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Fractal Dimensions and Mixing Structures of Soot Particles during Atmospheric Processing

Yuanyuan Wang^{1,2}, Fengshan Liu³, Cenlin He⁴, Lei Bi², Tianhai Cheng⁵, Zhili Wang⁶, Hua
Zhang^{7,8}, Xiaoye Zhang⁶, Zongbo Shi⁹, Weijun Li^{*2}

¹Environment Research Institute, Shandong University, Jinan, Shandong 250100, China

²Department of Atmospheric Sciences, School of Earth Sciences, Zhejiang University, Hangzhou,
310027, China

³Measurement Science and Standards, National Research Council, Ottawa, Ontario K1A 0R6,
Canada

⁴Department of Atmospheric and Oceanic Sciences and Joint Institute for Earth System Science
and Engineering, University of California, Los Angeles, CA90095, USA

⁵State Key Laboratory of Remote Sensing Science, Institute of Remote Sensing and Digital Earth,
Chinese Academy of Sciences, Beijing, 100101, China

⁶Chinese Academy of Meteorological Sciences, Beijing 100081, China

⁷Collaborative Innovation Center on Forecast and Evaluation of Meteorological Disasters, Nanjing
University of Information Science & Technology, Nanjing 210044, China

⁸Laboratory for Climate Studies, National Climate Center, China Meteorological Administration,
Beijing 100081, China

⁹School of Geography, Earth and Environmental Sciences, University of Birmingham,
Birmingham B15 2TT, U.K

* Corresponding author: liweijun@zju.edu.cn

+86-57187952453

1 **Abstract**

2 Soot particles strongly absorb sunlight and hence act as a short-lived warming agent.
3 Atmospheric aging of soot particles changes their morphology and mixing state and
4 consequently alter their optical properties. Here we collected soot particles at tunnel,
5 urban, mountaintop, and background sites in Northern China and analyzed their
6 mixing structures and morphology using transmission electron microscopy. Soot
7 particles were further classified into three types: bare-like, partly coated, and
8 embedded. Bare-like soot particles were dominant at the tunnel site, while most soot
9 particles were partly coated or embedded type at other sites. Fractal dimensions (D_f)
10 of different types of soot particles ranged from 1.80 to 2.16 and were ordered as:
11 bare-like < partly coated < embedded. Moreover, their average D_f changed from 1.8
12 to 2.0 from the tunnel to the background site. We conclude that the D_f can
13 characterize the shape of soot aggregates reasonably well and its variation reflects
14 soot aging processes. Compared with the reported D_f of soot particles, we found that
15 $D_f = 1.8$ used in previous optical models primarily represents freshly emitted soot
16 aggregates, rather than the ambient ones.

17

18 **1 Introduction**

19 Soot particles, also known as black carbon (BC) or elemental carbon (EC), are
20 fractal-like aggregates produced from the incomplete combustion of biomass and
21 fossil fuels. Soot particles strongly absorb sunlight and heat the air, altering the
22 radiative forcing of the atmosphere and affecting global and regional climate.¹⁻⁴
23 During transport and aging, fresh soot particles mix with organic and inorganic
24 aerosols, changing their morphology and compactness, which leads to changes of
25 their optical properties and radiative forcing.^{5,6} *Jacobson*⁷ proposed that the sulfate
26 coating on soot particles can enhance optical absorption by ~2 through treating the
27 mixture of soot and sulfate as a core-shell model. However, *Cappa et al.*⁸ observed
28 that the absorption enhancement of aged soot particles in Sacramento was 6% on
29 average at 532 nm by in-situ measurements. Different conclusions about the optical
30 absorption of soot particles should be attributed to their complicated shapes and
31 various mixing states in the atmosphere.^{9,10} Due to the lack of quantification on the
32 variation of shapes and mixing structures of soot particles, the debate on optical
33 properties of soot particles still continues.

34 Some experimental methods such as combination of single-particle soot
35 photometer (SP2), three-wavelength photoacoustic soot spectrometer (PASS-3), and
36 Aerodyne soot particle-aerosol mass spectrometer (SP-AMS) were used to well
37 characterize physicochemical properties of soot and measured their optical
38 properties.¹¹⁻¹⁴ However, these measurements could not provide accurate morphology
39 of soot aggregates for the modeling study. Many numerical optical models such as the
40 Rayleigh-Debye-Gans (RDG) approximation¹⁵, T-Matrix^{16, 17}, and Discrete Dipole
41 Approximation (DDA)¹⁸ can be used to calculate the optical properties of soot
42 aggregates.^{10, 19-21} Except RDG, other numerical models require the morphology of
43 soot aggregates, which can be generated numerically using fractal dimension (D_f).
44 Among the available algorithms to generate fractal aggregates, the tunable method²² is
45 preferred due to its capability of generating aggregates of a prescribed D_f , which is the
46 most important morphological parameter of fractal aggregates. *Adachi et al.*²³ used

47 electron tomography in transmission electron microscopy (TEM) to calculate the D_f of
48 individual soot particles. The method requires a sophisticated system of TEM coupled
49 with tomography, which is not commonly available. *Xiong and Friedlander*²⁴
50 calculated the D_f of individual soot particles by drawing circles around the primary
51 particles and then determining the size and position of the primary particles in the
52 TEM image using scaling laws.^{25, 26} The method is inefficient in obtaining the D_f of
53 hundreds of soot particles, because it requires 10-30 minutes for each soot aggregate.
54 Later, an approach for image characterization of soot aggregates was proposed by
55 *Brasil et al.*²⁷ and *Oh and Sorensen*.²⁸ The method can conveniently derive various
56 parameters of individual soot particles in the scaling law and obtain a D_f to represent
57 their ensemble morphology. Recently, *China et al.*²⁹ successfully used this method to
58 calculate D_f of soot particles freshly emitted by wildfire. However, there are only
59 quite few available reports about the D_f of ambient soot particles, whose D_f values are
60 very important to understand their optical properties in different environments.

61 In this study, we report a detailed analysis of a large number of soot particles
62 collected at tunnel, urban, mountaintop, and background sites in polluted air in the
63 North China Plain (NCP). At each site, soot particles are classified into three types
64 based on their mixing states and morphology and then their corresponding D_f values
65 are calculated and compared systematically for the first time. We use a method
66 combining TEM analysis and numerical calculation to obtain a D_f to represent the
67 ensemble morphology of soot aggregates. At last, we discuss their morphological
68 and mixing properties and the implication of these properties on aging.

69

70 **2 Materials and Methods**

71 **2.1 Aerosol Sampling**

72 The NCP was covered by the regional haze layer during the sampling period, so
73 we defined our samples from the continental polluted air. Aerosol samples were
74 collected at four sampling sites in NCP: a tunnel site, an urban site, a mountaintop
75 site, and a background site (Figure S1), where the relative humidities (RHs) were at

76 about 52%, 16%, 64%, and 56%, respectively. The RHs at the four sampling sites
77 were lower than 65% during the sampling period, indicating that the hazes were
78 mainly dry. The Kaiyuan tunnel site is a busy highway that enters Jinan City. The
79 urban site in Jinan City is a typical downtown site with strong vehicle and residential
80 emissions. The Mountain Tai (at 1534 m above sea level) is the highest mountain in
81 NCP. The aerosol particles collected at the mountaintop site reflect regional transport
82 of aerosol particles in NCP.³⁰ The background Changdao Island in the Bohai Sea is a
83 downwind site of Shandong province and the Jing-Jin-Ji area (i.e., Beijing, Tianjin,
84 and Hebei province) during winter (Figure S1). Aerosol samples were
85 simultaneously collected at the urban, mountaintop, and background sites during
86 13-23 December 2014. At the tunnel site, aerosol samples were collected on 8
87 November 2016. A total of 779 soot particles from 31 samples were analyzed to
88 determine their size and elemental composition using TEM/EDS. We note that the
89 distribution of aerosol particles on TEM grids was not uniform. Therefore, we chose
90 three to four areas from the center and periphery of each grid to ensure that the
91 analyzed particles were representative. Once the internally mixed soot particles are
92 under the strong electron beam (Figure S2), they can easily damage the sulfates and
93 nitrates but do not change morphology of soot aggregates. This microscopic analysis
94 is explained in the Supporting Information.

95

96 **2.2 Morphology Analysis of Soot Particles**

97 Fractal dimension of soot particles can be characterized using the scaling law²⁵:

$$98 \quad N = k_g \left(\frac{2R_g}{d_p} \right)^{D_f} \quad (1)$$

99 where N is the total number of monomers in each aggregate, R_g is the radius of
100 gyration of the soot aggregate, d_p is the monomer diameter, k_g is the fractal prefactor,
101 and D_f is the mass fractal dimension. Note that the D_f in this study is the mass fractal
102 dimension of soot aggregates that excludes the coating. In this study, the D_f and k_g
103 are estimated from a power law fit of a scatter plot of N vs the values of $2R_g/d_p$.

104 N can also be scaled with the aggregate projected area in the following

105 power-law relationship:

$$106 \quad N = k_a \left(\frac{A_a}{A_p} \right)^\alpha \quad (2)$$

$$107 \quad \delta = \frac{2a}{l} \quad (3)$$

108 where A_a is the projected area of the soot aggregate, A_p is the mean projected area of
109 the monomer, k_a is a constant, and α is an empirical projected area exponent. The
110 exact values of k_a and α depend on the overlap parameter (δ),²⁸ which can be
111 calculated using equation (3) with a being the monomer radius and l the lattice
112 spacing in TEM images. The number of monomers N can then be calculated using
113 equation (2).²⁸

114 The parameters d_p and R_g are also required to determine D_f . While d_p can be
115 obtained directly from analysis of TEM images, estimation of the actual radius of
116 gyration (R_g) is complicated. Here we used the following simple correlation

$$117 \quad L_{\max} / (2R_g) = 1.50 \pm 0.05 \quad (4)$$

118 to calculate R_g ,²⁷ where L_{\max} is the maximum length of the soot aggregate obtained
119 from TEM images.

120

121 **3 Results and Discussion**

122 **3.1 Morphology and Mixing State of Soot Particles**

123 Fresh soot particles are normally chain-like aggregates. Once soot particles mix
124 with other aerosol components in the air, the aging process can rearrange the
125 structure of the inner soot aggregates.³¹ Based on their morphology and the visual
126 estimation of coating on soot particles in TEM images, we classified them into three
127 types: bare-like, partly coated, and embedded. Bare-like soot particles in TEM
128 images display clear monomers without any visible coating on their surface (Figure
129 1a-1/1b-1/1c-1). Partly coated soot particles mean that individual soot particles are
130 partly coated by other aerosol components (Figure 1a-2/1b-2/1c-2). Embedded soot
131 particles refer to individual soot particles that are heavily coated or are entirely

132 embedded within other aerosol components (Figure 1a-3/1b-3/1c-3). Figure 1 shows
133 the three types of soot particles collected at the urban, mountaintop, and background
134 sampling sites. Bare-like soot particles are dominant in the tunnel samples, because
135 vehicles emit large amounts of fresh soot particles (Figure S3). Similar results have
136 been found near freeways.³² Based on their different mixing structures, embedded
137 soot particles are normally considered as more aged than the partly coated soot
138 particles.³³ We also calculated the area ratios of coating/soot core for internally
139 mixed soot particles. Figure S4 shows partly coated soot particles mostly have ratios
140 smaller than one, indicating smaller coatings. In contrast, embedded soot particles
141 have larger ratios, some of which are more than 20 times larger. These results are
142 consistent with our classification.

143 Figure 2 shows the fractions of three types of soot particles in different
144 atmospheric environments. The result shows that the bare-like soot particles
145 accounted for 64% of all particles in tunnel air but only 1~25% in urban polluted air
146 (Figure 2). *Wang et al.*³⁴ also found a fairly low fraction (31.2%) of externally mixed
147 soot particles in urban Xi'an City of China through a single-particle soot photometer
148 (SP2). As a result, the polluted air likely accelerated the transformation from
149 bare-like into partly coated or embedded soot particles.³³ It should be noted that
150 bare-like soot particles accounted for 25% at the urban site and 21% at the
151 background site, but embedded soot particles significantly increased from 12% to 39%
152 (Figure 2). These results indicate that the polluted air masses from the Jing-Jin-Ji
153 area and Shandong province (Figure S1) brought a large number of aged soot
154 particles into the downwind background air. In addition, the fraction of embedded
155 soot particles at the mountaintop site is largest at 55% and bare-like soot is lowest at
156 1% among the three sampling sites. *China et al.*³⁵ found that most soot particles from
157 North America became internally mixed at the summit caldera of the Pico Volcano.
158 Therefore, soot particles that are emitted mostly at ground level but transported into
159 the upper atmospheric layers could undergo intense aging processes during their
160 transports. The RH is a critical factor to enhance heterogeneous reactions of acidic
161 gases on particle surface because secondary aerosols can deliquesce at about 60-80%

162 RH and form liquid phases.³⁶ During the sampling period, there was higher RH
163 around 64% in the upper air than the 16-55% on the ground. Indeed, many
164 embedded soot particles on the mountaintop left a water rim around sulfate coating
165 after drying on the substrate (Figure 1b-3), which indicates that secondary aerosol
166 components existed as the liquid phase in the air.³³ We conclude that soot particles
167 likely underwent more complicated ageing processes due to the higher RH of the
168 upper layers than at the polluted ground sites.

169

170 3.2 Quantifying the Shapes of Soot Particles

171 It is widely acknowledged that D_f of soot particles reflects their combustion
172 conditions and aging processes.²³ Compact soot particles often have larger D_f than
173 lacy aggregates.³⁷ Here we calculated the D_f of soot particles collected at the four
174 sampling sites (Figure 3). D_f of bare-like soot particles at different sampling sites was
175 very close, at ~ 1.82 (Figure 3a, 3b, 3d). Bare-like soot particles have the lowest D_f
176 followed by partly coated and embedded soot particles (Figure 3), suggesting that
177 bare-like soot particles were more lacy compared to the partly coated and embedded
178 types. D_f of partly coated soot particles tends to be ~ 1.87 , smaller than the 1.90~2.16
179 of embedded soot particles (Figure 3). Similarly, *China et al.*²⁹ found the same
180 properties (i.e., bare-like < partly coated < embedded) of D_f of the three types of soot
181 particles emitted by wildfires. *Peng et al.*³⁸ also found that the morphology of soot
182 particles was modified heavily during aging processes. For the background soot
183 particles, D_f ranges between 1.83 and 2.16, with a medium of 2.00 (Figure 3d). In
184 contrast, D_f of the urban soot particles has lower values, between 1.83 and 1.90. We
185 multiplied the number fraction of each type of soot by their corresponding D_f to
186 calculate the statistical weighting of D_f . The statistical weighting of D_f values of the
187 urban, mountaintop, and background site are 1.87, 1.90, and 1.97, respectively, which
188 have an average value of 1.91.

189 The convexity (CV), roundness (RN), and D_f of the three types of soot particles
190 at the four sampling sites are listed in Table S1. The CV and RN distributions of the
191 three types of soot particle at the same sampling site (Figure S5) clearly prove their

192 D_f changes (Figure 3). The CV and RN of bare-like soot particles are smallest
193 followed by those of partly coated and embedded soot particles at the four sampling
194 sites. We therefore conclude that larger CV and larger RN represent more
195 compactness for aged soot particles, consistent with the study of *China et al.*²⁹

196 We found that D_f of fresh soot particles retained a consistent value (~ 1.82) at
197 different sampling sites in the polluted air (Figure 3), although fresh soot particles
198 display slightly different D_f due to their different sources and combustion
199 conditions.³⁹ Many researchers obtained D_f of soot particles of the primary sources,
200 such as D_f from biomass burning at 1.67-1.83⁴⁰, D_f from vehicle emissions
201 1.52-1.94³², and D_f from diesel at 1.6-1.9⁴¹. D_f of soot particles becomes larger when
202 soot aggregates are coated by other components during atmospheric processes.⁴²
203 This indicates that soot particles likely collapse during the coating processes. In
204 addition, the wide range of D_f of soot particles in the background air is somewhat
205 expected because they originate from multiple sources, such as industries, residential
206 heating, and transportation,³⁰ and have undergone different atmospheric aging
207 durations and processes.²³ In addition, the D_f of embedded soot particles at
208 1.90~2.16 in this study are much lower than 2.3~2.6 reported by some previous
209 studies.^{21, 23, 43} *Adachi et al.*^{21, 23} used cube-counting method to calculate D_f of soot
210 particles. In most cases the images of fractal aggregates cannot be decomposed at all
211 scales into an integer number of square boxes using this method,⁴⁴ which may lead
212 to a larger D_f . In the study by *Bambha et al.*,⁴³ the smaller monomer diameter may
213 cause lesser structural compaction.⁴⁵ Besides, the coating material condensed at a
214 low humidity often causes no restructuring, whereas the coating liquefies at a higher
215 humidity and restructuring occurs promptly.⁴⁶ In a word, these differences could be
216 attributed to data processing methods, aging environments, and soot aggregate
217 properties.

218 Using the scaling law method, the previous studies reported D_f at 1.52~1.94 for
219 soot particles at road side³² and $D_f > 2$ for soot particles at a remote marine
220 troposphere site.³⁵ Here we systematically studied D_f of ambient soot particles
221 collected at three representative polluted sites. These data are crucial to assess the

222 accurate shape of soot particles in the dry continental air.

223

224 4 Atmospheric Implications

225 Previous studies reported that the fractal dimensions (D_f) of fresh soot particles
226 from vehicles, biomass, diesel, and wildfire emissions are around 1.73³², 1.75⁴⁰,
227 1.75⁴¹, and 1.89²⁹, respectively, which are close to 1.80~1.83 (D_f) of the bare-like
228 soot particles obtained in this study (Figure 3). The reason is that fresh soot particles
229 are generally formed via a cluster-dilute aggregation mechanism in a small-scale
230 burning regime.^{39, 47} These fresh soot particles are hydrophobic before being affected
231 by secondary aerosols and condensable vapors in the atmosphere.⁴⁸ Therefore, fresh
232 soot particles can hardly collapse and their structures remain largely unchanged. In
233 contrast, once soot particles interact with secondary organic and inorganic aerosols
234 and water vapor during long-range transport, they became more compact as
235 evidenced by the larger D_f in mountaintop and background air (Figure 3). TEM
236 images further show that the morphology of soot particles not only became more
237 compact from vehicular emission to background air (Figure 1), but also possibly
238 underwent reconstruction under the influence of water vapor.^{5, 49} Therefore, these
239 hygroscopic secondary aerosols heavily caused morphological changes of soot
240 particles in the atmosphere.

241 In this study, the D_f of soot particles were found to vary from 1.80 to 2.16
242 (Figure 3d) for different mixing structures, which indicate that the mixing structure
243 of soot particles can represent their aging degree.^{31, 33} At present, many studies set D_f
244 as ~1.8 to simulate the complex structure of soot particles and to further calculate
245 their optical properties.^{10, 50-52} However, some studies have suggested that the highly
246 compact soot particles have substantially different optical properties from the lacy
247 ones.^{20, 53, 54} In particular, the mass-specific scattering cross sections (MSC) of soot
248 particles follow the order: $D_f = 2.1 > D_f = 1.78 > D_f = 1.4$.²⁰ Therefore, it is essential
249 to select suitable D_f values to construct accurate optical models of soot particles. Our
250 results show that the statistical weighting of D_f of soot samples collected at the urban,

251 mountaintop, and background site has an average value at 1.91, suggesting that $D_f =$
252 1.91 could be more representative for ambient soot particles in continental polluted
253 air. In particular, $D_f = 1.91$ can well represent soot particles in dry ($RH < 65\%$), winter
254 polluted air in North China. Further studies are required to quantify the D_f of soot
255 particles in different atmospheric environments, such as in humid, troposphere, and
256 strongly photochemical air, because they all can accelerate soot aging in the
257 atmosphere.^{5, 34}

258

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264

265 **Associated Contents**

266 **Supporting Information Available:** specific microscopic analysis, related
267 geometric parameters of soot particles, and some supplementary tables and figures.

268

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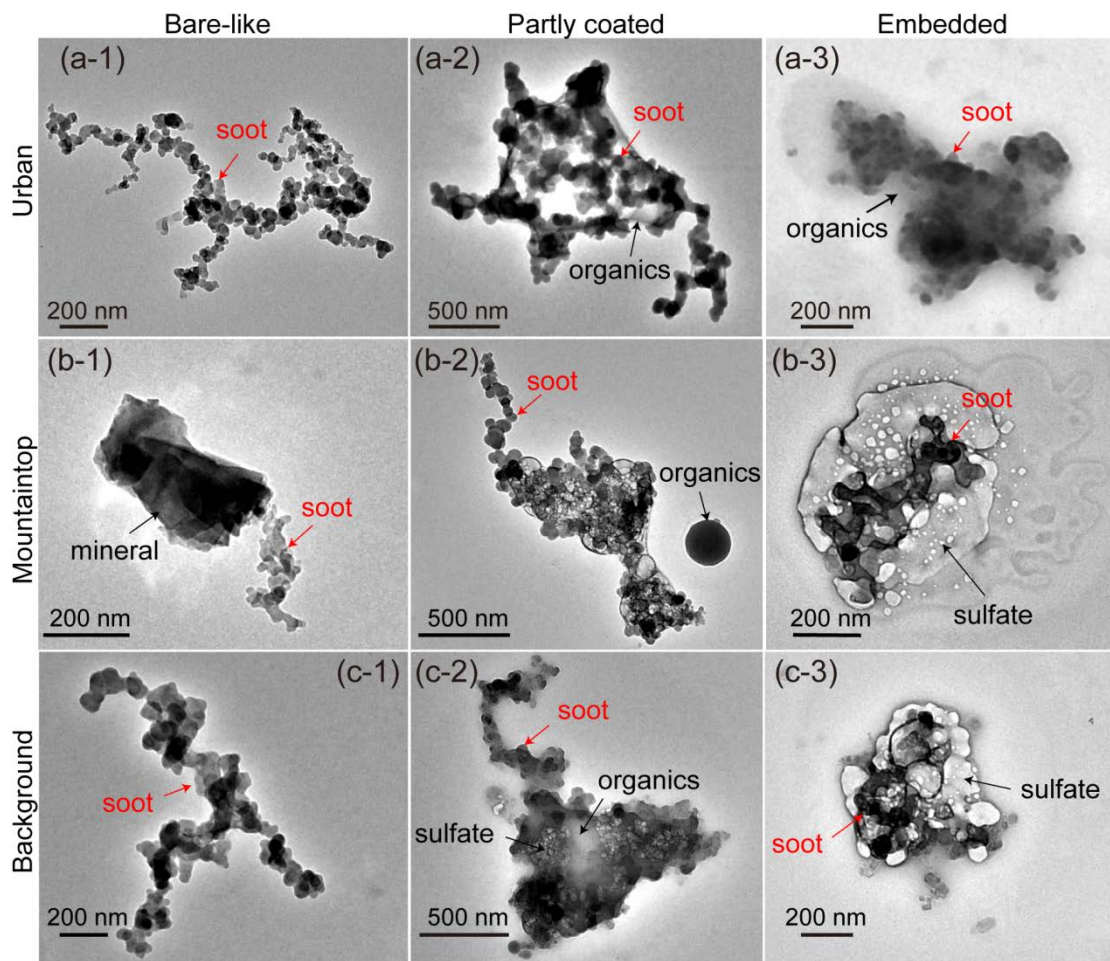
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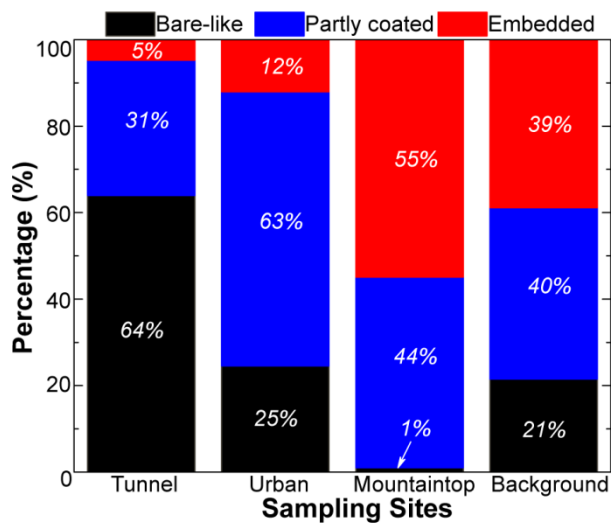
Figure Captions



432

433 **Figure 1.** TEM images of individual soot particles collected at the urban site (a-1/2/3), the
 434 mountaintop site (b-1/2/3), and the background site (c-1/2/3). Soot particles are classified into
 435 three types: bare-like (a/b/c-1), partly coated (a/b/c-2), and embedded (a/b/c-3).

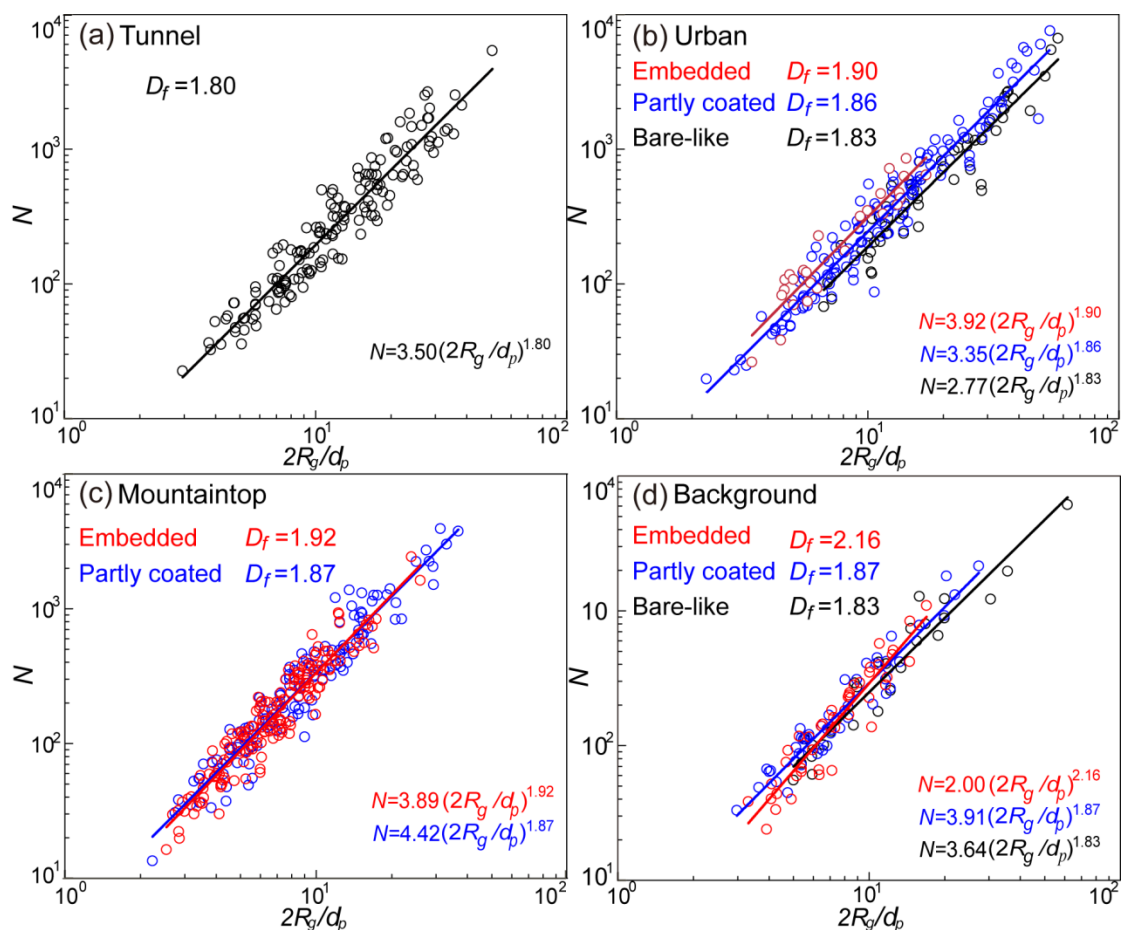
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438 **Figure 2.** The percentages of bare-like, partly coated, and embedded soot particles collected at
 439 four sampling sites. 147, 216, 295, and 121 soot particles were analyzed in the samples collected
 440 at the tunnel, urban, mountaintop, and background sites, respectively.

441



442

443 **Figure 3.** The fractal dimensions of different types of soot collected at the tunnel (a), urban (b),
 444 mountaintop (c), and background (b) site. For each site, the lines and circles represent bare-like
 445 (black), partly coated (blue), and embedded (red) soot particles.

446

447 **For Table of Contents Use Only**

448 **Fractal Dimensions and Mixing Structures of Soot Particles**
449 **during Atmospheric Processing**

450
451 Yuanyuan Wang^{1,2}, Fengshan Liu³, Cenlin He⁴, Lei Bi², Tianhai Cheng⁵, Zhili Wang⁶, Hua
452 Zhang^{7,8}, Xiaoye Zhang⁶, Zongbo Shi⁹, Weijun Li^{*2}

453 ¹Environment Research Institute, Shandong University, Jinan, Shandong 250100, China

454 ²Department of Atmospheric Sciences, School of Earth Sciences, Zhejiang University, Hangzhou,
455 310027, China

456 ³Measurement Science and Standards, National Research Council, Ottawa, Ontario K1A 0R6,
457 Canada

458 ⁴Department of Atmospheric and Oceanic Sciences and Joint Institute for Earth System Science
459 and Engineering, University of California, Los Angeles, CA90095, USA

460 ⁵State Key Laboratory of Remote Sensing Science, Institute of Remote Sensing and Digital Earth,
461 Chinese Academy of Sciences, Beijing, 100101, China

462 ⁶Chinese Academy of Meteorological Sciences, Beijing 100081, China

463 ⁷Collaborative Innovation Center on Forecast and Evaluation of Meteorological Disasters,
464 Nanjing University of Information Science & Technology, Nanjing 210044, China

465 ⁸Laboratory for Climate Studies, National Climate Center, China Meteorological Administration,
466 Beijing 100081, China

467 ⁹School of Geography, Earth and Environmental Sciences, University of Birmingham,
468 Birmingham B15 2TT, U.K

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