

1 **Persistent residential burning-related primary organic particles during**  
2 **wintertime hazes in North China: insights into their aging and optical changes**

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4 Lei Liu<sup>1</sup>, Jian Zhang<sup>1</sup>, Yinxiao Zhang<sup>1</sup>, Yuanyuan Wang<sup>1</sup>, Liang Xu<sup>1</sup>, Qi Yuan<sup>1</sup>, Dantong Liu<sup>1</sup>, Yele  
5 Sun<sup>2</sup>, Pingqing Fu<sup>3</sup>, Zongbo Shi<sup>4</sup>, and Weijun Li<sup>1,\*</sup>

6

7 <sup>1</sup>Department of Atmospheric Sciences, School of Earth Sciences, Zhejiang University, Hangzhou  
8 310027, China

9 <sup>2</sup>State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute  
10 of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

11 <sup>3</sup>Institute of Surface-Earth System Science, Tianjin University, Tianjin 300072, China

12 <sup>4</sup>School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham  
13 B15 2TT, UK

14

15 *\*Correspondence to:* Weijun Li (liweijun@zju.edu.cn)

## 16    **Abstract**

17        Primary organic aerosol (POA) is a major component of PM<sub>2.5</sub> in winter polluted air in the North  
18    China Plain (NCP), but our understanding on the atmospheric aging process of POA particles and the  
19    resulting influences on their optical properties is limited. As part of the Atmospheric Pollution and  
20    Human Health in a Chinese Megacity (APHH-Beijing) programme, we collected airborne particles  
21    at an urban site (Beijing) and an upwind rural site (Gucheng, Hebei province) in the NCP during 13–  
22    27 Nov. 2016 for microscopic analyses. We confirmed that large amounts of light-absorbing spherical  
23    POA (i.e., tarball) and irregular POA particles with high viscosity were emitted from the domestic  
24    coal and biomass burning at the rural site and were further transported to the urban site during regional  
25    wintertime hazes. During the heavily polluted period (PM<sub>2.5</sub> > 200 µg m<sup>-3</sup>), more than 60% of these  
26    burning-related POA particles were thickly coated with secondary inorganic aerosols (named as core–  
27    shell POA–SIA particle) through the aging process, suggesting that POA particles can provide  
28    surfaces for the heterogeneous reactions of SO<sub>2</sub> and NO<sub>x</sub>. As a result, their average particle-to-core  
29    diameter ratios at the rural and urban sites in the heavily polluted period increased to 1.60 and 1.67,  
30    respectively. Interestingly, we found that the aging process did not change the morphology and sizes  
31    of POA cores, indicating that these POA particles are quite inert in the atmosphere and can be  
32    transported long distances. Using Mie theory we estimated that the absorption capacity of POA  
33    particles was enhanced by ~1.39 times in the heavily polluted period at the rural and urban sites due  
34    to the “lensing effect” of secondary inorganic coatings. We highlight that the “lensing effect” on  
35    burning-related POA particles should be considered in radiative forcing models and the governments  
36    should continue to promote clean energy in rural areas to effectively reduce primary emissions.

## 1 Introduction

Atmospheric aerosol particles can affect regional and global energy budgets by scattering or absorbing solar radiation, modify microphysical properties of clouds by acting as cloud condensation nuclei (CCN), and exert adverse effects on human health such as respiratory and cardiovascular diseases (IPCC, 2013; West et al., 2016). With rapid industrialization and urbanization in past decades, severe air pollution characterized by high concentrations of fine particulate matter (PM<sub>2.5</sub>) frequently occurs in China, especially the regional hazes in the North China Plain (NCP), which has received wide concerns from the public, governments, and scientists (Sun et al., 2016). Many previous studies have shown that synergetic effects from extensive emissions of primary particles and gaseous precursors, efficient secondary aerosol formation, regional transport, and unfavorable meteorological conditions are main factors contributing to haze formation in the NCP (Chang et al., 2018; Liu et al., 2016; Zhong et al., 2019). In particular, long-term measurements have confirmed that wintertime haze episodes in Beijing are commonly initiated by regional transport of air pollutants from the south parts of NCP (e.g., Hebei and Henan provinces) under weak southerly winds and then evolved through the massive secondary aerosol formation via heterogeneous reactions (Ma et al., 2017; Sun et al., 2014; Zheng et al., 2015).

During the regional transport and evolution of haze episodes, complex physical and chemical processes in the atmosphere, such as condensation, coagulation, and heterogeneous reactions, could largely alter the morphology, composition, size, and mixing state of individual particles, which is also known as “particle aging” (Li et al., 2016a). Particle aging could further influence the optical property, health effects, hygroscopicity, and CCN activity of aerosol particles, although different types of particles might have different impacts (Fan et al., 2020; Li et al., 2016b; Riemer et al., 2019). Up to now, most of the studies conducted in the NCP mainly applied various bulk online and offline aerosol analytical techniques (e.g., online aerosol mass spectrometry (AMS) and offline ion chromatography (IC)) to explore mass concentrations, possible sources, and formation mechanisms of different aerosol

62 components, such as sulfate, nitrate, and organic aerosols (Chen et al., 2020; Cheng et al., 2016; J. Li  
63 et al., 2020; Sun et al., 2016; Wang et al., 2020). However, knowledge on the aging process of aerosol  
64 particles remains limited. Therefore, further to document the aging processes of different particles in  
65 the NCP through microscopic individual particle analysis is of great significance for revealing the  
66 particle transformation in the atmosphere and better assessing the aerosol climatic effects (Du et al.,  
67 2019; Li et al., 2016a).

68 Field observations have shown that carbonaceous aerosols, including organic aerosol (OA) and  
69 black carbon (BC), are the dominant components of PM<sub>2.5</sub> during heating seasons in the NCP, which  
70 accounts for more than 50% of the total PM<sub>2.5</sub> (Liu et al., 2020; P. Liu et al., 2017; Zhang et al., 2020).  
71 Source apportionment results reveal that residential coal and biomass burning in rural areas are the  
72 major contributors to the carbonaceous aerosols during wintertime hazes in the NCP (Li et al., 2017).  
73 BC is the major light-absorbing aerosol in the atmosphere, which can strongly absorb solar radiation  
74 and thus affect the regional and global climate (Bond et al., 2013; D. Liu et al., 2017; Wang et al.,  
75 2014). In recent years, a bunch of studies have well documented the aging process of BC particles  
76 and revealed that the secondary inorganic and organic coatings (e.g., sulfate and organics) can  
77 significantly enhance the light absorption capacity of the internally mixed BC particles via the  
78 “lensing effect” (Chakrabarty and Heinson, 2018; Wang et al., 2017). Recently, light-absorbing  
79 organic aerosols, also known as brown carbon (BrC), have been reported to be ubiquitous in the  
80 atmosphere in the NCP (Wang et al., 2018; Xie et al., 2019). Many studies have demonstrated that  
81 primary OA (POA) emitted from residential coal and biomass burning is the major source of BrC,  
82 and the chemical composition and optical properties of BrC in freshly emitted POA as well as the  
83 BrC in the ambient atmosphere were analyzed in detail using bulk techniques such as mass  
84 spectrometry and UV–visible spectrophotometry (M. Li et al., 2019; X. Li et al., 2020; Song et al.,  
85 2018; Sun et al., 2017; Yan et al., 2017). However, only a few studies characterized microscopic  
86 properties such as the morphology and mixing state of fresh burning-related POA particles by

87 transmission electron microscopy (TEM) (L. Liu et al., 2017; Zhang et al., 2018). The abundance and  
88 aging process of burning-related POA particles in the atmosphere and the resulting influences on their  
89 optical properties remain unknown in the NCP.

90 This study, as part of the Atmospheric Pollution and Human Health in a Chinese Megacity  
91 (APHH-Beijing) programme (Shi et al., 2019), aims to explore the atmospheric aging process of POA  
92 particles emitted from the residential coal and biomass burning in rural areas following the regional  
93 transport and evolution of haze episodes. Individual particle samples were collected in urban Beijing  
94 and the surrounding rural regions during the winter campaign and then were analyzed by microscopic  
95 methods to obtain the morphology, composition, size, and mixing state of different individual particle  
96 types. Besides, bulk analyses of aerosol chemical composition were also conducted to help understand  
97 the evolution of haze episodes. We found that large amounts of POA particles were emitted from the  
98 domestic coal and biomass burning in winter in the NCP. For the first time, we characterized the aging  
99 process of such burning-related POA particles based on microscopic analyses and Mie theory was  
100 used to further explore the resulting influences on their optical properties.

## 101 **2 Experimental methods**

### 102 **2.1 Sampling sites and sample collections**

103 Field observations were carried out simultaneously at the Beijing (BJ) urban site (39°58'27" N,  
104 116°22'16" E) and Gucheng (GC) rural site (39°08'58" N, 115°44'00" E) during 13–27 Nov. 2016.  
105 Locations of two sampling sites in the NCP are displayed in Fig. 1a. The BJ urban site, located on the  
106 rooftop of a two-story building (8 m above ground level (a.g.l.)) in the Tower Division of the Institute  
107 of Atmospheric Physics, Chinese Academy of Sciences, is between the north 3rd and 4th ring roads  
108 and surrounded by commercial area and residential apartments (Fig. 1b). The GC rural site, located  
109 on the rooftop of a three-story building (12 m a.g.l.) at the Gucheng Integrated Ecological–  
110 Meteorological Observation and Experimental Station of the Chinese Academy of Meteorological  
111 Sciences in Dingxing county, Hebei province, is 120 km to the southwest of the BJ urban site and

112 surrounded by many villages and farmlands (Fig. 1c). The detailed information about the two  
113 sampling sites can be found in the introduction paper of APHH-Beijing programme (Shi et al., 2019).  
114 The 24-h backward trajectories of air masses ending at the height of 100 m (a.g.l.) over the BJ urban  
115 site (Fig. 1a) were calculated using the NOAA Air Resources Laboratory's HYbrid Single-Particle  
116 Lagrangian Integrated Trajectory (HYSPLIT) model (Stein et al., 2016).

117 At the BJ urban site, the species in non-refractory submicron aerosols (NR-PM<sub>1</sub>) including  
118 organic matter (OM), SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and Cl<sup>-</sup> were measured by a high-resolution aerosol mass  
119 spectrometer (HR-AMS, Aerodyne Inc., USA). At the GC rural site, PM<sub>2.5</sub> samples were collected  
120 twice a day during the daytime (8:00 to 20:00) and nighttime (20:00 to 8:00 the next day) onto 90  
121 mm-diameter quartz filters (Pallflex 7204, Pall Corporation, USA) using a medium-volume sampler  
122 (TH-150A, Wuhan Tianhong Instruments Co., Ltd., China) at a flow rate of 100 L min<sup>-1</sup>. Field blank  
123 samples were collected for approximately 15 min without starting the sampler. The filters were  
124 prebaked at 450°C for 6 h before sampling to remove any possible contaminants. All the collected  
125 samples were sealed individually in aluminum foil bags and stored in a refrigerator at -20 °C for  
126 further analyses.

127 Individual particle samples were collected onto copper (Cu) TEM grids coated by formvar and  
128 carbon films (carbon type-B, 300 mesh, Beijing XXBR Technology Co., Ltd., China) at the GC rural  
129 and BJ urban sites using an individual particle sampler (DKL-2, Qingdao Genstar Electronic  
130 Technology Co., Ltd., China) at a flow rate of 1 L min<sup>-1</sup>. The DKL-2 sampler consists of a single-  
131 stage impactor with a 0.5 mm-diameter jet nozzle. Sampling duration ranged from 8 s to 3 min  
132 depending on the pollution levels to avoid overlap of particles on the TEM grids. Individual particle  
133 samples were placed in a clean and airtight container with controlled temperature ( $T$ , 25±1°C) and  
134 relative humidity (RH, 20±3%) for further analyses. The detailed information about the individual  
135 particle samples collected at the two sites is listed in Table S1.

136 Meteorological parameters including  $T$ , pressure ( $P$ ), RH, wind speed (WS), and wind direction

(WD) were recorded every 5 min at two sampling sites using a pocket weather station (Kestrel 5500, Nielsen-Kellermann Inc., USA). The hourly concentrations of PM<sub>2.5</sub> and gaseous pollutants (i.e., SO<sub>2</sub>, NO<sub>2</sub>, CO, and O<sub>3</sub>) during the sampling period at two monitoring stations (i.e., Dingxing government station: 39°15'42" N, 115°48'06" E; Beijing Olympic center station: 40°00'11" N, 116°24'25" E) close to GC rural and BJ urban sites were downloaded from the website of air quality online monitoring and analysis platform (<https://www.aqistudy.cn/>). All the data in this study are presented at the Beijing local time (UTC+8).

## 2.2 PM<sub>2.5</sub> chemical analysis

PM<sub>2.5</sub> samples collected at the GC rural site were analyzed to obtain their water-soluble inorganic ions (WSIIs), organic carbon (OC), and elemental carbon (EC). For the analysis of WSIs, two 16 mm-diameter punches from each PM<sub>2.5</sub> sample were put into a vial, followed by adding 20 mL deionized water (18.2 MΩ). Then these vials were placed in an ultrasonic water bath for 30 min to extract WSIs. The solutions were further filtered using PTFE syringe filters with 0.45 μm pore size to remove insoluble components and then analyzed by an ion chromatography system (Dionex ICS 600, ThermoFisher Scientific, USA). Finally, concentrations of three anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>) and five cations (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>) were obtained. Concentrations of OC and EC in PM<sub>2.5</sub> samples were determined by analyzing a 1×1.5 cm<sup>2</sup> punch from each filter with an OCEC analyzer (Model 5L, Sunset Laboratory Inc. USA), which adopted the NIOSH870 temperature protocol with thermal-optical transmittance for charring correction. The OM concentration was estimated via multiplying OC concentration by a factor of 1.6, based on the previous studies (Xing et al., 2013; Zheng et al., 2015).

## 2.3 AMS data analysis

The HR-AMS V-mode data were analyzed using standard data analysis software (PIKA V1.56D). A constant collection efficiency (CE) of 0.5, similar to the previous study conducted in winter at the BJ site (Sun et al., 2014), was applied to the HR-AMS datasets to obtain mass concentrations of NR-

162 PM<sub>1</sub> species. The relative ionization efficiencies used for OM, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and Cl<sup>-</sup> were 1.4,  
163 1.2, 1.1, 5.0, and 1.3, respectively. Positive matrix factorization (PMF) is a receptor model to identify  
164 potential sources without local source profiles provided (Xu et al., 2020). PMF was performed on the  
165 high-resolution mass spectra of organics measured by HR-AMS. Six OA factors were identified  
166 including fossil fuel-related OA (FFOA), cooking OA (COA), biomass burning OA (BBOA),  
167 oxidized primary OA (OPOA), oxygenated OA (OOA), and aqueous-phase OOA (aqOOA). Detailed  
168 information on the processing of HR-AMS data can be found in the related paper during the same  
169 campaign (Xu et al., 2019).

## 170 **2.4 Individual particle analysis**

171 Individual particle samples were analyzed using TEM (JEM-2100, JEOL Ltd., Japan) operated  
172 at a 200 kV accelerating voltage to acquire morphology and sizes of individual particles and mixing  
173 state (i.e., internally or externally mixed) of different aerosol components within one individual  
174 particle. TEM is equipped with an energy-dispersive X-ray spectrometer (EDS, INCA X-Max<sup>N</sup> 80T,  
175 Oxford Instruments, UK) to semi-quantitatively detect the elemental composition of individual  
176 particles with atomic number greater than six ( $Z \geq 6$ ). It should be noted that Cu peaks in the EDS  
177 spectra are not considered due to the interference from the Cu substrate of TEM grids. The distribution  
178 of aerosol particles on TEM grids is not uniform, with particle size decreasing from the center to the  
179 edge of distribution area. Therefore, to ensure the analyzed particles are representative, five grid  
180 meshes from the center to the edge of particle distribution area in each sample were selected to  
181 conduct TEM analysis. TEM images were manually processed by the RADIUS 2.0 software (EMSIS  
182 GmbH, Germany) to determine the particle types, areas, perimeters, and equivalent circle diameters  
183 (ECD). After a labor-intensive operation, a total of 1197 particles at the BJ urban site and 2443  
184 particles at the GC rural site were analyzed.

185 Scanning electron microscope (SEM, Ultra 55, Carl Zeiss Microscopy GmbH, Germany) was  
186 operated at the 10 kV accelerating voltage and secondary electron (SE2) mode to observe the particle

187 surface topography. Furthermore, particles were imaged at a tilt angle of  $75^\circ$  to realize the  
188 visualization of their morphology in the vertical dimension.

## 189 2.5 Optical property calculation

190 Mie theory has been widely used to calculate the optical properties of individual particles by  
191 assuming a spherical core-shell structure (Chylek et al., 2019; Wu et al., 2018; Yu et al., 2019). In  
192 this study, the light absorption cross sections (ACS) of internally mixed POA particles with secondary  
193 inorganic aerosol (SIA) shell (named as core-shell POA-SIA particle), as well as the POA cores and  
194 bare POA particles at the wavelength of 550 nm were calculated with BHCOAT Mie code (Bohren  
195 and Huffman, 1983). Details for the classification of POA and POA-SIA particles, please refer to  
196 Section 3.2. For the core-shell POA-SIA particles, a refractive index (RI) of  $1.55-0i$  for non-light-  
197 absorbing SIA coating (Denjean et al., 2014) and  $1.67-0.27i$  for light-absorbing POA core (Alexander  
198 et al., 2008) were adopted at the wavelength of 550 nm; and the ECD of each POA-SIA particle and  
199 its POA core obtained from the TEM images were used respectively as the input particle diameter  
200 ( $D_p$ ) and core diameter ( $D_c$ ) in the Mie calculation, which made the calculation sufficient to  
201 approximate reality. Because a core-shell structure is considered in the Mie model (Bond et al., 2006),  
202 for the uncoated POA particles (including POA cores without SIA shell and bare POA particles), the  
203 ECD of each POA particle and one-tenth of it were input as the  $D_p$  and  $D_c$ , respectively. Then in the  
204 case of vanishing the refractive index difference between the shell and core (i.e., POA core and POA  
205 shell,  $RI=1.67-0.27i$ ), the Mie model can be applied to homogeneous particles. Besides, we also  
206 constructed models of core-shell POA-SIA particles with different POA core diameters (i.e.,  $D_c=100$ ,  
207 200, 300, 400, 500, 700, 900, 1100, 1300, and 1500 nm) and particle-to-core diameter ratios (i.e.,  
208  $D_p/D_c$  ranged from 1 to 6 with an interval of 0.1), and calculated their ACS to further explore the  
209 effects of  $D_c$  and  $D_p/D_c$  changes on the light absorption enhancement factors ( $E_{abs}$ ) of POA particles.

210 After running the Mie calculation, attenuation efficiency ( $Q_{atn}$ ), scattering efficiency ( $Q_{sca}$ ), and  
211 absorption efficiency ( $Q_{abs}$ ) of an individual particle were output with their definitions as follows

212 (Aden and Kerker, 1951; Toon and Ackerman, 1981):

$$213 \quad Q_{\text{atn}} = \left(\frac{2}{x^2}\right) \sum_{n=1}^{\infty} (2n+1) [\text{Re}(a_n + b_n)] \quad (1)$$

$$214 \quad Q_{\text{sca}} = \left(\frac{2}{x^2}\right) \sum_{n=1}^{\infty} (2n+1) (|a_n|^2 + |b_n|^2) \quad (2)$$

$$215 \quad Q_{\text{abs}} = Q_{\text{atn}} - Q_{\text{sca}} \quad (3)$$

216 where  $x = \frac{\pi D}{\lambda}$ , is the dimensionless size parameter of the particle diameter  $D$  and the wavelength of  
 217 incident light  $\lambda$ ;  $a_n$  and  $b_n$  are calculated from Riccati–Bessel functions of the particle sizes and  
 218 refractive indices (Bohren and Huffman, 1983); The symbol Re denotes the real part of the complex  
 219 quantity  $a_n + b_n$ . The ACS of a particle can be obtained via multiplying the  $Q_{\text{abs}}$  by geometric cross  
 220 section of the particle shown as follow:

$$221 \quad \text{ACS} = Q_{\text{abs}} \times \frac{\pi D^2}{4} \quad (4)$$

## 222 3 Results and Discussion

### 223 3.1 Overview of a regional haze episode

224 A typical regional heavy haze episode in the NCP was observed at the GC rural and BJ urban  
 225 sites during 22–27 Nov. 2016. Based on variations of hourly  $\text{PM}_{2.5}$  concentrations, three pollution  
 226 levels are defined: clean ( $\text{PM}_{2.5} \leq 75 \mu\text{g m}^{-3}$ ), moderate pollution ( $75 \mu\text{g m}^{-3} < \text{PM}_{2.5} \leq 200 \mu\text{g m}^{-3}$ ),  
 227 and heavy pollution ( $\text{PM}_{2.5} > 200 \mu\text{g m}^{-3}$ ). According to the above criteria, we classified clean period  
 228 (21 Nov. 0:00 to 22 Nov. 19:00) and heavily polluted period (22 Nov. 20:00 to 27 Nov. 10:00) at the  
 229 GC rural site; clean period (21 Nov. 0:00 to 24 Nov. 9:00), moderately polluted period (24 Nov. 10:00  
 230 to 25 Nov. 16:00), and heavily polluted period (25 Nov. 17:00 to 27 Nov. 2:00) at the BJ urban site  
 231 (Fig. 2). Furthermore, we divided the heavily polluted period at the GC rural site into the early stage  
 232 (22 Nov. 20:00 to 23 Nov. 20:00), middle stage (23 Nov. 20:00 to 24 Nov. 20:00), and late stage (24  
 233 Nov. 20:00 to 27 Nov. 8:00) based on the evolution of chemical species in  $\text{PM}_{2.5}$  (Fig. 2a). The average

234 meteorological parameters and mass concentrations of PM<sub>2.5</sub>, aerosol chemical species, OA factors,  
235 and gaseous pollutants in different periods at two sampling sites are summarized in Table S2.

236 Strong northwesterly winds ( $> 4 \text{ m s}^{-1}$ ) accompanied with rain and snow invaded the NCP during  
237 20–21 Nov. (Fig. S1), leading to fast dispersion of air pollutants (Figs. 2 and S2). The low  $T$  ( $-8$  to  
238  $5^{\circ}\text{C}$ ) and WS ( $< 2 \text{ m s}^{-1}$ ) were displayed after the cold front (Fig. S1), which can facilitate the  
239 accumulation of air pollutants (Zhong et al., 2019). At the GC rural site, PM<sub>2.5</sub> concentration began  
240 to increase at 18:00 on 22 Nov. and quickly reached a peak of  $394 \mu\text{g m}^{-3}$  within six hours (Fig. 2a).  
241 PM<sub>2.5</sub> chemical analysis reveals that OM ( $252.8 \mu\text{g m}^{-3}$ ) accounted for 83% of the PM<sub>2.5</sub> in the  
242 nighttime sample on 22 Nov. (i.e., 22 Nov. 20:00 to 23 Nov. 8:00), causing the fast transition from  
243 the clean to heavily polluted period directly (Figs. 2a and S3a). In the early stage of heavily polluted  
244 period, the average PM<sub>2.5</sub> concentration ( $288.3 \mu\text{g m}^{-3}$ ) increased by a factor of seven compared with  
245 that ( $39.8 \mu\text{g m}^{-3}$ ) in the clean period, with OM being the largest contributor ( $185.1 \mu\text{g m}^{-3}$ ) followed  
246 by SIA (i.e., sum of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ ;  $36.4 \mu\text{g m}^{-3}$ ) (Table S2). At the BJ urban site, the air  
247 quality remained clean before 24 Nov. under continuous northerly winds (Figs. 2b and S1b). With  
248 prevailing winds changing from northerly to southerly on 24 Nov. (Fig. S1), polluted air parcels in  
249 the south of NCP were transported to Beijing (Fig. 1a), which has also been confirmed by another  
250 study conducted in the APHH-Beijing winter campaign (Du et al., 2019). Thus, the concentrations of  
251 PM<sub>2.5</sub>, chemical species in NR-PM<sub>1</sub>, CO, and SO<sub>2</sub> at the BJ urban site increased simultaneously and  
252 sharply from 09:00 on 24 Nov., causing the transition from the clean period to the moderately polluted  
253 period (Figs. 2b and S2b). The average PM<sub>2.5</sub> concentration in the moderately polluted period was  
254  $111.0 \mu\text{g m}^{-3}$ , 10 times higher than that ( $10.8 \mu\text{g m}^{-3}$ ) in the clean period, and the OM and SIA  
255 contributed equally in NR-PM<sub>1</sub> with their average concentrations being  $44.4$  and  $43.4 \mu\text{g m}^{-3}$ ,  
256 respectively (Table S2). Following the haze evolution, PM<sub>2.5</sub> levels increased gradually to  $312.3$  and  
257  $396.8 \mu\text{g m}^{-3}$  in the middle and late stages of heavily polluted period at the GC rural site and to  $281.0$   
258  $\mu\text{g m}^{-3}$  in the heavily polluted period at the BJ urban site (Fig. 2 and Table S2). Contrasting to the

259 above transition periods at two sampling sites, we found that the SIA concentration increased  
260 significantly, meanwhile, the OM concentration only slightly increased at the GC rural and BJ urban  
261 sites with the consistent decreasing WS and increasing RH during the heavily polluted period (Figs.  
262 2 and S1). In a word, we observed that the SIA fraction in fine particles increased and the OM fraction  
263 decreased following the haze evolution (Fig. S3).

264 The concentrations and fractions of OM and EC at nighttime were much higher than those at  
265 daytime during the whole haze episode at the GC rural site (Figs. 2a and S3a), suggesting the  
266 continuous strong local combustion emissions at nighttime. Furthermore, the concentration of  $\text{Cl}^-$  ( $8\text{--}$   
267  $22\text{ }\mu\text{g m}^{-3}$ ) was much higher than that of  $\text{K}^+$  ( $1\text{--}3\text{ }\mu\text{g m}^{-3}$ ) (Fig. 2a), which suggests more contributions  
268 from coal combustion than biomass burning at the GC rural site (Sun et al., 2014; Zhang et al., 2020).  
269 Based on the field investigation and  $\text{PM}_{2.5}$  analysis, we concluded that the explosive increase of  $\text{PM}_{2.5}$   
270 at the GC rural site was initiated by strong local emissions and accumulation of POA from residential  
271 coal combustion for heating and a small fraction of biomass burning for cooking in rural areas. The  
272 PMF analysis shows that FFOA and BBOA ( $14.6\text{--}30.6\text{ }\mu\text{g m}^{-3}$ ) contributed significantly ( $> 30\%$ ) to  
273 OM in the polluted period at the BJ urban site (Fig. S4 and Table S2), suggesting that POA emitted  
274 in rural areas were transported to Beijing under southerly winds. In summary, bulk analyses show  
275 that POA from residential coal and biomass burning consistently contributed to the regional haze, and  
276 SIA produced from the secondary formation had an increasing contribution at higher RH following  
277 the haze evolution.

### 278 3.2 Classification of individual particle types

279 In this study, TEM observations show abundant spherical and irregular particles comprised of C,  
280 O, and Si elements during this haze episode (Fig. 3a). These particles are stable under strong electron  
281 beams and appear as dark features in TEM images, reflecting their high thickness and refractory  
282 properties (Ebert et al., 2016; Liu et al., 2018). The SEM image acquired at a  $75^\circ$  tilt angle shows that  
283 these particles did not deform upon impaction and retained high vertical dimensions (Fig. 4),

284 indicating that these particles are in a solid state with high viscosity (Reid et al., 2018; Wang et al.,  
285 2016). By contrast, the secondary particles (i.e., SIA and organic coating) became flat on the substrate  
286 (Fig. 4). Previous studies have confirmed that these solid spherical and irregular particles are POA  
287 particles emitted from coal and biomass burning (L. Liu et al., 2017; Zhang et al., 2018), especially  
288 the spherical POA particles shown in Fig. 3a-1 are defined as tarballs containing light-absorbing BrC  
289 (Adachi et al., 2019; C. Li et al., 2019; Pósfai et al., 2003; Zhang et al., 2018). The tarballs (Fig. 3a-  
290 1) and irregular POA particles (Fig. 3a-2) are both burning-related POA particles and have similar  
291 chemical composition and physical characteristics under the TEM despite their different shapes, thus  
292 in this study we consider that irregular POA particles also contain light-absorbing BrC like tarballs.

293 Other typical individual particle types, such as SIA (Fig. 3b), mineral (Fig. 3c), soot (Fig. 3d),  
294 and fly ash/metal (Fig. 3e) particles were also classified during this haze episode. The detailed  
295 classification criteria of these particle types derived from the TEM images and their sources can be  
296 found in our previous paper (Li et al., 2016a). It should be noted that some SIA particles were coated  
297 with secondary organic coatings (Fig. 3b) which were produced from the chemical oxidation of  
298 volatile organic compounds (Li et al., 2016b). TEM observations further show the internal mixture of  
299 POA or soot particles with SIA, i.e., POA-SIA (Fig. 3f) and soot-SIA (Fig. 3g). To better understand  
300 number variations of different particle types, we classified the bare POA and POA-SIA particles as  
301 the POA-containing particles, and bare soot and soot-SIA particles as soot-containing particles.

### 302 **3.3 Relative abundance of individual particle types**

303 Figure 5 shows number fractions of different particle types in different periods at GC rural and  
304 BJ urban sites. At the GC rural site, POA-containing and soot-containing particles were the major  
305 particle types with their corresponding contributions being 37.6% and 35.9% by number, followed  
306 by SIA particles (22.4%) in the clean period. When the haze episode occurred at the GC rural site,  
307 POA-containing particles became dominant in the early stage of heavily polluted period and its  
308 number fraction (64.8%) was nearly twice that (37.6%) in the clean period (Fig. 5a). This result agrees

309 well with the bulk PM<sub>2.5</sub> analysis which shows a sharp increase in OM concentration in the early  
310 stage of heavily polluted period (Fig. 2a). With increasing pollution levels from the early stage to the  
311 late stage of heavily polluted period, the fraction of POA-containing particles slightly decreased from  
312 64.8% to 50.8%, by contrast, the fraction of SIA particles increased from 4.6% to 12.4% (Fig. 5a).  
313 The variations of POA-containing and SIA particles are similar to the results from the bulk PM<sub>2.5</sub>  
314 analysis as shown in Fig. 2a.

315 At the BJ urban site, the contribution of POA-containing particles (15.1%) in the clean period  
316 was much lower than that (37.6%) at the GC rural site (Fig. 5). Following the transition from the  
317 clean period to the moderately polluted period at the BJ urban site, the fraction of POA-containing  
318 particles (66.2%) increased significantly by more than a factor of four compared with that (15.1%) in  
319 the clean period. Meanwhile, fractions of soot-containing, mineral, and SIA particles decreased  
320 largely. When the pollution level changed to the heavily polluted period, similar to the situation at the  
321 GC rural site, the fraction of SIA particles increased from 7.8% to 13.2% and the fraction of POA-  
322 containing particles decreased slightly from 66.2% to 52.8% (Fig. 5b). Overall, the individual particle  
323 analysis results consist well with changes in aerosol chemical components obtained by the bulk  
324 analysis as shown in Fig. 2. Furthermore, individual particle analysis reveals that POA-containing  
325 particles dominated (> 50% by number) in the rural and urban air during the regional wintertime haze  
326 episode.

### 327 **3.4 Atmospheric aging of POA particles**

328 TEM images clearly show the morphology and mixing state of individual particles in different  
329 polluted periods at GC rural and BJ urban sites (Fig. 6). At the GC rural site, we found that large  
330 amounts of bare POA particles, especially tarballs occurred in the early stage of heavily polluted  
331 period (Fig. 6a). Based on the integrated analyses of individual particles and bulk samples, we  
332 confirmed that POA particles emitted from the intense domestic coal and biomass burning for heating  
333 and cooking contributed significantly to the deterioration of air quality in rural areas. When the haze

334 episode evolved into the late stage of heavily polluted period, we found that most of the POA particles  
335 were coated with SIA (i.e., POA–SIA particle) forming the core–shell structure (Fig. 6b). This result  
336 indicates that POA particles in the regional haze layer provided surfaces for the heterogeneous  
337 reactions of SO<sub>2</sub> and NO<sub>x</sub>, which promotes the formation of SIA on POA particles in the humid  
338 polluted air (Ebert et al., 2016; Zhang et al., 2017).

339       Following the regional transport of polluted air masses from the south to the north of the NCP,  
340 abundant POA particles occurred in the moderately polluted period at the BJ urban site (Fig. 6c).  
341 Therefore, we conclude that the POA particles emitted in the rural areas in the south of the NCP could  
342 be transported to the BJ urban site and significantly affect the urban air quality. Following the haze  
343 evolution, similar to those at the GC rural site, the POA particles aged and became core–shell POA–  
344 SIA particles at the BJ urban site in the heavily polluted period (Fig. 6d).

345       Based on the mixing state of POA-containing particles, we found that following evolution of the  
346 haze episode, the fraction of bare POA particles was reduced by twice from 91.4% in the early stage  
347 to 39.6% in the late stage of heavily polluted period at the GC rural site, and the fraction of POA–  
348 SIA particles correspondingly increased by seven times from 8.6% to 60.4% (pie charts in Fig. 7).  
349 Similarly, at the BJ urban site, the fraction of bare POA particles decreased from 70.4% in the  
350 moderately polluted period to 31.4% in the heavily polluted period, and the fraction of POA–SIA  
351 particles increased correspondingly from 29.6% to 68.6% (pie charts in Fig. 7). Consequently, the  
352 average size of POA-containing particles increased from 505 nm in the early stage to 837 nm in the  
353 late stage of heavily polluted period at the GC rural site and from 443 nm in the moderately polluted  
354 period to 732 nm in the heavily polluted period at the BJ urban site (Fig. 7a). Interestingly, the average  
355 sizes of uncoated POA particles (i.e., POA cores and bare POA) remained similar following the haze  
356 evolution, with their respective values being 469, 508, and 465 nm in the early, middle, and late stages  
357 of heavily polluted period at the GC rural site and 381 and 379 nm in the moderately and heavily  
358 polluted periods at the BJ urban site (Fig. 7b). The average sizes of uncoated POA particles at the BJ

359 urban site were slightly smaller than those at the GC rural site, which is reasonable because the fresh  
360 POA particles with larger sizes could be collected at the GC rural site close to emission sources and  
361 larger ones are more likely to be removed during the regional transport (Seinfeld and Pandis, 2006).  
362 Adachi et al. (2018) reported that tarballs retained their spherical shapes and the particle masses and  
363 sizes did not change largely when heated to 300°C in TEM. As a result, we conclude that the POA  
364 particles should be quite physically stable and chemically inert in the atmosphere, which can be  
365 transported over long distances.

366 The  $D_p/D_c$  ratio can be used to indicate the aging degree of POA-containing particles in the  
367 atmosphere (Chen et al., 2017; Li et al., 2011). By calculating the  $D_p/D_c$  ratio, we realized  
368 quantification of the aging degree of POA-containing particles as shown in Fig. 8. In the early stage  
369 of heavily polluted period at the GC rural site, the POA-containing particles were mainly fresh bare  
370 POA particles with a fraction of 91.4% (Fig. 7), therefore, the average  $D_p/D_c$  ratio was close to one  
371 (1.02). Following the haze evolution at the GC rural and BJ urban sites, average  $D_p/D_c$  ratios increased  
372 from 1.08 in the middle stage to 1.60 in the late stage of heavily polluted period at the GC rural site,  
373 and from 1.11 in the moderately polluted period to 1.67 in the heavily polluted period at the BJ urban  
374 site. The results indicate that POA particles were thickly coated with SIA due to the particle aging  
375 process. Here we can obtain two conclusions based on the individual particle analysis: (1) more POA  
376 particles continuously aged and were coated with SIA following the haze evolution; (2) the SIA  
377 coating gradually grew through the heterogeneous conversion of gaseous precursors (e.g., SO<sub>2</sub> and  
378 NO<sub>x</sub>) in the polluted air. Therefore, the aging process of individual POA particles in wintertime hazes  
379 well reflects the regional haze evolution in the NCP.

### 380 **3.5 Changes in light absorption of POA particles**

381 It is well known that organic aerosols emitted from coal and biomass burning are the main source  
382 of light-absorbing BrC (M. Li et al., 2019; Lin et al., 2016; Sun et al., 2017). Recently, some  
383 observation and modeling works show that BrC in haze layers over the NCP can affect the regional

energy budget (Feng et al., 2013; Wang et al., 2018; Xie et al., 2019). However, there is no answer on how the aging process of burning-related light-absorbing POA particles influences their optical absorption in the regional haze. Here using Mie theory we further explored variations in the optical absorption of individual POA particles following the haze evolution at the GC rural and BJ urban sites (Fig. 9). It should be noted that another RI of  $1.84-0.21i$  for tarballs was reported by Hoffer et al. (2016). The average Mie calculation results at the GC rural and BJ urban sites obtained by the RIs of  $1.67-0.27i$  (used in this study) and  $1.84-0.21i$  were compared and we found that the two RIs only cause little differences between the results (Table S3). Therefore, only the results from the RI of  $1.67-0.27i$  were used and discussed in this study.

At the GC rural site, the average ACS of individual POA-containing particles under the actual scenario ( $ACS_{\text{actual}}$ ) in the early, middle, and late stages of heavily polluted period were estimated to be  $3.09 \times 10^{-14}$ ,  $3.97 \times 10^{-14}$ , and  $4.43 \times 10^{-14} \text{ m}^2$ , respectively (Fig. 9a). If all the POA-containing particles were not coated with SIA in each period (i.e., particle non-aging scenario), the corresponding average ACS of individual uncoated POA particles ( $ACS_{\text{non-aging}}$ ) were  $3.01 \times 10^{-14}$ ,  $3.53 \times 10^{-14}$ , and  $3.18 \times 10^{-14} \text{ m}^2$ , respectively (Fig. 9a). Therefore, we obtained that the  $E_{\text{abs}}$  (i.e., ratio of  $ACS_{\text{actual}}$  to  $ACS_{\text{non-aging}}$ ) were 1.02, 1.12, and 1.39 in the early, middle, and late stages of heavily polluted period, respectively, at the GC rural site (Fig. 9a). Similarly, at the BJ urban site, the  $E_{\text{abs}}$  were 1.10 and 1.39 in the moderately and heavily polluted periods, respectively, with the corresponding average  $ACS_{\text{actual}}$  being  $2.06 \times 10^{-14}$  and  $3.00 \times 10^{-14} \text{ m}^2$  and  $ACS_{\text{non-aging}}$  being  $1.86 \times 10^{-14}$  and  $2.15 \times 10^{-14} \text{ m}^2$  (Fig. 9b). The light absorption capacity of individual POA particles at the BJ urban site was a little lower than that at the GC rural site (Fig. 9), which was mainly attributed to the smaller sizes of POA particles at the BJ urban site (Fig. 7).

To better understand the influence of SIA-coating thickness and POA-core diameter on the light absorption of POA-SIA particles, we modeled the variations in  $E_{\text{abs}}$  of POA-SIA particles (i.e., ratio of  $ACS_{\text{POA-SIA}}$  to  $ACS_{\text{POA core}}$ ) with different  $D_c$  as a function of  $D_p/D_c$  ratios (Fig. 10). Results show

that  $E_{\text{abs}}$  is sensitive to the changes in both  $D_c$  and  $D_p/D_c$  ratio. When  $D_p/D_c < 1.5$ , the  $E_{\text{abs}}$  increases sharply with the increase of  $D_p/D_c$  ratio for different POA core sizes; but when  $D_p/D_c > 1.5$ , the  $E_{\text{abs}}$  does not show an increase any more for particles with  $D_c > 200$  nm, and the  $E_{\text{abs}}$  is limited to between 1.5 and 2 for particles with  $D_c$  ranging from 200 to 1500 nm (Fig. 10). The diameters of observed POA cores at GC rural and BJ urban sites in this study were mainly in the range of 200 to 800 nm (Fig. 7), thus the  $E_{\text{abs}}$  of observed POA–SIA particles in the NCP were mostly below 1.75 (Fig. 10). All the above results indicate that the atmospheric aging process could significantly improve the light absorption capacity of POA particles along with the evolution of haze episodes due to the “lensing effect” of SIA coating.

#### 4 Conclusions and implications

This study demonstrates that primary pollutants especially large amounts of POA particles emitted from the residential coal and biomass burning in rural areas initiated the wintertime regional haze episode in the NCP. The presence of abundant burning-related POA particles in the atmosphere could further provide surfaces for heterogeneous reactions promoting the large production of SIA under stagnant metrological conditions with high RH, which further elevated the pollution level. Compared with the tarballs which have been confirmed as BrC with strong light-absorbing capacities in previous studies (Adachi et al., 2019; C. Li et al., 2019), the spherical POA (i.e., tarball) and irregular POA particles observed in this study can better represent burning-related light-absorbing primary organic particles in the wintertime hazes. Therefore, the ubiquitous light-absorbing POA particles in the atmosphere of NCP unquestionably affect the energy balance (Feng et al., 2013). We found that burning-related POA particles remained quite stable during the regional transport from the rural areas to urban Beijing in the NCP and were coated with SIA through the atmospheric aging process in the haze layer, which could significantly enhance the light absorption capacity of POA particles via the “lensing effect” of SIA coating. We estimated that  $E_{\text{abs}}$  values were within the upper limit of 1.75 in core–shell Mie calculations considering the typical size distribution of POA particles

434 (200–800 nm) in the NCP. Furthermore, Alexander et al. (2008) found plenty of primary brown  
435 carbon spheres with strong light absorption capacity in East Asian outflow, which indicates that the  
436 POA particles could be transported over long distances and still retain their strong light-absorbing  
437 properties, and thus can affect the regional and even global radiative forcing. Therefore, we highlight  
438 that the “lensing effect”, which has been adequately reported on BC particles but not on light-  
439 absorbing POA particles in previous studies, should be further considered on these POA particles in  
440 radiative forcing models.

441 Considering the adverse effects of residential coal and biomass burning on the haze formation  
442 and climate change, we suggest that the governments should continue to implement the “Clean Air  
443 Actions” (Zhang and Geng, 2019), especially encourage the use of clean energy such as electricity  
444 and natural gas for heating and cooking in rural areas of North China in winter.

#### 445 **Data availability**

446 All data presented in this paper are available upon request. Please contact the corresponding  
447 author (liweijun@zju.edu.cn).

#### 448 **Author Contributions**

449 WL and LL designed the research. LL performed the data analysis and wrote the manuscript and  
450 WL revised it. JZ and YZ assisted with the sample collection. YS provided the AMS data at the  
451 Beijing site. LL, JZ, YZ, LX, QY, and YW carried out the chemical analysis of PM<sub>2.5</sub> and TEM  
452 analysis of individual particles. ZS, YS, DL, and PF contributed to the improvement of this  
453 manuscript. All the authors approved the final version of this paper.

#### 454 **Competing interests**

455 The authors declare that they have no conflict of interest.

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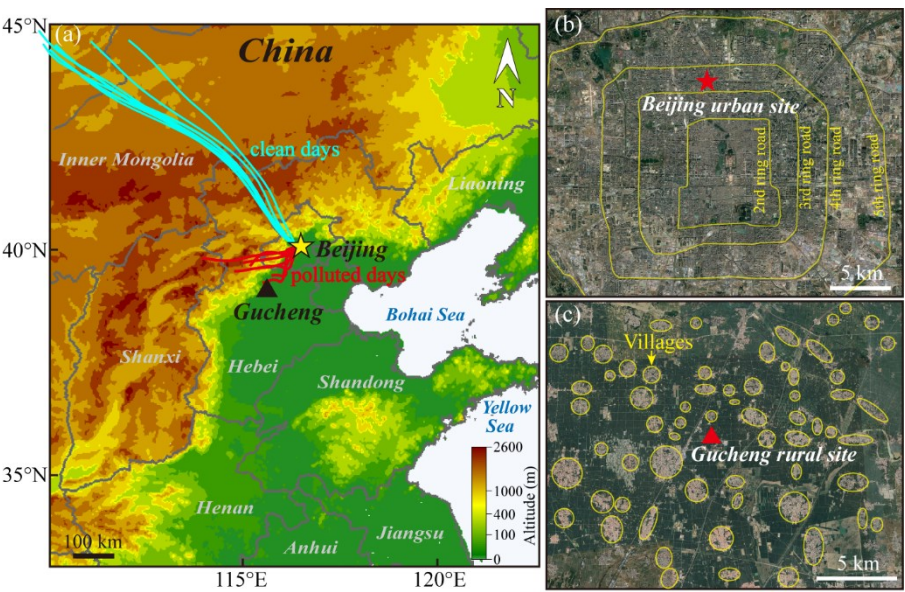
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701 Figure 1. Locations of Beijing and Gucheng in the North China Plain (a) and the expanded view of surrounding  
702 topographies around the Beijing urban site (b) and Gucheng rural site (c). The 24-h backward trajectories of air  
703 masses ending at the height of 100 m (a.g.l) over the Beijing urban site in clean and polluted days during 20–27  
704 November, 2020 are also shown in (a). (Map copyright @2020 Google Maps)

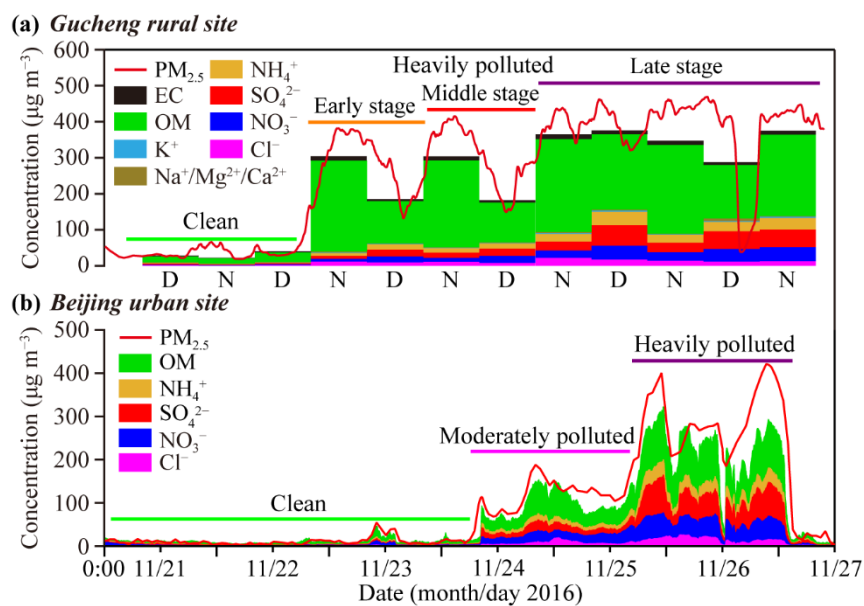


Figure 2. Time series of PM<sub>2.5</sub> and major aerosol chemical species at the (a) Gucheng rural site and (b) Beijing urban site. Chemical species were obtained by offline analysis of daytime (D) and nighttime (N) PM<sub>2.5</sub> filter samples at the rural site and were obtained by online analysis of NR-PM<sub>1</sub> using a high-resolution aerosol mass spectrometer (HR-AMS) at the urban site. The different periods of the haze episode at rural and urban sites are marked in this figure.

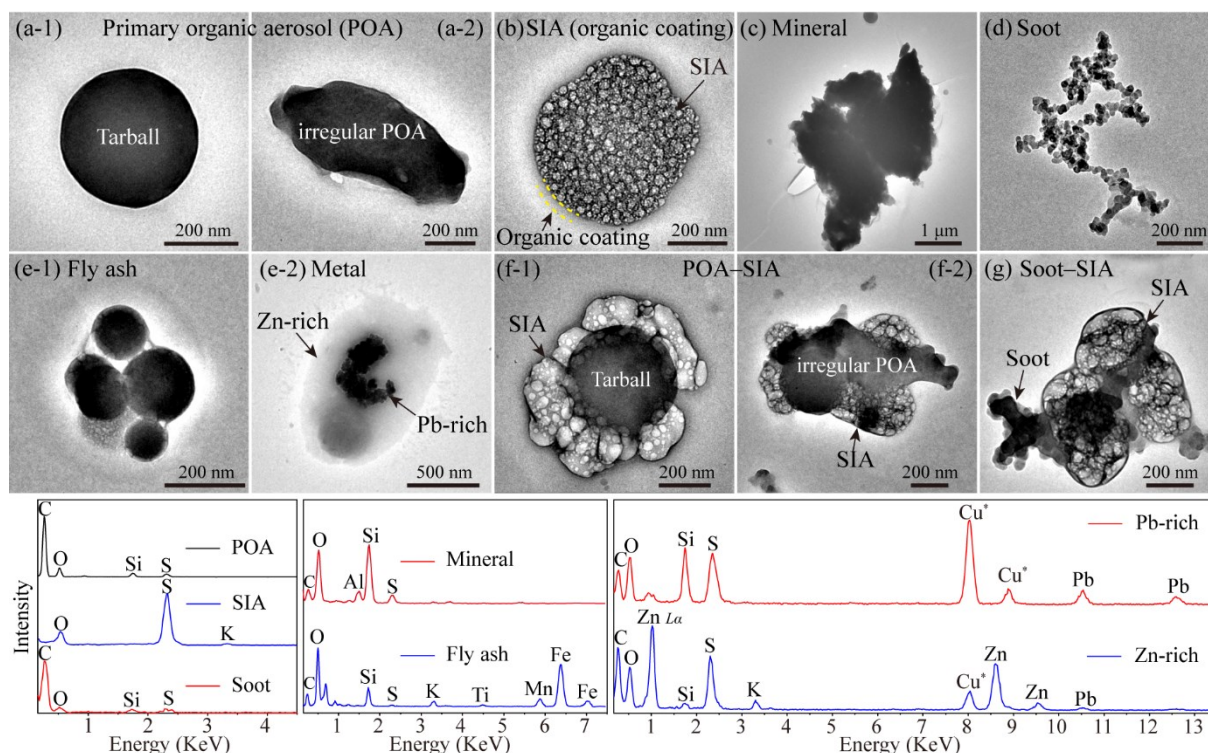
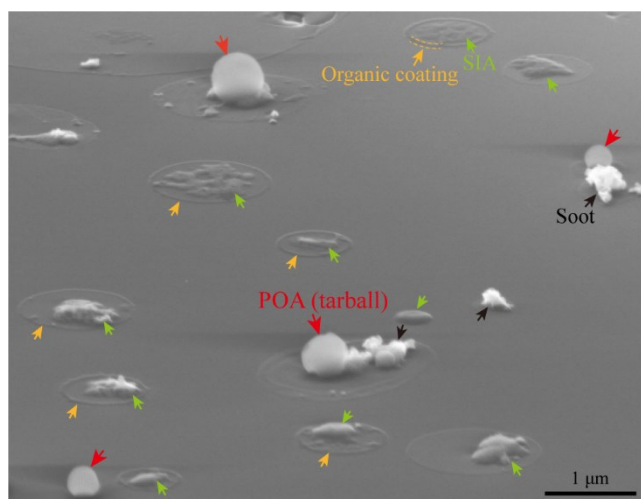


Figure 3. Typical transmission electron microscopy (TEM) images and energy-dispersive X-ray spectrometry (EDS) spectra showing the morphology, composition, and mixing structures of different individual particle types. (a) primary organic aerosol (POA) particles with (a-1) spherical (i.e., tarball) or (a-2) irregular shapes; (b) secondary inorganic aerosol (SIA) particle with secondary organic coating; (c) mineral; (d) soot; (e-1) fly ash and (e-2) metal; (f) internally mixed POA particle with SIA coating (POA-SIA); (g) internally mixed soot particle with SIA coating (soot-SIA).



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Figure 4. Scanning electron microscopy (SEM) image acquired in the secondary electron (SE2) mode at a 75° tilt angle showing the surface morphology of individual particles in the vertical dimension. The red, black, green, and orange arrows indicate primary organic aerosol (POA) particle (mainly tarball), soot particle, secondary inorganic aerosol (SIA) particle, and secondary organic coating, respectively.

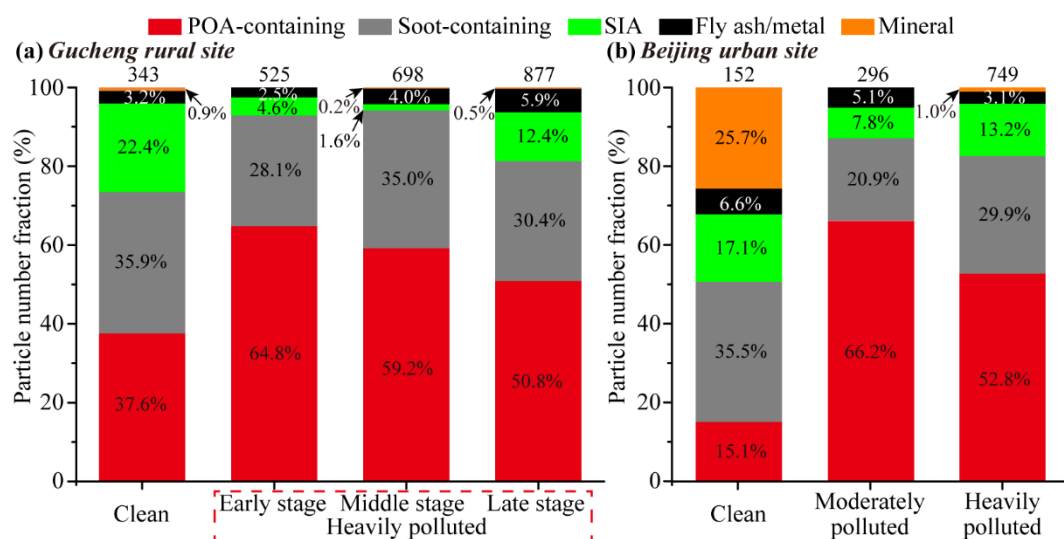


Figure 5. Relative abundance of different particle types in different periods at the (a) Gucheng rural site and (b) Beijing urban site. The numbers of analyzed particles in different periods are shown on the top of each column.

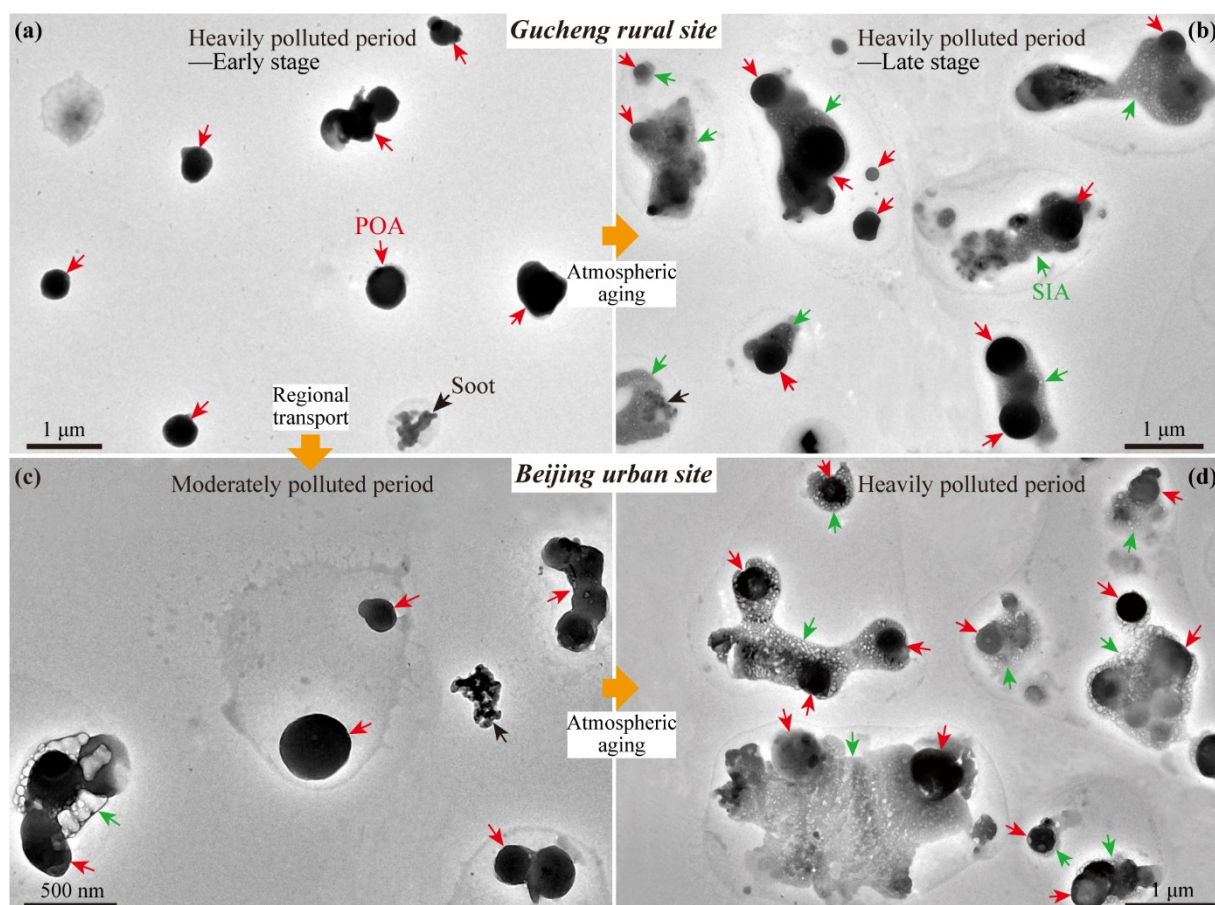


Figure 6. TEM images showing individual particles collected in the (a) early stage and (b) late stage of heavily polluted period at the Gucheng rural site and in the (c) moderately polluted and (d) heavily polluted periods at the Beijing urban site. The red, green, and black arrows indicate primary organic aerosol (POA) particle, secondary inorganic aerosol (SIA) particle, and soot particle, respectively.

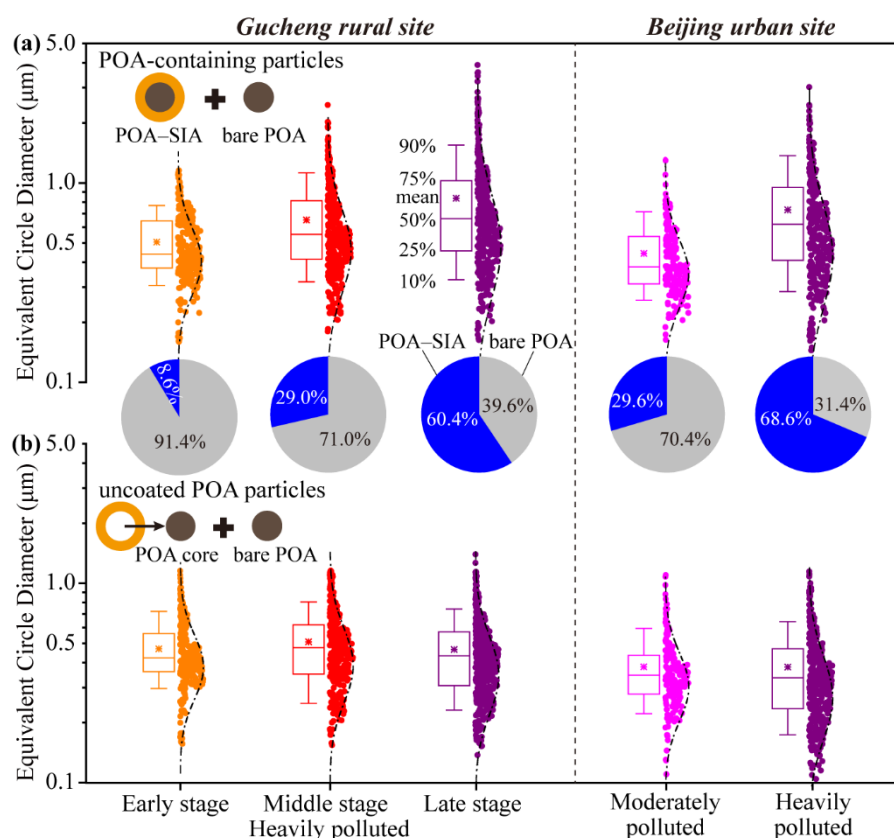


Figure 7. Box plots showing equivalent circle diameters (ECD) of (a) POA-containing particles (including core-shell POA-SIA and bare POA) and (b) uncoated POA particles (including POA cores without SIA shell and bare POA) in different polluted periods at the Gucheng rural site and Beijing urban site. The solid circles (right of the box) represent the ECD of individual particles with lognormal distributions. The pie charts present the relative number fractions between POA-SIA and bare POA in different polluted periods.

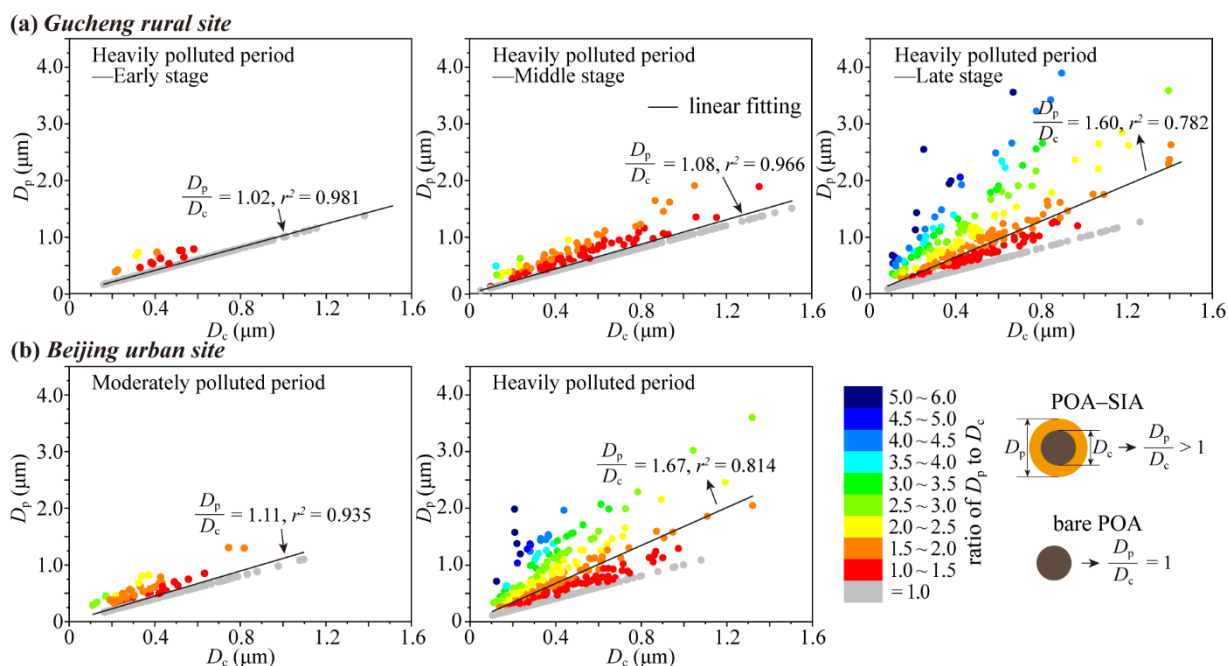


Figure 8. Relationship between the diameter of POA-containing particle ( $D_p$ ) and its POA core ( $D_c$ ) in the early stage, middle stage, and late stage of heavily polluted period at the Gucheng rural site (a) and in the moderately polluted and heavily polluted periods at the Beijing urban site (b).

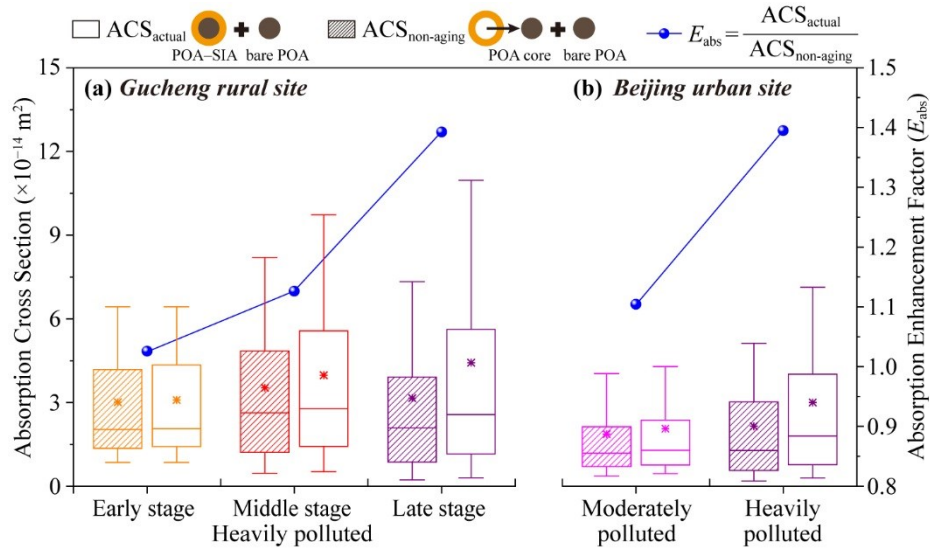


Figure 9. Box plots of light absorption cross sections (ACS) of individual POA-containing particles (including core-shell POA-SIA and bare POA) under the actual scenario ( $ACS_{actual}$ ) and uncoated POA particles (including POA cores without SIA shell and bare POA) under the particle non-aging scenario ( $ACS_{non-aging}$ ) at the wavelength of 550 nm; and variations in the light absorption enhancement factors ( $E_{abs}$ , i.e., ratio of  $ACS_{actual}$  to  $ACS_{non-aging}$ ) in different polluted periods at the (a) Gucheng rural site and (b) Beijing urban site. A refractive index of  $1.55-0i$  for non-light-absorbing SIA coating (Denjean et al., 2014) and  $1.67-0.27i$  for light-absorbing POA core (Alexander et al., 2008) were adopted at the wavelength of 550 nm. The box represents the 25th (lower line), 50th (middle line), and 75th (top line) percentiles; the asterisk in the box represents the mean value; and the end lines of the vertical bars represent the 10th (below the box) and 90th (above the box) percentiles.

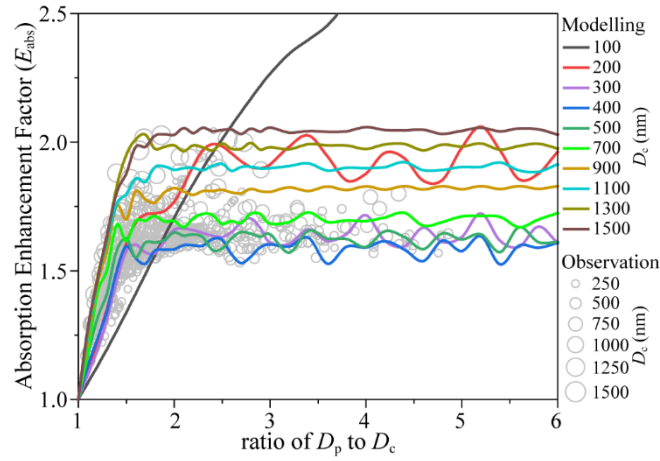


Figure 10. Mie theory-calculated light absorption enhancement factors ( $E_{\text{abs}}$ ) of modeled core-shell POA-SIA particles (i.e., ratio of  $\text{ACS}_{\text{POA-SIA}}$  to  $\text{ACS}_{\text{POA pore}}$ ) with different POA core diameters ( $D_c$ ) as a function of particle-to-core diameter ratio ( $D_p/D_c$ ) at the wavelength of 550 nm (solid lines). A refractive index of  $1.55-0i$  for non-light-absorbing SIA coating (Denjean et al., 2014) and  $1.67-0.27i$  for light-absorbing POA core (Alexander et al., 2008) were adopted at the wavelength of 550 nm. The open circles represent all the observed POA-SIA particles during the whole polluted periods at Gucheng rural and Beijing urban sites.