



## Supplement of

## The real part of the refractive indices and effective densities for chemically segregated ambient aerosols in Guangzhou by a single particle aerosol mass spectrometer

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## 16 **1** The meteorological conditions over the study

<ul> <li>including solar radiation, temperature (Temp), relative humidity (RH), wind di</li> <li>(WD) and wind speed (WS), and air quality parameters (i.e., NO<sub>x</sub>, SO<sub>2</sub>, O<sub>3</sub>, Pl</li> <li>shown in Fig. S1. These parameters were provided by Guangdong Enviror</li> <li>Monitoring Center (http://www.gdemc.gov.cn/). Ambient Temp, RH, and WS c</li> <li>study varied between 10.8–31 °C, 20.7–89.8%, and 0.2–3.9 m/s, with average</li> <li>of 21.2 °C, 59.9%, and 1.1 m/s, respectively. The concentration peaks for NO</li> <li>and PM<sub>1</sub> were often observed during the nighttime, due to the accumula</li> <li>pollutants under unfavorable meteorological conditions with lower WS and</li> <li>boundary layer depth.</li> <li><b>2 The mass spectral patterns for the single particle types</b></li> <li>The mass spectral characteristics are displayed in Fig. S4, and a brief desc</li> <li>is provided as follows.</li> <li>OC group: Mass spectra for OC particles mainly contain the OC markers, a</li> </ul>	ological parameters,
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31 OC group: Mass spectra for OC particles mainly contain the OC markers, a	
	OC markers, and also

32 some other OC peaks such as  $50[C_4H_2]^+$ ,  $51[C_4H_3]^+$ ,  $55[C_4H_7]^+$  and  $63[C_5H_3]^+$ . Besides,

33 a large peak at m/z 39 is also observed in mass spectra of OC, which might be explained

34 by coagulation between OC and 39[K]<sup>+</sup> or condensation of organic species onto

35 biomass seed [Moffet et al., 2008]. Particle mass spectra in HMOC type show the

36 presence of m/z 50, 51, 63, 77, 91, 115, and 128 [Silva and Prather, 2000; Sodeman et

*al.*, 2005]. By including the ion peak from sulfate/nitrate, OC particles were subdivised
into OC-S, OC-SN, and HMOC.

39 EC group: Mass spectra of LC-EC type are dominated by the distinct carbon ion 40 clusters ranged from m/z -120 to m/z 180, with minor ion intensities from other species. 41 SC-EC type is associated with short carbon clusters ions peaks ( $C_n^{+/-}$ , n < 6), generally 42 internally mixed with intense sulfate ion peak. Differently, NaK-EC type shows the 43 carbon ion clusters mainly in the negative mass spectra, combined with dominant peaks 44 from 23[Na]<sup>+</sup> and 39[K]<sup>+</sup> in the positive ones.

ECOC group: ECOC particles have typical carbon ion clusters  $(12[C]^{+/-},$ 45  $24[C_2]^{+/-}, \ldots, 12n[C_n]^{+/-}$  with  $36[C_3]^+$  as dominant fragments, together with OC 46 markers (e.g.,  $27[C_2H_3]^+$ ,  $29[C_2H_5]^+$ ,  $37[C_3H]^+$ , and  $43[C_2H_3O]^+$ ). K-rich particles 47 48 contain potassium (39[K]<sup>+</sup>), sulfate (-97[HSO<sub>4</sub>]<sup>-</sup>), nitrate (-46[NO<sub>2</sub>]<sup>-</sup> and -62[NO<sub>3</sub>]<sup>-</sup>), 49 and carbonaceous species (e.g.,  $12[C]^+$ ,  $27[C_2H_3]^+$ ,  $29[C_2H_5]^+$ ,  $36[C_3]^+$ ,  $37[C_3H]^+$ , 50  $43[C_2H_3O]^+$ ,  $-26[CN]^-$ ,  $-42[CNO]^-$ ) as major components, similar to those reported in 51 other studies [Moffet et al., 2008; Silva et al., 1999]. The association of sulfate and/or 52 nitrate separated the ECOC particles into ECOC-S, ECOC-SN, K-S, K-SN, and K-N 53 [*Zhang et al.*, 2015].

Metal rich group: Peaks corresponding to **23**[Na]<sup>+</sup>, 39[K]<sup>+</sup>, 46[Na<sub>2</sub>]<sup>+</sup>, 81/83[Na<sub>2</sub>Cl]<sup>+</sup>, nitrate and chloride (-35[Cl]<sup>-</sup> and -37[Cl]<sup>-</sup>) are present in mass spectra of Na-rich, indicating transport and evolution of sea salt particles [*Gaston et al.*, 2011; *Gaston et al.*, 2013]. Na-K type is characterized by dominant peaks from 39[K]<sup>+</sup>,

58	relatively less intense peak from $23[Na]^+$ , nitrate and silicate (-76[SiO <sub>3</sub> ] <sup>-</sup> ). They are
59	probably from dust and/or industry sources [Moffet et al., 2008]. Fe-rich type is
60	identified by strong peaks from iron at m/z 54, 56 and 57, according to their isotopic
61	components. Similarly, Pb-rich type is identified by strong peaks m/z 206-208, and Cu-
62	rich is characterized by the presence of isotopic peaks at m/z 63 and 65. Fe-Cu-Pb
63	represents the internally mixed Fe, Cu, Pb in the individual particles.

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Fig. S1. Temporal profiles (in 1 h resolution) of PM<sub>1</sub>, visibility, and black carbon (BC),
gaseous pollutants (SO<sub>2</sub>, NO<sub>x</sub>, and O<sub>3</sub>) and meteorological parameters, during the 13<sup>th</sup>
October–26<sup>th</sup> November 2012 in Guangzhou.



Fig. S2. (a) Upper limit of light scattering signals and theoretical PSCS for PSL as a function of size (0.15, 0.3, 0.5, 0.72, 1, and 2  $\mu$ m) and (b) their relationship. For PSL, n = 1.59 and  $\rho_{eff} = \rho_p = 1.054$  g cm<sup>-3</sup>.



Fig. S3. Mass spectra for the observed single particle types in the atmosphere of Guangzhouduring fall of 2012.



80 Fig. S4. Measured and best fit theoretical PSCS for OC-SN particle type.

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Fig. S5. Measured and best fit theoretical PSCS for various particle types observedin the present study.

## 85 **REFERENCES**

- 86 Gaston, C. J., H. Furutani, S. A. Guazzotti, K. R. Coffee, T. S. Bates, P. K. Quinn, L. I.
- 87 Aluwihare, B. G. Mitchell, and K. A. Prather (2011), Unique ocean-derived particles
- serve as a proxy for changes in ocean chemistry, J. Geophys. Res.-Atmos., 116(D18310),
- 89 1-13, doi:10.1029/2010jd015289.
- 90 Gaston, C. J., P. K. Quinn, T. S. Bates, J. B. Gilman, D. M. Bon, W. C. Kuster, and K. A.
- 91 Prather (2013), The impact of shipping, agricultural, and urban emissions on single
- 92 particle chemistry observed aboard the R/V Atlantis during CalNex, J. Geophys. Res.-

93 Atmos., 118(10), 5003-5017, doi:10.1002/Jgrd.50427.

94 Moffet, R. C., B. de Foy, L. T. Molina, M. J. Molina, and K. A. Prather (2008), Measurement

95 of ambient aerosols in northern Mexico City by single particle mass spectrometry,

- 96 *Atmos. Chem. Phys.*, 8(16), 4499-4516.
- 97 Silva, P. J., D. Y. Liu, C. A. Noble, and K. A. Prather (1999), Size and chemical
- 98 characterization of individual particles resulting from biomass burning of local Southern
  99 California species, *Environ. Sci. Technol.*, *33*(18), 3068-3076.
- Silva, P. J., and K. A. Prather (2000), Interpretation of mass spectra from organic compounds
  in aerosol time-of-flight mass spectrometry, *Anal. Chem.*, 72(15), 3553-3562.
- 102 Sodeman, D. A., S. M. Toner, and K. A. Prather (2005), Determination of single particle
- 103 mass spectral signatures from light-duty vehicle emissions, *Environ. Sci. Technol.*,

*39*(12), 4569-4580.

- Song, X. H., P. K. Hopke, D. P. Fergenson, and K. A. Prather (1999), Classification of single
  particles analyzed by ATOFMS using an artificial neural network, ART-2A, *Anal. Chem.*, 71(4), 860-865.
- 108 Zhang, G. H., B. X. Han, X. H. Bi, S. H. Dai, W. Huang, D. H. Chen, X. M. Wang, G. Y.
- 109 Sheng, J. M. Fu, and Z. Zhou (2015), Characteristics of individual particles in the
- 110 atmosphere of Guangzhou by single particle mass spectrometry, *Atmos. Res.*, 153(0),
- 111 286-295, doi:10.1016/j.atmosres.2014.08.016.