary NOCs, produced by mixed carbonyls and ammonium (Woo et al., 2013). In the present study, the Nfs of ammonium-containing particles internally mixed with NOCs, varied within a wider range (~40-90%) (Fig. 2), as compared to the variation in oxidized organics. The enhanced mixing of NOCs with ammonium suggests that the uptake of gas phase oxidized organics and their interaction with particulate ammonium might also contribute to the formation of NOCs (Gen et al., 2018; De Haan et al., 2017). However, no enhancement occurred during spring and the enhancement was limited in ammonium-containing particles, as compared to oxidized organics-containing particles (Fig. 2). This phenomenon may be attributed to the limited oxidized organics fraction during spring (< 20%), in comparison to other seasons (~40%) (Fig. S3). Interestingly, the relationship between NOCs and ammonium was distinctly different from the relationship between NOCs and oxidized organics. A positive correlation (R² = 0.50, p < 0.01) was observed between the hourly detected number of NOCs and ammonium. In contrast, a negative correlation (R² = 0.55, p < 0.01) was observed between the hourly average relative peak areas (RPAs) of NOCs and ammonium (Fig. 3). These results imply that the controlling factors on the formation of NOCs from ammonium are different from those controlling oxidized organics.
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. By this pathway, 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 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, 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).

As discussed, the formation of oxidized organics is mainly attributed to gas-phase photochemical reactions followed by condensation. One may expect that NOCs were formed through the interaction 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. Consistent results were also obtained from the PMF model analysis (Norris et al., 2009) (detailed information is provided in the SI). Fig. 5 presents the PMF factor profiles and their diurnal variations.

Around 75% of NOCs could be well explained by two factors, with 33% of the modelled NOCs mainly associated with ammonium and carbonaceous ion peaks (ammonium factor), while 59% were mainly associated with oxidized organics (oxidized organics factor). 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, this factor contributed to ~80% (Fig. S9) of the modelled NOCs during spring when the highest RH was observed (Table S1), while the oxidized organics factor dominated in all other seasons. This may indicate 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, which may correspond to the photochemical production of oxidized organics and follow-up interaction with condensed ammonium. This pathway may explain the slightly late peaking of NOCs compared to oxidized organics, as condensation of ammonium is favorable overnight (Hu et
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 modelled NOCs in the oxalate factor, which contained ~80% of the modelled oxalate. As previously discussed, these oxidized organics are also precursors for the formation of oxalate (Zhang et al., 2019) and therefore, these results 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, resulted in a diurnal pattern of variation and concentration peaks during the afternoon (Fig. 5), while others interact with ammonium to form NOCs. This However, the controlling factors for these pathways could not be determined in the present study.

Several laboratory studies have confirmed the importance of ammonium in the formation of NOCs from carbonyls in atmospheric aerosols (Sareen et al., 2010; Shapiro et al., 2009; Noziere et al., 2009; Kampf et al., 2016; Galloway et al., 2009). Similarly, SOA generated from a large group of biogenic and anthropogenic VOCs can be further aged by NH$_3$/NH$_4^+$ (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).
3.2 Seasonal variations in the observed NOCs

A clear seasonal variation in 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 NH₃/NH₄⁺. 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 NH₃ concentrations have also been reported during the warmer seasons, corresponding to the peak emissions from agricultural activities and high temperatures, while the low NH₃ 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 also obtained in a model simulation, showing that the conversion of NH₃ into NOCs would result in a significantly higher reduction of gas-phase NH₃ during summer (67%) than winter (31%), due to the higher NH₃ and SOA concentrations present in the summer (Zhu et al., 2018). Since NOCs have been commonly observed in air masses affected by biomass burning (Desyaterik et al., 2013), 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 the seasonal variations in NOCs can be adequately explained by the variations in concentrations of oxidized organics and ammonium (Fig. 4), the hourly variations during each season were not well explained, as indicated by the lower R² values (Table S2).
correlation coefficients ($R^2$) ranged from 0.24 to 0.57 for inter-seasonal variations, although all regressions were found to be significant. As shown in Fig. 3, the seasonal dependence of NOCs on oxidized organics and ammonium varies, despite the correlations between NOCs and oxidized organics/ammonium being significant ($p < 0.01$) over different seasons. During spring, NOCs exhibited a limited dependence on oxidized organics (Fig. 3a and 3b), while during summer, the hourly detected number of NOCs showed a limited dependence on ammonium (Fig. 3d). These findings 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. S9). A detailed discussion of this issue is provided in the SI.

### 3.3 Influence of RH and particle acidity

The importance of RH on NOC RPAs and peak ratios of NOCs and oxidized organics, are shown in Fig. 6. While NOCs did not show a clear dependence on RH, the ratio of NOCs to oxidized organics showed a clear increase with higher RH. This finding is consistent with the observations reported by Xu et al. (2017), in which the N/C ratio significantly increased as a function of RH in the atmosphere of Beijing. In addition, the diurnal variations of NOCs with peaks values around 20:00 were also similar to those reported by Xu et al. (2017). 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.,
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 NH₃, an increase in aerosol acidity would be expected due to the reduction in NH₄, 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 (R² = 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).

### 3.4 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 photochemical products with NH₃/NH₄⁺, 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 be considered. 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 NOCs correlated well and 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 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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Aiona, P. K., Lee, H. J., Leslie, R., Lin, P., Laskin, A., Laskin, J., and Nizkorodov, S. A.: Photochemistry of Products of the Aqueous Reaction of Methylglyoxal with Ammonium Sulfate, Acs Earth Space Chem., 1, 522-532, doi:10.1021/acsearthspacechem.7b00075, 2017.

Altieri, K. E., Turpin, B. J., and Seitzinger, S. P.: Composition of Dissolved Organic Nitrogen in Continental Precipitation Investigated by Ultra-High Resolution FT-ICR Mass Spectrometry, Environ. Sci. Technol., 43, 6950-6955, doi:10.1021/es9007849, 2009.

Andreae, M. O., and Gelencser, A.: Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols, Atmos. Chem. Phys., 6, 3131-3148, 2006.

Bones, D. L., Henricksen, D. K., Mang, S. A., Gonsior, M., Bateman, A. P., Nguyen, T. B., Cooper, W. J., and Nizkorodov, S. A.: Appearance of strong absorbers and fluorophores in limonene-O-3 secondary organic aerosol due to NH4+-mediated chemical aging over long time scales, J. Geophys. Res.-Atmos., 115, D05203, doi:10.1029/2009jd012864, 2010.

Cape, J. N., Cornell, S. E., Jickells, T. D., and Nemitz, E.: Organic nitrogen in the atmosphere — Where does it come from? A review of sources and methods, Atmos. Res., 102, 30-48, doi:10.1016/j.atmosres.2011.07.009, 2011.

Chen, Y., Ge, X., Chen, H., Xie, X., Chen, Y., Wang, J., Ye, Z., Bao, M., Zhang, Y., and Chen, M.: Seasonal light absorption properties of water-soluble brown carbon in atmospheric fine particles in Nanjing, China, Atmos. Environ., doi:https://doi.org/10.1016/j.atmosenv.2018.06.002, 2018.

Chu, B. W., Zhang, X., Liu, Y. C., He, H., Sun, Y., Jiang, J. K., Li, J. H., and Hao, J. M.: Synergetic formation of secondary inorganic and organic aerosol: effect of SO2 and NH3 on particle formation and growth, Atmos. Chem. Phys., 16, 14219-14230, doi:10.5194/acp-16-14219-2016, 2016.

De Gouw, J., and Jimenez, J. L.: Organic Aerosols in the Earth's Atmosphere, Environ. Sci. Technol., 43, 7614-7618, doi:10.1021/Es9006004, 2009.

De Haan, D. O., Hawkins, L. N., Kononenko, J. A., Turley, J. J., Corrigan, A. L., Tolbert, M. A., and Jimenez, J. L.: Formation of Nitrogen-Containing Oligomers by Methylglyoxal and
Amines in Simulated Evaporating Cloud Droplets, Environ. Sci. Technol., 45, 984-991, doi:10.1021/es102933x, 2011.

De Haan, D. O., Hawkins, L. N., Welsh, H. G., Pednekar, R., Casar, J. R., Pennington, E. A., de Loera, A., Jimenez, N. G., Symons, M. A., Zauscher, M., Pajunoja, A., Caponi, L., Cazaunau, M., Formenti, P., Gratien, A., Pangui, E., and Doussin, J.-F.: Brown Carbon Production in Ammonium- or Amine-Containing Aerosol Particles by Reactive Uptake of Methylglyoxal and Photolytic Cloud Cycling, Environ. Sci. Technol., 51, 7458-7466, doi:10.1021/acs.est.7b00159, 2017.

De Haan, D. O., Jimenez, N. G., de Loera, A., Cazaunau, M., Gratien, A., Pangui, E., and Doussin, J.-F.: Methylglyoxal Uptake Coefficients on Aqueous Aerosol Surfaces, J. Phys. Chem. A, 122, 4854-4860, doi:10.1021/acs.jpca.8b00533, 2018.

Denkenberger, K. A., Moffet, R. C., Holecek, J. C., Rebotier, T. P., and Prather, K. A.: Real-time, single-particle measurements of oligomers in aged ambient aerosol particles, Environ. Sci. Technol., 41, 5439-5446, doi:10.1021/es070329l, 2007.

Desyaterik, Y., Sun, Y., Shen, X., Lee, T., Wang, X., Wang, T., and Collett, J. L., Jr.: Speciation of "brown" carbon in cloud water impacted by agricultural biomass burning in eastern China, J. Geophys. Res.-Atmos., 118, 7389-7399, doi:10.1002/jgrd.50561, 2013.

El-Sayed, M. M. H., Wang, Y. Q., and Hennigan, C. J.: Direct atmospheric evidence for the irreversible formation of aqueous secondary organic aerosol, Geophys. Res. Lett., 42, 5577-5586, doi:10.1002/2015gl064556, 2015.

Feng, Y., Ramanathan, V., and Kotamarthi, V. R.: Brown carbon: a significant atmospheric absorber of solar radiation?, Atmos. Chem. Phys., 13, 8607-8621, doi:10.5194/acp-13-8607-2013, 2013.

Fry, J. L., Draper, D. C., Barsanti, K. C., Smith, J. N., Ortega, J., Winkle, P. M., Lawler, M. J., Brown, S. S., Edwards, P. M., Cohen, R. C., and Lee, L.: Secondary Organic Aerosol Formation and Organic Nitrate Yield from NO3 Oxidation of Biogenic Hydrocarbons, Environ. Sci. Technol., 48, 11944-11953, doi:10.1021/es502204x, 2014.
Galloway, M. M., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Flagan, R. C., Seinfeld, J. H., and Keutsch, F. N.: Glyoxal uptake on ammonium sulphate seed aerosol: reaction products and reversibility of uptake under dark and irradiated conditions, Atmos. Chem. Phys., 9, 3331-3345, doi:10.5194/acp-9-3331-2009, 2009.

Gen, M., Huang, D. D., and Chan, C. K.: Reactive Uptake of Glyoxal by Ammonium-Containing Salt Particles as a Function of Relative Humidity, Environ. Sci. Technol., 52, 6903-6911, doi:10.1021/acs.est.8b00606, 2018.

Guo, H., Weber, R. J., and Nenes, A.: High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production, Sci. Rep., 7, 12109, doi:10.1038/s41598-017-11704-0, 2017.

Hawkins, L. N., Lemire, A. N., Galloway, M. M., Corrigan, A. L., Turley, J. J., Espelien, B. M., and De Haan, D. O.: Maillard Chemistry in Clouds and Aqueous Aerosol As a Source of Atmospheric Humic-Like Substances, Environ. Sci. Technol., 50, 7443-7452, doi:10.1021/acs.est.6b00909, 2016.

He, L. Y., Huang, X. F., Xue, L., Hu, M., Lin, Y., Zheng, J., Zhang, R. Y., and Zhang, Y. H.: Submicron aerosol analysis and organic source apportionment in an urban atmosphere in Pearl River Delta of China using high-resolution aerosol mass spectrometry, J. Geophys. Res.-Atmos., 116, 1-15, doi:10.1029/2010jd014566, 2011.

Healy, R. M., Sciare, J., Poulain, L., Crippa, M., Wiedensohler, A., Preovot, A. S. H., Baltensperger, U., Sarda-Esteve, R., McGuire, M. L., Jeong, C. H., McGillicuddy, E., O’Connor, I. P., Sodeau, J. R., Evans, G. J., and Wenger, J. C.: Quantitative determination of carbonaceous particle mixing state in Paris using single-particle mass spectrometer and aerosol mass spectrometer measurements, Atmos. Chem. Phys., 13, 9479-9496, doi:10.5194/acp-13-9479-2013, 2013.

Herrmann, H., Schaefer, T., Tilgner, A., Styler, S. A., Weller, C., Teich, M., and Otto, T.: Tropospheric Aqueous-Phase Chemistry: Kinetics, Mechanisms, and Its Coupling to a Changing Gas Phase, Chem. Rev., 115, 4259-4334, doi:10.1021/cr500447k, 2015.
Ho, K. F., Ho, S. S. H., Lee, S. C., Kawamura, K., Zou, S. C., Cao, J. J., and Xu, H. M.: Summer and winter variations of dicarboxylic acids, fatty acids and benzoic acid in PM2.5 in Pearl Delta River Region, China, Atmos. Chem. Phys., 11, 2197-2208, doi:10.5194/acp-11-2197-2011, 2011.

Ho, K. F., Ho, S. S. H., Huang, R. J., Liu, S. X., Cao, J. J., Zhang, T., Chuang, H. C., Chan, C. S., Hu, D., and Tian, L. W.: Characteristics of water-soluble organic nitrogen in fine particulate matter in the continental area of China, Atmos. Environ., 106, 252-261, doi:10.1016/j.atmosenv.2015.02.010, 2015.

Hu, M., Wu, Z., Slanina, J., Lin, P., Liu, S., and Zeng, L.: Acidic gases, ammonia and water-soluble ions in PM2.5 at a coastal site in the Pearl River Delta, China, Atmos. Environ., 42, 6310-6320, 2008.

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

Huang, R. J., Zhang, Y., Bozzetti, C., Ho, K. F., Cao, J. J., Han, Y., Daellenbach, K. R., Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaspazade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., El Haddad, I., and Prevot, A. S.: High secondary aerosol contribution to particulate pollution during haze events in China, Nature, 514, 218-222, doi:10.1038/nature13774, 2014.

Jang, M., Czoschke, N. M., Lee, S., and Kamens, R. M.: Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions, Science, 298, 814-817, 2002.

Jeong, C. H., McGuire, M. L., Godri, K. J., Slowik, J. G., Rehbein, P. J. G., and Evans, G. J.: Quantification of aerosol chemical composition using continuous single particle measurements, Atmos. Chem. Phys., 11, 7027-7044, doi:10.5194/acp-11-7027-2011, 2011.

Jia, S. G., Sarkar, S., Zhang, Q., Wang, X. M., Wu, L. L., Chen, W. H., Huang, M. J., Zhou, S. Z., Zhang, J. P., Yuan, L., and Yang, L. M.: Characterization of diurnal variations of
| Page | Text |
|------|------|
| 520  | PM2.5 acidity using an open thermodynamic system: A case study of Guangzhou, China, Chemosphere, 202, 677-685, doi:10.1016/j.chemosphere.2018.03.127, 2018. |
| 522  | Kampf, C. J., Filippi, A., Zuth, C., Hoffmann, T., and Opatz, T.: Secondary brown carbon formation via the dicarbonyl imine pathway: nitrogen heterocycle formation and synergistic effects, Phys. Chem. Chem. Phys., 18, 18353-18364, doi:10.1039/c6cp03029g, 2016. |
| 525  | Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, Atmos. Chem. Phys., 5, 1053-1123, 2005. |
| 530  | Kroll, J. H., Ng, N. L., Murphy, S. M., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds, J. Geophys. Res.-Atmos., 110, doi:10.1029/2005JD006004, 2005. |
| 533  | Laskin, A., Smith, J. S., and Laskin, J.: Molecular Characterization of Nitrogen-Containing Organic Compounds in Biomass Burning Aerosols Using High-Resolution Mass Spectrometry, Environ. Sci. Technol., 43, 3764-3771, doi:10.1021/es803456n, 2009. |
| 536  | Laskin, A., Laskin, J., and Nizkorodov, S. A.: Chemistry of Atmospheric Brown Carbon, Chem. Rev., 115, 4335-4382, doi:10.1021/cr5006167, 2015. |
| 538  | Lee, A. K. Y., Zhao, R., Li, R., Liggio, J., Li, S. M., and Abbatt, J. P. D.: Formation of Light Absorbing Organo-Nitrogen Species from Evaporation of Droplets Containing Glyoxal and Ammonium Sulfate, Environ. Sci. Technol., 47, 12819-12826, doi:10.1021/es402687w, 2013. |
| 541  | Lee, S. H., Murphy, D. M., Thomson, D. S., and Middlebrook, A. M.: Nitrate and oxidized organic ions in single particle mass spectra during the 1999 Atlanta Supersite Project, J. Geophys. Res., 108, 8417, doi:10.1029/2001jd001455, 2003. |
| 545  | Lehtipalo, K., Yan, C., Dada, L., Bianchi, F., Xiao, M., Wagner, R., Stolzenburg, D., Ahonen, L. R., Amorim, A., Baccarini, A., Bauer, P. S., Baumgartner, B., Bergen, A., Bernhammer, A.-K., Breitenlechner, M., Brilke, S., Buchholz, A., Mazon, S. B., Chen, D., Chen, |
X., Dias, A., Dommen, J., Draper, D. C., Duplissy, J., Ehn, M., Finkenzeller, H., Fischer, L., Frege, C., Fuchs, C., Garmash, O., Gordon, H., Hakala, J., He, X., Heikkinen, L., Heinritzi, M., Helm, J. C., Hofbauer, V., Hoyle, C. R., Jokinen, T., Kangasluoma, J., Kerminen, V.-M., Kim, C., Kirkby, J., Kontkanen, J., Kürten, A., Lawler, M. J., Mai, H., Mathot, S., Mauldin, R. L., Molteni, U., Nichman, L., Nie, W., Nieminen, T., Ojdanic, A., Onnela, A., Passananti, M., Petäjä, T., Piel, F., Pospisilova, V., Quéléver, L. L. J., Rissanan, M. P., Rose, C., Sarnela, N., Schallhart, S., Schuchmann, S., Sengupta, K., Simon, M., Sipilä, M., Tauber, C., Tomé, A., Tröstl, J., Väisänen, O., Vogel, A. L., Volkamer, R., Wagner, A. C., Wang, M., Weitz, L., Wimmer, D., Ye, P., Ylisimio, A., Zha, Q., Carslaw, K. S., Curtius, J., Donahue, N. M., Flagan, R. C., Hansel, A., Riipinen, I., Virtanen, A., Winkler, P. M., Baltensperger, U., Kulmala, M., and Worsnop, D. R.: Multicomponent new particle formation from sulfuric acid, ammonia, and biogenic vapors, Sci. Adv., 4, eaau5363, doi:10.1126/sciadv.aau5363, 2018.

Li, J., Fang, Y. T., Yoh, M., Wang, X. M., Wu, Z. Y., Kuang, Y. W., and Wen, D. Z.: Organic nitrogen deposition in precipitation in metropolitan Guangzhou city of southern China, Atmos. Res., 113, 57-67, doi:10.1016/j.atmosres.2012.04.019, 2012.

Li, L., Huang, Z. X., Dong, J. G., Li, M., Gao, W., Nian, H. Q., Fu, Z., Zhang, G. H., Bi, X. H., Cheng, P., and Zhou, Z.: Real time bipolar time-of-flight mass spectrometer for analyzing single aerosol particles, Intl. J. Mass. Spectrom., 303, 118-124, doi:10.1016/j.ijms.2011.01.017, 2011.

Li, X., Rohrer, F., Brauers, T., Hofzumahaus, A., Lu, K., Shao, M., Zhang, Y. H., and Wahner, A.: Modeling of HCHO and CHOCHO at a semi-rural site in southern China during the PRIDE-PRD2006 campaign, Atmos. Chem. Phys., 14, 12291-12305, doi:10.5194/acp-14-12291-2014, 2014.

Li, Z. J., Nizkorodov, S. A., Chen, H., Lu, X. H., Yang, X., and Chen, J. M.: Nitrogen-containing secondary organic aerosol formation by acrolein reaction with ammonia/ammonium, Atmos. Chem. Phys., 19, 1343-1356, doi:10.5194/acp-19-1343-2019, 2019.

Liggio, J., Li, S. M., and McLaren, R.: Reactive uptake of glyoxal by particulate matter, J. Geophys. Res.-Atmos., 110, doi:10.1029/2004jd005113, 2005.
Lin, P., Aiona, P. K., Li, Y., Shiraiwa, M., Laskin, J., Nizkorodov, S. A., and Laskin, A.: Molecular Characterization of Brown Carbon in Biomass Burning Aerosol Particles, Environ. Sci. Technol., 50, 11815-11824, doi:10.1021/acs.est.6603024, 2016.

Liu, Y., Liggio, J., Staebler, R., and Li, S. M.: Reactive uptake of ammonia to secondary organic aerosols: kinetics of organonitrogen formation, Atmos. Chem. Phys., 15, 13569-13584, doi:10.5194/acp-15-13569-2015, 2015.

Mace, K. A., Kubilay, N., and Duce, R. A.: Organic nitrogen in rain and aerosol in the eastern Mediterranean atmosphere: An association with atmospheric dust, J. Geophys. Res.-Atmos., 108, doi:10.1029/2002jd002997, 2003.

Mang, S. A., Henricksen, D. K., Bateman, A. P., Andersen, M. P. S., Blake, D. R., and Nizkorodov, S. A.: Contribution of Carbonyl Photochemistry to Aging of Atmospheric Secondary Organic Aerosol, J. Phys. Chem. A, 112, 8337-8344, doi:10.1021/jp804376c, 2008.

Miyazaki, Y., Fu, P. Q., Ono, K., Tachibana, E., and Kawamura, K.: Seasonal cycles of water-soluble organic nitrogen aerosols in a deciduous broadleaf forest in northern Japan, J. Geophys. Res.-Atmos., 119, 1440-1454, doi:10.1002/2013JD020713, 2014.

Mohr, C., Lopez-Hilfiker, F. D., Zotter, P., Prévôt, A. S. H., Xu, L., Ng, N. L., Herndon, S. C., Williams, L. R., Franklin, J. P., Zahniser, M. S., Worsnop, D. R., Knighton, W. B., Aiken, A. C., Gorkowski, K. J., Dubey, M. K., Allan, J. D., and Thornton, J. A.: Contribution of Nitrated Phenols to Wood Burning Brown Carbon Light Absorption in Detling, United Kingdom during Winter Time, Environ. Sci. Technol., 47, 6316-6324, doi:10.1021/es400683v, 2013.

Moise, T., Flores, J. M., and Rudich, Y.: Optical Properties of Secondary Organic Aerosols and Their Changes by Chemical Processes, Chem. Rev., 115, 4400-4439, doi:10.1021/cr5005259, 2015.

Neff, J. C., Holland, E. A., Dentener, F. J., McDowell, W. H., and Russell, K. M.: The origin, composition and rates of organic nitrogen deposition: A missing piece of the nitrogen cycle?, Biogeochemistry, 57, 99-136, 2002.
Nguyen, T. B., Lee, P. B., Updyke, K. M., Bones, D. L., Laskin, J., Laskin, A., and Nizkorodov, S. A.: Formation of nitrogen- and sulfur-containing light-absorbing compounds accelerated by evaporation of water from secondary organic aerosols, J. Geophys. Res.-Atmos., 117, D01207, doi:10.1029/2011jd016944, 2012.

Norris, G., Vedantham, R., Wade, K., Zahn, P., Brown, S., Paatero, P., Eberly, S., and Foley, C. (2009), Guidance document for PMF applications with the Multilinear Engine, edited, Prepared for the U.S. Environmental Protection Agency, Research Triangle Park, NC.

Noziere, B., Dziedzic, P., and Cordova, A.: Products and Kinetics of the Liquid-Phase Reaction of Glyoxal Catalyzed by Ammonium Ions (NH4+), J. Phys. Chem. A, 113, 231-237, doi:10.1021/jp8078293, 2009.

Noziere, B., Kaberer, M., Claeys, M., Allan, J., D'Anna, B., Decesari, S., Finessi, E., Glasius, M., Grigic, I., Hamilton, J. F., Hoffmann, T., Inumya, Y., Jaoui, M., Kahno, A., Kampf, C. J., Kourtchev, I., Maenhaut, W., Marsden, N., Saarikoski, S., Schnelle-Kreis, J., Surratt, J. D., Szidat, S., Szmigielski, R., and Wisthaler, A.: The Molecular Identification of Organic Compounds in the Atmosphere: State of the Art and Challenges, Chem. Rev., 115, 3919-3983, doi:10.1021/cr5003485, 2015.

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.

Pan, Y. P., Tian, S. L., Zhao, Y. H., Zhang, L., Zhu, X. Y., Gao, J., Huang, W., Zhou, Y. B., Song, Y., Zhang, Q., and Wang, Y. S.: Identifying Ammonia Hotspots in China Using a National Observation Network, Environ. Sci. Technol., 52, 3926-3934, doi:10.1021/acs.est.7b05235, 2018.

Paulot, F., Wunch, D., Crounse, J. D., Toon, G. C., Millet, D. B., DeCarlo, P. F., Vigouroux, C., Deutscher, N. M., González Abad, G., Notholt, J., Warneke, T., Hannigan, J. W., Warneke, C., de Gouw, J. A., Dunlea, E. J., De Mazière, M., Griffith, D. W. T., Bernath, P., Jimenez, J. L., and Wennberg, P. O.: Importance of secondary sources in the atmospheric
Qin, X. Y., Bhave, P. V., and Prather, K. A.: Comparison of two methods for obtaining quantitative mass concentrations from aerosol time-of-flight mass spectrometry measurements, Anal. Chem., 78, 6169-6178, doi:10.1021/ac060395q, 2006.

Rastogi, N., Zhang, X., Edgerton, E. S., Ingall, E., and Weber, R. J.: Filterable water-soluble organic nitrogen in fine particles over the southeastern USA during summer, Atmos. Environ., 45, 6040-6047, doi:10.1016/j.atmosenv.2011.07.045, 2011.

Sareen, N., Schwier, A. N., Shapiro, E. L., Mitroo, D., and McNeill, V. F.: Secondary organic material formed by methylglyoxal in aqueous aerosol mimics, Atmos. Chem. Phys., 10, 997-1016, doi:10.5194/acp-10-997-2010, 2010.

Shapiro, E. L., Szprengiel, J., Sareen, N., Jen, C. N., Giordano, M. R., and McNeill, V. F.: Light-absorbing secondary organic material formed by glyoxal in aqueous aerosol mimics, Atmos. Chem. Phys., 9, 2289-2300, 2009.

Shrivastava, M., Cappa, C. D., Fan, J. W., Goldstein, A. H., Guenther, A. B., Jimenez, J. L., Kuang, C., Laskin, A., Martin, S. T., Ng, N. L., Petaja, T., Pierce, J. R., Rasch, P. J., Roldin, P., Seinfeld, J. H., Shilling, J., Smith, J. N., Thornton, J. A., Volkamer, R., Wang, J., Worsnop, D. R., Zaveri, R. A., Zelenyuk, A., and Zhang, Q.: Recent advances in understanding secondary organic aerosol: Implications for global climate forcing, Rev. Geophys., 55, 509-559, doi:10.1002/2016RG000540, 2017.

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.
Part I, biogenic influences and day/night chemistry in summer, Atmos. Chem. Phys. Discuss., 2019, 1-36, doi:10.5194/acp-2019-361, 2019.

Sullivan, R. C., and Prather, K. A.: Investigations of the diurnal cycle and mixing state of oxalic acid in individual particles in Asian aerosol outflow, Environ. Sci. Technol., 41, 8062-8069, 2007.

Sun, J. Z., Zhi, G. R., Hitzenberger, R., Chen, Y. J., Tian, C. G., Zhang, Y. Y., Feng, Y., Cheng, M. M., Zhang, Y. Z., Cai, J., Chen, F., Qiu, Y., Jiang, Z., Li, J., Zhang, G., and Mo, Y.: Emission factors and light absorption properties of brown carbon from household coal combustion in China, Atmos. Chem. Phys., 17, 4769-4780, doi:10.5194/acp-17-4769-2017, 2017.

Sun, Y. L., Zhang, Q., Schwab, J. J., Demerjian, K. L., Chen, W. N., Bae, M. S., Hung, H. M., Hogrefe, O., Frank, B., Rattigan, O. V., and Lin, Y. C.: Characterization of the sources and processes of organic and inorganic aerosols in New York city with a high-resolution time-of-flight aerosol mass spectrometer, Atmos. Chem. Phys., 11, 1581-1602, doi:10.5194/acp-11-1581-2011, 2011.

Updyke, K. M., Nguyen, T. B., and Nizkorodov, S. A.: Formation of brown carbon via reactions of ammonia with secondary organic aerosols from biogenic and anthropogenic precursors, Atmos. Environ., 63, 22-31, doi:10.1016/j.atmosenv.2012.09.012, 2012.

Wang, X. F., Gao, S., Yang, X., Chen, H., Chen, J. M., Zhuang, G. S., Surratt, J. D., Chan, M. N., and Seinfeld, J. H.: Evidence for High Molecular Weight Nitrogen-Containing Organic Salts in Urban Aerosols, Environ. Sci. Technol., 44, 4441-4446, 2010.

Wang, X. F., Wang, H. L., Jing, H., Wang, W. N., Cui, W. D., Williams, B. J., and Biswas, P.: Formation of Nitrogen-Containing Organic Aerosol during Combustion of High-Sulfur-Content Coal, Energ. Fuel., 31, 14161-14168, doi:10.1021/acs.energyfuels.7b02273, 2017.

Woo, J. L., Kim, D. D., Schwier, A. N., Li, R. Z., and McNeill, V. F.: Aqueous aerosol SOA formation: impact on aerosol physical properties, Faraday Discuss., 165, 357-367, doi:10.1039/c3fd00032j, 2013.
Xu, W. Q., Sun, Y. L., Wang, Q. Q., Du, W., Zhao, J., Ge, X. L., Han, T. T., Zhang, Y. J., Zhou, W., Li, J., Fu, P. Q., Wang, Z. F., and Worsnop, D. R.: Seasonal Characterization of Organic Nitrogen in Atmospheric Aerosols Using High Resolution Aerosol Mass Spectrometry in Beijing, China, Acs Earth Space Chem., 1, 673-682, doi:10.1021/acsearthspacechem.7b00106, 2017.

Yan, J., Wang, X., Gong, P., Wang, C., and Cong, Z.: Review of brown carbon aerosols: Recent progress and perspectives, Sci. Total. Environ., 634, 1475-1485, doi:https://doi.org/10.1016/j.scitotenv.2018.04.083, 2018.

Yu, X., Yu, Q. Q., Zhu, M., Tang, M. J., Li, S., Yang, W. Q., Zhang, Y. L., Deng, W., Li, G. H., Yu, Y. G., Huang, Z. H., Song, W., Ding, X., Hu, Q. H., Li, J., Bi, X. H., and Wang, X. M.: Water Soluble Organic Nitrogen (WSON) in Ambient Fine Particles Over a Megacity in South China: Spatiotemporal Variations and Source Apportionment, J. Geophys. Res.-Atmos., 122, 13045-13060, doi:10.1002/2017JD027327, 2017.

Yuan, B., Liggio, J., Wentzell, J., Li, S. M., Stark, H., Roberts, J. M., Gilman, J., Lerner, B., Warneke, C., Li, R., Leithead, A., Osthoff, H. D., Wild, R., Brown, S. S., and de Gouw, J. A.: Secondary formation of nitrated phenols: insights from observations during the Uintah BasinWinter Ozone Study (UBWOS) 2014, Atmos. Chem. Phys., 16, 2139-2153, doi:10.5194/acp-16-2139-2016, 2016.

Yuan, Q., Lai, S., Song, J., Ding, X., Zheng, L., Wang, X., Zhao, Y., Zheng, J., Yue, D., Zhong, L., Niu, X., and Zhang, Y.: Seasonal cycles of secondary organic aerosol tracers in rural Guangzhou, Southern China: The importance of atmospheric oxidants, Environ. Pollut., 240, 884-893, doi:10.1016/j.envpol.2018.05.009, 2018.

Zauscher, M. D., Wang, Y., Moore, M. J. K., Gaston, C. J., and Prather, K. A.: Air Quality Impact and Physicochemical Aging of Biomass Burning Aerosols during the 2007 San Diego Wildfires, Environ. Sci. Technol., 47, 7633-7643, doi:10.1021/es4004137, 2013.

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.
Zhang, G., Lin, Q., Peng, L., Yang, Y., Jiang, F., Liu, F., Song, W., Chen, D., Cai, Z., Bi, X., Miller, M., Tang, M., Huang, W., Wang, X., Peng, P., and Sheng, G.: Oxalate Formation Enhanced by Fe-Containing Particles and Environmental Implications, Environ. Sci. Technol., 53, 1269-1277, doi:10.1021/acs.est.8b05280, 2019.

Zhang, G. H., Bi, X. H., He, J. J., Chen, D. H., Chan, L. Y., Xie, G. W., Wang, X. M., Sheng, G. Y., Fu, J. M., and Zhou, Z.: Variation of secondary coatings associated with elemental carbon by single particle analysis, Atmos. Environ., 92, 162-170, doi:10.1016/j.atmosenv.2014.04.018, 2014.

Zhang, G. H., Lin, Q. H., Peng, L., Yang, Y. X., Fu, Y. Z., Bi, X. H., Li, M., Chen, D. H., Chen, J. X., Cai, Z., Wang, X. M., Peng, P. A., Sheng, G. Y., and Zhou, Z.: Insight into the in-cloud formation of oxalate based on in situ measurement by single particle mass spectrometry, Atmos. Chem. Phys., 17, 13891-13901, doi:10.5194/acp-17-13891-2017, 2017.

Zhang, Q., Duan, F., He, K., Ma, Y., Li, H., Kimoto, T., and Zheng, A.: Organic nitrogen in PM2.5 in Beijing, Frontiers of Environmental Science & Engineering, 9, 1004-1014, doi:10.1007/s11783-015-0799-5, 2015.

Zhang, Y. S., Shao, M., Lin, Y., Luan, S. J., Mao, N., Chen, W. T., and Wang, M.: Emission inventory of carbonaceous pollutants from biomass burning in the Pearl River Delta Region, China, Atmos. Environ., 76, 189-199, doi:10.1016/j.atmosenv.2012.05.055, 2013.

Zhao, R., Lee, A. K. Y., and Abbatt, J. P. D.: Investigation of Aqueous-Phase Photooxidation of Glyoxal and Methylglyoxal by Aerosol Chemical Ionization Mass Spectrometry: Observation of Hydroxyhydroperoxide Formation, J. Phys. Chem. A, 116, 6253-6263, doi:10.1021/jp211528d, 2012.

Zhao, R., Lee, A. K. Y., Huang, L., Li, X., Yang, F., and Abbatt, J. P. D.: Photochemical processing of aqueous atmospheric brown carbon, Atmos. Chem. Phys., 15, 6087-6100, doi:10.5194/acp-15-6087-2015, 2015.

Zheng, J. Y., Yin, S. S., Kang, D. W., Che, W. W., and Zhong, L. J.: Development and uncertainty analysis of a high-resolution NH3 emissions inventory and its implications with
precipitation over the Pearl River Delta region, China, Atmos. Chem. Phys., 12, 7041-7058, doi:10.5194/acp-12-7041-2012, 2012.

Zhou, S. Z., Wang, T., Wang, Z., Li, W. J., Xu, Z., Wang, X. F., Yuan, C., Poon, C. N., Louie, P. K. K., Luk, C. W. Y., and Wang, W. X.: Photochemical evolution of organic aerosols observed in urban plumes from Hong Kong and the Pearl River Delta of China, Atmos. Environ., 88, 219-229, doi:10.1016/j.atmosenv.2014.01.032, 2014.

Zhou, Y., Huang, X. H. H., Griffith, S. M., Li, M., Li, L., Zhou, Z., Wu, C., Meng, J. W., Chan, C. K., Louie, P. K. K., and Yu, J. Z.: A field measurement based scaling approach for quantification of major ions, organic carbon, and elemental carbon using a single particle aerosol mass spectrometer, Atmos. Environ., 143, 300-312, doi:10.1016/j.atmosenv.2016.08.054, 2016.

Zhu, S. P., Horne, J. R., Montoya-Aguilera, J., Hinks, M. L., Nizkorodov, S. A., and Dabdub, D.: Modeling reactive ammonia uptake by secondary organic aerosol in CMAQ: application to the continental US, Atmos. Chem. Phys., 18, 3641-3657, doi:10.5194/acp-18-3641-2018, 2018.
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.

Figure 7. The dependence of NOCs on the relative acidity ratio. The relative acidity ratios were logarithmically transformed to follow a normal distribution.
Fig. 1.
Fig. 2.
Fig. 3.
Fig. 4.

R² = 0.71

Fitted function: Y = X
Fig. 5.
Fig. 6.
Fig. 7.