

1     **The influence of impactor size cut-off shift caused by hygroscopic growth**  
2             **on particulate matter loading and composition measurements**

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15

16    **Highlights:**

- 17    • Hygroscopic growth leads to a shift in the size of dry particles cut off by impactors used in  
18    measurements of particle mass and composition.
- 19    • We propose a method for evaluating this influence on analysis of aerosol composition,  
20    quantifying its global importance for the first time.
- 21    • Observational comparisons and model validation must account for the large temporal and  
22    spatial variations in this influence.

23

24 **Abstract:**

25 The mass loading and composition of atmospheric particles are important in determining their  
26 climate and health effects, and are typically measured by filter sampling. However, particle  
27 sampling under ambient conditions can lead to a shift in the size cut-off threshold induced by  
28 hygroscopic growth, and the influence of this on measurement of particle loading and  
29 composition has not been adequately quantified. Here, we propose a method to assess this  
30 influence based on  $\kappa$ -Köhler theory. A global perspective is presented based on previously  
31 reported annual climatological values of hygroscopic properties, meteorological parameters  
32 and particle volume size distributions. Measurements at background sites in Europe may be  
33 more greatly influenced by the cut-off shift than those from other continents, with a median  
34 influence of 10-20% on the total mass of sampled particles. However, the influence is generally  
35 much smaller (<7%) at urban sites, and is negligible for dust and particles in the Arctic. Sea-  
36 salt particles experience the largest influence (median value ~50%), resulting from their large  
37 size, high hygroscopicity and the high relative humidity (RH) in marine air-masses. We  
38 estimate a difference of ~30% in this influence of sea-salt particle sampling between relatively  
39 dry (RH=60%) and humid (RH=90%) conditions. Given the variation in the cut-off shift in  
40 different locations and at different times, a consistent consideration of this influence using the  
41 approach we introduce here is critical for observational studies of the long-term and spatial  
42 distribution of particle loading and composition, and crucial for robust validation of aerosol  
43 modules in modelling studies.

44 **Keywords:** aerosol measurement; chemical composition; filter sampling; growth factor.

**Graphical abstract:**



## 45 **1. Introduction**

46 Particulate matter (PM) is currently of major concern around the world due to its effects on  
47 human health (Meister et al., 2012; Pope et al., 2009) and climate change (IPCC, 2013;  
48 Ramanathan & Carmichael, 2008; Seinfeld & Pandis, 2006). The mass loading and  
49 composition of particles are crucial factors in these effects (Putaud et al., 2004; Seinfeld &  
50 Pandis, 2006; Van Dingenen et al., 2004). Filter sampling and subsequent laboratory analysis  
51 is one of the major ways to obtain particle composition and loading (Chow, 1995; Mader &  
52 Pankow, 2001; Schaap et al., 2011). An impactor (or inlet head) is employed at the start of the  
53 airflow to cut off particles larger than a certain size (Aufschnaiter, 2009; Berner & Luerzer,  
54 1980; Marple et al., 1991; Schauer et al., 2003), so that PM<sub>1</sub>, PM<sub>2.5</sub> and PM<sub>10</sub> (particulate matter  
55 with an aerodynamic diameter smaller than 1, 2.5 and 10 µm, respectively) can be collected on  
56 filters for offline analysis. However, ambient particle diameter is strongly influenced by aerosol  
57 liquid water (ALW), a ubiquitous and abundant aerosol constituent (Heintzenberg 1989; EPA  
58 1999), whose amount is governed by particle hygroscopic growth. Global ALW may exceed  
59 dry particle mass by a factor of more than two (Lee & Adams, 2010; Liao & Seinfeld, 2005;  
60 Nguyen et al., 2016). Therefore, particle hygroscopic growth and ALW of ambient particles  
61 can significantly influence the cut-off diameter of dry particles, and hence lead to a  
62 considerable shift in the cut-off that impacts the particle composition and loading measured  
63 using filter-based sampling.

64 The cut-off shift is determined by particle hygroscopicity, of which large variations have been  
65 observed on a global scale (Liu et al., 2011; Nguyen et al., 2016; Pringle et al., 2010; Wu et al.,  
66 2013a, 2013b; Wu et al., 2011). Furthermore, hygroscopic growth is strongly influenced by  
67 relative humidity (RH), which also varies greatly in space and time (Köppen, 1900; Dai, 2006;  
68 Willett et al., 2014). Measurements made in different seasons and locations may suffer the cut-  
69 off shift to different extents. Without sufficient understanding of the cut-off shift, it is difficult  
70 to derive consistent seasonal variations and yearly trends of particle composition or compare  
71 different locations. Moreover, insufficient knowledge of the cut-off shift can hinder effective  
72 model validation. Most modelling results provide the mass loading and chemical composition  
73 of dry particles (e.g., Archer-Nicholls et al., 2015; Mann et al., 2014; Mann et al., 2010; Tsyro,  
74 2005; Zaveri et al., 2008), but filter measurements report results under ambient RH (i.e., wet  
75 particles). The impact of this on model validation is expected to be important over humid

76 regions, e.g. marine and coastal regions where high RH and abundant hygroscopic sea-salt  
77 particles are both present (Chen et al., 2016; Neumann et al., 2016a, 2016b).

78 Despite the important influence of hygroscopic growth and cut-off shift on particle composition  
79 and loading measurements, there is no efficient way to dry the airflow for a high-volume  
80 aerosol sampler. The airflow better not be heated or dried during the sampling, since these  
81 processes change the gas-particle equilibrium and lead to a loss of semi-volatile compounds  
82 (Chow, 1995; Grassian, 2001; Mader & Pankow, 2001; Schaap et al., 2011; Van Dingenen et  
83 al., 2004; Shingler, et al., 2016; ), e.g. nitrate (Chow et al., 2005; Hering & Cass, 1999; Schaap  
84 et al., 2004; Slanina et al., 2001; Vecchi et al., 2009; Chen et al., 2018) and secondary organic  
85 aerosols (Iinuma et al., 2010; Mader & Pankow, 2000). As recommended by EPA and  
86 WMO/GAW (EPA, 1999; WMO/GAW, 2016), the inlet should sample the particles under  
87 ambient conditions. It is worth noting that some experiments dry airflow in inlet manifolds due  
88 to different scientific focuses, this would lead to evaporative losses of semi-volatile compounds  
89 and Shingler et al. (2016) estimated the losses based on thermo-kinetic simulations.  
90 Consequently, the influence due to cut-off shift is inherent in measurements of particle  
91 composition, and requires full investigation and careful assessment to ensure consistent  
92 comparisons between measurements.

93 In this study, we propose a method to assess the influence of this cut-off shift on particle  
94 composition and loading measured using filter-based sampling. A global perspective on the  
95 influence is presented first, based on  $\kappa$ -Köhler theory (which describes the hygroscopic growth  
96 of particles, Köhler, 1936; Petters & Kreidenweis, 2007) together with previously reported  
97 annual climatological values of hygroscopic properties, meteorological parameters (RH and  
98 temperature) and particle volume size distributions. This work enables us to quantify the  
99 influence of cut-off shift on analysis of particulate matter loading and composition, provides a  
100 firm foundation for more consistent studies of the long-term characteristics and spatial  
101 distributions, and brings more confidence to model validation.

## 102 **2. Method and Data**

103 To explore the influence of cut-off shift on filter-based particle sampling driven by hygroscopic  
104 growth, we calculate the aerodynamic diameter of ambient particles based on the hygroscopic  
105 diameter growth factor (GF). The GFs are derived from  $\kappa$ -Köhler theory (Petters &  
106 Kreidenweis, 2007), with consideration of particle composition and size as well as

107 meteorological conditions (Eq. 1). In this study, particles are assumed to be homogeneously  
 108 internally mixed with the same chemical constitution throughout each size mode, and the  
 109 influence of the cut-off shift on total particulate matter loading is assessed. The influence on  
 110 each particle component can also be assessed, although there is uncertainty resulting from the  
 111 assumption about the particle mixing state (discussed in the section 3.3). More precise  
 112 assessment of the influence of cut-off shift on particle components can be derived using the  
 113 approach we propose here if detailed observations of particle mixing state and size-segregated  
 114 composition are available. The collection efficiency, which depends on aerodynamic design of  
 115 the impactor, air flow rate and pressure drop (Hillamo & Kauppinen, 1991; Marple et al., 1991;  
 116 Wang & John, 1988), influences the sampled particles. This will influence the cut-off shift,  
 117 which is generally less than 10% and is discussed in detail in section 3.4. In this study, we  
 118 assume that the influence of sampling collection efficiency is corrected during chemical post-  
 119 processing, so that particles larger than the nominal cut-off thresholds are totally blocked by  
 120 the impactor and are not collected on the filter.

121 The  $\kappa$ -Köhler theory proposes a single parameter ( $\kappa$ ) to describe the hygroscopic properties of  
 122 particles, representing the dependence of hygroscopicity on chemical composition. The  
 123 original Köhler equation (Köhler, 1936) can be transformed into the following Eq. (1), which  
 124 describes the relationship between RH,  $\kappa$  and dry particle diameter (Liu et al., 2014; Petters &  
 125 Kreidenweis, 2007):

$$RH/100 = \frac{GF^3 - 1}{GF^3 - 1 + \kappa} \exp\left(\frac{4\sigma_{s/a}M_w}{R(T + 273.15)\rho_w D_{dry}GF}\right) \quad (1)$$

126 where  $RH$  has units of [%],  $GF$  is the diameter of an ambient particle divided by its dry diameter  
 127 ( $D_{dry}$ , [m]),  $T$  is the temperature [°C],  $\sigma_{s/a}$  is the surface tension of the solution–air interface,  $R$   
 128 is the universal gas constant,  $M_w$  is the water molar weight,  $\rho_w$  is the water density, and  $\kappa$  is the  
 129 hygroscopicity parameter. More details of the  $\kappa$  value and density of each components from  
 130 previous studies are given in Table S1, please see also the references (Asa-Awuku et al., 2010;  
 131 Bond & Bergstrom, 2006; Cross et al., 2007; Fountoukis & Nenes, 2007; Liu et al., 2014;  
 132 McMeeking et al., 2010; Petters & Kreidenweis, 2007; Pringle et al., 2010).

133 The  $\kappa$  value of an internally mixed particle can be derived from its composition using the  
 134 Zdanovskii-Stokes-Robinson (ZSR) mixing rule (Stokes & Robinson, 1966; Zdanovskii, 1948),  
 135 which weights the  $\kappa$  of each component according to its respective volume fraction. A previous

136 modelling study (Pringle et al., 2010) provided the global distribution of  $\kappa$  for fine (0.1-1  $\mu\text{m}$ )  
137 particles, showing a fair agreement with most measurement-derived  $\kappa$ . The deviations between  
138 the modelled and observed  $\kappa$  values were less than 0.05 at 10 out of the 14 locations (Pringle  
139 et al., 2010). We adopt their statistical  $\kappa$  value for each continent in this study (Tables 1 and 2  
140 in Pringle et al., 2010), and assume that the coarse particles (1-10  $\mu\text{m}$ ) have the same  $\kappa$  as fine  
141 particles in the absence of size-resolved  $\kappa$  studies. The measured chemical properties or size-  
142 resolved  $\kappa$  of particles is applied where available (Marine, Beijing and Melpitz cases described  
143 below). O'Dowd et al. (2004) reported that coarse marine particles are very close to pure sea-  
144 salt with more than 90% sodium chloride, whereas fine marine particles consist of more organic  
145 components. Therefore,  $\kappa$  of sodium chloride is adopted for coarse marine particles in this study;  
146 while the  $\kappa$  of fine marine particles follows Pringle et al. (2010). Liu et al. (2014) investigated  
147 the size-resolved  $\kappa$  based on chemical composition measurements at a background station on  
148 the North China Plain (NCP) near Beijing. The HOPE-Melpitz campaign (part of the HD(CP)2  
149 Observational Prototype Experiment, Macke et al., 2017) provided size-segregated ( $\text{PM}_{10}$  and  
150  $\text{PM}_{10}$ ) chemical ions and composition from filter measurements with a high-volume DIGITEL  
151 DHA-80 sampler (Walter Riemer Messtechnik, Germany), more details of sampling and  
152 laboratory analysis are given elsewhere (Spindler et al., 2013; Spindler et al., 2004). The  
153 ISORROPIA II thermodynamic model (Fountoukis & Nenes, 2007) is used to derive the  
154 inorganic components (e.g. ammonium nitrate and ammonium sulfate, please see details in  
155 Table S1 and Fountoukis & Nenes, 2007) from ions measured by filter sampling at Melpitz.  
156 We then follow the approach proposed by Liu et al. (2014) to derive  $\kappa$  for fine and coarse  
157 modes based on their chemical composition. Homogeneous mixing is assumed for all chemical  
158 components in fine and coarse modes in the absence of size-resolved particle composition  
159 information. Therefore,  $\kappa$  is different between fine and coarse modes, but is consistent within  
160 each mode.

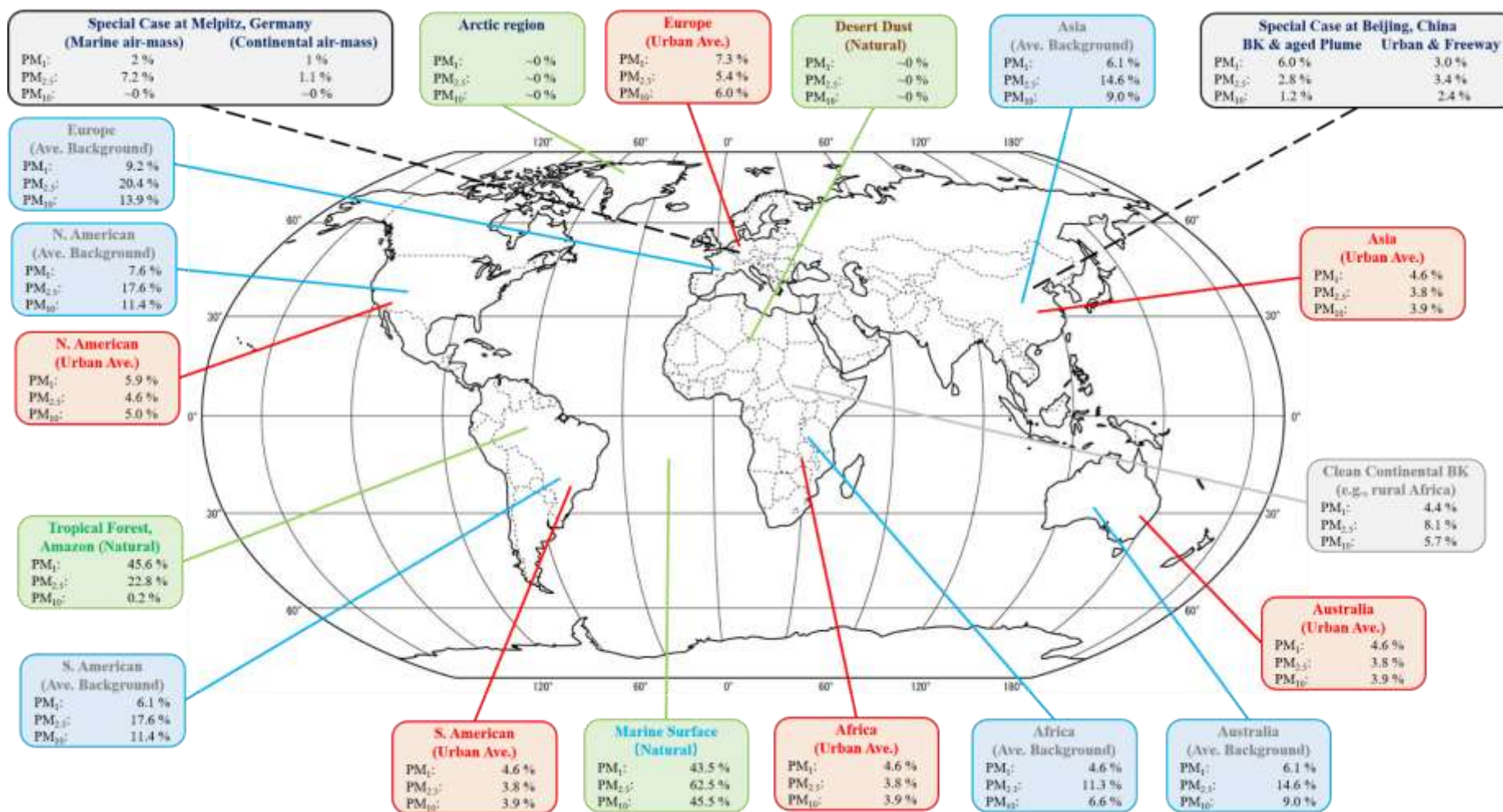
161 Dry particle volume size distributions (PVSD) can be described by a multimodal distribution,  
162 namely a lognormal distribution in the fine/accumulation (0.1-1  $\mu\text{m}$ ) and coarse ( $> 1\mu\text{m}$ ) modes  
163 (Whitby, 1978). In this study, we follow the typical PVSDs in different air-mass/aerosol-  
164 type/site categories in Whitby (1978), which are based on a compilation of global in-situ  
165 measurements. For a specific case at Melpitz, we derive the PVSD from measurements using  
166 an Aerodynamic Particle Sizer (APS Model 3320, TSI, Inc., Shoreview, MN USA) and a Twin  
167 Differential Mobility Particle Sizer (TDMPS, Birmili et al., 1999, TROPOS, Leipzig,  
168 Germany). Both APS and TDMPS were operated under dry conditions, and measured particle

169 number size distribution in the coarse and fine modes, respectively. PVSD is then calculated  
170 assuming a spherical shape. The mobility diameter is converted to an aerodynamic diameter  
171 following Chen, et al. (2016) and Heintzenberg et al. (1998). It is worth noting that fine  
172 particles also include the Aitken mode ( $< 0.1 \mu\text{m}$ ), which is not considered in this study since  
173 it is negligible for the mass/volume loading and too small to be cut off.

174 To estimate the hygroscopic growth and cut-off shift, we use the annual climatological global  
175 distribution of surface RH reported by (Dai, 2006) for each continent and for marine regions.  
176 This is based on an analysis of long-term (1976-2002) global measurements from over 15,000  
177 weather stations and ships. A recent study (Willett et al., 2014) based on 1976-2005 global  
178 measurements reported annual climatological surface temperatures (T) and RH, and shows a  
179 good agreement with Dai (2006). The reported surface temperature is adopted for each  
180 continent, and a fixed surface temperature of  $26.85^\circ\text{C}$  (300 K) is assumed over marine regions  
181 due to absence of data. Although this does not provide a realistic T variation, GF is insensitive  
182 to T in the range  $-30^\circ\text{C}$  to  $+30^\circ\text{C}$ , and less than 5% difference is observed for a  $1 \mu\text{m}$  sea-salt  
183 particle when  $\text{RH}=90\%$ , according to  $\kappa$ -Köhler theory (Fig. S1). For specific cases in Beijing  
184 (Liu et al., 2014) and Melpitz (September 2013), the average RH and T observed during the  
185 corresponding sampling periods were used.

### 186 **3. Results and Discussion**

187 The cut-off shift due to aerosol hygroscopic growth is ubiquitous in particle composition  
188 measurements made with filter-based sampling. Fig. 1 and Table S2 summarize the influences  
189 of cut-off shift on particle sampling ( $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ ) for different site/aerosol-type  
190 categories following the classification in Whitby (1978), including marine surface (sea-salt),  
191 desert dust, tropical forest, urban-average, average background, clean continental background,  
192 background and aged urban plume, as well as urban and freeway. These assessments are based  
193 on annual climatological datasets, but it is worth noting that the cut-off shift can vary  
194 substantially during different measurement periods. The resulting influence for a specific  
195 observation can be assessed using the corresponding measurement data via this proposed  
196 approach, as shown later for specific measurement campaigns in Beijing and Melpitz.



**Figure 1.** The influence of cut-off shift on particle mass loading. Green box (natural source aerosols), red box (urban-average over continents), blue box (average background over continents), grey box (clean continental background, taking Africa for example), and black box (two specific cases: Beijing & Melpitz). Annual climatological values are shown in this figure, more detailed parameters and uncertainties are given in Table S2 and S3.

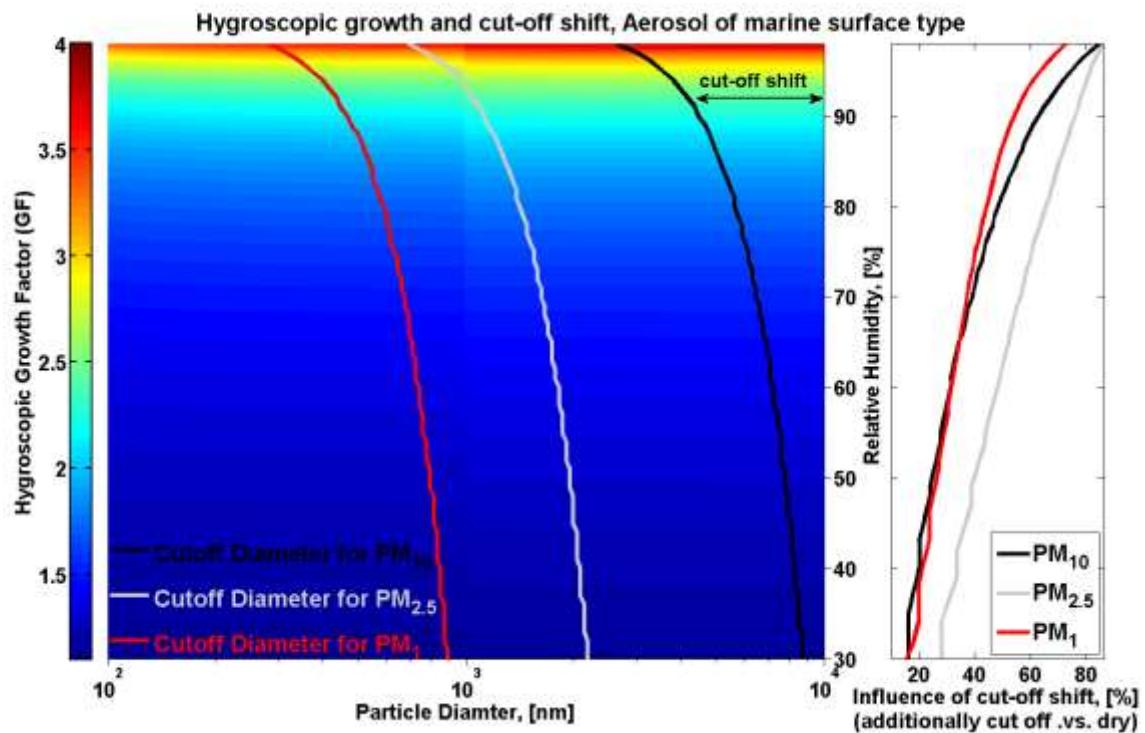


### 198 3.1 Influences of the cut-off shift on particle measurements

199 Of particles from natural sources, sea-salt experiences the most significant influence of cut-off  
200 shift, due to its high hygroscopicity (Twomey, 1954; Petters & Kreidenweis, 2007), high  
201 volume/mass fraction at large sizes (Fig. S2), and high RH over marine surfaces (Dai, 2006).  
202 As shown in Fig. 2, the influence on sampled sea-salt particles in PM<sub>2.5</sub> can exceed 80% when  
203 RH is higher than 90%. Over marine surfaces, as much as ~60% (median value) of sea-salt is  
204 estimated to be additionally cut off by a PM<sub>2.5</sub> impactor/inlet head compared with dry  
205 conditions, and up to ~45% by a PM<sub>1</sub>/PM<sub>10</sub> impactor (Table S2). In contrast, there is almost no  
206 influence on hydrophobic dust particles (Pringle et al., 2010) and Arctic particles. Arctic  
207 particles rarely reach sizes larger than 0.5 μm (Heintzenberg & Leck, 2012; Heintzenberg et  
208 al., 2006; Korhonen et al., 2008), far below the cut off threshold. The influence on PM<sub>10</sub>  
209 sampling is negligible for biogenic particles over tropical regions, due to their low  
210 hygroscopicity ( $\kappa \sim 0.1$ , (Pringle et al., 2010) and very limited volume/mass fraction around  
211 10 μm (Huffman et al., 2012). However, the influence on tropical forest particles sampled by  
212 PM<sub>1</sub> impactor can reach up to ~45%, and more than 20% by PM<sub>2.5</sub> impactor. This is because  
213 there is a large contribution from biogenic particles with sizes around 1 μm and 2.5 μm to the  
214 total volume of PM<sub>1</sub> and PM<sub>2.5</sub>, respectively (Huffman et al., 2012), see Fig. S2. Generally, the  
215 influence of cut-off shift on filter-based sampling is negligible for dust, but should be  
216 comprehensively considered for aerosols over marine and coastal regions, as well as tropical  
217 forest. Greater care should be taken for a size-segregated particle composition analysis, where  
218 the cut-off shift not only influences the total PM mass, but may also shift particles from smaller  
219 size bins to larger bins.

220 Over regions influenced by anthropogenic activities, our estimated ALW is consistent with  
221 previously reported values (Nguyen et al., 2016) all over the world. The highest contribution  
222 of ALW (in percentage) to continental ambient total particle mass concentrations is found to  
223 be in Europe. ALW contributes 22-56% (median 40%) of ambient total particle mass  
224 concentrations in an urban-average air-mass over Europe (Table S2), but less than 30% over  
225 other continents. This is because urban-average particles generally have a relatively low  
226 hygroscopicity, with median  $\kappa$  values less than 0.3 on continents other than Europe, where a  
227 higher median  $\kappa$  value of 0.36 (Pringle et al., 2010) and a relatively humid atmosphere (average  
228 RH  $\sim$  75%, Dai, 2006) are both present. In an extreme case with high RH and highly  
229 hygroscopic particles present simultaneously, the contribution of ALW to the ambient total

230 particle mass concentrations may reach up to ~95% in a European average background air-  
 231 mass, much higher than in an urban-average air-mass. In general, average background particles  
 232 are larger than urban-average particles (Whitby, 1978), resulting in a reduction of the Kelvin  
 233 effect and therefore an enhancement in water vapour condensation and cut-off shift.  
 234 Correspondingly, the median value of the resulting influences on PM<sub>1</sub>/PM<sub>2.5</sub>/PM<sub>10</sub> sampling  
 235 over European cities (urban-average sites) can be 5.5-7.5%, and may reach 50-60% (median  
 236 value ~10-20%) for average background sites. Over other continents, the influence for urban  
 237 sites is almost negligible (<5%), and for average background sites is about 10-17% for PM<sub>2.5</sub>  
 238 and less than 10% for PM<sub>1</sub> and PM<sub>10</sub>. Taking rural regions in Africa as an example of clean  
 239 continental background, the influence is ~5% for PM<sub>1</sub> and PM<sub>10</sub> measurements and ~8% for  
 240 PM<sub>2.5</sub> measurements. Reported measurements over the NCP/Beijing region in summer 2007  
 241 are adopted in this study as examples of ‘background and aged urban plume’ and ‘urban and  
 242 freeway’ (Liu et al., 2014), and the influences are found to be negligible (<6%) for PM<sub>1</sub>, PM<sub>2.5</sub>,  
 243 and PM<sub>10</sub> here.



**Figure 2.** The hygroscopic diameter growth factor (GF, left panel) of marine surface aerosol, including fine mode (considerable organic components) and coarse mode (nearly pure sea salt), under different RH condition. The cut-off point of dry particles under different RH condition is indicated by the colourful lines (red: PM<sub>1</sub>; grey: PM<sub>2.5</sub>; black: PM<sub>10</sub>). The influences of cut-off shift on particle volume concentrations are given in the right panel.

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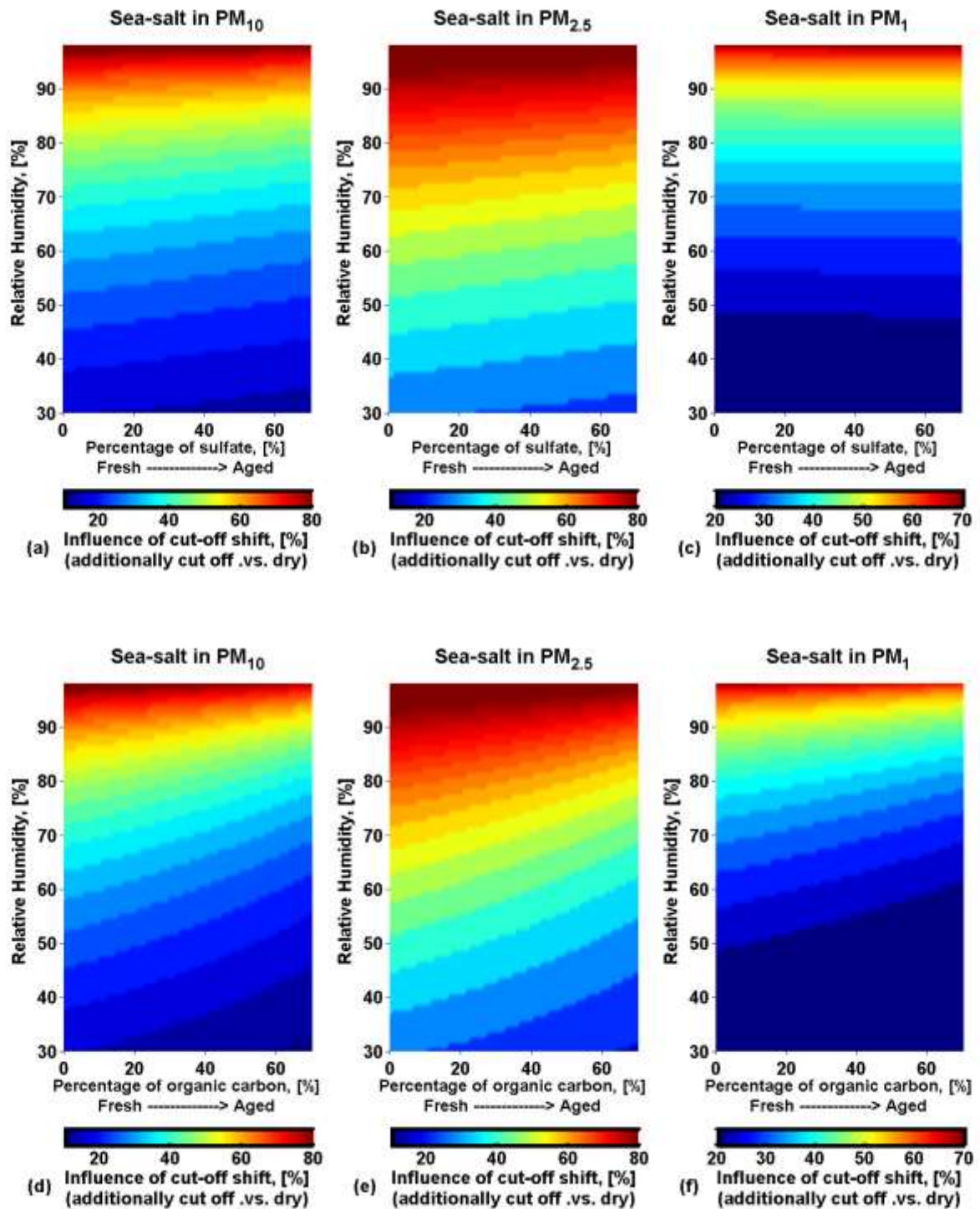
### 245 **3.2 Variability of the cut-off shift**

246 The influence of the cut-off shift varies greatly with time as well as location. Understanding  
247 this variability is critical for study of the long-term and spatial distribution of particle  
248 composition and for model validation. Observational data from the HOPE-Melpitz campaign  
249 are used to illustrate this variability. Generally, the influence is small (<10%) at Melpitz, a  
250 central European background site, where the coarse particle volume concentration is very  
251 limited during this campaign (Fig. S3). However, the influence rapidly increased from ~1% to  
252 ~7% for PM<sub>2.5</sub> measurements (Fig. 1) when a marine air-mass brought hygroscopic coarse  
253 particles to Melpitz (Fig. S3 and Fig. S4). Super-micron (1-2.5 μm) sea-salt particles  
254 experienced substantial hygroscopic growth, and were strongly influenced by the cut-off shift.  
255 This issue is of great importance for measurements at marine and coastal locations, where sea-  
256 salt is an important contributor to total particulate matter. As shown in Fig. 2, there is a 30%  
257 difference in the sampled sea-salt mass between RH=60% and RH=90% conditions due to the  
258 cut-off shift alone.

### 259 **3.3 Impact of mixing state and aging process on cut-off shift**

260 The mixing state of particles can impact the cut-off shift. For instance, aging processes can mix  
261 sea-salt with sulfate and organic carbon (OC) internally via heterogeneous reaction and  
262 condensation, moderating the hygroscopic growth of sea-salt particle and influencing the cut-  
263 off shift during sampling. Taking this aging process of sea-salt as an example, we conduct a  
264 simplified theoretical investigation of the impact of mixing state on the cut-off shift. We make  
265 the simplified assumptions that sea-salt is homogeneously internally mixed with more  
266 hygroscopic sulfate (Na<sub>2</sub>SO<sub>4</sub> with κ=0.76, Fountoukis & Nenes, 2007; Liu et al., 2014) and  
267 less hygroscopic water soluble organic carbon (OC with κ=0.3, Asa-Awuku et al., 2011; Asa-  
268 Awuku et al., 2010). A consistent percentage of sulfate and OC is assumed throughout all  
269 particle sizes, and this percentage is used to indicate the extent of aging. We use the PVSD for  
270 marine aerosol shown in Table S2, and assume that it remains unchanged during the aging  
271 process. The Zdanovskii-Stokes-Robinson (ZSR) mixing rule is applied to calculate the κ  
272 values of aged sea-salt-sulfate and sea-salt-OC particles, respectively. As shown in Fig. 3, the  
273 influence of cut-off shift on the measured sea-salt mass loading decreases as aging increases.  
274 This reduction in the influence is larger for PM<sub>10</sub>/PM<sub>2.5</sub> than PM<sub>1</sub> for sea-salt, and can decrease

275 by ~10% for sea-salt-sulfate and by 15-20% for sea-salt-OC particle once the aging level  
 276 reaches 70%. The influence of cut-off shift reduces more slowly as RH falls. The influence of



**Figure 3.** Impact of mixing state or aging process on the cut-off shift. (a, b, c) internally mixed between sea-salt and sulfate; (d, e, f) internally mixed between sea-salt and water soluble organic carbon. The percentage of sulfate or organic carbon indicates the aging level of sea-salt particles.

278

279 cut-off shift for sea-salt-OC particles is more sensitive to the aging level than sea-salt-sulfate  
280 particles, due to the different hygroscopicity of sulfate and OC. Conversely, mixing with sea-  
281 salt enhances the cut-off shift in measurements of sulfate and OC. For example, with RH=90%,  
282 the influence of cut-off shift on sulfate measurements increases from 60% to 70% in PM<sub>10</sub> (70%  
283 to 80% in PM<sub>2.5</sub>) when the percentage of sea-salt increases from 30% to 80% (Fig. 3a and 3b).  
284 Similarly, with RH=90%, the influence of cut-off shift on OC measurements increases from  
285 55% to 70% in PM<sub>10</sub> (65% to 80% in PM<sub>2.5</sub>) when the percentage of sea-salt increases from  
286 30% to 80% (Fig. 3d and 3e). Detailed observations of mixing state are therefore needed in  
287 future field measurements to refine assessment of the influence of cut-off shift on each particle  
288 component.

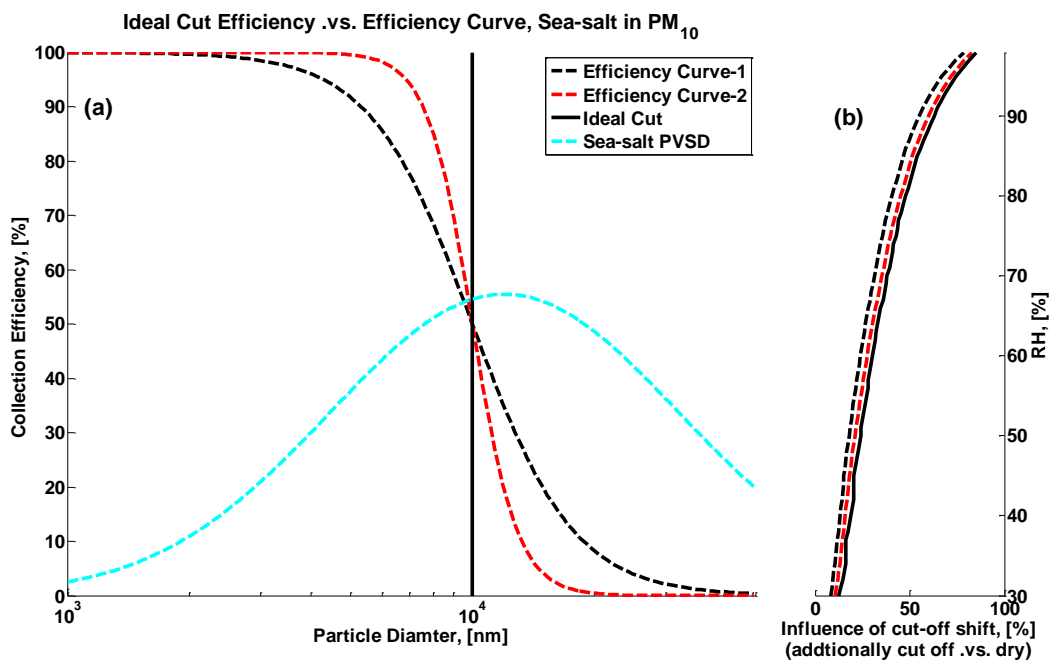
### 289 **3.4 Impact of collection efficiency on cut-off shift**

290 The collection efficiency, depending on aerodynamic design of the impactor, air flow rate and  
291 pressure drop influences the particle sampling. A ~2% over-sampling of sea-salt due to the  
292 shallow collection efficiency curve (Fig. 4) is found, and this may decrease the influence of  
293 cut-off shift. Here, we take the sampling of sea-salt particles with two PM<sub>10</sub> impactors as  
294 examples to illustrate the impact of collection efficiency on cut-off shift. The PVSD of sea-salt  
295 (Whitby, 1978) and collection efficiency curves of demonstrated impactors, TEOM PM<sub>10</sub> low  
296 volume sampler (EPA, 1991) and impactor (Marple et al., 1991), are shown in Fig. 4. Taking  
297 the collection efficiency curve into account, the influence of cut-off shift decreases slightly.  
298 Generally, this impact of collection efficiency on cut-off shift increases slowly as RH increases;  
299 however, as shown in Fig. 4, it remains less than 10% for the demonstrated shallow efficiency  
300 curve (EPA, 1991) and less than 5% for the steep curve (Marple et al., 1991). This impact of  
301 collection efficiency on cut-off shift is expected to be smaller on the PM<sub>1</sub>/PM<sub>2.5</sub> sampling of  
302 sea-salt or sampling other types of aerosol. Since a single peak close to the cut-off threshold is  
303 essential for a sensible impact of efficiency curve on particle sampling or cut-off shift. Dust  
304 has a similar single peak PVSD to sea-salt, but it is hydrophobic and therefore there is no cut-  
305 off shift due to hygroscopic growth.

### 306 **3.5 Impact of particle volume size distribution on the cut-off shift**

307 To investigate the impact of PVSD on the cut-off shift, we conduct sensitivity studies by  
308 varying the geometric mean diameter by volume (D<sub>GV</sub>), standard deviation ( $\sigma$ ) and volume

309 concentration ( $V$ ) of PVSD by  $\pm 10\%$ , as shown in Table S3. Two types of aerosol are chosen  
 310 as examples. The first is marine surface aerosol, representing highly hygroscopic aerosol  
 311 predominantly in the coarse mode; and the second is averaged urban aerosol in Asia,  
 312 representing less hygroscopic aerosol with clearly defined fine and coarse modes in PVSD.  
 313 Negligible impact ( $< 2\%$ ) on the cut-off shift is observed for the second aerosol type due to its  
 314 limited hygroscopicity. No impact from  $V$  can be observed for either aerosol type, since  
 315 varying  $V$  does not change the shape of PVSD. Small differences (1-3%) in the influence of  
 316 cut-off shift can be observed due to the variation of DGV in both aerosol types, although this  
 317 effect could be larger in aerosols with a DGV lying close to the cut-off threshold of the impactor.  
 318 However, a large impact can be observed for the highly hygroscopic marine aerosol with a  $\pm 10\%$   
 319 variation of  $\sigma$ . Although the differences for  $PM_{2.5}$  and  $PM_{10}$  marine aerosol are generally  
 320 smaller than 5%, an 8-14% difference in the influence of cut-off shift can be observed for  $PM_{10}$   
 321 marine aerosol when  $RH=60\%$  (and 5-11% when  $RH=90\%$ ). The particle size distribution is  
 322 important for assessing the cut-off shift, and therefore it is very helpful if this can be measured  
 323 during field campaigns.



**Figure 4.** Impact of collection efficiency on cut-off shift during sea-salt sampling. Left panel (a) shows the PVSD (light blue dashed line) of sea-salt, an ideal efficiency curve (black solid line) and two collection efficiency curves of demonstrated impactors. The dashed black line indicates the TEOM  $PM_{10}$  low volume sampler (shallow curve, EPA, 1991); and the dashed red line indicates a steep-curve impactor (Marple et al., 1991). Right panel (b) shows the corresponding influences of

cut-off shift with consideration of two collection efficiency curves (dashed lines) and ideal cut (black solid line).

#### 324 **4. Conclusions**

325 This study highlights the importance of the shift in the size of dry particles cut off by impactors,  
326 resulting from hygroscopic growth. A method for assessing the influence of this cut-off shift  
327 on analysis of particulate matter loading and composition is proposed, and an algorithm in  
328 MATLAB language is provided in the supplementary materials. We present the first global  
329 perspective of this influence.

330 Large temporal and spatial variation of the influence is found. On average, particles over  
331 marine surfaces are found to experience the largest influence of cut-off shift, where as much as  
332 ~60% of particle mass is estimated to be additionally cut off by a  $PM_{2.5}$  impactor compared  
333 with sampling under dry condition, and up to ~45% by a  $PM_1/PM_{10}$  impactor. In contrast, the  
334 cut-off shift has no influence for dust and particles in the Arctic region. The influence for  
335 biogenic particles in tropical forest is negligible for  $PM_{10}$  measurements, but considerable (23-  
336 46%) for  $PM_{2.5}$  and  $PM_1$  measurements. The influence is generally negligible (less than 7%)  
337 over urban areas, but need to be considered (about 10-20%) over continental background areas.  
338 This influence needs to be assessed for each measurement period individually even at the same  
339 location, since it is highly dependent on the ambient conditions. We estimate a difference of  
340 ~30% in this influence of sea-salt particle sampling between relatively dry (RH=60%) and  
341 humid (RH=90%) conditions. Our sensitivity studies show that detailed measurements of  
342 particle size distribution and mixing state are helpful for refining assessments of this influence.

343 This work proposes a method to quantify the influence of cut-off shift on analysis of particulate  
344 matter loading and composition, and to investigate the variability of this influence from a  
345 temporal and spatial perspective. It is critical for observational studies focusing on long-term  
346 and spatial distribution of particle loading and composition, and crucial for robust validation  
347 of aerosol modules in modelling studies.

348

349 **Supplementary Materials**

350 Figure S1-S4;

351 Table S1-S3;

352 The MATLAB script in the '.m' files.

353

354

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