

1 **Measurements of non-volatile aerosols with a VTDMA and**  
2 **their correlations with carbonaceous aerosols in**  
3 **Guangzhou, China**

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17

## 1 Abstract


2 Simultaneous measurements of aerosols of varying volatilities and carbonaceous matters were  
3 conducted at a suburban site in Guangzhou, China in February and March 2014 using a  
4 volatility tandem differential mobility analyzer (VTDMA) and an organic carbon/ elemental  
5 carbon (OC/EC) analyzer. Low-volatility (LV) particles, with a volatility shrinkage factor (*VSF*)  
6 at 300 °C exceeding 0.9, contributed to 5% of number concentrations of 40 nm particles and  
7 11–15% of 80–300 nm particles. They were non-volatile materials externally mixed with the  
8 volatile ones and therefore did not evaporate significantly at 300 °C. Non-volatile materials  
9 mixed internally with the volatile ones are referred to as the medium volatility (MV,  $0.4 < VSF$   
10  $< 0.9$ ) and high volatility (HV,  $VSF < 0.4$ ) particles. These MV and HV particles contributed to  
11 57–71% of number concentrations for particles between 40 nm and 300 nm in size. The average  
12 EC and OC concentrations measured by the OC/EC analyzer were  $3.4 \pm 3.0 \mu\text{g m}^{-3}$  and  $9.0 \pm$   
13  $6.0 \mu\text{g m}^{-3}$ , respectively. Non-volatile OC evaporating at 475 °C or above, together with EC,  
14 contributed to 67% of the total carbon mass. The diurnal variations in the volume fraction of  
15 the volatile materials, HV, MV and LV residuals were less than 15% for most of the particles  
16 except for the 40 nm ones, although a daily maximum and a daily minimum were still observed.  
17 Back trajectory analysis also suggests that over 90% of the air masses influencing the sampling  
18 site were well-aged as they were transported at low altitudes (below 1500 m) for over 40 h  
19 before arrival. Further comparison with the diurnal variations in the mass fractions of EC and  
20 non-volatile OC in  $\text{PM}_{2.5}$  suggests that the non-volatile residuals may be related to both EC and  
21 non-volatile OC in the afternoon, during which the concentration of aged organics increased.  
22 The closure analysis of the total mass of LV and MV residuals and the mass of EC or the sum  
23 of EC and non-volatile OC also suggests that non-volatile OC, in addition to EC, was one of  
24 the components of the non-volatile residuals measured by the VTDMA in this study.

25


# 1 1 Introduction

2 Carbonaceous aerosols comprising organic carbon (OC) and elemental carbon (EC) or black  
3 carbon (BC) are one of the major light absorption constituents and are abundant in particulate  
4 matter (PM) (Rosen et al., 1978; Hansen et al., 1984; Japar et al., 1986; Chow et al., 1993;  
5 Horvath, 1993; Liousse et al., 1993; Fuller et al., 1999; Putaud et al., 2010; Tao et al., 2014;  
6 Zhang et al., 2015). In China, the worsening of visibility degradation associated with PM is of  
7 increasing concern in recent years. In particular, numerous studies on air pollution were carried  
8 out in different cities in China including the Pearl River Delta (PRD) region which is a fast-  
9 developing economic zone (Cheng et al., 2006; Wu et al., 2007; Andreae et al., 2008; Chan and  
10 Yao, 2008; Gnauk et al., 2008; Tan et al., 2013a). In 2007, the mass concentrations of EC and  
11 OC measured at an urban Guangzhou (GZ) site were reported to be from 6.8 to 9.4  $\mu\text{g m}^{-3}$  and  
12 from 13.4 to 22.5  $\mu\text{g m}^{-3}$  respectively (Yu et al., 2010).

13 Soot particles are often characterized in terms of EC and BC, depending on whether they are  
14 measured thermally or optically (Penner and Novakov, 1996; Lavanchy et al., 1999; Cheng et  
15 al., 2011 and references therein). Their optical properties are distinct when they are freshly  
16 produced (Novakov et al., 2003). After aging processes such as cloud processing, ~~reaction with~~  
17 ~~other species~~ and coagulation, their structure, shape, size, mixing state and thus optical  
18 properties change (Horvath, 1993; Liousse et al., 1993; Ghazi and Olfert, 2012). EC is typically  
19 measured by thermal method such as the OC/EC analyzer (Chow et al., 2007), ~~BC are~~ optically  
20 measured using instruments such as aethalometer (Hansen et al., 1984), multi-angle absorption  
21 photometer (Petzold and Schönlinner, 2004) and particle soot absorption photometer (Virkkula  
22 et al., 2005). However, it is not possible to retrieve the mixing state of soot particles ~~from above~~  
23 techniques. To determine the mixing state of soot particles, single particle soot photometer  
24 (Stephens et al., 2003), soot particle aerosol mass spectrometer (Onasch et al., 2012) and  
25 Volatility Tandem Differential Mobility Analyzer (VTDMA) (Philippin et al., 2004) have been  
26 used.

27 Ambient aerosols have varying volatility properties based on their chemical compositions.  
28 VTDMA was first duced by Rader and McMurry (1986) to study the behavior of aerosols  
29 upon thermal **treatment**. ~~Philippin et al. (2004) later~~ developed a VTDMA which is capable of  
30 evaporating volatile materials in aerosols at temperatures up to 300 °C. Non-volatile ~~materials~~  
31 at 300 °C, such as EC, non-volatile organics and sea salt, can internally mix with (or be coated  
32 with) volatile materials. Note that the terms “volatile” and “non-volatile” are ~~defined at the~~

1 ~~heating temperature of 300 °C in the VTDMA.~~ They are different from the volatilities defined  
2 under ambient conditions (Donahue et al., 2009; Murphy et al., 2014) or in other measurement  
3 techniques (Twomey, 1968; Pinnick et al., 1987; Huffman et al., 2009). The composition of  
4 these non-volatile residuals can vary spatially and temporally ~~in VTDMA measurements.~~  
5 Previous studies have demonstrated good agreement between the mass of black carbon and the  
6 mass of particles ~~with small volatile fractions, which~~ experienced size reductions of 5 to 10%  
7 upon heating at 300 °C in the VTDMA. Various studies have also used an VTDMA to estimate  
8 the mixing states of soot particles. **Particles with small volatile fractions are often assumed to**  
9 **be soot particles externally mixed with particles with volatile materials at 300 °C. Particles with**  
10 **larger volatile fractions, which experienced size reductions of more than 10% upon heating at**  
11 **300 °C in the VTDMA, were assumed to represent soot** particles internally mixed (coated) with  
12 the volatile materials (Philippin et al., 2004; Cheng et al., 2006; Frey et al., 2008; Wehner et al.,  
13 2009; Rose et al., 2011; Levy et al., 2014; Zhang et al., 2016).

14 Organics also contribute to light absorption by atmospheric particles (Bond, 2001; Kirchstetter  
15 et al., 2004; Chen and Bond, 2010). Laboratory studies have shown that organic aerosols may  
16 form low volatility oligomers after aging for a long time (e.g. Kalberer et al., 2004). Huffman  
17 et al. (2009) showed that highly oxygenated, aged organic aerosols exhibited similar or lower  
18 volatility than the primary organic aerosols or the less oxygenated **ones**. Recently, Häkkinen et  
19 al. (2012) found that the mass fraction remaining (MFR) of non-BC residuals, i.e. the difference  
20 between the residual mass derived from a volatility differential mobility particle sizer at 280 °C  
21 and black carbon mass derived from  aethalometer, is positively correlated with the mass  
22 fraction of organics measured by an **AMS**.

23 In this study, simultaneous measurements of aerosols volatility and carbonaceous matter were  
24 made at a suburban site in Guangzhou, China during wintertime in February and March 2014  
25 using a VTDMA and a semi-continuous OC/EC analyzer, respectively. Volatility  
26 measurements were made for ambient aerosols ranging from 40 nm to 300 nm in diameter.  
27 Residuals remaining after heating at 300 °C in the VTDMA are referred to as non-volatile in  
28 this study. We report the average values, time series and diurnal variations in the number and  
29 volume fractions of the volatile and non-volatile materials, as well as the OC and EC  
30 concentrations. We examine the relationships of the non-volatile materials upon heating at  
31 300 °C to EC and to the non-volatile OC, based on analyses of the diurnal patterns and mass  
32 closures of the OC/EC and VTDMA data. Finally, we discuss the influence of air mass origins

1 on the volatility of the sampled aerosols and concentrations of OC and EC based on back  
2 trajectory analysis.

3

## 4 **2 Methodology**

### 5 **2.1 Experimental**

#### 6 **2.1.1 Measurement details**

7 The campaign ~~was taken~~ place at the China Meteorological Administration (CMA)  
8 Atmospheric Watch Network (CAWNET) Station in Panyu, Guangzhou, China in summer  
9 from July to September 2013 and winter from 6 February to 21 March 2014, ~~which~~ is operated  
10 by the Institute of Tropical and Marine Meteorology (ITMM) of the CMA. The Panyu station  
11 is located at the center of the PRD region and on the top of Dazhengang Mountain (23°00' N,  
12 113°21' E) with an altitude of about 150 m (Figure S1 in Supplemental Information) (Tan et al.,  
13 2013a). It is about 120 m above the city ~~average elevation~~ and is surrounded by residential  
14 neighborhoods with no significant industrial pollution sources nearby. Measurements of  
15 particle number size distributions, volatility, mass concentrations of EC and OC were made in  
16 winter from 6 Feb to 21 Mar 2014. Some of the measurements were not made continuously due  
17 to maintenance work and hence only ~~both~~ VTDMA and OC/EC measurements  
18 were analyzed.

#### 19 **2.1.2 VTDMA measurements**

20 We used a custom-made VTDMA based on a Hygroscopic TDMA system developed in ITMM  
21 (Tan et al., 2013b), with the humidifier between the two DMAs replaced by a heated tube which  
22 ~~effect~~ evaporation of volatile materials. In our VTDMA system shown in Figure 1, ambient  
23 aerosols sampled by a PM<sub>2.5</sub> inlet ~~first~~ passed through a dryer at relative humidity below 20%.  
24 The dry aerosols ~~then passed~~ through a neutralizer and entered the first differential mobility  
25 analyzer (DMA<sub>1</sub>) (Stream 1) to produce mono-disperse aerosols of diameter between 40 nm  
26 and 300 nm,  $D_0$ . The mono-disperse aerosols went either ~~path~~ (a) or (b) in Fig. 1 after leaving  
27 ~~DMA~~<sub>1</sub>. In path (a), they (Stream 2) were directed to a condensation particle counter (CPC, TSI  
28 Model 3772) to obtain particle counts,  $N_{D_0}$ . The particle number size distribution of the ambient  
29 aerosols,  $dN/d\log D_p$ , was also measured by varying the DMA<sub>1</sub> voltage (SMPS scan).  
30 Afterwards, the mono-disperse aerosols were directed via path (b) to a heated tube for volatility


1 measurement (V-Mode) sequentially at 25 °C, 100 °C and 300 °C. The heating tube was a 1/2",  
2 80 cm long stainless steel tube with an inner diameter of 8 mm. With a sample flow rate of 1 L  
3 min<sup>-1</sup>, the resulting residence time in the heated section of the VTDMA was 2.4 s. The estimated  
4 aerosol velocity on the center line was 0.33 m s<sup>-1</sup>. Compared to the residence time of 0.3 s to 1  
5 s in other VTDMA systems (e.g. Brooks et al., 2002; Philippin et al., 2004; Villani et al., 2007),  
6 the residence time in our VTDMA is assumed to be long enough for the volatile materials to be  
7 effectively vaporized. After leaving the heating tube, the flow entered a heat exchanger  
8 measuring 30 cm in length to ensure sufficient cooling before entering DMA<sub>2</sub>.



9 Upon heating ~~at 100 °C and above~~, volatile components of particles such as sulfate, nitrate and  
10 volatile organics ~~would~~ vaporize at different temperatures depending on their volatilities. A  
11 volatility shrinkage factor, *VSF*, is defined as the ratio of particle diameter after heating at  
12 temperature *T*, *D<sub>p,T</sub>*, to ~~that~~ before heating, *D<sub>0</sub>*, ~~to indicate~~ the size reduction of the ambient  
13 particles (Eq. (1)). The value of *VSF* is always smaller than or equal to one, depending on the  
14 amount of volatile materials vaporized at the heating temperature *T*.



$$15 \quad VSF(T) = \frac{D_{p,T}}{D_0} \quad (1)$$

16 The *VSF* is ~~also~~ used to divide the particles into three groups, namely ~~the~~ low volatility (LV),  
17 medium volatility (MV) and high volatility (HV) particles. In this study, we focus on the  
18 measurements made at 300 °C. The *VSF* ranges for LV, MV and HV particles upon heating at  
19 300 °C are ~~above~~ 0.9, between 0.4 and 0.9 and below 0.4, respectively (Fig. 2) (Wehner et al.,  
20 2004; Wehner et al., 2009). **The LV particles are assumed to represent EC particles externally**  
21 **mixed with the volatile materials, while MV and HV particles are assumed to represent EC**  
22 **particles internally mixed with volatile materials. While the volatile materials in the MV and**  
23 **HV particles are referred to as VM, those exist as external mixtures with the LV, MV and HV**  
24 **particles are referred to as completely vaporized (CV) particles.** The CV particles evaporate  
25 completely without ing behind any residuals at 300 °C. Excluding particle diffusional and  
26 thermophoretic losses, the evaporation of VM and CV does not change the number  
27 concentrations of LV, MV and HV particles.

28 The ~~new~~ size distribution,  $dN'/d\log D_p$  of the remaining particles (hereafter the residuals) were  
29 measured by DMA<sub>2</sub> and CPC ~~before they were heated at another temperature~~ (Fig. 2b). Overall  
30 it took around one and a half to two hours to complete a cycle of measurements which consisted  
31 of SMPS scans and V-Mode measurements at 25 °C, 100 °C and 300 °C. At each temperature,  
32 the sampling time for six selected diameters from DMA<sub>1</sub> (40 nm, 80 nm, 110 nm, 150 nm, 200

1 nm and 300 nm) took about half an hour and SMPS scans were made in-between. Hereafter,  
2 notations with the superscript prime refer to the LV, MV or HV residuals measured by DMA<sub>2</sub>  
3 and CPC after heating, while the corresponding ones without the prime refer to the LV, MV or  
4 HV residuals in ambient aerosols prior to heating.

### 5 **2.1.3 OC/EC measurements**

6 A semi-continuous Sunset OC/EC Analyzer (Model 4) was used to measure PM<sub>2.5</sub> mass  
7 concentrations of organic carbon and elemental carbon,  $m_{OC}$  and  $m_{EC}$  respectively, on an hourly  
8 basis (Turpin et al., 1990; Birch and Cary, 1996; Wu et al., 2012). The OC/EC Analyzer adopts  
9 the ACE-Asia protocol (a NIOSH-derived protocol), where OC evaporates at four set  
10 temperatures of 310 °C, 475 °C, 615 °C and 870 °C with pure helium (He) as the carrier gas, and  
11 EC is combusted at temperatures between 550 °C and 870 °C under He and 2% oxygen (O<sub>2</sub>)  
12 (Schauer et al., 2003; Wu et al., 2012). The OC contents are named OC<sub>1</sub> to OC<sub>4</sub> based on the  
13 temperature protocol of the OC/EC analyzer (Table 1). The mass of EC determined at different  
14 temperatures will be grouped together for discussions. In the VTDMA measurements, there  
15 were volatile or semi-volatile OC which vaporize at 300 °C or below. These vaporized OC are  
16 assumed to be OC<sub>1</sub>, which vaporizes at 310 °C, although this OC/EC set temperature is slightly  
17 higher than the set temperature of 300 °C in the VTDMA. With this assumption, the residuals  
18 of the VTDMA at 300 °C (LV and MV residuals) are postulated to consist of (1) OC<sub>2</sub> to OC<sub>4</sub>,  
19 which vaporize at 475 °C and above, and (2) EC and other refractory PM components. We have  
20 ignored the HV residuals as their contributions to the total volume of the particles are  
21 insignificant when compared to LV and MV residuals (Section 3.1). We will conduct a mass  
22 closure analysis based on the VTDMA and OC/EC measurements to examine this assumption.

## 23 **2.2 Data analysis**

### 24 **2.2.1 Number fractions**

25 The number fractions of LV, MV and HV residuals ( $\Phi'_{N,LV}$ ,  $\Phi'_{N,MV}$  and  $\Phi'_{N,HV}$ , with their sum  
26 being equal to unity) in Stream 2 on Fig. 1 were obtained from  $dN'/d\log D_p$  measured by the  
27 CPC. However, these fractions do not represent the actual number fractions of LV, MV and HV  
28 particles ( $\Phi_{N,LV}$ ,  $\Phi_{N,MV}$  and  $\Phi_{N,HV}$ ) before heating because they have not taken into account the  
29 CV particles and particle diffusional and thermophoretic losses. The number fraction of CV

1 ( $\Phi_{N,CV}$ ) is first obtained by considering the number fractions ~~due to~~ the residuals ( $1-\Phi_{N,CV}$ ) and  
 2 the number concentrations at a selected diameter  $D_0$  before heating ( $N_{D_0}$ ) and after heating ( $N'$ ):

$$3 \quad N_{D_0} \times \eta_{D_0} \times (1 - \Phi_{N,CV}) = N' \quad (2)$$

4 where  $\eta_{D_0}$  is the transport efficiency of particles.

5 ~~Equation (2) assumes~~ that  $\eta$  is the same for LV, MV and HV particles.  $\eta$  accounts for particle  
 6 loss between DMA<sub>1</sub> and DMA<sub>2</sub> due to diffusion and thermophoretic forces (Philippin et al.,  
 7 2004), and it varies with particle size and heating temperature.  $\eta$  at each particle diameter and  
 8 VTDMA temperature was determined by laboratory calibrations with sodium chloride (NaCl)  
 9 particles, which do not evaporate (i.e.,  $\Phi_{N,CV} = 0$ ) at the temperatures used in our experiments.  
 10 The transmission efficiency of NaCl of several selected diameters ~~heated at~~ temperatures  
 11 between 50 °C and 300 °C is provided in the supplemental information (Fig. S2). From the  
 12 known  $\eta$  and ~~field measurements~~  $N_{D_0}$  and  $N'$ ,  $\Phi_{N,CV}$  ~~was obtained~~ from Eq. (2). Afterwards,  
 13  $\Phi_{N,LV}$ ,  $\Phi_{N,MV}$  and  $\Phi_{N,HV}$  were obtained by renormalizing  $\Phi'_{N,LV}$ ,  $\Phi'_{N,MV}$  and  $\Phi'_{N,HV}$  with  $(1-\Phi_{N,CV})$   
 14 so that the sum of  $\Phi_{N,LV}$ ,  $\Phi_{N,MV}$ ,  $\Phi_{N,HV}$  and  $\Phi_{N,CV}$  equals to unity.

## 15 2.2.2 Volume fractions

16 The volume fractions of LV, MV, HV residuals and CV ( $\Phi_{V,LV}$ ,  $\Phi_{V,MV}$ ,  $\Phi_{V,HV}$  and  $\Phi_{V,CV}$ ) at each  
 17 selected diameter  $D_0$  are defined as the ratios of the volume of LV, MV, HV residuals and CV  
 18 to the total volume of the mono-disperse particles before heating. By assuming that the residuals  
 19 are ~~in~~ spherical shape,  $\Phi_{V,LV}$ ,  $\Phi_{V,MV}$  and  $\Phi_{V,HV}$  can be calculated by:

$$20 \quad \Phi_{V,i} = \frac{N_i \times \frac{\pi}{6} D_{p,i}^3}{N_{D_0} \times \frac{\pi}{6} D_0^3} = \Phi_{N,i} \times \frac{D_{p,i}^3}{D_0^3} \quad (3)$$

21 where  $N_i$  and  $D_{p,i}$  are the number concentration and mean residual diameter of  $i = LV, MV$  or  
 22 HV residuals.

23 For LV particles, it is assumed that  $D_0$  and mean  $D_p$  are the same and hence  $\Phi_{V,LV}$  is the same  
 24 as  $\Phi_{N,LV}$ . For MV and HV particles, the mean  $D_p$  is smaller than  $D_0$  due to the evaporation of  
 25 volatile materials. The number weighted mean residual diameter ( $D_p$ ) is calculated by:

$$26 \quad D_{p,i} = \frac{\sum_j D_{p,i} \times N_{i,j}}{N_i} \quad (4)$$

27 where  $D_{p,i}$  and  $N_{i,j}$  are the residual diameter and number concentration of  $i = MV$  or HV at the  
 28 75 diameter bins ( $j$ ) of VSF, respectively.



1

2 The volume fractions of the evaporated materials are calculated from the volume fractions of  
3 the residuals. The calculation for  $\Phi_{V,CV}$  is similar to that for  $\Phi_{V,LV}$ . Since the particle has  
4 completely vaporized, the vaporized volume is equivalent to the volume of the original particle.  
5 Hence,  $\Phi_{V,CV}$  is the same as  $\Phi_{N,CV}$ :

$$6 \quad \Phi_{V,CV} = \frac{N_{CV} \times \frac{\pi}{6} D_{p,CV}^3}{N_{D0} \times \frac{\pi}{6} D_0^3} = \Phi_{N,CV} \quad (5)$$

7 where  $D_{p,CV} = D_0$ . Since the sum of the total volume fraction of CV, VM and the residuals of  
8 LV, MV, HV equals to unity,  $\Phi_{V,VM}$  was obtained after the above volume fractions were  
9 calculated. Furthermore, we also calculated the volume fraction remaining (*VFR*), defined as  
10 the volume ratio of the residual to its host particle, to aid our discussions later:

$$11 \quad VFR_i = \frac{N_i \times \frac{\pi}{6} D_{p,i}^3}{N_i \times \frac{\pi}{6} D_0^3} = \frac{D_{p,i}^3}{D_0^3} \quad (6)$$

12 where  $N_i$  and  $D_{p,i}$  are the number concentration and mean residual diameter of  $i = MV$  or  $HV$   
13 after heating, respectively.

### 14 **2.2.3 Particle size distributions of number, volume and mass concentrations of** 15 **LV, MV and HV residuals**

16 Due to the differences in the size cuts of the VTDMA and the OC/EC Analyzer, log-normal fits  
17 extrapolated to 5  $\mu\text{m}$  were applied to the particle number size distributions of the residuals of  
18 LV, MV and HV ( $dN/d\log D_{p,i}$ , where  $i = LV, MV$  or  $HV$ ) to estimate the volume and then mass  
19 concentrations (~~calculated later~~) of the ambient aerosols for comparison with  $\text{PM}_{2.5}$  OC/EC  
20 measurements. The volume size distributions ( $dV/d\log D_{p,i}$ ) ~~are~~ calculated by:

$$21 \quad \frac{dV}{d\log D_{p,i}} = \frac{dN}{d\log D_{p,i}} \times \frac{\pi}{6} D_{p,i}^3 \quad (7)$$

22 where  $D_{p,i}$  is the mean residual diameter as defined in Section 2.2.2.

23 Volume ( $V$ ) concentrations of LV, MV and HV residuals can ~~then~~ be calculated by integrating  
24 the area under the fitted curves. As we only focus on LV and MV, densities of  $1.0 \text{ g cm}^{-3}$   
25 (Hitzenberger et al., 1999) and  $1.5 \text{ g cm}^{-3}$  are applied to  $V_{LV}$  and  $V_{MV}$  to obtain mass ( $m$ )  
26 concentrations of LV and MV residuals, respectively. The choice of the densities is based on  
27 the assumption that LV and MV residuals are dominated by soot and non-volatile OC,  
28 respectively.

## 1 3 Results and Discussions



### 2 3.1 Overview

3 The time series of meteorological conditions, particle number size distribution, PM<sub>2.5</sub>, OC and  
4 EC concentrations during the campaign are presented in Fig. 3. Overall, the campaign ~~came~~  
5 under the influence of the prevailing northerly wind with an average wind speed and  
6 temperature ( $\pm$ one standard deviation) of  $1.73 \pm 0.95 \text{ m s}^{-1}$  and  $14.8 \pm 5.1 \text{ }^\circ\text{C}$ , respectively. The  
7 average PM<sub>2.5</sub> concentration was  $48 \pm 26 \text{ } \mu\text{g m}^{-3}$ . A few ~~cold-front~~ periods were observed,  
8 during which the wind speed increased and the temperature decreased. In general, the low wind  
9 speed favored the accumulation of PM<sub>2.5</sub>. OC concentrations ranged from 0.5 to  $47.0 \text{ } \mu\text{g m}^{-3}$   
10 with an average of  $9.0 \pm 6.0 \text{ } \mu\text{g m}^{-3}$ , while EC concentrations ranged from 0.2 to  $23.0 \text{ } \mu\text{g m}^{-3}$   
11 with an average of  $3.4 \pm 3.0 \text{ } \mu\text{g m}^{-3}$ . OC<sub>1</sub>, the most volatile group among OC<sub>1</sub> to OC<sub>4</sub> in OC/EC  
12 analysis, accounted for one-third of the total carbon mass (Fig. 4).

13 On Feb 17, and Mar 12 and 17, the daily-averaged PM<sub>2.5</sub> concentrations exceeded  $95 \text{ } \mu\text{g m}^{-3}$ ;  
14 they were nearly twice the daily-averaged values ~~on~~ other days (Fig. 3, shaded area in grey).  
15 Results of 72 h back trajectories (Stein et al., 2015; Rolph, 2016) showed that air masses  
16 arriving at the site on or before these three days mostly originated from the continental or  
17 oceanic area close to Eastern China (Fig. S3). The SMPS data also showed a mode near 100  
18 nm with a high particle number concentration (Fig. 3).

19 The temporal variation of the number concentration of MV particles having an initial diameter  
20 of 80 nm or above tracked reasonably well with the accumulation ~~of~~ PM<sub>2.5</sub> as particles aged and  
21 became more internally mixed (Fig. 3 and S4). Furthermore, a **size dependence** was observed  
22 for 80 nm to 300 nm MV particles. There were days, e.g., from Feb 24 to Mar 10, when the  
23 number concentration of 300 nm MV particles did not track well with PM<sub>2.5</sub>. The mode of total  
24 particle number size distribution was below 100 nm and the number concentrations of 300 nm  
25 particles were low (Fig. 3). PM<sub>2.5</sub> tracked better ~~with~~ the number concentrations of 80 nm to  
26 150 nm MV particles (Fig. 4a to S4c) than those of 200 nm and 300 nm MV particles (Fig. S4d  
27 and S4e).

28 The average number and volume fractions of CV, HV, MV and LV in VTDMA measurements  
29 at 300 °C are summarized in Table 2. VM is internally mixed with ~~(or coated on)~~ MV and HV  
30 residuals, and hence does not have a separate contribution to number concentrations. Overall,  
31 HV and MV particles, indicator for aged aerosols with internally mixed non-volatile and

1 volatile materials, accounted for 57% to 71% of the total particle number concentration. Non-  
2 volatile materials (LV, MV and HV residuals) accounted for 15% to 26% of the total volume  
3 of selected particles before heating. While the CV and HV fractions were larger in the finest  
4 particles selected ( $D_0 = 40$  nm), MV and LV were more abundant in larger particles ( $D_0 > 80$   
5 nm). As in Rose et al. (2006), fresh emissions like soot adsorbed or absorbed volatile materials  
6 during atmospheric processing. ~~Smaller particles grew to a greater extent~~ than the larger ones  
7 because of their higher ratios of surface area to volume. When they were heated in the VTDMA  
8 at 300 °C, ~~these~~ smaller particles reduced more substantially in size, as reflected in the higher  
9 CV and HV fractions and lower MV and LV fractions. The higher abundance of MV and LV  
10 in larger size particles could also be explained by ~~the~~ non-volatile primary particles. Yu et al.  
11 (2010) reported that the **condensation and droplet modes** of EC and  in urban sites of  
12 Guangzhou were approximately 400 nm and  nm, respectively. The mode of fresh EC  
13 emitted from vehicles is also **approximately 400 nm** (Huang et al., 2006). Larger particles also  
14 likely contain more internally mixed aged aerosols (secondary pollutants) than the smaller ones.  
15 Nevertheless, the detection limit of the downstream DMA and CPC in the VTDMA system is  
16 10 nm. ~~It was assumed that the residuals having a diameter below 10 nm were small enough to~~  
17 ~~be considered as completely vaporized.~~ However, ~~such assumption would lead to an~~  
18 overestimation of CV and an underestimation of the non-volatile residuals for the finest  
19 particles selected (with an initial diameter of 40 nm).

### 20 **3.2 Diurnal variations**

21 Figure 5 shows ~~the~~ diurnal variation of the fraction of CV, HV residual, MV residual, LV  
22 residual and VM in the total volume of particles of dry initial diameters of 40, 150 and 300 nm.  
23 For 40 nm particles, clear maximum and minimum of the fraction of CV, VM and HV residuals  
24 are observed at 08:00 and 13:00, respectively. The diurnal variation of the HV and MV particles  
25 in 40 nm particles was clearer in terms of number fraction (Fig. S5). Furthermore, the trend of  
26 CV is opposite to those of VM, HV and MV. The increase of CV in 40 nm particles and to a  
27 lesser extent of LV in 150 nm and 300 nm particles in the morning is consistent with traffic  
28 pattern, where freshly emitted volatile and non-volatile materials, likely OC and EC, are  
29 externally mixed and contributed to CV and LV, respectively. As time progresses in a day, the  
30 highly volatile species (CV) which were freshly emitted in the morning, may evaporate and  
31 react to form less volatile particles and become VM instead of CV (Robinson et al., 2007).  
32 Alternatively, these CV particles could also coagulate with smaller particles to form VM

1 containing particles. Less fresh emissions with more CV particles turning into VM on MV and  
2 HV particles can explain the trend that the number and volume fractions of CV decreased while  
3 those of MV and HV increased (Fig. 5 and Fig. S5).

4 We also used the diurnal variations in the volume fraction remaining (*VFR*), again defined as  
5 the volume ratio of the residual to its *host* particle (not to the total volume of all particles), to  
6 examine the size changes of the non-volatile residuals of HV and MV particles. The *VFR* of  
7 HV did not exhibit any obvious diurnal variations but the *VFR* of MV peaked near 18:00. The  
8 *VFR* of 40 nm MV particles increased after 14:00 while those of 150 nm and 300 nm MV  
9 particles increased after 15:00. Since the *VFR* of HV and MV were relatively constant during  
10 the day, the increase in VM fraction after the morning rush hours is likely attributed to the  
11 increase in number concentrations of HV and MV particles instead of changes in the amount of  
12 VM on the MV or HV residuals.

13 The diurnal variations for particles larger than 80 nm were much less obvious than those for 40  
14 nm particles in this study and in others (Rose et al., 2011; Cheng et al., 2012; Zhang et al.,  
15 2016). In winter, the atmosphere is more stable, resulting in a poorer dilution of aged particles  
16 with the less polluted aerosols from higher up (Rose et al., 2006). When the aged pollutants  
17 were trapped near the ground surface, the effect of aging of fresh emissions weakened.  
18 Therefore, although a daily maximum and a daily minimum were still observed for particles  
19 larger than 80 nm, the variation was mostly within 15%.

20 The diurnal variations in the mass fractions of OC and EC in PM<sub>2.5</sub> provided further insights to  
21 the observations above (Fig. 6). The OC and EC data on Mar 12 and 17 were excluded since  
22 they were more than two standard deviations higher than those on other days. Subtle morning  
23 peaks between 06:00 and 10:00 were observed for the volume fraction of LV residuals (Fig. 5).  
24 A similar peak was observed for the mass fraction of EC in PM<sub>2.5</sub> in the morning (Fig. 6). This  
25 suggests that LV particles may be related to the EC from vehicle emissions in the morning. This  
26 EC was relatively less aged and externally mixed with other volatile materials. In the late  
27 afternoon, LV residuals showed another peak between 17:00 and 19:00 whereas the mass  
28 fraction of EC in PM<sub>2.5</sub> exhibited a minimum at 15:00, after which it increased continuously.  
29 The continuous increase in EC at night is likely related to the increase of heavy-duty diesel  
30 vehicles (Zhang et al., 2015), which was restricted during daytime (Bradsher, 2007).

31 Although OC<sub>1</sub> contributed to about half of the total OC mass, the diurnal variation in the mass  
32 fraction of OC in PM<sub>2.5</sub> was driven by the total mass of OC<sub>2</sub>, OC<sub>3</sub> and OC<sub>4</sub> (OC<sub>2-4</sub>), which

1 reached a minimum between 05:00 and 09:00 and increased until 19:00. OC can be attributed  
2 to both primary and secondary sources. The increased mass fraction of OC in PM<sub>2.5</sub> and OC-  
3 to-EC ratio in the afternoon suggest that the sources of OC were less related to traffic but more  
4 to the aging and formation of secondary organic aerosols (Turpin et al., 1990; Chow et al.,  
5 1996). These OC<sub>2</sub>, OC<sub>3</sub> and OC<sub>4</sub> may be highly oxygenated species or oligomers that are less  
6 volatile than primary or less oxygenated organics (Kalberer et al., 2004; Huffman et al., 2009).  
7 It is interesting to note that the volume fraction of LV residuals and the VFR of MV particles at  
8 different sizes showed a dip in the afternoon (Fig. 5, third column from the left). The VFR of  
9 40 nm MV particles showed a dip at 14:00 while those in 150 nm and 300 nm particles showed  
10 a dip at 15:00. The volume fraction of LV residuals in 150 nm and 300 nm particles reached a  
11 minimum at 13:00 and 15:00, respectively. Because EC decreased between 12:00 and 15:00,  
12 the increase in the volume fraction of LV residuals in 150 nm particles since 13:00 and the VFR  
13 of 40 nm MV particles since 14:00 may be related to the increased presence of aged organics  
14 as well as the EC particles which aged via coagulation and condensation.

### 15 **3.3 Back trajectory analyses**

16 We calculated ~~the~~ 72 h back trajectories of ~~the~~ air masses arriving at the sampling site (23°00  
17 N, 113°25' E) at 4 h intervals (at 00:00, 04:00, 08:00, 12:00, 16:00 and 20:00 local time, UTC  
18 +8) using the PC version of the HYSPLIT4 (Hybrid Single Particle Lagrangian Integrated  
19 Trajectory, version 4) model (Stein et al., 2015; Rolph, 2016). Archived meteorological data  
20 from the Global Data Assimilation System (GDAS) 1-deg was employed and the receptor  
21 height was set at 500 m above ground level (a.g.l.). The 191 back trajectories calculated were  
22 grouped into six clusters based on their spatial distribution (Fig. 7).

23 Overall, the sampling site was mostly affected by northwesterly and northeasterly air masses.  
24 Cluster 1 and 3 are coastal and continental air masses, respectively, although both originated  
25 from the northeast. Clusters 4, 5 and 6 represent continental air masses originating from the  
26 northwest. Cluster 2 is a group of maritime air masses originating from the East China Sea  
27 northeast or east of Guangzhou. While air masses in cluster 6 were transported at relatively high  
28 speeds and altitudes (over 3000 m a.g.l.), air masses in all the other clusters were transported at  
29 an altitude below 1500 m a.g.l. for over 40 h before arriving at the site. ~~Nevertheless,~~ air masses  
30 in cluster 6 only ~~persisted for~~ less than three days. ~~Since~~ the corresponding VTDMA and OC/EC  
31 data were sometimes unavailable, cluster 6 will be excluded from the following discussion.

1 The average PM<sub>2.5</sub>, OC and EC concentrations associated with air masses from the northeast of  
2 Guangzhou (clusters 1, 2 and 3) were higher than those from the northwest (clusters 4 and 5,  
3 Table 3). Days associated with coastal and maritime air masses were more polluted than days  
4 associated with continental air masses for several reasons. First, south China as a region is often  
5 affected by the high pressure system moving eastward or southward from the continent out to  
6 sea in winter. When the maritime or coastal air streams entered from the southeast of the  
7 sampling site at Panyu, the atmosphere at the sampling site became more stable with low local  
8 wind speeds (e.g. the polluted days on Feb 17 and Mar 12, 16 and 17, Fig. 3 and S3). Local  
9 pollutants accumulated and the city was also affected by pollutants from the southeastern areas  
10 of the site (e.g. Shenzhen, Nansha and Dongguan). Second, land-sea breeze cycles were  
11 observed when the sampling site was under the influence of maritime air masses from Mar 18  
12 to 20. During the day, southeasterly wind prevailed and the wind speed was higher. In the  
13 evening, the southeasterly wind was gradually replaced by a southwesterly or northwesterly  
14 wind and the wind speed decreased (Fig. 3). The cycle started again in the morning when the  
15 westerly wind was gradually replaced by southeasterly wind. Such land-sea breeze effects can  
16 result in an effective redistribution and accumulation of air pollutants within the PRD region  
17 (Lo et al., 2006).

18 Furthermore, PM<sub>2.5</sub> in the northeastern parts of China can exceed 200 µg m<sup>-3</sup> due to both  
19 enhanced emissions from coal combustion for heating and poor dispersion during wintertime  
20 (Gu et al., 2014). Under the influence of the prevailing northerly or northeasterly wind in China,  
21 these pollutants were often transported to southern China and the East China Sea (Chen et al.,  
22 2012). Pollutants might also have accumulated when the maritime air masses spent about two  
23 days across Taiwan and the coast of south China. In contrast, continental air masses in cluster  
24 5 moved slightly faster, and were often associated with the cold front period during which the  
25 local wind speed and pressure increased but the temperature decreased (Fig. 3). As the cold air  
26 masses passed through the city, dispersion and clearance of pollutants were promoted, resulting  
27 in lower PM<sub>2.5</sub> concentrations (Tan et al., 2013a). Therefore, unlike in other coastal cities like  
28 Hong Kong (Lee et al., 2013), in Panyu maritime air masses could lead to more severe pollution  
29 than the continental ones in winter.


30 The five clusters were further analyzed to study the influence of air mass history on aerosol  
31 volatility. The number fractions of CV, HV, MV and LV of the six selected diameters in  
32 VTDMA measurements are regrouped based on the clusters as shown in Fig. 8. The total

1 number fractions of the non-volatile residuals (sum of HV, MV and LV) were similar in all  
2 clusters. Maritime air masses (cluster 2) had a slightly higher fraction of LV particles while  
3 continental air masses originating from the northwest of the site (clusters 4 and 5) had a higher  
4 fraction of HV particles. Although the air masses in clusters 1 and 5 originated from farther  
5 away and traveled at relatively higher speeds than those in clusters 2, 3 and 4, all clusters  
6 involved transport at low altitudes (below 1500 m) for over 40 h, likely due to the generally  
7 lower mixing heights in winter. Therefore, aerosols in these air masses were all well-aged upon  
8 arrival (Wehner et al., 2009). This could be another reason for the lack of size dependence of  
9 the number, volume fractions and diurnal variation for particles larger than 80 nm. When the  
10 transported air masses mixed with local pollutants, the size dependence of the number fractions  
11 of different volatility groups as well as the aging of local emissions was further reduced.

12 We also examine the volatility shrinkage factor (*VSF*) distributions of 40 nm, 110 nm and  
13 300 nm particles upon heating at 300 °C (Fig. 9). Log-normal fittings with a three-peak solution  
14 were applied to the distributions. The average *VSF* modes of the peaks were located at  $0.38 \pm$   
15  $0.021$  (peak 1),  $0.60 \pm 0.066$  (peak 2) and  $0.95 \pm 0.007$  (peak 3), respectively. The standard  
16 deviation of the corresponding normal distribution ( $\sigma$ ) of peak 3 was the smallest among the  
17 three peaks ( $\sigma < 0.1$ ). For the same particle size, the *VSF* distributions in the *VSF* range between  
18 0.3 and 0.8 in cluster 5 was relatively more uni-modal than those of other clusters (Fig. 9b and  
19 9c). This suggests that the composition in cluster 5 was more homogeneous. Cluster 1 also  
20 consisted of long-range transported air masses but they likely passed through areas that are  
21 more polluted and mixed with different types of pollutants. Note that the fractions of HV, MV  
22 and LV have been traditionally defined based on the values of *VSF*, i.e.  $HV < 0.4$ ;  $0.4 < MV <$   
23  $0.9$ ;  $LV > 0.9$  (Wehner et al., 2009). The *VSF* distributions above suggest that these definitions  
24 using  $VSF = 0.4$  and  $0.9$  may need to be re-visited in the future.



### 25 3.4 New particle formation

26 o new particle formation (NPF) events were observed in the campaign on Feb 20 and Mar  
27 13 (Fig. 3). Since VTDMA data were not available during the NPF event on Mar 13, we only  
28 focus on the NPF event on Feb 20 which happened after a cold front under a low  $PM_{2.5}$   
29 concentration. On Feb 20, a sub-20 nm particle mode was first observed at 12:00. This particle  
30 mode grew continuously until it reached 120 nm at 02:00 on Feb 21. In VTDMA measurements,  
31 a sharp increase in the number concentration of HV particles having an initial diameter of 40  
32 nm was observed at 17:00 on Feb 20 (Fig. 10). This event is likely related to the growth of the

1 newly formed particles when they mixed with the volatile materials via condensation or  
2 adsorption. As these particles aged further, they grew larger as reflected in the increase in  
3 number concentrations of larger MV particles and the increase in PM<sub>2.5</sub> mass (Fig. 10). The  
4 growth of the newly formed particles can also be observed from the number size distributions  
5 of HV, MV and LV particles at different times on Feb 20 and 21 (Fig. 11). The mode of HV  
6 particles increased from 40 nm at 17:00 to 80 nm at 21:00 on Feb 20 Feb. The mode stayed at  
7 80 nm while the corresponding number concentration decreased at 02:00 on Feb 21 Feb. In  
8 contrast, the number concentrations of MV particles grew continuously. The HV and MV  
9 particle concentrations and diameter modes underwent much smaller changes on the non-event  
10 day of Feb 28 (Fig. 11).

### 11 **3.5 Closure analysis for LV and MV residuals at 300°C, OC and EC**

12 Closure analysis of EC or the sum of EC, OC<sub>2</sub>, OC<sub>3</sub>, and OC<sub>4</sub> and the total mass of LV and MV  
13 residuals is conducted (Fig. 12). Good correlations ( $R^2 > 0.9$ ) for both EC and the sum of EC,  
14 OC<sub>2</sub>, OC<sub>3</sub>, and OC<sub>4</sub> with the total mass of LV and MV residuals were obtained. Nonetheless,  
15 the slope for the total mass of LV and MV residuals to the mass of EC (2.94) is more than two  
16 times of that for the total mass of LV and MV residuals to the sum of EC, OC<sub>2</sub>, OC<sub>3</sub>, and OC<sub>4</sub>  
17 (1.22), indicating that EC alone cannot account for the total mass of LV and MV residuals.  
18 Including non-volatile OC (sum of OC<sub>2</sub> to OC<sub>4</sub>) give better mass closure with the total of LV  
19 and MV residuals. This further supports our initial postulation that the non-volatile residuals  
20 which remained intact upon heating at 300 °C in the VTDMA may contain a significant amount  
21 of non-volatile OC. However, the total mass of EC, OC<sub>2</sub>, OC<sub>3</sub>, and OC<sub>4</sub> do not explain all the  
22 mass of LV and MV residuals. A possible explanation could be that the vaporizing temperatures  
23 of some OC<sub>1</sub> are close to the upper limit (310 °C), hence they were not completely vaporized in  
24 the heated tube and remained in non-volatile residuals. The presence of other refractory  
25 materials and the assumption made about the density of LV and MV are two other possible  
26 explanations.

27 Other possible errors for the closure could be related to the different heating environments in  
28 the VTDMA and the OC/EC analyzer. In the OC/EC analyzer, OC was measured when the  
29 samples were heated in the presence of a non-oxidative carrier gas (He). In the VTDMA,  
30 aerosols were heated in air which contained O<sub>2</sub>. Therefore, some “OC<sub>2-4</sub>” that evaporated at  
31 475 °C or above in the OC/EC analyzer may have been oxidized at 300 °C in the VTDMA.  
32 Charring of organic matter could also occur (Philippin et al., 2004). Further study is needed to



1 quantify the effect of oxygen on the oxidation of OC in the VTDMA. The extrapolated  
2 lognormal fitting of the size distribution of non-volatile particles can also cause errors if the  
3 mode diameter of the fitting is beyond the VTDMA's range of measurements. While the  
4 VTDMA measured the size distribution of particles between 10 nm and 400 nm in diameter,  
5 the OC/EC analyzer took into account particles up to 2.5  $\mu\text{m}$  in diameter. Yu et al. (2010)  
6 reported three EC and OC modes between 0.4  $\mu\text{m}$  and 10  $\mu\text{m}$  in ambient aerosols in Guangzhou:  
7 0.4, 0.9 and 5  $\mu\text{m}$ . The 0.4  $\mu\text{m}$  mode accounted for 44% to 49% of the measured EC but only  
8 17% to 20% of the measured OC.

9

#### 10 **4 Conclusions**

11 This study presents the first VTDMA measurements in a suburban area of Guangzhou in the  
12 Pearl River Delta, China during wintertime. The LV fraction was assumed to be EC particles.  
13 These particles were externally mixed with volatile materials at 300  $^{\circ}\text{C}$  and contributed to less  
14 than 20% of the total particle number concentration at the sampling site. The diurnal variations  
15 in the number and volume fractions of LV, MV and HV were much less obvious in this study  
16 than in **other studies** likely because of the more stable atmosphere and poorer dilution of aged  
17 aerosols in winter. Back trajectory analysis showed that the measured  $\text{PM}_{2.5}$ , EC and OC  
18 concentrations were higher when the sampling site came under the influence of maritime and  
19 coastal air masses originating from the east or northeast of the site. These observations ~~are~~  
20 attributed to ~~the~~ high pressure system on ~~the~~ continent, the prevailing northerly wind and ~~the~~  
21 enhanced pollution from north China in winter. Long-range transport continental trajectories  
22 were often associated with the cold front periods during which the dispersion of pollutants was  
23 promoted. The number fractions of LV, MV and HV particles did not show much variations  
24 among the ~~clusters~~, likely because the air masses in all ~~clusters~~ were transported at low altitudes  
25 (below 1500 m) for over 40 h. They were therefore well-aged upon arrival at the site.

26 While **previous studies have demonstrated** soot as a major component of the non-volatile  
27 residuals at 300  $^{\circ}\text{C}$  measured by the VTDMA, this work identified **non-volatile organics** as  
28 another possible component. The diurnal variations in the LV fractions and the size of the MV  
29 residuals may be related to the variation in the abundance of both EC and non-volatile OC,  
30 which evaporated at 475  $^{\circ}\text{C}$  and above in the OC/EC analyzer. Analyses of the diurnal variations  
31 in the LV fractions and the *VFR* of MV particles, the latter of which reflects the change in size  
32 of the non-volatile materials in the MV particles, suggest that the increase in ~~non-volatile~~

1 fractions and size in the early afternoon may be related to the increase in non-volatile OC in  
2 addition to the effects of EC coagulation and condensation. The mass closure analysis of EC  
3 and non-volatile OC and the total mass of LV and MV residuals also suggest that non-volatile  
4 OC may have contributed to non-volatile residuals in our VTDMA measurements.

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7

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41



1 Table 1. Temperature (T) and residence time (RT) protocol of the semi-continuous Sunset  
 2 OC/EC analyzer (Wu et al., 2012)

| Carbon Fraction | Carrier Gas              | T (°C) | RT (s) |
|-----------------|--------------------------|--------|--------|
| OC <sub>1</sub> | He                       | 310    | 80     |
| OC <sub>2</sub> |                          | 475    | 60     |
| OC <sub>3</sub> |                          | 615    | 60     |
| OC <sub>4</sub> |                          | 870    | 90     |
| EC <sub>1</sub> | He and 2% O <sub>2</sub> | 550    | 45     |
| EC <sub>2</sub> |                          | 625    | 45     |
| EC <sub>3</sub> |                          | 700    | 45     |
| EC <sub>4</sub> |                          | 775    | 45     |
| EC <sub>5</sub> |                          | 850    | 45     |
| EC <sub>6</sub> |                          | 870    | 45     |

3

4

1 Table 2. Summary of average number and volume fractions in VTDMA measurements at 300 °C.

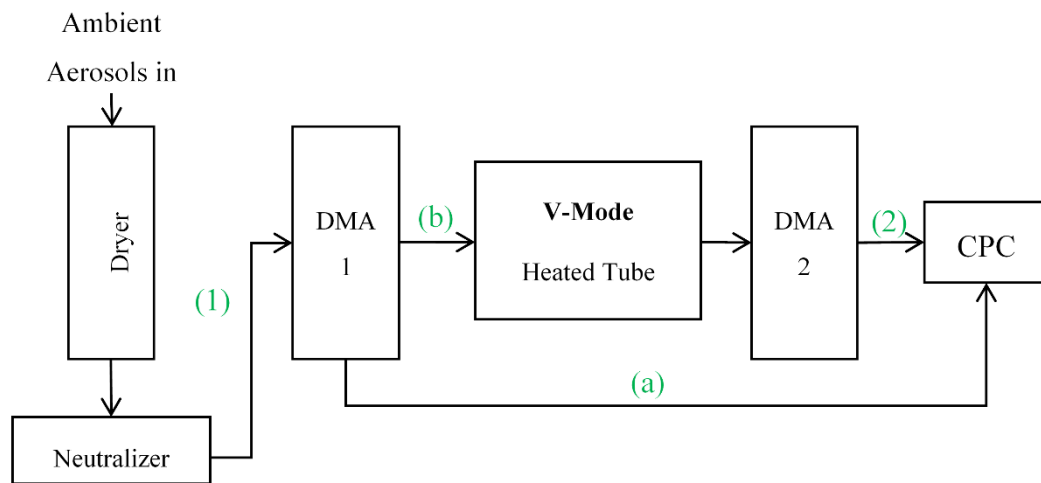
| Diameter (nm)   | 40                | 80                | 110               | 150               | 200               | 300               |
|-----------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Number fraction |                   |                   |                   |                   |                   |                   |
| CV              | $0.380 \pm 0.153$ | $0.174 \pm 0.097$ | $0.188 \pm 0.081$ | $0.167 \pm 0.074$ | $0.153 \pm 0.070$ | $0.141 \pm 0.065$ |
| HV              | $0.255 \pm 0.097$ | $0.198 \pm 0.052$ | $0.165 \pm 0.055$ | $0.163 \pm 0.064$ | $0.178 \pm 0.081$ | $0.214 \pm 0.097$ |
| MV              | $0.314 \pm 0.097$ | $0.513 \pm 0.089$ | $0.515 \pm 0.098$ | $0.530 \pm 0.105$ | $0.523 \pm 0.116$ | $0.497 \pm 0.125$ |
| LV              | $0.051 \pm 0.026$ | $0.113 \pm 0.040$ | $0.132 \pm 0.041$ | $0.140 \pm 0.041$ | $0.146 \pm 0.044$ | $0.148 \pm 0.047$ |
| Volume fraction |                   |                   |                   |                   |                   |                   |
| VM              | $0.503 \pm 0.131$ | $0.600 \pm 0.082$ | $0.580 \pm 0.073$ | $0.590 \pm 0.066$ | $0.602 \pm 0.064$ | $0.627 \pm 0.064$ |
| CV              | $0.361 \pm 0.168$ | $0.163 \pm 0.105$ | $0.166 \pm 0.098$ | $0.148 \pm 0.086$ | $0.134 \pm 0.080$ | $0.127 \pm 0.073$ |
| HV              | $0.014 \pm 0.005$ | $0.011 \pm 0.003$ | $0.008 \pm 0.002$ | $0.007 \pm 0.003$ | $0.007 \pm 0.003$ | $0.007 \pm 0.003$ |
| MV              | $0.070 \pm 0.025$ | $0.112 \pm 0.024$ | $0.112 \pm 0.025$ | $0.115 \pm 0.026$ | $0.109 \pm 0.027$ | $0.091 \pm 0.025$ |
| LV              | $0.052 \pm 0.026$ | $0.114 \pm 0.040$ | $0.134 \pm 0.044$ | $0.140 \pm 0.042$ | $0.148 \pm 0.048$ | $0.148 \pm 0.047$ |

2

1 Table 3. Summary of concentrations of PM<sub>2.5</sub>, OC, EC and the ratio of OC to EC (OC/EC) in  
 2 the five clusters.

|   | Cluster     |              |              |             |             |
|---|-------------|--------------|--------------|-------------|-------------|
|   | Coastal     | Maritime     |              | Continental |             |
|   | 1           | 2            | 3            | 4           | 5           |
| Origin (to the site)                    | NE          | NE/E         | NE           | NW          | NW          |
| PM <sub>2.5</sub> (µg m <sup>-3</sup> ) | 58.5 ± 24.4 | 58.9 ± 30.9  | 47.5 ± 28.4  | 33.9 ± 15.9 | 33.8 ± 19.3 |
| OC (µg m <sup>-3</sup> )                | 10.8 ± 6.01 | 10.84 ± 7.22 | 10.13 ± 6.89 | 5.51 ± 3.3  | 7.32 ± 2.75 |
| EC (µg m <sup>-3</sup> )                | 4.38 ± 2.97 | 4.98 ± 4.21  | 3.43 ± 3.12  | 1.8 ± 0.98  | 2.46 ± 0.59 |
| OC/EC                                   | 2.83 ± 1.05 | 2.62 ± 1.03  | 3.65 ± 1.6   | 3.18 ± 1.26 | 2.94 ± 0.73 |

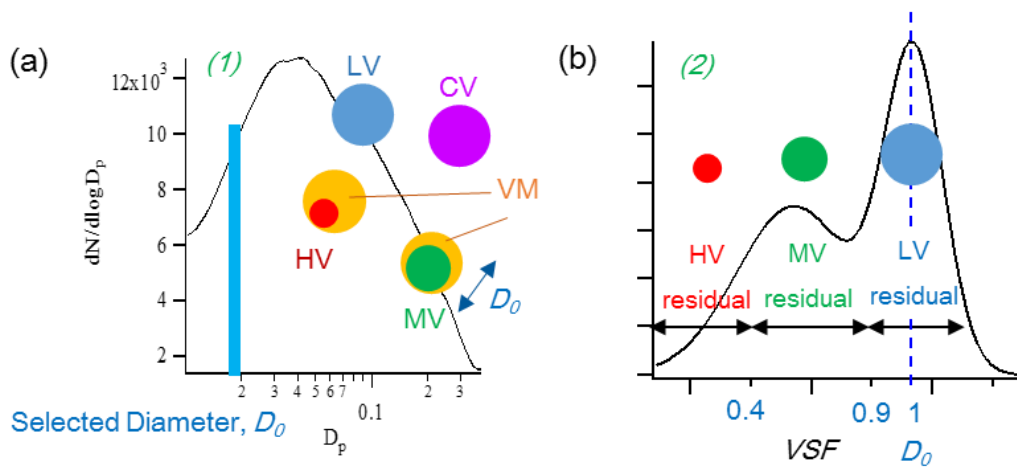
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2 Fig. 1. Schematic diagram of the volatility tandem differential mobility analyzer (VTDMA).

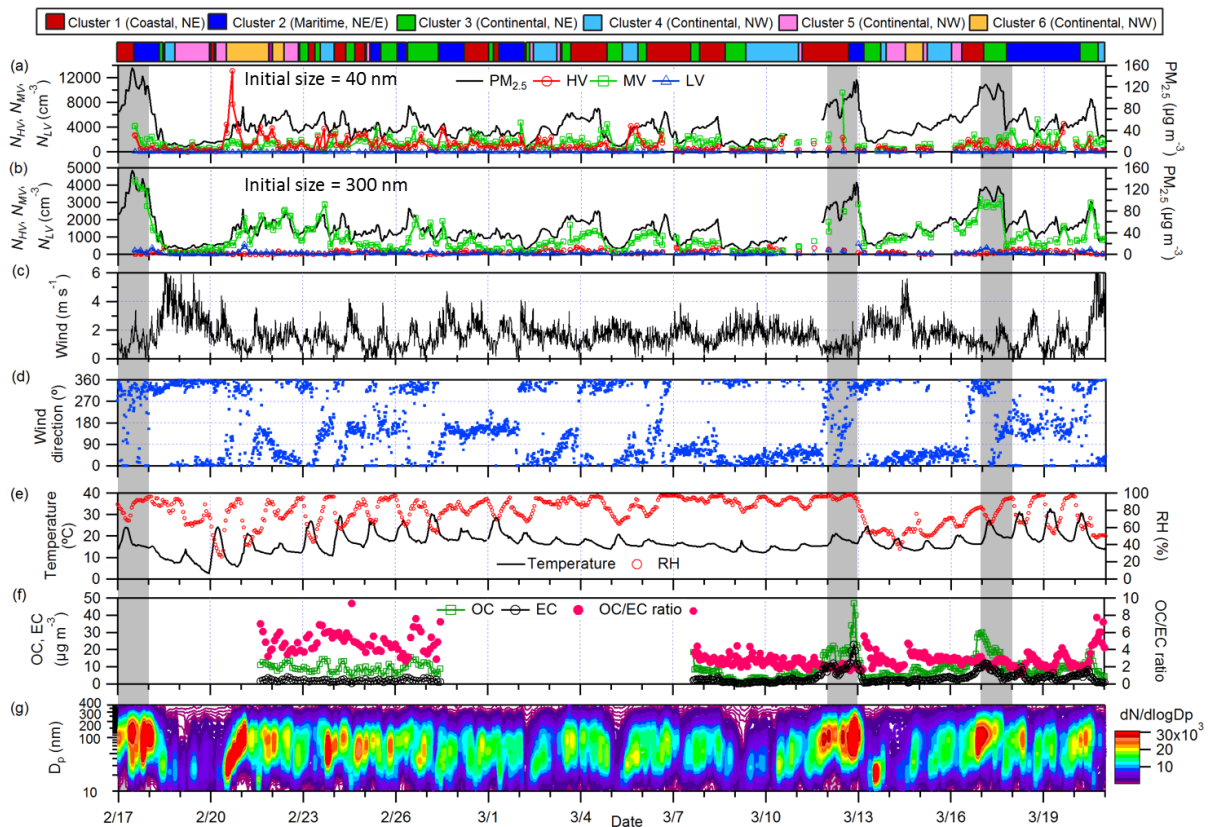
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1

2 Fig. 2. Examples of particle size distributions of (a) ambient aerosols before entering DMA<sub>1</sub>  
 3 and (b) residuals of the size-selected particles ( $D_0$ ) after heating. at 300 °C. The distributions in  
 4 Fig. 2a and 2b correspond to (1) and (2) in Figure 1 respectively. Residuals are divided into  
 5 three groups—LV (blue), MV (green) and HV (red)—based on their *VSF*. CV (purple) and VM  
 6 (orange) are vaporized and hence not measured as residuals. VM appears as coating for  
 7 illustration purposes only. It does not necessarily reflect the morphology of the particles.

8



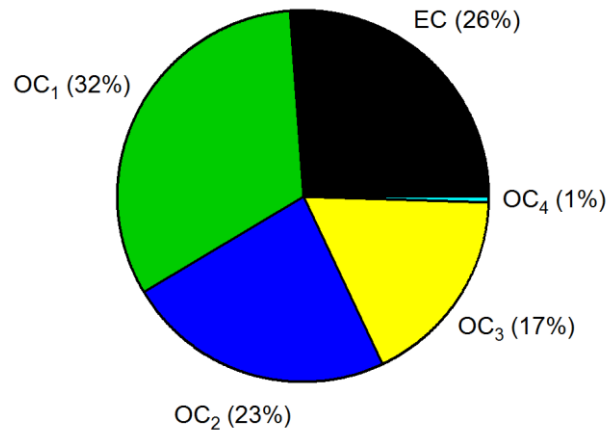
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2 Fig. 3. Temporal variation of number concentrations of HV, MV and LV in 40 nm  
 3 particles,  $PM_{2.5}$ , major meteorological parameters, OC and EC concentrations, OC-to-EC ratio  
 4 and particle number size distributions in the campaign. Air mass clusters are depicted at the top  
 5 and the shaded areas indicate days with daily-averaged  $PM_{2.5}$  concentrations exceeding  $95 \mu g$   
 6  $m^{-3}$ .

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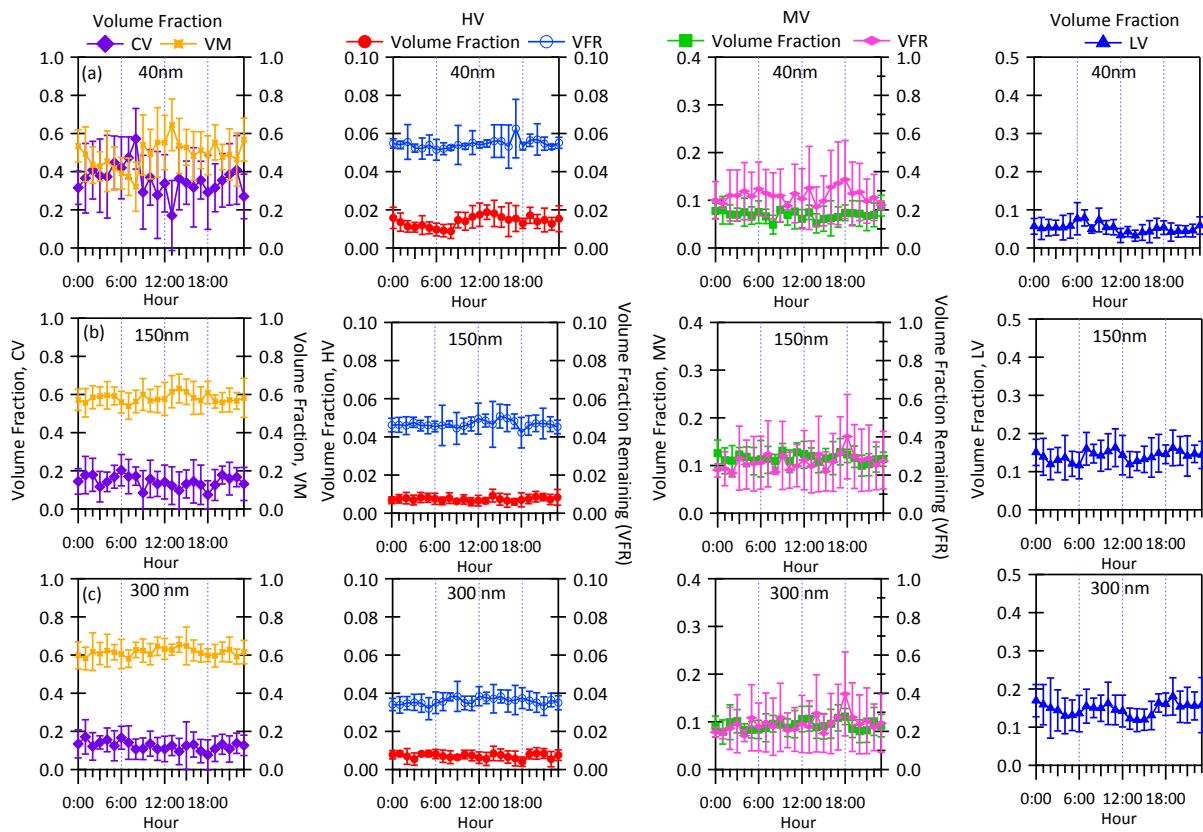
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2 Fig. 4. Average mass fractions of EC, OC<sub>1</sub>, OC<sub>2</sub>, OC<sub>3</sub> and OC<sub>4</sub> in PM<sub>2.5</sub>.

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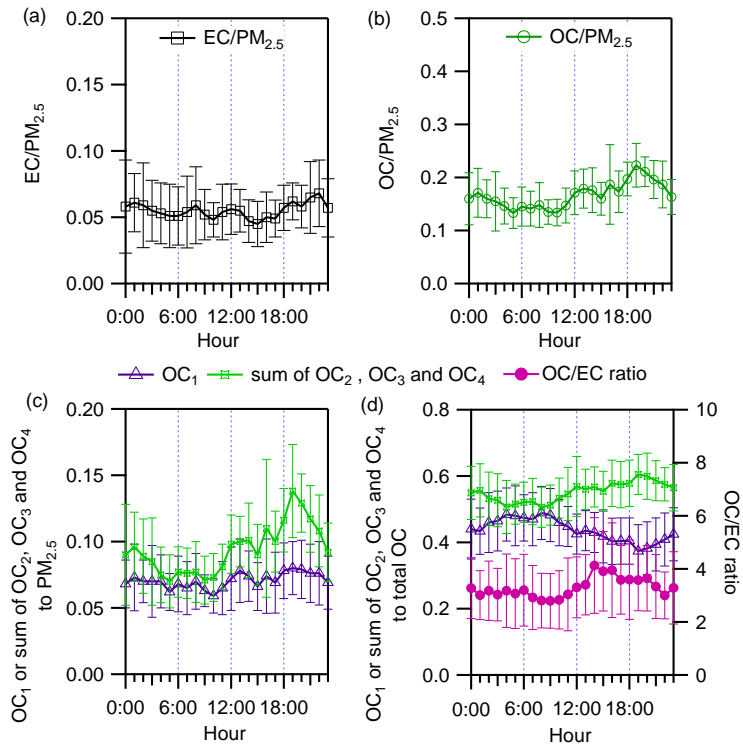
1

2 Fig. 5. Diurnal variations in volume fractions of (columns from left to right) CV, VM, HV  
 3 residuals, MV residuals and LV residuals in (a) 40 nm, (b) 150 nm and (c) 300 nm particles.  
 4 Diurnal variations in the volume fraction remaining (*VFR*) of HV and MV particles are plotted  
 5 on the right axis. Error bars represent one standard deviation.

6

7



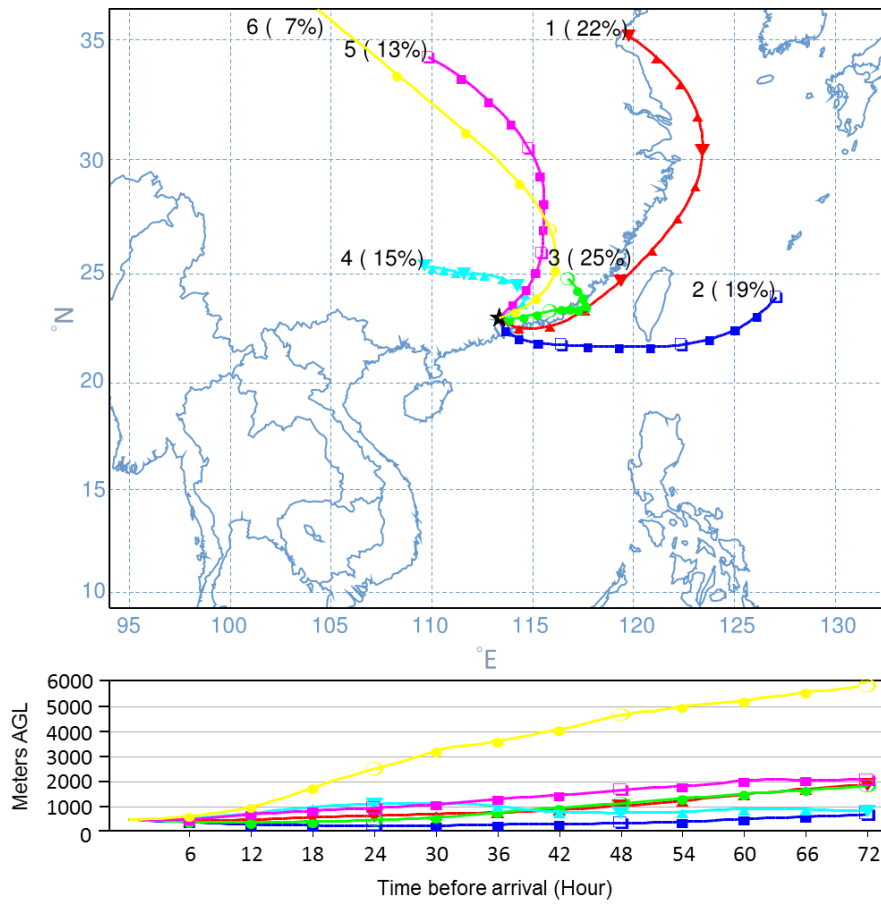


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2 Fig. 6. Diurnal variations in the mass fractions of EC, OC, OC<sub>1</sub> and the sum of OC<sub>2</sub>, OC<sub>3</sub> and  
 3 OC<sub>4</sub> in PM<sub>2.5</sub>, the ratio of OC to EC, mass fractions of OC<sub>1</sub> and the sum of OC<sub>2</sub>, OC<sub>3</sub> and OC<sub>4</sub>  
 4 to total OC in February and March. Error bars represent one standard deviation.

5

6



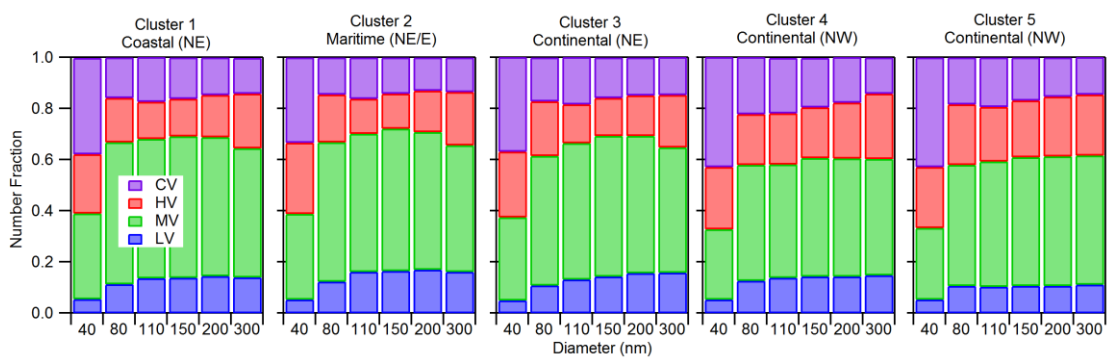
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2 Fig. 7. Mean back trajectories of the six types of air masses arriving at the sampling site.

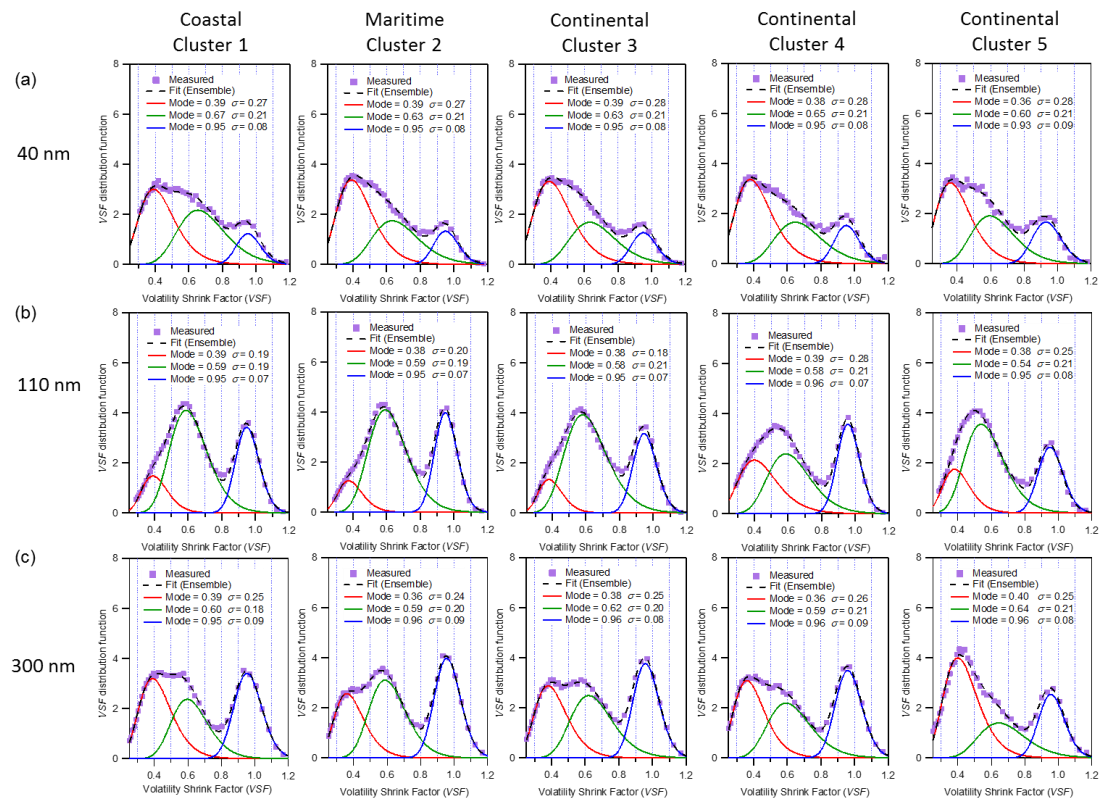
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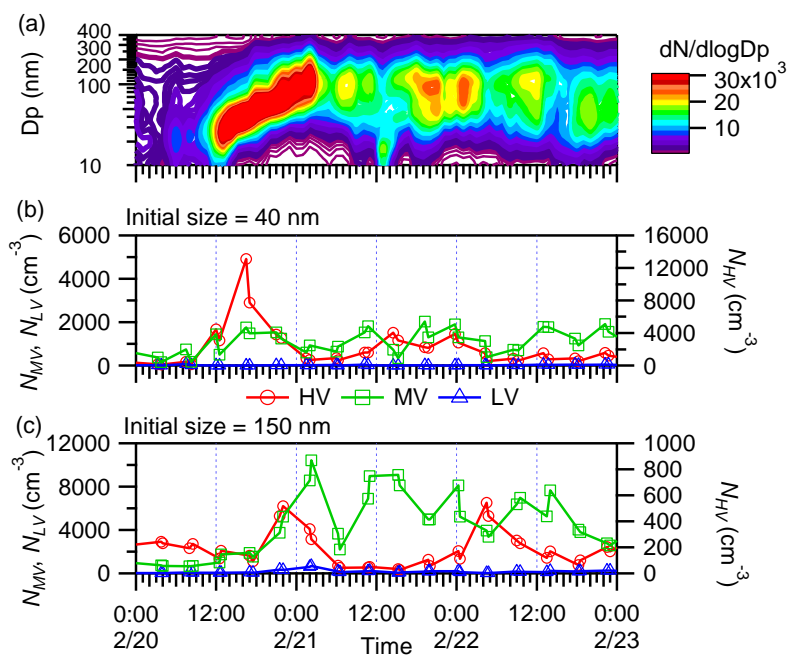
1  
 2 Fig. 8. Average number fractions of CV, HV, MV and LV in clusters 1 to 5 at different selected  
 3 diameters.  
 4



1

2 Fig. 9. Volatility shrinkage factor (VSF) distribution function in different clusters. Solid and  
 3 dotted lines are the peaks fitted with log-normal function and the ensemble distributions,  
 4 respectively.

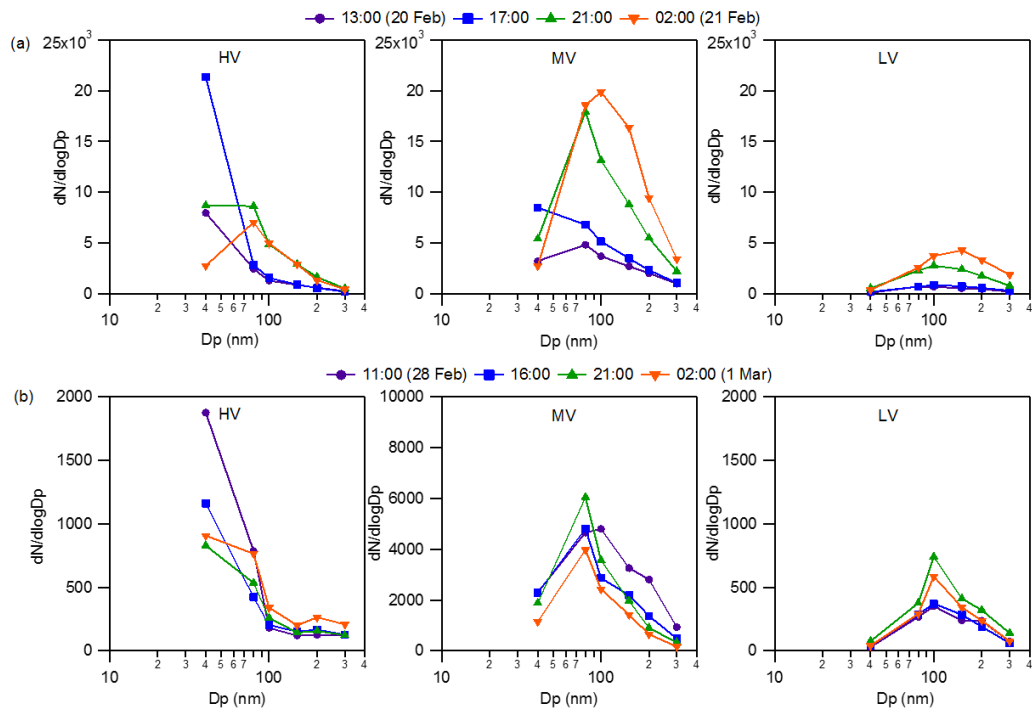
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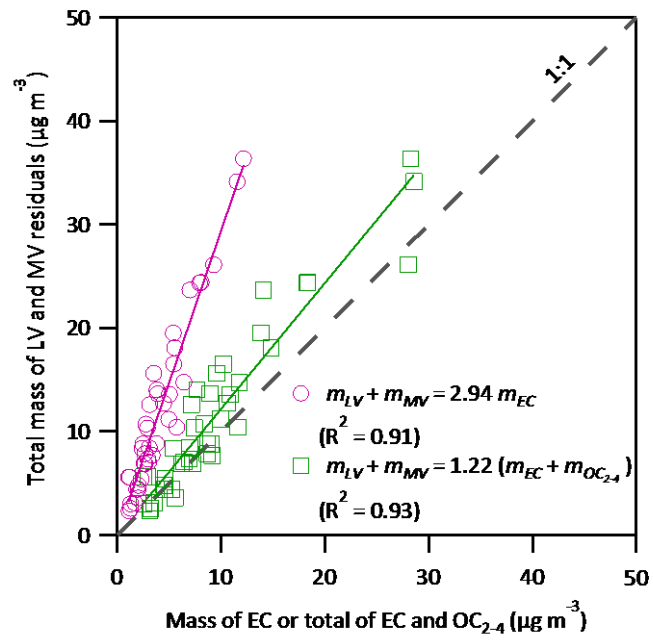


Fig. 10. Time series of (a) particle number size distribution, (b) number concentrations of HV, MV and LV in 40 nm particles and (c) number concentrations of HV, MV and LV in 150 nm particles.



1  
 2 Fig. 11. Particle number size distribution of (columns from left to right) HV, MV and LV  
 3 particles (a) at 13:00, 17:00, 21:00 on 20 Feb and 02:00 on 21 Feb and (b) at 11:00, 16:00,  
 4 21:00 on 28 Feb and 02:00 on 1 Mar.

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Fig. 12. Closure analysis of the total mass of LV and MV residuals from VTDMA at 300 °C and measured mass of EC or total of EC and OC<sub>2.4</sub> from the OC/EC analyzer.