

## **Supporting Information:**

### **An alternative method for evaluating the contribution of light absorption from brown carbon with high-time resolution**

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## Single Particle Aerosol Mass Spectrometer

Particles are introduced into SPAMS through a critical orifice, then focused and accelerated to specific velocities that would be determined by two continuous diode Nd:YAG laser beams (532 nm) installed downstream in sizing region. Individual particle is then desorped/ionized by a pulsed laser (266 nm) triggered exactly based on the specific velocity, and the corresponding positive and negative fragments are also recorded. The velocities are then converted to  $d_{va}$  using a calibration curve, created from the measured velocities of polystyrene latex spheres (Nanosphere Size Standards, Duke Scientific Corp., Palo Alto) with defined sizes.

The collected dataset including particles sizes and mass spectra were imported into MATLAB (The Mathworks Inc.) and analyzed with YAADA ([www.yaada.org](http://www.yaada.org)). We focused on particles with vacuum aerodynamic diameter ( $d_{va}$ ) ranging from 0.1 to 1.6  $\mu\text{m}$ , which were more effectively detected. The SPAMS collected 472931 individual particles (234012 and 238919 respectively for ambient and heated particles) with both positive and negative ion mass spectra. An adaptive resonance theory based neural network algorithm (ART-2a) is applied to cluster individual particles into separate groups based on the presence and intensities of ion peaks in single particle mass spectrum (Song et al., 1999), with a vigilance factor of 0.5, learning rate of 0.05, and 20 iterations. Several major particle types with distinct chemical patterns were obtained, representing ~97% of population of both the ambient and heated particles. The majority of single particle types were similar to those observed in Guangzhou (Zhang et al., 2015). Internally mixed OC and sulfate type discussed in the present

study contained both OC markers (e.g.,  $27[\text{C}_2\text{H}_3]^+$ ,  $29[\text{C}_2\text{H}_5]^+$ ,  $37[\text{C}_3\text{H}]^+$ , and  $43[\text{C}_2\text{H}_3\text{O}]^+$ ) and sulfate signals ( $-97[\text{HSO}_4]^-$ ) in the mass spectra.

### **Monitor for Aerosols & Gases in Ambient Air (MARGA)**

Water-soluble gases and aerosols can be measured simultaneously and continuously with MARGA ([www.metrohm.com](http://www.metrohm.com)). The analytical part of the instrument consists of two ion chromatograph systems for cation and anion measurements, respectively. The detection system is continuously calibrated by the internal standard of LiBr.

### **Organic/Elemental Carbon Measurement and estimation of Secondary organic aerosols**

The concentrations of organic carbon (OC) and elemental carbon (EC) were measured by Semi-Continuous OC-EC analyzer (Model-4, Sunset laboratory Inc.), which has been a successful development for on-line OC and EC measurement. The analysis methods and techniques utilized by the Sunset OCEC analyzer have been well documented elsewhere (Arhami et al., 2005; Zheng et al., 2014). Briefly, the air was drawn through two quartz-fiber filters packed together, and ambient  $\text{PM}_{2.5}$  was collected onto a sampling spot, and was subsequently analyzed by the thermal–optical method. Carbon fraction thermally evolved during each heating step and was converted to  $\text{CO}_2$  and detected by the Non-Dispersive Infra-Red (NDIR) sensor, which is calibrated by injection of methane gas as an internal standard at the end of

each analysis. Optical charring correction by light transmittance over the analysis provide the concentration of optical EC, in addition to the thermal–optical analyzed OC/EC. Optical OC was then defined as thermal–optical analyzed TC minus optical EC.

In order to provide further insight into the formation of SOA, secondary organic carbon (SOC) was estimated according to the minimum ratio method (Turpin and Huntzicker, 1995; Castro et al., 1999), which is described in the following equation:

$$\text{SOC} = \text{OC}_{\text{total}} - \text{EC} \times (\text{OC}/\text{EC})_{\text{min}}$$

Where  $\text{OC}_{\text{total}}$  refers to the total measured ambient OC, and  $(\text{OC}/\text{EC})_{\text{min}}$  is the corresponding minimum OC/EC ratio. The lower limit values (regarding the lowest 10% values as outliers) of the bar plot in Fig. S5 are applied in the calculation. The estimated SOC based on thermal and optical methods is also compared in Fig. S5. Highly correlation and similar diurnal variation of them were obtained, and thus only the SOC calculated by optical method was used in the discussion.

### **The correction factor for multiple scattering in AE33 measurements**

The optical attenuation (ATN) for aerosol samples collected on AE33 filter can be parameterized as a function of filter loading (B) by an empirical relationship:

$$\text{ATN} = \frac{1}{k}(1 - e^{-\sigma k B})$$

where  $\sigma$  represents the mass attenuation cross section of BC, and k refers to the loading effect parameter or multiple scattering. The correction factor for the loading effect is depends on chemo physical properties of the measured aerosol and affected

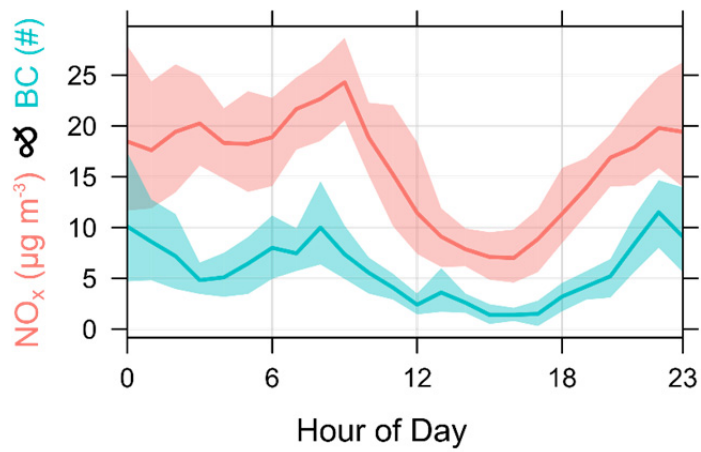
strongly the accuracy of the measured data, and therefore it needs to be evaluated in ambient measurements. The AE33 were operated with two filter spots, collecting the same aerosol with different rate. Therefore, different loading can be obtained, assuming the same value of the loading parameter k:

$$e^{-\sigma k B_1} = 1 - k \cdot \text{ATN}_1$$

$$e^{-\sigma k B_2} = 1 - k \cdot \text{ATN}_2$$

The optical attenuations  $\text{ATN}_1$  and  $\text{ATN}_2$  are simultaneously measured. The filter loading values for the two sample spots B1 and B2 are proportional to the airflows ( $F_1$  and  $F_2$ ) through the two sample spots, respectively. The parameter k is then determined by numerically solving the following equation:

$$\frac{F_1}{F_2} = \frac{\ln(1 - k \cdot \text{ATN}_1)}{\ln(1 - k \cdot \text{ATN}_2)}$$



1

2

3 Fig. S1. The diurnal variations of the mean hourly detected number of  
 4 BC-containing particles and NO<sub>x</sub>. The BC-containing particles were detected with  
 5 obvious carbon clusters (C<sub>n</sub><sup>+/-</sup>, n = 1,2,3,...) (Zhang et al., 2017).

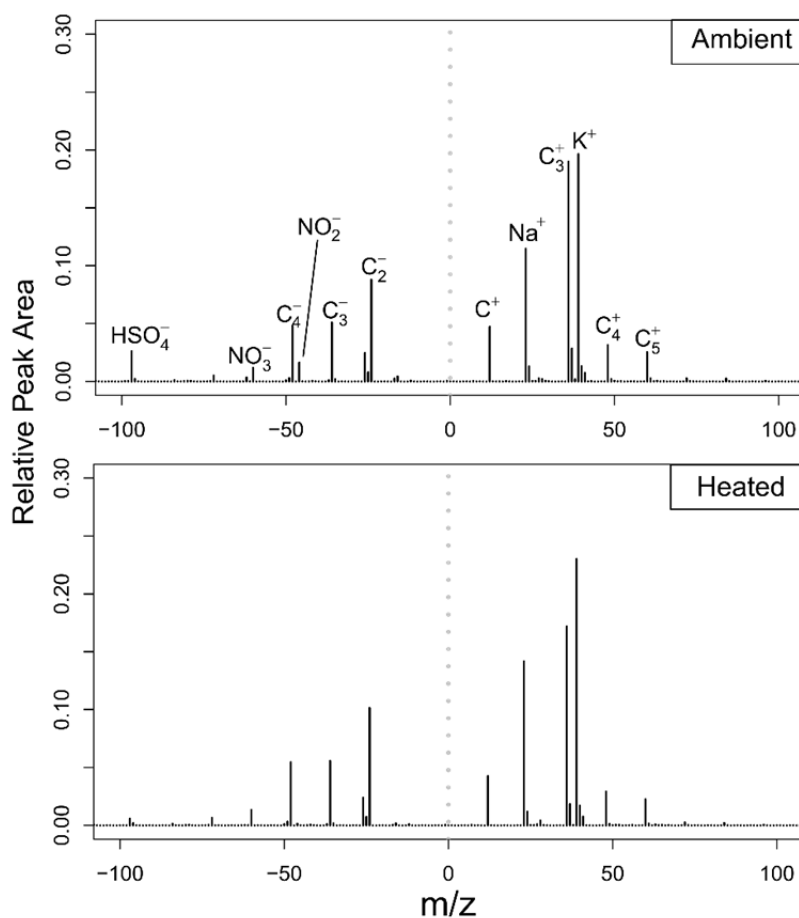


Fig. S2. Comparison of the average mass spectrum of the ambient and heated BC-containing particles around 200 nm (150-250 nm). It can be seen that the ambient BC-containing particles contained relatively small fraction of sulfate ( $m/z$  -97[ $\text{HSO}_4^-$ ]) and nitrate ( $-46[\text{NO}_2^-]$  and  $-62[\text{NO}_3^-]$ ). For the heated BC-containing particles, the associated sulfate and nitrate were further evaporated to a negligible fraction. The intense potassium ( $39\text{K}^+$ ) peak is attributed to the highly sensitive of potassium to the desorption laser used in the SPAMS (Gross et al., 2000). Some organics ( $m/z$  -26[ $\text{CN}^-$ ] and  $m/z$  37[ $\text{C}_3\text{H}^+$ ]) were retained after heated.

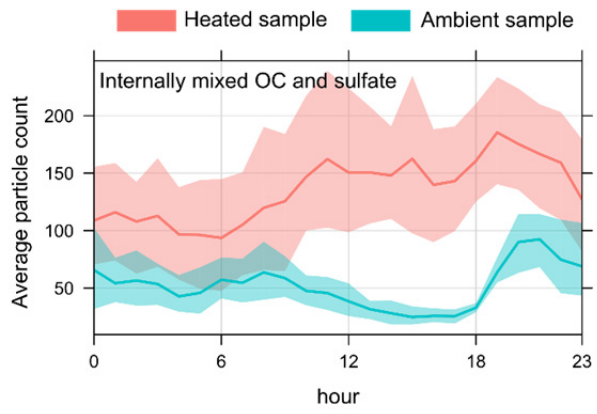


Fig. S3. Comparison of average diurnal variations of internally mixed OC and sulfate particles.



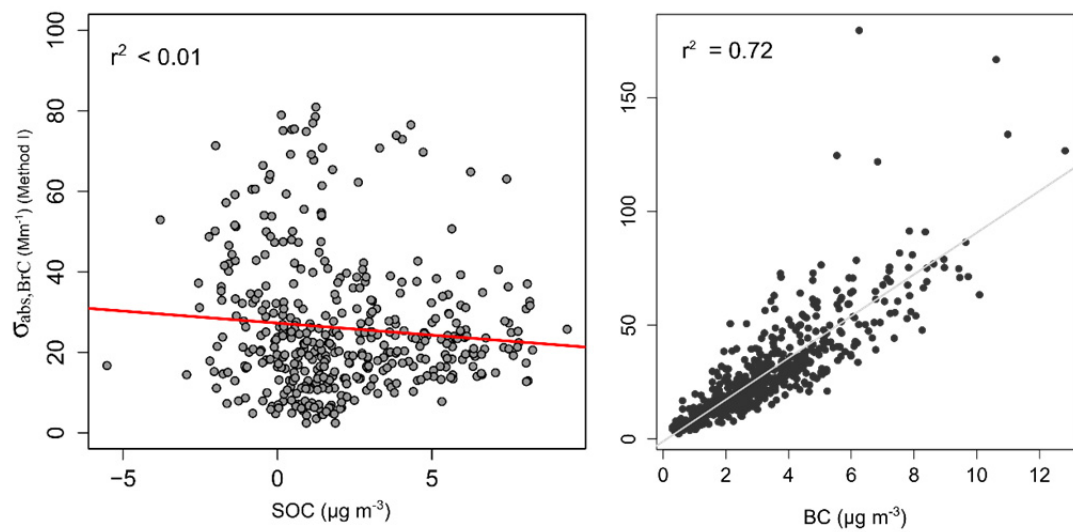


Fig. S4. Correlation analysis between  $\sigma_{\text{abs, BrC}}$  by the developed method and (left) SOC and (right) BC.

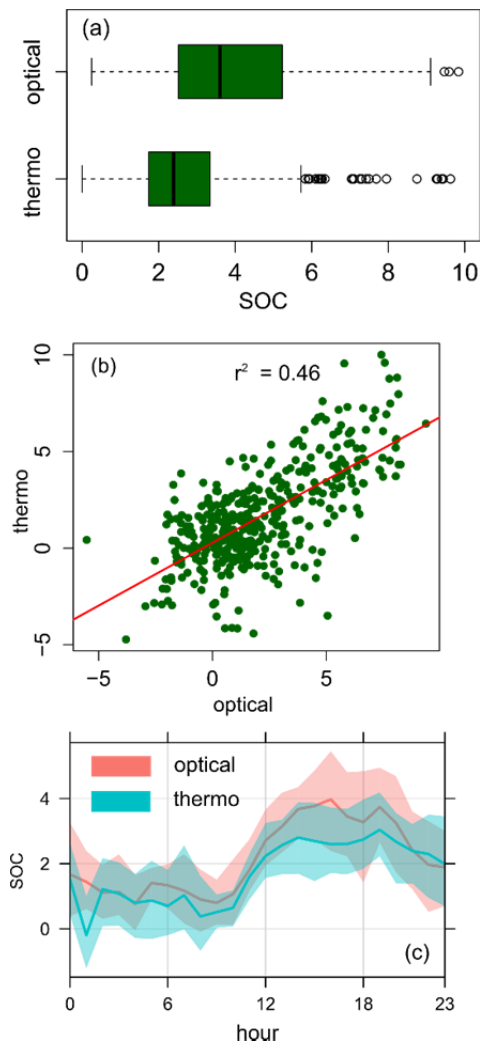


Fig. S5. (a) bar plot and (b) correlation analysis of the OC/EC by thermo and optical methods, and (c) comparison between average diurnal variations of SOC by thermo and optical methods.

## References

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