

1    **Light Absorption Properties and Composition of Brown carbon in North China**

2    **Plain: Implication for an Enhancing Role of Nitrogenous Organic Compounds**

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**Abstract:** Brown carbon (BrC), an efficiently light-absorbing carbonaceous aerosol, exerts significant impacts on the global energy budget and regional climate, attracting growing scientific attention. To advance understanding of the spatial variability of atmospheric BrC and its dominant formation pathways in the North China Plain (NCP), light absorption properties, chemical composition and formation process of the water-soluble BrC in 2023 winter were investigated by conducting simultaneous measurements at five sites across the NCP, namely, Beijing, Tianjin, Luancheng (rural site), Handan and Jinan. Our results showed that the average light absorption coefficient at 365 nm ( $\text{abs}_{365}$ ) in Luancheng was approximately 1.1–3.5 times higher than those in urban ones. However, mass absorption efficiency displayed a distinctly different spatial pattern, with the strongest light-absorptivity ( $1.40 \pm 0.02 \text{ m}^2 \text{ g}^{-1}$ ) recorded in Jinan. Notably, average  $\text{abs}_{365}$  in four urban sites exhibited a decline of ~45% from 2018 to 2023 compared to those previous observations. Furthermore, the light-absorptivity of BrC was enhanced from clean to haze period at the most sampling sites along with the increasing N:C ratio, indicating that nitrogenous organic compounds (NOCs) were important BrC chromophores in the NCP. Additionally, over 50% of NOCs were found to formed predominantly via aqueous reactions, where ammonia played an important role. Above results elucidate the substantial contribution of NOCs to atmospheric BrC in the NCP, and further confirm the importance of ammonia emission for alleviating haze and BrC pollution in this region.

**Keywords:** Brown carbon; Nitrogenous organic compounds; Spatiotemporal characteristics; Biomass burning; Secondary formation

## 1. Introduction

Light-absorbing organic aerosol, optically defined as brown carbon (BrC), is prevalent in the troposphere and efficiently absorbs solar radiation, thereby perturbing the global energy budget and influencing regional climate (Liu et al., 2020; Laskin et al., 2015; Samset et al., 2018). Recent modeling studies demonstrates that BrC is responsible for >20% of the direct radiative effect (DRE) caused by carbonaceous aerosols (Zeng et al., 2020; Feng et al., 2013; Zhang et al., 2017; Liu et al., 2015a). Most significantly, BrC even dominates the DRE in certain regions of the Earth, e.g., in the remote tropical upper troposphere (Zhang et al., 2020). However, these reported BrC DRE have large uncertainty, partly stemming from the poor understanding of optical properties and atmospheric evolution of BrC. Unlike black carbon (BC), BrC is characterized by a pronounced dependence of light-absorption on wavelength, with absorbance increasing steeply near UV wavelengths (Andreae and Gelencsér, 2006). Consequently, abundant BrC can also reduce the amount of ultraviolet sunlight reaching surface, subsequently altering tropospheric photochemistry. Indeed, growing evidence reveal a nonnegligible reduction in photolysis rates of the ozone and radicals with enhanced BrC load (Hammer et al., 2016; Gligorovski et al., 2015; Jo et al., 2016; He and Carmichael, 1999). Beyond the climatic and atmospheric effects, multiple BrC chromophores (e.g, polycyclic aromatic and nitro-heterocyclic compounds) also pose adverse health effects because of their strong oxidative potential (Fang et al., 2019; Daellenbach et al., 2020).

Diverse sources of atmospheric BrC have been identified, including the various primary emissions and complex secondary formation. Primary BrC is known to be

directly emitted from the incomplete combustion of biomass and other fuels (Washenfelter et al., 2015; Lack et al., 2012; Chen et al., 2017; Yan et al., 2017), of which optical properties are inherently related to combustion conditions and fuel types (Ni et al., 2021; Xie et al., 2017; Stockwell et al., 2015). And field measurements and laboratory studies indicated that the aromatics, conjugated systems, and highly functionalized species with high light-absorptivity can be secondarily formed via  $\text{OH}\cdot/\text{NO}_3\cdot/\text{O}_3$  photooxidation of various precursors (Hems and Abbatt, 2018; Jiang et al., 2019; Finewax et al., 2018), or reactions initiated by ammonia/amines with atmospherically relevant carbonyls (Updyke et al., 2012; Powelson et al., 2014; Grace et al., 2020). These processes would generate abundant N-containing compounds (NOCs), which have been recognized as significant components of BrC (Lin et al., 2015; Yang et al., 2022; Wang et al., 2025a). Notably, the latest modeling study suggested that the NOCs dominate the global organic aerosol absorption, accounting for 18% of global DRE induced by carbonaceous aerosols (Li et al., 2025). These absorptive NOCs are probably responsible for an enhanced light absorption of BrC in the upper boundary layer, as a result of their efficient formation in the lifting air masses (Wu et al., 2024a; Wu et al., 2024b). Moreover, the further aging processes would chemically modify the BrC composition, subsequently leading to either an increase (photodarkening) or decrease (photobleaching) in light-absorptivity of BrC chromophores (Wong et al., 2017; Jiang et al., 2022; Hems et al., 2021). These dynamic natures of BrC drive pronounced spatiotemporal heterogeneity in its chemical components and optical properties, propagating significant uncertainties in climate models that limit the reliable

projection and mitigation of the climate effects caused by diverse BrC.

Over the past decade, stringent emission control measures, such as shifting residential coal to natural gas/electricity, eliminating small coal-fired industrial boilers, and banning straw burning, etc., have been implemented in the North China Plain (NCP) (Chen et al., 2024b; Zheng et al., 2018). Given the substantial contribution of primary emissions to atmospheric BrC, BrC level in this region was expected to drastically decrease. Nevertheless, high loads of strongly light-absorbing BrC were still detected frequently in this region (Wang et al., 2025c; Chen et al., 2024a; Gong et al., 2023; Sun et al., 2026). Therefore, the sources and formation mechanism remain elusive in the NCP. Moreover, the atmospheric environment in this region also undergone significant changes, characterized particularly by enhanced atmospheric oxidation capacity driven by reduced NO<sub>x</sub> emissions and elevated O<sub>3</sub> levels, as well as persistently high NH<sub>3</sub> loadings due to insufficient controls on agricultural emissions (Li et al., 2019; Zheng et al., 2018; Zhu et al., 2023). Our recent studies demonstrate that such an ammonia-rich environment plays a key role in enhancing BrC absorption, primarily by reducing aerosol acidity and facilitating the formation of light-absorbing NOCs (Liu et al., 2023; Zhang et al., 2024). These findings imply that the primary drivers of BrC formation may have changed relative to those in the past. Motivated by this, atmospheric BrC in the NCP were collected during the 2023 winter and analyzed for the characteristics of BrC. We investigated the spatial difference of chemical composition and light-absorption of BrC, and discussed the role of NOCs in the BrC light absorption and their formation pathways.

## **2. Materials and Methods**

### **2.1 Sampling**

The multi-site observations were synchronously conducted on the North China Plain from 15 November to 31 December 2023 (Figure S1). Four of the sampling sites are located in urban areas, namely Beijing (BJ), Tianjin (TJ), Handan (HD) and Jinan (JN), which are surrounded by the traffic arteries and dense residential and commercial buildings. And the remaining one, adjacent to Luancheng (LC), serves as a rural station free from significant industrial influences. At each site, the PM<sub>2.5</sub> samples with a 12-hr interval were collected onto prebaked (at 450°C for 6 hrs) quartz filters using high- (1.13 m<sup>3</sup> min<sup>-1</sup>) or medium-volume (100 L min<sup>-1</sup>) air samplers; All the samplers located on the rooftops approximately 15–20 m above ground level. After sampling, the filter samples were wrapped in prebaked aluminum foils and stored in a freezer (at -18°C) prior to analysis.

Hourly concentrations of PM<sub>2.5</sub> and associated pollutants (e.g., NO<sub>2</sub>, O<sub>3</sub>, CO) at the sampling sites were obtained from the National Urban Air Quality Real-time Release Platform of China (<https://air.cnemc.cn:18007/>, last access: 6 April 2025), of which monitoring sites are adjacent to ours with a distance of < 10 km. The meteorological data including ambient temperature (T) and relative humidity (RH) were downloaded from National Climatic Data Center (<https://www.ncei.noaa.gov/>, last access: 6 April 2025).

### **2.2 Chemical analysis**

A piece of each filter was extracted with 40 ml ultrapure Milli-Q water (18.2 MΩ) under

151 ultrasonication for 30 min. A part of the extract was used for the detection of water-  
152 soluble ions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) by using an ion  
153 chromatography; The remaining part was detected for the water-soluble organic carbon  
154 (WSOC) and water-soluble total nitrogen (WSTN) via a total organic carbon (TOC)  
155 analyzer (Model TOC-L CPH, Shimadzu, Japan). And the water-soluble organic  
156 nitrogen (WSON) can be quantified by deducting the water-soluble inorganic nitrogen  
157 (WSIN) from WSTN (i.e.,  $\text{WSON} = \text{WSTN} - \text{WSIN}$ ). A DRI-model 2001 thermal-optical  
158 carbon analyzer following the IMPROVE-A protocol was applied here to measure  
159 organic carbon (OC) and element carbon (EC) of  $\text{PM}_{2.5}$ .

160 The molecular compositions in  $\text{PM}_{2.5}$  samples, including nitro-aromatic compounds  
161 (NACs, Table S1), polycyclic aromatic hydrocarbons (PAHs) and others organic tracers,  
162 were extracted with a mixture of dichloromethane and methanol (2: 1, v/v);  
163 Subsequently, the extracts were derivatized via derivatization reagent (a mixture of 50  
164  $\mu\text{l}$  of N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) and 1% trimethylsilyl  
165 chloride and 10  $\mu\text{l}$  of pyridine) prior to GC/MS analyses. More details of the extraction,  
166 derivatization and the GC/MS analyses can refer to elsewhere (Wang et al., 2006; Wu  
167 et al., 2025).

168 Additionally, the aerodyne high-resolution time-of-flight aerosol mass spectrometer  
169 (HR-AMS) was applied here to characterize the imidazole-related fragments (e.g.,  
170  $\text{C}_3\text{H}_3\text{N}_2^+$  and  $\text{C}_3\text{H}_4\text{N}_2^+$ ) in a typical humid haze event (12 to 31 December of 2023,  
171 Figure S2), following the method reported by Ge et al. (2024). It should be pointed out  
172 that above fragments may stem from other nitrogen-containing precursors, which

inevitably introduces uncertainties into the quantification. Accordingly, the concentrations derived from these fragment ions cannot represent the actual abundances of the real molecules. Even so, the fragment ion levels can still indicate the variation trends of imidazole N-heterocycles. Because imidazole concentrations measured by orbitrap mass spectrometry in our previous field campaign showed a significant positive correlation with offline-AMS signals of  $C_3H_3N_2^+$  and  $C_3H_4N_2^+$  (Figure S3).

The details of the extraction and derivatization can be found elsewhere (Wu et al., 2024a). Briefly, a part of the  $PM_{2.5}$  filter was extracted following the procedure similar to that of other water-soluble components; then the extracts were atomized using argon as the carrier gas, dehydrated by a diffusion drier, and ultimately quantified by HR-AMS. Each sample was continuously monitored by HR-AMS for >10 min to obtain stable signal, and above procedure was also applied to the blank samples to account for any potential contamination or background signals. A deep post-processing was conducted for the V-mode data in this study using the Igor-based Aerosol Mass Spectrometer Analysis Toolkit. The mass concentration of imidazole-related fragments was calculated as the follow:

$$C_{IMs} = F_{IMs} \times WSOM \quad (1)$$

Where  $C_{IMs}$  denotes to the concentration of the imidazole-related fragments.  $F_{IMs}$  is mass contribution of the imidazole-related fragments to the total fragments measured by HR-AMS; WSOM refers to atmospheric concentration of water-soluble organic matter ( $\mu g\ m^{-3}$ )

### 2.3 Optical Absorption of BrC

The light-absorbing chromophores (i.e., BrC) were also extracted with 10 ml ultrapure Milli-Q water, following the procedure for water-soluble ions. A UV–vis spectrometer was applied here to record the absorption spectra of all the extracts, which were finally converted into absorption coefficient ( $abs_{\lambda}$ , M/m) at a given wavelength ( $\lambda$ ) using the following equation:

$$abs_{\lambda} = (A_{\lambda} - A_{700}) \frac{V_L}{V_a \times l} \times \ln(10) \quad (2)$$

Where  $A_{\lambda}$  is the absorbance at wavelength  $\lambda$  (nm),  $V_L$  and  $V_a$  refer to the volume of the extractant and air through corresponding to filter punches, respectively. The optical path length is 1 cm (i.e.,  $l$ ). From  $abs_{\lambda}$ , the mass absorption coefficient ( $MAE_{\lambda}$ ,  $m^2/g$ ) can be characterized as:

$$MAE_{\lambda} = \frac{abs_{\lambda}}{C} \quad (3)$$

Where  $C$  is the mass concentration of water-soluble organic carbon.

#### 2.4 Random forest analysis for water-soluble organic nitrogen

Random forest (RF), as a powerful tool for regression and prediction (Hu et al., 2017; Vu et al., 2019), was employed here to elucidate the relationships between secondary WSON (WSONsec) and potential factors ( $NH_4^+$ ,  $NO_2$ ,  $O_3$ , ALWC, pH and meteorological factors). The importance of each factor to WSONsec can be determined by a SHAP method originally proposed by Lundberg and Lee (2017). Rooted in cooperative game theory, SHAP framework as a model-agnostic additive feature attribution method enables an in-depth exploration of interaction effects and effectively alleviates poor interpretability of machine learning models. In the RF model design, 70% of the dataset including all the samples from the five monitoring sites was randomly divided into a training subset to construct the RF model, and the remaining 30% (i.e., test set) was used to assess the model performance. Following systematic hyperparameter optimization, the decision tree ( $n_{tree}$ ) was set to 300 to balance model

performance and computational efficiency; and number of variables split at each node ( $n_{\text{mtry}}$ ) was limited to 12 to avoid overfitting. Additionally, a 10-fold cross-validation strategy was adopted here to optimize model parameters and estimate model performance. The RF model was constructed using the “randomForest” R package, of which performance was evaluated by coefficient of determination ( $R^2$ ), mean square error (MSE) or root-mean-square error (RMSE) and mean absolute error (MAE). As summarized in Table S2, the simulated WSONsec corrected strongly with observed ones, and the error metric remained at low levels; These indicated that the model could reconstruct commendably the variations of WSONsec in this study.

## 2.5 Theoretical estimation of particulate fraction of NACs ( $F_p$ )

Since gas-phase nitro-aromatic compounds (NACs) were not detected in this study, the particulate-phase fraction ( $F_p$ ) of NACs was calculated based on absorption equilibrium theory (Pankow et al., 2001; Zuend and Seinfeld, 2012), and the specific calculation method referred to that reported by Chen et al. (2025). As shown in the following equations:

$$F_p = \frac{C_p}{C_p + C_g} = \frac{K_p \times PM}{1 + K_p \times PM} \quad (4)$$

$$K_p = \frac{C_p}{C_g \times PM} = \frac{760 \times f \times R \times T}{10^6 \times P_v \times M \times \xi} \quad (5)$$

Herein,  $C_g$  and  $C_p$  are the mass concentrations of the organic molecule in gas and particle phase, respectively.  $K_p$  refers to gas–particle partitioning coefficient, and is determined by many factors in Eq. 5. Specifically,  $P_v$  is the saturation pressure (Pa), which is 0.00378 torr for 4-nitrophenol (at 298 K).  $\xi$  is the activity coefficient of the species, adopting from the values reported by Wang et al. (2019).  $M$  refers to the molecular weight of NAC species ( $\text{g mol}^{-1}$ ). Additionally,  $R$  is the gas constant (8.314

$J \text{ (mol K)}^{-1}$ ),  $T$  is the temperature (K),  $f$  denotes the fraction of organic matter in particle, and  $PM$  is the mass concentration of  $PM_{2.5}$ .

### 3. Result and discussion

#### 3.1 Spatial variation of $PM_{2.5}$ Chemical Composition

As shown in Table 1 and Figure S2, the  $PM_{2.5}$  concentration across the North China Plain (NCP) exhibited significant spatial heterogeneity, ranging from 4.0 to 223.7  $\mu\text{g m}^{-3}$ . Specifically, the highest average  $PM_{2.5}$  load was recorded in JN ( $94.1 \pm 37.8 \mu\text{g m}^{-3}$ ), partially attributed to unfavorable topographic conditions and intensive anthropogenic emissions. The average  $PM_{2.5}$  level at remaining sampling sites decreased gradually from south to north. Notably, the  $PM_{2.5}$  concentration in Beijing during the campaign was only a quarter of that recorded a decade ago ( $158 \mu\text{g m}^{-3}$ ), indicating a notable air quality improvement in BJ over recent years. Even so, multi-day haze episodes ( $PM_{2.5} > 75 \mu\text{g m}^{-3}$ ) still occurred frequently in BJ (Figure S2), of which hourly peak concentration even reached up to  $203 \mu\text{g m}^{-3}$ , about 3-fold of National Air Quality Standard grade-II ( $75 \mu\text{g m}^{-3}$ ). Additionally, these events were also observed simultaneously at other sites, suggesting that regional  $PM_{2.5}$  pollution remains a persistent challenge during winter across the NCP, particularly in its southern region.

The spatiotemporal differences in chemical compositions, sources of organic matter (OM) in  $PM_{2.5}$  among sampling sites are illustrated in Figure 1. As the major component of  $PM_{2.5}$ , water soluble ions (WSIs) accounted for approximately 30%-53% of  $PM_{2.5}$ ; Similar to the spatial pattern of  $PM_{2.5}$ , WSIs also exhibited high loads in JN ( $40.4 \pm 23.2 \mu\text{g m}^{-3}$ ) and HD ( $44.1 \pm 34.3 \mu\text{g m}^{-3}$ ), which were  $\sim 1.2$ -4 fold of those measured in other

sites. From Figure 1, nitrate was the most abundant ion across the NCP, accounting for 14%-27% of PM<sub>2.5</sub>, followed by sulfate (5%-9%) and ammonium (4%-11%), respectively. Compared to those in urban sites, relative abundance of SNA (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) in rural site (LC) moderately enhanced by 10%-23%, indicating a significant influence of secondary aerosol formation in the rural area. Furthermore, a relatively high concentration of chloride was detected among the sampling sites, even with a molarity being >1.5-fold of that of sulfate (Figure S4a). A strong correlation between chloride and levoglucosan+Benzo[k]fluoranthene (BkF) across the sampling sites (R<sup>2</sup>=0.97) implied that combustion emissions were the primary source for the abundant chloride in the NCP (Figure S4b). These abundant chlorides could promote heterogeneous formation of sulfate as evidenced by a robust relationship chloride and SOR (SO<sub>4</sub><sup>2-</sup>/(SO<sub>4</sub><sup>2-</sup>+SO<sub>2</sub>)) (Figure S4c). This finding was consistent with the results of our laboratory experiments (Wang et al., 2025b; Wang et al., 2016), which demonstrated that the abundant chloride could significantly enhance the uptake of NO<sub>2</sub> by interfacial electrostatic attraction, subsequently accelerating sulfate formation.

The average concentration of OM ranged from 7.9±5.7 µg m<sup>-3</sup> to 18.7±10.7 µg m<sup>-3</sup>, accounting for 17%-25% of PM<sub>2.5</sub>. Although OM was a predominant species in PM<sub>2.5</sub> at most sites, its spatial distribution differed slightly from that of PM<sub>2.5</sub>, with high loads in LC (18.5±11 µg m<sup>-3</sup>) and HD (18.7±10.7 µg m<sup>-3</sup>). To determine the sources of the abundant OM, a PMF was applied here and identified three types OM sources (Figure S4, Text S1). From Figure 1, a significant fraction of OM (40%-55%) at urban sites was associated with secondary formation, comparable to that in northern regions of China

(50%) (Chen et al., 2024b). In contrast, combustion-derived primary OM accounted for less than 40% of the total OM. This finding was consistent with the field observations, which demonstrated a widespread decline in primary OM in NCP during 2013-2020 due to the significant reduction in residential fuel burning (Chen et al., 2024b). Notably, about 55% of OM at rural site was derived from combustion, reflecting an urban-rural variation in sources.

### 3.2 Spatial variability in optical properties of BrC

Figure 2a displays the average absorption spectra of WSOC across the sampling sites, which exhibits the marked feature of BrC with the reduced light absorption from the ultraviolet to the visible ranges. As illustrated in Table 1 and Figure 2, the light absorption coefficient at 365 nm ( $\text{abs}_{365}$ ) displayed a spatial pattern similar to that of organic matter (OM) across the five sampling sites. Specifically, the highest average  $\text{abs}_{365}$  was observed at LC site, with average of  $(8.0 \pm 4.7 \text{ Mm}^{-1})$ , followed by HD ( $7.9 \pm 5.0 \text{ Mm}^{-1}$ ), JN ( $6.9 \pm 3.0 \text{ Mm}^{-1}$ ), TJ ( $5.7 \pm 3.8 \text{ Mm}^{-1}$ ) and BJ ( $2.3 \pm 1.9 \text{ Mm}^{-1}$ ), respectively. Across the sampling sites,  $\text{abs}_{365}$  correlated robustly ( $R^2 = 0.73$ ,  $p < 0.05$ ) with levoglucosan being a known tracer for biomass burning (BB). This implied that BrC in the NCP was significantly affected by fresh emissions from BB, which aligns with the prior observations in China (Li et al., 2022b; Desyaterik et al., 2013; Li et al., 2023). Additionally, the BB emission was more pronounced in rural areas, as indicated by a higher mass fraction of levoglucosan to OM ( $0.67 \pm 0.39\%$ ), which was approximately 2.1 to 5 times higher than those in urban areas. These findings highlight the significant impact of anthropogenic combustion on air quality in the rural NCP.

From Figure 2b, the average light-absorption of urban BrC in the NCP exhibited a decline of ~45% from  $10.7 \pm 3.0 \text{ Mm}^{-1}$  in 2018 to  $5.8 \pm 2.2 \text{ Mm}^{-1}$  in 2023. Beijing exhibited a more substantial reduction, where the  $\text{abs}_{365}$  was only 16% of that recorded a decade ago (Figure 2b). Even so, the averaged  $\text{abs}_{365}$  in the NCP still remains higher than that in Nanjing, Guangzhou and urban areas in developed countries (Table S3).

As a metric for characterizing the light absorptivity of BrC, the MAE at 365 nm ( $\text{MAE}_{365}$ ) was quantified by the linear regression slope of  $\text{abs}_{365}$  against WSOC. As illustrated in Figure 2c,  $\text{MAE}_{365}$  exhibits a distinctly different spatial pattern relative to  $\text{abs}_{365}$ . A strikingly high  $\text{MAE}_{365}$  value was measured in JN ( $1.4 \pm 0.04 \text{ m}^2 \text{ g}^{-1}$ ), on par with those found in severely polluted regions like Xingtai, Xi'an and Delhi, India ( $1.2\text{--}1.6 \text{ m}^2 \text{ g}^{-1}$ , in the cold season) (Li et al., 2023; Wu et al., 2020; Kirillova et al., 2014). And the  $\text{MAE}_{365}$  value also falls within the range for documented BrC emitted from residential coal combustion (e.g.,  $1.20\text{--}1.59 \text{ m}^2 \text{ g}^{-1}$  for bituminous coal) (Ni et al., 2021), suggesting that coal combustion is one of the potential sources of atmospheric BrC in JN. Additionally, TJ, LC and HD shared a comparable  $\text{MAE}_{365}$  value of approximately  $1.1 \text{ m}^2 \text{ g}^{-1}$ , which closely matches the values associated with biomass burning-derived BrC ( $1.2 \pm 0.3 \text{ m}^2 \text{ g}^{-1}$ ) (Cao et al., 2021). This finding further indicated a significant effect of biomass burning on the wintertime BrC in the NCP, which can be corroborated by the concentration-weighted trajectory (CWT) analysis. As shown in Figure 3, high CWT loadings for  $\text{abs}_{365}$  were predominantly associated with regions characterized by concentrated fire hotspots, especially in LC, HD and their adjacent areas. Of note, the  $\text{MAE}_{365}$  of the BrC in BJ was the lowest ( $0.71 \pm 0.02 \text{ m}^2 \text{ g}^{-1}$ ), only half that of JN. This

relatively weak light absorptivity of BrC in BJ may be attributable to substantial vehicle emissions, as BrC from this source typically exhibits relatively low MAE values, ranging from approximately 0.35 to 0.71 m<sup>2</sup> g<sup>-1</sup> (Tang et al., 2020; Huang et al., 2022). Another possibility is that the aerosol in BJ was more aged, because BrC light-absorption would decay in the aerosol aging process as revealed by observational and experimental findings (Hems et al., 2021; Qiu et al., 2024). This can be confirmed by the Benzo[e]pyrene/(Benzo[a]pyrene+Benzo[e]pyrene) ratio (BeP/(BaP+BeP)). Since BaP is easily degraded via atmospheric oxidation while BeP is chemically stable, a higher BeP/(BaP+BeP) value indicates more aged atmospheric aerosols. As shown in Figure S6a, the BeP/(BaP+BeP) ratio in BJ was relatively higher than those at other sampling sites. Moreover, a negative correlation between BeP/(BaP+BeP) and MAE<sub>365</sub> further supported this hypothesis (Figure S6b). In Figure 2d, we can note that unlike the temporal evolution of abs<sub>365</sub>, the MAE<sub>365</sub> of the BrC at most sampling sites undergone indistinctive variations in response to the reduction in anthropogenic emission.

As depicted in Figure 4a, the optical properties of BrC in different periods are plotted in the AAE-MAE<sub>405</sub> (log scale) space, with reference to the optically defined BrC classes proposed by Saleh (2020). On average, BrC across the sampling sites exhibits optical properties akin to those from biomass burning or coal combustion, falling into the "weakly" absorbing BrC class. This observation reinforced remarkable impacts of combustion sources on BrC in the NCP. Of particular note, the BrC light-absorptivity was enhanced from clean (PM<sub>2.5</sub> < 75 µg m<sup>-3</sup>) to haze (PM<sub>2.5</sub> > 75 µg m<sup>-3</sup>) periods at most sampling sites, coinciding with the increasing N:C ratio (Figure 4a and S7). And

a positive correlation between N:C ratio and  $\text{abs}_{365}$  was also found across the NCP (Figure 4b), indicating that NOCs likely serve as the potential chromophores modulating BrC optical properties in this region (Figure S8). Accordingly, the high N:C ratio was also associated with an elevated WSOC/OC ratio (Figure 4b), implying that the secondary formation was likely the predominant source of the N-containing chromophores in the NCP.

### **3.3 Secondary formation N-containing compounds in the NCP**

To quantify the contribution of secondary formation to the water-soluble organic nitrogen, a tracer method analogous to that used for estimating secondary organic carbon (SOC) with EC as a tracer was adopted here (Text S2 in the Supplement). The fundamental assumption underlying this method is that primary WSON and EC share the common sources, both being predominantly sourced from combustion emissions. Accordingly, when a fraction of primary WSON stems from non-combustion emissions, secondary WSON would be overestimated. Based on statistical analysis, our found that the estimation results of secondary WSON was robust using this method (Table S4). Moreover, the strong positive correlations between primary WSON and CO at all sampling sites can further indirectly validate that this method is credible for capturing temporal variations in secondary WSON in this study. From the results illustrated in Figure 5a, a dominant role of secondary formation in WSON accumulation was observed across five sites. Specifically, secondary WSON (WSON<sub>sec</sub>) in BJ explained more than  $64 \pm 21\%$  of the total WSON, which was comparable to those at other urban sites but was approximately 1.2-fold of that in LC. Such spatial pattern was attribute to

the enhanced primary emission (e.g., biomass burning) in rural site. Additionally, the fractional contribution of WSONsec increased with the rising PM<sub>2.5</sub> levels (Figure S7) across sampling sites, particularly in BJ. Above findings further highlighted the critical role of secondary formation in regulating the abundance of strongly light-absorbing N-containing chromophores during haze periods.

### **3.3.1 Aerosol aqueous formation of light-absorbing NOCs**

The secondary WSON formation can be affected by multiple factors, e.g., NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub>, O<sub>3</sub>, ALWC, pH, NACs and meteorological factors. To investigate the contributions of these factors to WSONsec, a random forest analysis was conducted here and demonstrated that atmospheric WSONsec in the NCP was largely affected by NH<sub>4</sub><sup>+</sup> (~48%) and ALWC (~28%). Given the limited capability of the RF model to capture interactive and nonlinear relationships between driving factors and WSONsec, a generalized additive model (GAM) was applied here, which is a nonparametric modeling framework (Text S3). As shown in Figure S9 and Table, the GAM model can robustly rebuild the WSONsec variation, and identified NH<sub>4</sub><sup>+</sup> and ALWC as the primary driving factors of WSONsec. In addition, we also analyzed the ionic fragments of hydroxy methanesulfonic acid (MSA) predominantly formed via aqueous-phase reactions, which exhibited a significant positive correlation with WSONsec during humid haze episode (Figure S10). All the above evidence underscored the critical role of aqueous processing in WSONsec formation. Above phenomenon is presumably prevalent across China, as it has been observed in the rural site (Xianghe) in the NCP, Yangtze River Delta, the Guanzhong Plain, and even the upper boundary layer (Liu et

al., 2023; Wu et al., 2024a; Xiao et al., 2025). Previously, aqueous-phase reaction via  $\alpha$ -dicarbonyls (e.g., methylglyoxal and glyoxal) with  $\text{NH}_3$  have been identified as an important formation pathway for N-heterocyclic species (e.g., imidazoles, IMs) (Yang et al., 2024; Aiona et al., 2017; Lin et al., 2015), of which yield can be regulated by the chemical forms of ammonium in aerosol. Specially, the uptake coefficient of methylglyoxal/glyoxal (the prevalent  $\alpha$ -dicarbonyls in the atmosphere) on  $(\text{NH}_4)_2\text{SO}_4$  seed was significantly higher than on  $\text{NH}_4\text{HSO}_4$  seed, thereby leading to an enhanced yield of N-heterocycles and their oligomers (Li et al., 2021b). Whereas it has been confirmed theoretically that the aerosol across five sites were characterized by abundant  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$  as shown in Figure S11a and Text S4. These hygroscopic  $(\text{NH}_4)_2\text{SO}_4$  particles would promote N-containing compounds formation via  $\text{NH}_3$ -mediated aqueous-phase chemistry. To further validate above assumption, IMs-related fragments (e.g.,  $\text{C}_3\text{H}_3\text{N}_2^+$  and  $\text{C}_3\text{H}_4\text{N}_2^+$ ) were quantified by offline AMS analysis during a humid haze episode across the NCP (Figure S2). During this event, the  $\text{ALWC}/(\text{ALWC}+\text{PM}_{2.5})$  was approximately 1.5-fold of that observed in the remaining periods (Figure S11b), indicating that aerosols were far more likely to be in the liquid phase during this period. In the atmosphere, IMs can be either directly emitted from biomass burning or secondarily produced via aqueous reactions (Gao et al., 2021). As illustrated in Figure 5c and S12, IMs-related fragments weakly correlated with the levoglucosan+BkF ( $R^2=0.02$ ,  $p>0.05$ ) but strongly with ammonium ( $R^2=0.93$ ,  $p<0.01$ ), suggesting that a major fraction of the IMs-like heterocyclic compounds was secondarily formed during the humid event. Notably, as the haze episode evolved, the

IMs/WSO<sub>N</sub> (N:N) ratio increased dramatically across the NCP, reaffirming an important role of NH<sub>3</sub>-induced chemistry in NOCs formation under moist environments.

Additionally, aerosol acidity also modulated the WSO<sub>N</sub> formation, with relative importance being ~8% (Figure 5b). Figure 5d clearly demonstrates a negative correlation between the mass fraction of WSO<sub>N</sub>sec in the total WSO<sub>N</sub> and aerosol pH, indicating that acidic condition likely favors NOCs formation. It is possible that ammonia would be more readily partitioned into acidic aerosol, thereby promoting the formation of NOCs. Consistent with this hypothesis, our estimation of the gas-to-particle partitioning coefficient for NH<sub>3</sub> ( $\epsilon_{\text{NH}_3}$ ) showed that  $\epsilon_{\text{NH}_3}$  at pH 3.0 was one order of magnitude higher than that at pH 5.0 (Text S4). And numerous experimental evidences have established that the reactions of NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> with carbonyl are generally acid catalyzed (Liu et al., 2015b; Zhang et al., 2015). Furthermore, our recent findings confirmed that compared to the neutral aerosols, acidic aerosols are more conducive to the formation of high-molecular-weight NOCs through carbonyl-to-NH<sub>3</sub> reactions, which exhibit stronger light-absorptivity (Zhang et al., 2024).

### 3.3.2 Gas-phase formation of light-absorbing NOCs

It is worth noting that NO<sub>2</sub> and O<sub>3</sub> explained over 8% and 6% of the variances in the WSO<sub>N</sub>sec (Figure 5b), implying that partial WSO<sub>N</sub>sec presumably formed by gas-phase photochemical oxidation under relatively high NO<sub>x</sub> loadings. To verify this, nine NACs herein were quantified, which typically derived from gas-phase reactions of polyphenols with OH/NO<sub>3</sub> radicals, and followed by partitioning into the aerosol. As shown in Figure 6a, 4-Nitrophenol (4NP) and 4-Nitrocatechol (4NC) were the dominant

species among the detected NACs. On average, they accounted for 56.8%–74.0% and 10.3%–20.7% of the total NACs across the five sites, respectively. This finding is consistent with previous observations reported in Shanghai (Liu et al., 2023), Dezhou (Li et al., 2021a), and Xinglong (Sun et al., 2026).

Furthermore, secondary NACs was also quantified following the method of WSONsec. As depicted in Figure 6b, secondary formation played a dominant role in NACs accumulation, contributing approximately 46%–64% of total NACs across the five sites. Notably, secondary NACs ( $\text{NACs}_{\text{[sec]}}$ ) at all sites except TJ correlated strongly with  $\text{NO}_2$  ( $p < 0.05$ ) but displayed no significant relationships with levoglucosan and BkF, highlighting that gas-phase oxidation was a major formation pathway for NACs during the campaign. Previously, it is has been well established that nitrite is an important source of aerosol aqueous-phase  $\text{NO}_2$  radical (Vione et al., 2004), which can react with aromatic compounds (e.g., phenol or catechol) to yield corresponding NACs. However, secondary NACs ( $\text{NACs}_{\text{[sec]}}$ ) were correlated weakly with  $\text{NO}_2^-$  and ALWC (Figure 6c), suggesting a limited role of aqueous-phase reactions in  $\text{NACs}_{\text{[sec]}}$  formation. Similarly, no significant correlation was observed between the ionic fragments of MSA and secondary NACs (Figure S10), further supporting above inference.

Notably, the  $\text{NACs}_{\text{[sec]}}$  exhibited a temperature-dependent pattern across all sampling sites ( $P < 0.05$ , Figure 6c). It is possible that ambient temperature largely affected gas-to-particle partitioning of the NACs, thereby moderating the abundance of particulate NACs. On this basis, we theoretically estimated the fraction of particulate 4NP (Fp)

relative to the total based on the Pankow's absorption equilibrium theory, obtaining an average  $F_p$  of  $0.3 \pm 0.1$  across the NCP. This predicted value was within the range of field observations (0.2 in Hongkong to 0.75 on Mt. Tai) (Li et al., 2022a; Chen et al., 2025). As depicted in Figure 6d, the  $F_p$  correlated positively with the particulate 4NP, again suggesting that partial NOCs are formed by gas-phase photooxidation reactions, subsequently partitioning into the aerosol. In addition, temperature can also affect the abundance of NACs regulating the rates of numerous photochemical reactions. For instance, Lignell et al. (2014) found that low temperature substantially restrained the photolysis of 2, 4-Dinitrophenol in secondary organic aerosols, with its decay rate at 0 °C dropping by nearly one order of magnitude relative to 25 °C. Correspondingly, the low-temperature atmospheric environment likely inhibited the photolysis of NACs during the campaign, thereby facilitating their accumulation in the particle phase. This may be one of the reasons for the significant negative correlation between NACs and temperature.

#### **4 Conclusion and implications**

Synchronous observations of the optical properties and chemical compositions of atmospheric BrC were conducted at five sites across the NCP during the winter of 2023. The OM was identified as the predominant component of  $PM_{2.5}$  at all sampling sites, accounting for 40%-55% of the  $PM_{2.5}$ . BrC in rural area exhibited a higher light-absorption, being approximately 1.1–3.5 folds of those recorded at urban sites. Compared with the previous observations, the average light absorption of urban BrC decreased substantially by roughly 45 over the period 2018–2023, which was mainly

due to significant anthropogenic emission controls in the NCP. The average  $MAE_{365}$  ranged from  $0.7 \pm 0.04 \text{ m}^2 \text{ g}^{-1}$  to  $1.40 \pm 0.02 \text{ m}^2 \text{ g}^{-1}$ , with a distinctly different spatial pattern. Specially, a strikingly high  $MAE_{365}$  value ( $1.40 \pm 0.02 \text{ m}^2 \text{ g}^{-1}$ ) was measured in JN, falls within the range for BrC emitted from residential coal combustion. While, the  $MAE_{365}$  values of BrC ( $\sim 1.1 \text{ m}^2 \text{ g}^{-1}$ ) in TJ, LC and HD were closely matched the values associated with biomass burning-derived BrC. The  $MAE_{365}$  value in BJ was the lowest among all the sampling sites, which was likely ascribed to enhanced photobleaching during aerosol aging.

During the haze periods, we observe that the  $MAE_{365}$  of BrC at most sample sites was 1.5-fold of that in clean periods, indicating enhanced light-absorptivity of BrC the haze development. Of particular note, a parallel variation was also found for N:C ratio. These findings indicated that N-containing compounds (NOCs), as crucial chromophores governing BrC optical properties in the NCP, were abundantly formed in the aerosol aging process. Additionally, these secondary NOCs accounted for over 50% of the total on average and were mainly formed through the aerosol aqueous reactions, with ammonia playing an important role. In the previous observation conducted on Mt. Hua (Wu et al., 2024a), we also revealed that ammonia-driven aerosol aqueous reactions can also significantly promote BrC formation during the air mass lifting process. Consequently,  $\text{NH}_3$  is probably one of the important factors contributing to the high loading of strongly light-absorbing BrC within the boundary layer across China. This phenomenon would be pronounced under moist winter haze episodes, as such environments can accelerate aerosol liquid phase formation and promote aqueous

chemical processes. Thereby, targeted NH<sub>3</sub> emission control is indispensable for further alleviating haze and BrC pollution in the country.

**Data availability.** The primary data used in this study can be obtained from <https://doi.org/10.5281/zenodo.17947347> (Wu, 2025). Other data utilized in the present study are available from the corresponding author on request.

**Author contributions.** G.W. designed research and contributed analytic tools. C.W., Z.L. B.X. and R.L. collected the samples. C.W. and Y.C. conducted the sample analysis. C.W. performed the data interpretation. C.W. and G.W. wrote the paper. All authors contributed to the paper with useful scientific discussions.

**Competing interests.** The authors declare no competing interest.

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## Figure captions

**Figure 1** Chemical composition of PM<sub>2.5</sub> and sources for organic matters (OM) at different sampling sites. The mass concentration data correspond to PM<sub>2.5</sub>. The maps are the reproductions from ©Mapbox (<https://account.mapbox.com/>, last access: 03 December 2025)

**Figure 2** Optical properties of BrC at each sampling site. **(a and c)** Average absorption spectra and mass absorption coefficient of WSOC; **(b and d)** Comparison of  $\text{abs}_{365}$  and  $\text{MAE}_{365}$  in different cities of China (NJ, XA and GZ represent Nanjing, Xi'an and Guangzhou; Superscripts indicate the corresponding years, for instance, the superscript "11" refers to 2011; The datasets of (b) and (d) were derived from the literature, and given in Table S4).

**Figure 3** The CWT analysis of BrC at sampling sites along with fire hotspot. Fire hotspot data from Fire Information for Resource Management System (FIRMS) were applied to evaluate open biomass burning intensity during the campaign. The data were acquired from the Visible Infrared Imaging Radiometer Suite (VIIRS) sensor and processed using a fire detection algorithm to identify active fire hotspots.

**Figure 4** Graphical representation of optical-based BrC classes in  $\log_{10}(\text{MAE}_{405})$ -AAE space **(a)**. The shaded regions represent very weakly light-absorbing BrC (VW-BrC), weakly light-absorbing BrC (W-BrC), moderately light-absorbing BrC (M-BrC), strongly light-absorbing BrC (S-BrC), and absorbing BC, respectively. **(b)** shows the linear fit regressions for  $\text{abs}_{365}$  with N:C ratio (Diamonds indicate the averaged  $\text{abs}_{365}$  and N:C ratio of all sites in each binned N:C interval, with bars representing standard deviations).

**Figure 5** Aqueous formation of N-containing compounds in the NCP. Fractional contribution of primary water-soluble organic nitrogen (WSO<sub>N</sub>pri) and secondary WSON (WSO<sub>N</sub>sec) to the total **(a)**; SHAP feature importance assessment for the key factors affecting WSONsec **(b)**; Linear correlation between IMs-related fragments and  $\text{NH}_4^+$  with different PM<sub>2.5</sub> loads **(c)**; **(d)** show the linear fit regressions for WSONsec/WSO<sub>N</sub> with pH value across the NCP. (Circles in (c) and (d) show grouped mean statistics over all sampling site)

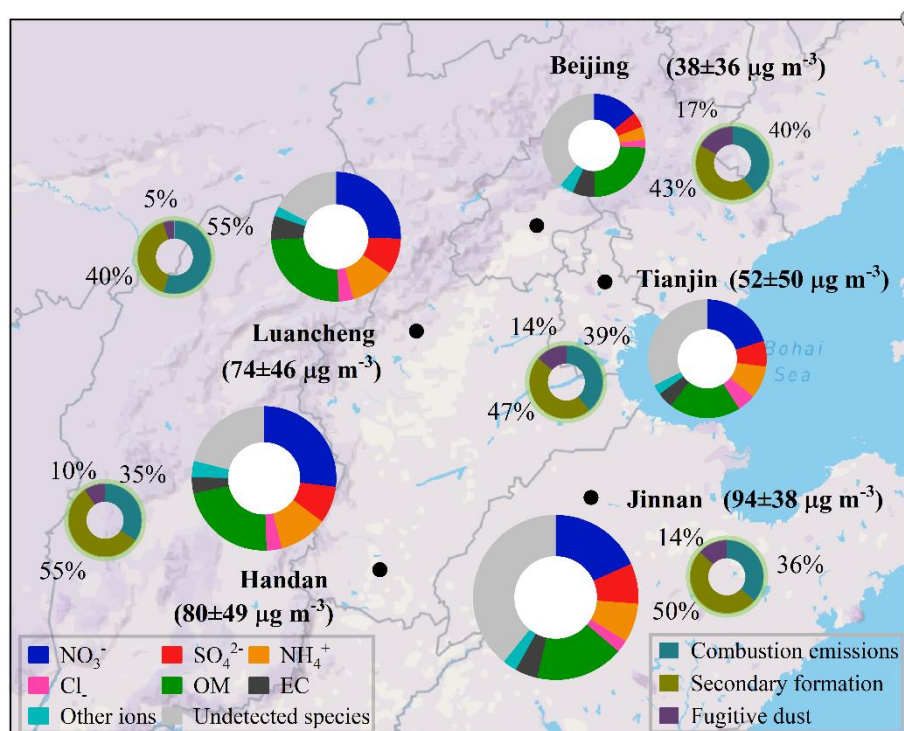
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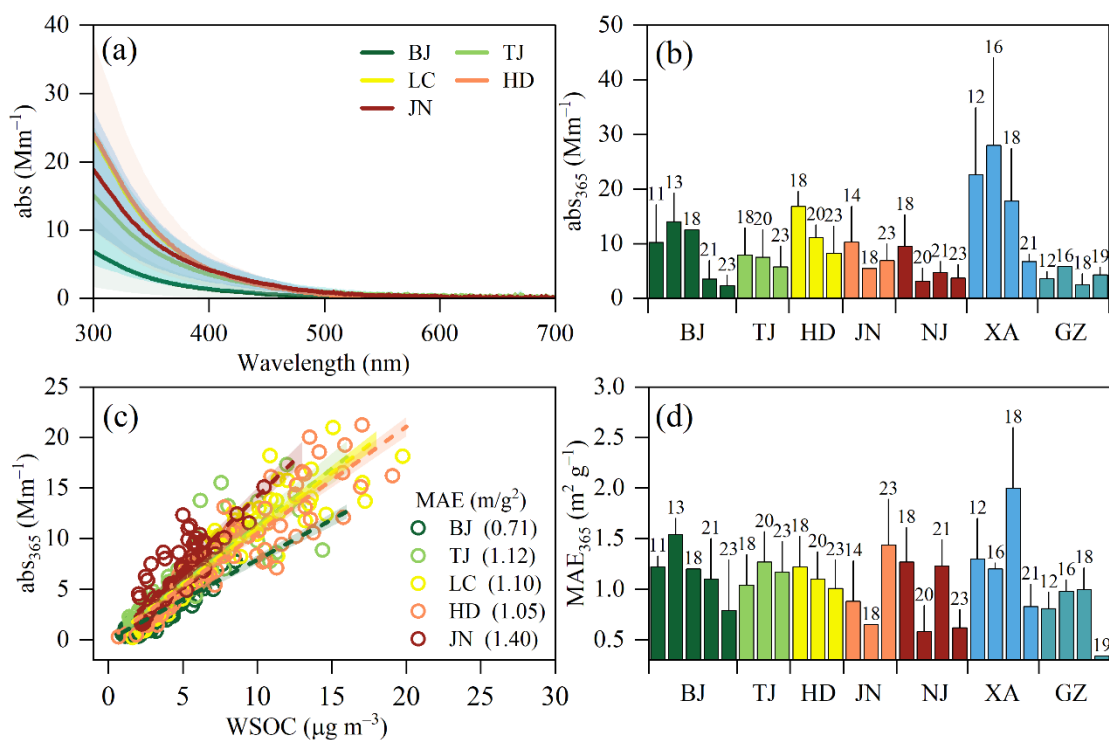
**Table 1** Optical properties of BrC, mass concentrations of chemical composition in PM<sub>2.5</sub>, and meteorological parameters at sampling sites.

|                                                                                                  | Beijing   | Tianjin   | Luancheng | Handan    | Jinan     |
|--------------------------------------------------------------------------------------------------|-----------|-----------|-----------|-----------|-----------|
| (i) Meteorological parameters and gaseous pollutants                                             |           |           |           |           |           |
| T (°C)                                                                                           | -1.1±5.6  | -1.2±4.9  | 1.2±6.3   | 1.7±6.6   | 3.1±5.9   |
| RH (%)                                                                                           | 49±21     | 50±19     | 54±22     | 59±21     | 54±23     |
| O <sub>3</sub> (µg m <sup>-3</sup> )                                                             | 29±20     | 31±18     | 31±18     | 28±17     | 35±26     |
| NO <sub>2</sub> (µg m <sup>-3</sup> )                                                            | 41±26     | 48±31     | 44±23     | 46±18     | 48±60     |
| SO <sub>2</sub> (µg m <sup>-3</sup> )                                                            | 4±5       | 4.7±2.4   | 8.8±4.5   | 5.9±3.8   | 10.0±11.0 |
| (ii) Mass concentrations of PM <sub>2.5</sub> and its chemical composition (µg m <sup>-3</sup> ) |           |           |           |           |           |
| PM <sub>2.5</sub>                                                                                | 38±36     | 52±50     | 74±46     | 80±49     | 94±38     |
| NO <sub>3</sub> <sup>-</sup>                                                                     | 5.4±7.3   | 13.0±14.6 | 19.0±18.2 | 22.7±20.8 | 17.3±13.4 |
| SO <sub>4</sub> <sup>2-</sup>                                                                    | 1.8±1.0   | 4.6±4.0   | 6.7±7.0   | 7.0±5.8   | 7.5±5.8   |
| NH <sub>4</sub> <sup>+</sup>                                                                     | 1.6±2.2   | 5.7±5.9   | 8.2±8.6   | 9.1±8.0   | 7.3±6.5   |
| Cl <sup>-</sup>                                                                                  | 1.0±0.7   | 3.2±2.7   | 2.8±1.7   | 2.9±1.9   | 2.3±1.2   |
| OM                                                                                               | 9.1±5.2   | 7.9±5.7   | 18.5±11   | 18.7±10.7 | 16.3±7.3  |
| EC                                                                                               | 2.7±2.4   | 2.8±1.7   | 4.4±2.5   | 3.1±1.9   | 4.2±1.4   |
| WSOC                                                                                             | 3.2±1.8   | 4.9±3.1   | 7.3±4.0   | 7.5±4.1   | 4.8±1.7   |
| WSON                                                                                             | 0.65±0.64 | 1.2±1.1   | 2.5±2.6   | 2.3±1.6   | 1.3±0.8   |
| (iii) Optical properties of BrC, ALWC and acidity of PM <sub>2.5</sub>                           |           |           |           |           |           |
| abs <sub>365</sub> (Mm <sup>-3</sup> )                                                           | 2.3±1.9   | 5.7±3.8   | 8.0±4.7   | 8.2±5.0   | 6.9±3.0   |
| MAE (m <sup>2</sup> g <sup>-1</sup> )                                                            | 0.71±0.5  | 1.12±0.05 | 1.10±0.04 | 1.05±0.02 | 1.4±0.02  |
| pH                                                                                               | 5.6±1.1   | 3.8±0.8   | 3.3±1.4   | 4.1±1.2   | 4.0±1.1   |
| ALWC (µg m <sup>-3</sup> )                                                                       | 9.7±21.6  | 21.0±38   | 36±74     | 47±72     | 41±70     |

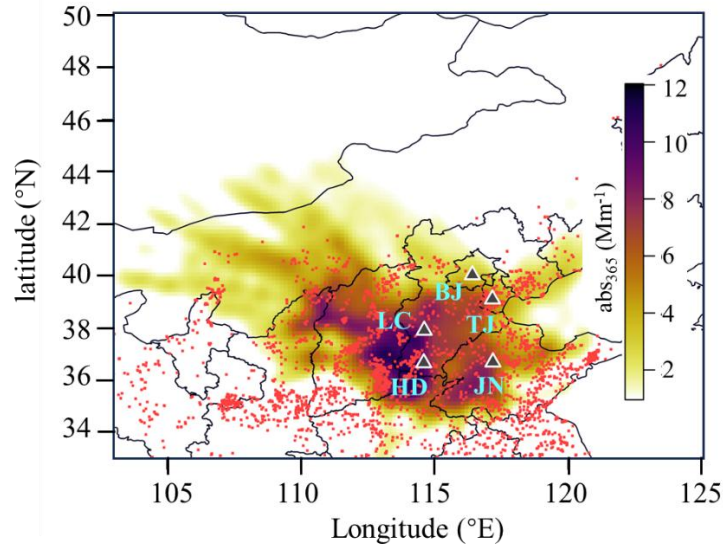
ALWC: aerosol liquid water content; ALWC and pH were simulated by thermodynamic model (ISORROPIA-II), details can be found in Text S5.



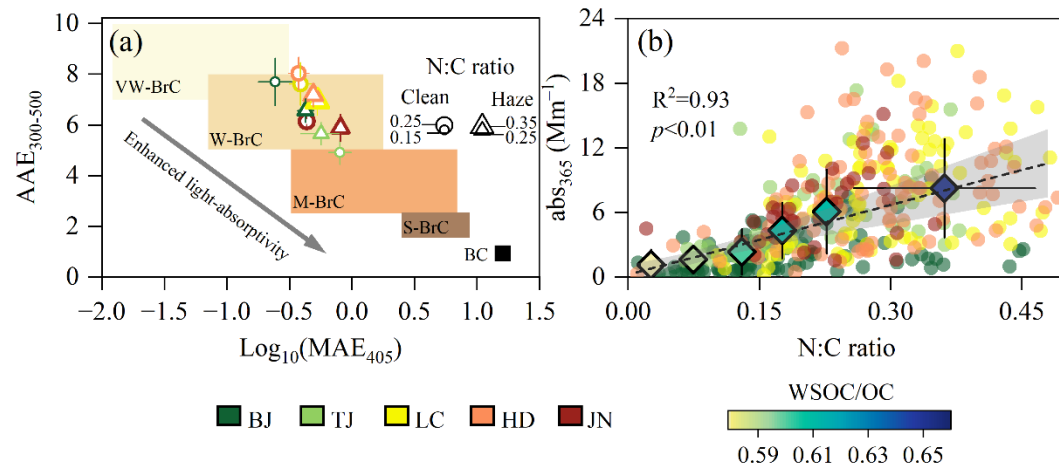
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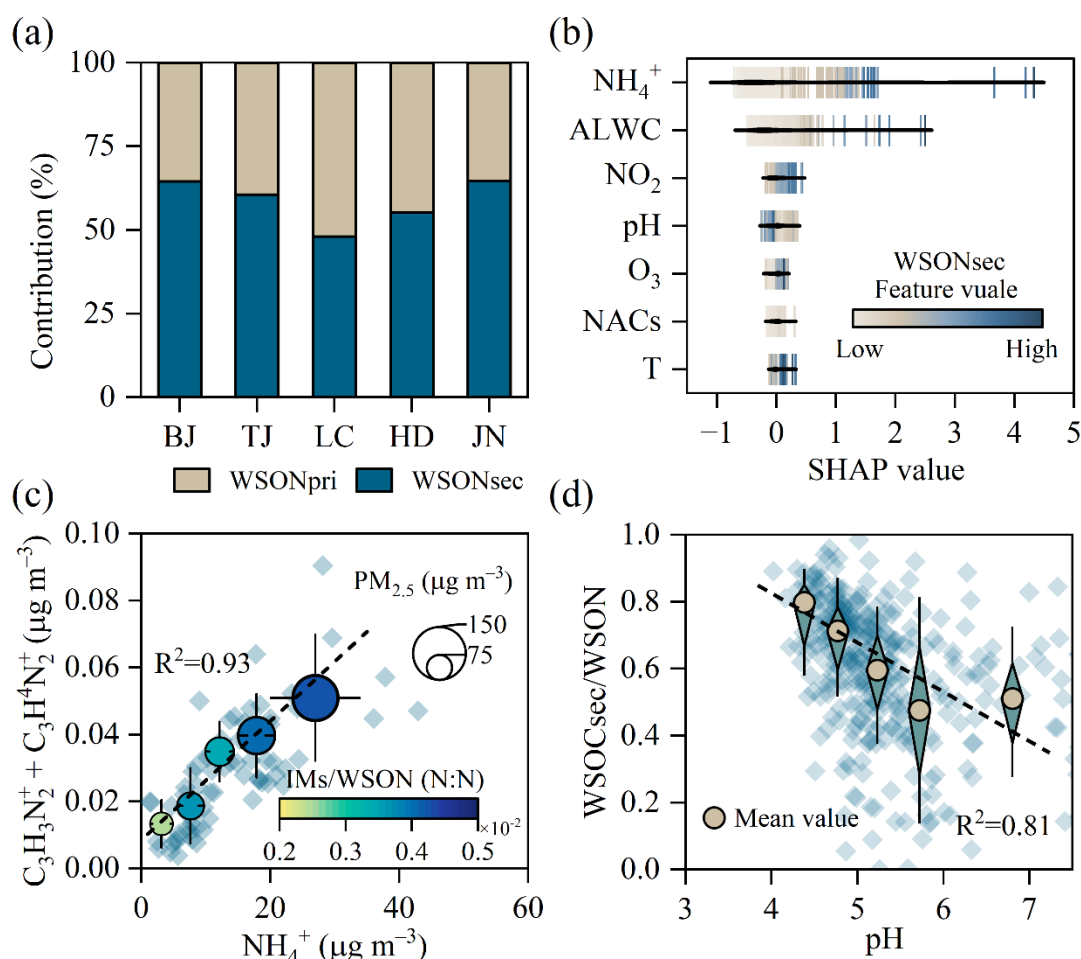
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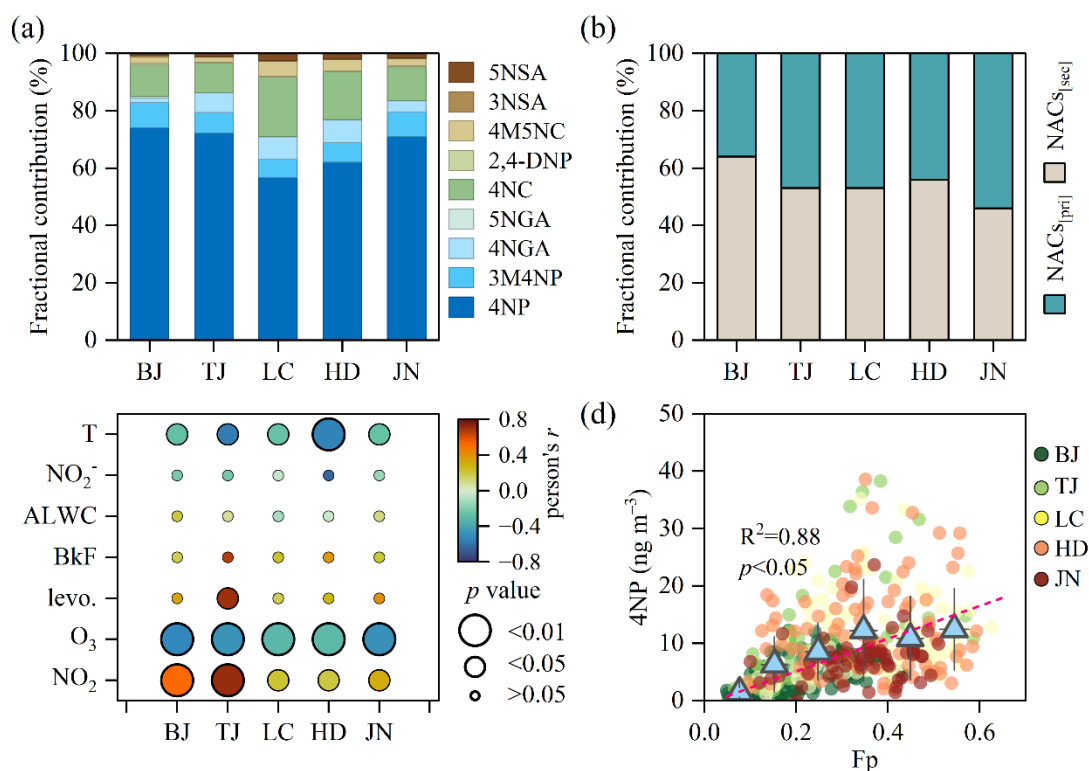
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 965 mean statistics over all sampling site)

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**Figure 6** Chemical composition and formation of NACs. Fractional mass contribution of individual NAC to the total (a); Relative contributions of primary emissions (NACs<sub>[pri]</sub>) and secondary formation (NACs<sub>[sec]</sub>) to the detected NACs (b); Pearson coefficients between NACs<sub>[sec]</sub> and various influencing factors (c); Linear regression analysis for particulate 4NP with its gas-to-particle-phase partitioning coefficient (d). (Triangles in (d) correspond to the bin-averaged 4NP versus Fp over all sampling sites, cross bars represent standard deviation).