



**Chemical mass  
balance of refractory  
particles ( $T = 300\text{ °C}$ )**

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# Chemical mass balance of refractory particles ( $T = 300\text{ °C}$ ) at the tropospheric research site Melpitz, Germany

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Received: 7 August 2013 – Accepted: 26 September 2013 – Published: 16 October 2013

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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## Abstract

In the fine particle mode (aerodynamic diameter  $< 1 \mu\text{m}$ ) refractory material has been associated with black carbon (BC) and low-volatile organics and, to a lesser extent, with sea salt and mineral dust. This work analyses refractory particles at the tropospheric research station Melpitz (Germany), combining experimental methods such as a mobility particle size spectrometer (3–800 nm), a thermodenuder operating at  $300^\circ\text{C}$ , a multi-angle absorption photometer (MAAP), and an aerosol mass spectrometer (AMS). The data were collected during two atmospheric field experiments in May/June 2008 as well as February/March 2009. As a basic result, we detected average refractory particle volume fractions of  $11 \pm 3\%$  (2008) and  $17 \pm 8\%$  (2009). In both periods, BC was in close linear correlation with the refractory fraction, but not sufficient to quantitatively explain the refractory particle mass concentration. Based on the assumption that BC is not altered by the heating process, the refractory particle mass fraction could be explained by the sum of black carbon BC (47% in summer, 59% in winter) and a refractory organic contribution estimated as part of the Low-Volatility Oxygenated Organic Aerosol (LV-OOA) (53% in summer, 41% in winter); the latter was identified from AMS data by factor analysis. Our results suggest that organics were more volatile in summer (May–June 2008) than in winter (February/March 2009). Although carbonaceous compounds dominated the sub- $\mu\text{m}$  refractory particle mass fraction most of the time, a cross-sensitivity to partially volatile aerosol particles of maritime origin could be seen. These marine particles could be distinguished, however, from the carbonaceous particles by a characteristic particle volume size distribution. The paper discusses the uncertainty of the volatility measurements and outlines the possible merits of volatility analysis as part of continuous atmospheric aerosol measurements.

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## 1 Introduction

Atmospheric aerosol particles are made of a large variety of organic and inorganic compounds. They affect global climate through direct and indirect radiative forcing (IPCC, 2007), the ecosystem (e.g. Bohlmann et al., 2005; Jickells et al., 2005; Molina and Molina, 2004) as well as human health (e.g. Gurjar et al., 2010; Ostro et al., 2007; Pope, 2000). Moreover, aerosol chemistry and thermodynamic properties (e.g. heterogeneous interactions and chemistry, condensation or evaporation of semi-volatile compounds on the particle phase) directly contribute to modify the chemical composition of both atmospheric gas and particle phases (e.g. Kolb and Worsnop, 2012; Pöschl et al., 2007). In a worldwide overview of sub- $\mu\text{m}$  chemical particle composition, Zhang et al. (2007) reported organic mass fractions between 20 and 90 % in  $\text{PM}_{10}$  depending on location and season. This organic fraction is difficult to characterize because it includes thousands of organic compounds, many of which have not been identified analytically. Organic aerosol particles are of biogenic and/or anthropogenic origin and can be emitted directly from these sources (primary organic aerosol – POA), or formed as a secondary organic aerosol (SOA) by chemical reactions of gas phase precursors such as Volatile Organic Compounds (VOCs) to form low volatility reaction products which can partition into particles (e.g. Kanakidou et al., 2005; Hallquist et al., 2009). The aerosol particle composition is strongly depending on the gas-to-particle partitioning of their constitutive compounds.

In studies related to the atmosphere, volatility analysis has proved to be useful to differentiate classes of inorganic compounds, such as particulate ammonium nitrate, ammonium sulfate, sulfuric acid, and sodium chloride (Schmid et al., 2002; Smith and O'Dowd, 1996). After the evaporation of high-volatile particulate compounds, volatility analysis leaves refractory particle cores containing material that is non-volatile at the given temperature. Hence, the volatilization temperature is, among others, a parameter that can be characteristic for certain classes of organic, but also inorganic compounds. In the fine particle mode (aerodynamic diameter  $< 1 \mu\text{m}$ ) non-volatile material has been

ACPD

13, 26981–27018, 2013

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associated with black carbon particles and low-volatile organic, and to a lesser extent with sodium chloride and crustal material (e.g. Engler et al., 2007; Huffman et al., 2009, 2008). While the volatilization temperatures of inorganic compounds are relatively well known (cf. Engler et al., 2007), they are more uncertainties for the organic phase; the ratio of more and less volatile compounds, in particular, strongly depends on the source of the particulate matter, and the stage of the aerosol within its atmospheric lifecycle. For example, the chemical composition as well as the thermodynamic properties of SOA are not constant over time but evolve during the aging processes of the aerosol (e.g. Donahue et al., 2012a). Therefore, Donahue et al. (2006) developed the Volatility Basis Set (VBS) approach, a model where organic aerosols formation and aging processes is described by their saturation vapor pressure ( $C^*$ ). SOA volatility depends on the cascade of reactions that happen during the aging processes, with functionalization leading to compounds with lower volatility, and fragmentation contributing to a higher volatility (Jimenez et al., 2009). A quantitative relationship between  $C^*$  and the organic aerosol oxidation state was introduced in an improved VBS model (2D-VBS, Donahue et al., 2011, 2012b).

A practical device to investigate aerosol particle volatility is the thermodenuder (TD). Here, aerosol particles are evaporated in the airborne state inside a heated flow tube at defined temperature. See Burtscher et al. (2001) for a survey of the design of different TDs. The TD can, in principle, be combined with most particle sampling techniques and on-line particle sizing and classification instruments. Volatility tandem differential mobility analyzers (V-TDMA; Rose et al., 2006; Philippin et al., 2004) have been used to measure the shrinkage of monodisperse particles after volatilization. The volatility twin differential mobility particle sizer (V-TDMPS; V-SMPS), in contrast, measures complete particle number size distributions upstream and downstream of the TD (Ehn et al., 2007; Engler et al., 2007). Comparing integral particle properties such as number and volume upstream and downstream of a TD allows estimating the refractory fraction at the given temperature. In order to investigate the refractory part of atmospheric aerosol particles on a long term basis, continuous V-TDMPS or V-SMPS measurements have

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been implemented at several atmospheric observation sites in Germany: the rural re-  
search site Melpitz (Engler et al., 2007), the HGMU urban monitoring site Augsburg  
(Birmili et al., 2010), and six other stations inside the German Ultrafine Aerosol Net-  
work (GUAN; Birmili et al., 2009). In all cases, a temperature of  $300\text{ }^{\circ}\text{C}$  was selected in  
the thermodenuder. The reason for choosing this temperature is that sulfates, nitrates  
and most organic compounds would be stripped off while the charring of organic matter  
would be prevented in the presence of atmospheric oxygen (cf. Engler et al., 2007).

The motivation to monitor black carbon and other refractory particle compounds in  
atmospheric networks involves, on the one hand, the necessity to help quantify the  
regional and global effect of light absorption (Cheng et al., 2009; Koch et al., 2009;  
Stier et al., 2007; Bond and Bergstrom, 2006). On the other hand, atmospheric soot  
particles and refractory compounds have been associated with certain adverse health  
effects by epidemiological and toxicological studies (Attfield et al., 2012; Janssen et al.,  
2012; Mazzarella et al., 2007; Totlandsdal et al., 2012). A monitoring strategy such as  
pursued in GUAN attempts to provide experimental data that can be used to address  
both issues mentioned above. As an additional issue, volatility instruments have also  
been used to examine the evolution of the atmospheric nucleation mode. A substantial  
observation has been that each particle of the evolving atmospheric nucleation mode  
seems to contain a refractory core at  $300\text{ }^{\circ}\text{C}$ , even though these particles were initially  
formed purely from gas-to-particle conversion at ambient temperatures (Ehn et al.,  
2007; Wehner et al., 2005).

Recently, an Aerosol Mass Spectrometer (AMS, e.g. Canagaratna et al., 2007) was  
combined with the TD, allowing a direct investigation of the chemical composition of  
the refractory fraction (Faulhaber et al., 2009; Huffman et al., 2009, 2008; Wu et al.,  
2009). These measurements point out that the refractory fraction is not only made of  
black carbon and crustal material (which cannot be detected by the AMS), even at tem-  
peratures higher than  $200\text{ }^{\circ}\text{C}$ , but that the presence of a refractory organic fraction has  
to be considered as well. These remaining organic compounds represent an important  
description parameter for a better estimation of the atmospheric organic aerosol (OA)

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since it should be only negligibly influenced by dilution and gas-to-particle equilibrium. Improving our understanding on this low-volatile organic fraction is necessary in order to improve the current SOA models, to better estimate the impact of the OA to the global aerosol mass loading and to finally better predict the organic contribution to both climate and human health.

In this study, a mass closure study based on parallel Thermodenuder (TD), Aerosol Mass Spectrometer (AMS), and MAAP measurements to identify the composition of refractory fraction at  $300\text{ }^{\circ}\text{C}$  during two intensive campaigns in May/June 2008 and February/March 2009 at the TROPOS Central European regional atmospheric research station Melpitz (Germany) is performed. A simple method will be used to estimate the refractory chemical composition, principally based on laboratory measurements performed using a similar TD running in comparable conditions as well as on comparisons with similar measurements available in the literature. The influence of the meteorological conditions as well as of the air mass origin on the non-volatile fraction will be discussed.

## 2 Experimental

### 2.1 The TROPOS research station Melpitz (Germany)

Atmospheric aerosol measurements were performed at the TROPOS research station Melpitz ( $51.54^{\circ}\text{N}$ ,  $12.93^{\circ}\text{E}$ ,  $86\text{ m a.s.l.}$ ),  $50\text{ km}$  to the east of Leipzig, Germany. The station has been used since 1992 to examine the effect of atmospheric long range transport on local air quality. The site itself is mainly surrounded by agricultural pastures and forests. The atmospheric aerosol observed at Melpitz can be regarded as representative for Central European regional conditions, as confirmed by multiple site comparisons within the programme EMEP (co-operative programme for monitoring and evaluation of the long-range transmissions of air pollutants in Europe, Aas et al., 2012) and the GUAN Network (Birmili et al., 2009).





tailed in Canonaco et al. (2013). Further details on the factor analysis results can be found in Crippa et al. (2013a).

## 2.2.2 MAAP

The Black carbon (BC) mass concentration was estimated by a Multi-Angle Absorption Photometer (MAAP, Model 5012, Thermo-scientific, Petzold and Schönlinner, 2004). This instrument internally converts the absorption coefficient measured at a wavelength of 637 nm to the soot mass concentration by applying a constant mass absorption coefficient of  $6.6 \text{ m}^2 \text{ g}^{-1}$ . This value was determined from a combination of independent measurements of the absorption coefficient using the MAAP and the soot mass concentration applying a thermographic method for urban aerosol samples (Petzold and Schönlinner, 2004). However, model calculations and experimental literature results suggest that the mass absorption coefficient of atmospheric soot particles is not constant, but may depend on the state of mixture with other compounds (Fuller et al., 1999). The analysis of graphitic carbon from MAAP filter samples at various GUAN sites using Raman-spectroscopy yielded an average mass absorption efficiency of  $5.3 \text{ m}^2 \text{ g}^{-1}$  for Germany (Nordmann et al., 2013), which differs from the default mass absorption efficiency of  $6.66 \text{ m}^2 \text{ g}^{-1}$ . This implies a systematic uncertainty of BC derived from the MAAP measurements, depending on which mass absorption efficiency is used.

An additional source of error is the measurement accuracy of an individual MAAP instrument. Direct intercomparison of multiple MAAP instruments yielded a variability of less than 5% around the mean value (Müller et al., 2011). Another correction was necessary in this work: at Melpitz, the MAAP is operated downstream of a  $\text{PM}_{10}$  inlet. Our subsequent calculations, however, refer to  $\text{PM}_1$ . We converted BC ( $\text{PM}_{10}$ ) to BC ( $\text{PM}_1$ ) by multiplication with a factor of 0.9, which was obtained by running two MAAPs at Melpitz side by side with different inlets (cf. Poulain et al., 2011). Considering instrumental, mass absorption efficiency and size cutting uncertainties, a global uncertainty of approximately 15% on the  $\text{PM}_1$  BC mass concentration can be expected.

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## 2.3 Ambient and refractory particle number size distributions

Particle number size distributions (3–800 nm) were continuously measured upstream and downstream of a TD using a volatility twin differential mobility particle sizer (V-TDMPS). The TD follows the design of Wehner et al. (2002). Briefly, it consists of a heating section (50 cm) followed by a cooling section filled with active carbon to remove evaporated material and to cool down the sample to room temperature. The TD was used at a flow rate between 2.5 and 3.0 L min<sup>-1</sup> (corresponding to a residence time on the heating section of approximately 1.0 and 0.8 s, respectively) and at a constant temperature of 300 °C.

A Twin Differential Mobility Particle Sizer (TDMPS, Birmili et al., 1999) was deployed to measure particle number size distributions from 3–800 nm mobility diameter with a time resolution of 10 min, changing its sampling inlet between atmosphere aerosol and this aerosol after passing through the thermodenuder. The system consisted of two Differential Mobility Analyzers (DMA, Hauke-type) and two Condensation Particle Counters (CPC, TSI model 3010 and TSI model 3025). The sheath air was circulated in closed loops for both DMAs. The evaluation of particle number size distributions includes a multiple charge inversion, the CPC efficiency and diffusional losses in the DMA and all internal and external sampling lines according to the recommendations in Wiedensohler et al. (2012). The V-TDMPS data was additionally corrected for particle losses due to diffusion inside the TD. The particle volume concentrations are calculated from the measured number size distribution assuming spherical particles. The volume fraction remaining (VFR) was determined by dividing the refractory volume concentration measured downstream of the TD by the total particle volume measured at ambient temperature, i.e. by-passing the TD.

## 2.4 Off-line chemical characterization

During the 2008 campaign, daily PM<sub>2.5</sub> High Volume DIGITEL filter samples (Digital Elektronik AG, Hegnau, Switzerland) were collected from midnight to midnight, while

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during the 2009 campaign, daily  $\text{PM}_{10}$  High Volume DIGITEL filter samples were taken. A 5-stage BERNER impactor (Hauke, Austria, Berner and Lurzer, 1980) was deployed on individual days (from midnight to midnight) during February/March 2009. All filters were analyzed according to the same analytical methods. Filters were weighted for the total particle mass and inorganic cations and anions as well as OC and EC were determined. Details on the different analytical methods and results for these two specific periods can be found in Spindler et al. (2010).

### 3 Results

#### 3.1 Mass closure

Before discussing the volatility measurements, the balance of  $\text{PM}_{10}$  particle mass obtained from AMS and MAAP on the one hand, and the TDMP5 on the other hand is examined. To convert the particle volume concentration from the TDMP5 into a mass concentration, we estimated the gravimetric particle density on the basis of measured chemical composition using Eq. (1) (Salcedo et al., 2006). In this equation, the density of ammonium nitrate and ammonium sulfate was assumed to be  $1.75\text{ g cm}^{-3}$  (Lide, 1991), the density of ammonium chloride as  $1.52\text{ g cm}^{-3}$  (Lide, 1991), the density of organic matter as  $1.2\text{ g cm}^{-3}$  (Turpin and Lim, 2001) and the density of BC as  $1.77\text{ g cm}^{-3}$  (Park et al., 2004).

$$\text{density} = \frac{[\text{Total}_{\text{AMS}} + \text{BC}]}{\frac{[\text{NO}_3^-] + [\text{SO}_4^{2-}] + [\text{NH}_4^-]}{1.75} + \frac{[\text{Cl}^-]}{1.52} + \frac{[\text{Org}]}{1.2} + \frac{[\text{BC}]}{1.77}} \quad (1)$$

Applying the density to measured particle composition, a mean density of  $1.4\text{ g cm}^{-3}$  for May/June 2008 and  $1.6\text{ g cm}^{-3}$  for February/March 2009 was obtained, respectively. The reconstructed mass concentrations are presented in Fig. 1 and show a reasonable correlation with  $R^2 = 0.90$  in 2008, and  $R^2 = 0.88$  in 2009.

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It needs to be noted that the mass concentrations derived from the TDMPs are on average 20 % higher than those derived from AMS and MAAP (Fig. 1) which is close to previous comparisons (e.g. Mensah et al., 2012; Setyan et al., 2012). This deviation is within the range of instrumental uncertainties provided by the methods used: TDMPs total particle volume ( $\pm 10\%$ ), BC PM<sub>1</sub> mass concentration (15 %), AMS mass concentrations (30 %), density estimation. In addition, another source of uncertainties related to the different size cut offs of the AMS and TDMPs has to be considered. The transmission efficiency of the AMS aerodynamic lenses starts decreasing towards 700 nm (mobility), so that the mass concentration of non-refractory compounds measured by the AMS might underestimate the one measured by the TDMPs (upper size range 800 nm mobility). Differences due to different amounts of water present in the particulate phase as a result of particle hygroscopicity can be neglected because the relative humidity in the sample aerosol was always below 30 %.

### 3.2 Ambient and refractory particle volume concentrations

Figure 2 shows the time series of the ambient and refractory particle volume concentrations obtained from the TDMPs, in conjunction with the volume fraction remaining (VFR) at 300 °C. The VFR is higher in the February/March 2009 period ( $17 \pm 8\%$ ; mean  $\pm$  standard deviation) compared to the May/June 2008 period ( $11 \pm 3\%$ ). It can also be seen that the VFR shows considerable variations with time, although to a lesser extent than the total particle volume concentrations. Such seasonality may be due to a change in the aerosol chemical composition as discussed in the following sections. In order to directly compare the refractory particle volume concentration (RVC) measured after the TD with the aerosol chemical composition, it is essential to convert it into refractory mass concentration (RMC). As discussed above, the particle density directly depends on its chemical composition. However, in contrary to ambient particles, the chemical composition of the refractory fraction is unknown. Therefore, in the following, a constant density of  $1.6\text{ g cm}^{-3}$  was applied to convert the TD measurements into mass concentration.

### 3.2.1 Black carbon contribution to the refractory mass concentration

Black carbon is considered as a major refractory component in sub- $\mu\text{m}$  PM (e.g. Pöschl, 2005). During the GUAN project, Birmili et al. (2009) found linear relationships between the BC mass concentrations and the refractory volume concentrations for 5 different atmospheric measurement sites. It is therefore a strong hypothesis that BC constitutes a major part of the RMC.

Detailed correlations between refractory particles and BC are shown in Fig. 3a and c. The correlations between the calculated refractory particle mass concentration and the BC concentration yield slopes well below 1, and measures of determination ( $R^2$ ) of 0.86 (May/June 2008) and 0.80 (February/March 2009). Similar slopes were obtained for the 2008 (0.38) and 2009 (0.36) periods. These results confirmed that BC alone cannot explain the entire refractory mass fraction.

### 3.2.2 Inorganic contribution to the refractory mass concentration

In the continental troposphere, the inorganic sub- $\mu\text{m}$  particulate fraction consists of major amounts of ammonium nitrate and ammonium sulfate. This was confirmed for Melpitz by Poulain et al. (2011). Ammonium nitrate is a semi-volatile compound that starts evaporating at 30 °C, while ammonium sulfate is a less volatile compound, evaporating only at around 150 °C from the particulate phase in a thermodenuder of our type (Wu et al., 2009). Consequently, no ammonium nitrate or sulfate are expected to remain in the particulate phase at 300 °C.

It can be thought that other inorganic compounds, such as chloride, sodium, calcium, potassium, or magnesium remain in the particulate phase at 300 °C. However, their concentrations were rather low compared to the concentrations of ammonium sulfate and nitrate, as suggested by Digital filter samples taken simultaneously with our study (Daily PM<sub>2.5</sub> filter samples were taken during May/June 2008, while daily PM<sub>1</sub> filter samples were taken during February/March 2009). Specifically, chloride, sodium, calcium, potassium, and magnesium accounted for around 13 % of the total inorganic

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PM<sub>2.5</sub> mass and for around 4 % of the total inorganic PM<sub>1</sub> mass (Poulain et al., 2011; Spindler et al., 2010).

### 3.2.3 Organic contribution to the refractory mass concentration

In this section, we discuss the possible organic contribution to the refractory particle mass concentration (RMC), based on the AMS measurements. Figure 4 illustrates the mass balance for the refractory particle mass, which is described in detail in the following.

As described in Sect. 2.2.1., factor analysis of organic aerosol matter was performed using the ME-2 approach to describe the organic aerosols. A detailed description of the ME-2 analysis can be found in Crippa et al. (2013a) and is summarized in Supplement SI-1. Only the main results will be discussed here. In May/June 2008, three factors were identified to explain the total organic aerosol (OA). These factors correspond to Low-Volatility Oxygenated Organic Aerosol (LV-OOA, 46.7 % of total OA), Semi-Volatile Oxygenated Organic Aerosol (SV-OOA, 45.7 % of total OA) and Hydrocarbon-like Organic Aerosol (HOA, 7.5 % of total OA). In February/March 2009, an additional factor was found, and identified as biomass burning emissions (Biomass Burning Organic Aerosol or BBOA, 13.3 % of total OA). During this period, LV-OOA, SV-OOA and HOA represent 43.4, 32.9 and 10.3 % of total OA, respectively. HOA and BBOA are related to primary organic aerosol sources: BBOA represents biomass burning while the HOA is more related to traffic and liquid domestic fuel combustion. LV-OOA and SV-OOA are more related to secondary organic aerosol. LV-OOA is known to be associated with more oxygenated OA with the lowest volatility, while the SV-OOA is commonly considered to be representative for freshly generated OA made of less oxygenated OA, with a higher volatility than LV-OOA (e.g. Jimenez et al., 2009; Lanz et al., 2007; Ulbrich et al., 2009).

Previous field measurements using coupled TD-AMS set-up (Huffman et al., 2009) demonstrated that at 250–270 °C, SV-OOA, HOA and BBOA nearly fully evaporated (with a mass fraction remaining (MFR) near or below 10 %), while LV-OOA presents

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a MFR of 70–30 %, depending on the location. Because LV-OOA has a similar mass spectrum as Humic Like Substances (HULIS), Wu et al. (2009) investigated the temperature dependency of the volatility of fulvic and humic acids as surrogate for HULIS, using a similar TD-AMS setup as in the present study. Within that study it was found that these two compounds present a MFR of 47 % for fulvic acid and 58 % for humic acid after being heated at 300 °C, in agreement with the field observations made by Huffman et al. (2009). Kondo et al. (2011) reported an evaporation of 10–30 % for laboratory generated monodisperse particles of different surrogates of atmospheric HULIS heated at 300 °C and 400 °C with a residence time inside the heated part of 0.3 s. Although direct comparisons between the different TD measurement can be strongly influenced by the residence time of the particle inside the heated section (An et al., 2007), the previous works are in good agreement and confirm that a large fraction of the HULIS are not evaporated even after being heated at high temperatures.

Since Wu et al. (2009) used the same TD setup as in the present work, the refractory organic aerosol (ROA) mass concentration was estimated to represent 52 % of the measured LV-OOA, which is the mean value of the measured surrogate of HULIS used by the authors. This is also in agreement with the mean value of the Huffman et al. (2009) observations.

Time series of the estimated ROA fraction for each season are presented in Fig. 4 and the relationship with the measured refractory mass concentration is shown in Fig. SI-2 (Supplement). The relationship between ROA and the measured refractory mass shows a correlation slope of 0.74 ( $R^2 = 0.51$ ) and 0.24 ( $R^2 = 0.34$ ) for 2008 and 2009, respectively (Fig. SI-2a and d). These results will be discussed in the following.

### 3.3 Assessment of the refractory particles chemical composition

Figures 4 and 5 illustrate the time series and inter-parameter correlations of BC, ROA, and the refractory mass concentration (RMC) derived from the V-TDMPS. Overall, the May/June 2008 period exhibits higher mass concentrations than the February/March 2009 period. In both periods, the RMC proves to be highly variable on the

scale of hours. A look at the time series of RMC estimated from AMS/MAAP and measured by the V-TDMPS shows a significant covariance, down to the time scale of hours, although the mean values do not coincide during all periods.

The good correlation (slope of 1.11,  $R^2 = 0.77$ ) during May/June 2008 indicates that the measured refractory fraction at 300 °C can be quantitatively explained by BC and ROA (Fig. 5a). In this case, the ROA represents  $66 \pm 8\%$  of the reconstructed refractory mass. In contrast, only 60 % of the measured refractory mass during February/March 2009 can be explained by the same approach (Figs. 4 and 5d). In that second case, the ROA represents  $41 \pm 13\%$  of the reconstructed refractory mass.

It should be noted that the discrepancy between estimated and measured RMC was not constant over the whole measurement period in February/March 2009. On some days, balance was matched (e.g. 16, 17, 25, 26, 27 March) while on others, a large discrepancy could be observed (e.g. 18–19 March 2009, and the first days of the measurement period). Interestingly, the largest differences usually occurred when particles consisted of a particularly large refractory fraction (Figs. 2 and 4). For example, on 18 March 2009, the VFR was 60 %. In order to better understand the limits of our approach and to draw some hypotheses to explain the discrepancies, it is essential to go into more details on the different factors that could influence each time period.

### 3.4 Discussion

Our results suggest that the refractory particle mass fraction (RMF) could be fully explained by BC and ROA during May/June 2008, while about one third of this balance remained unexplained in February/March 2009. We now scrutinize two reasons for this deviation: particle size distribution, and chemical particle composition.

#### 3.4.1 Influence of the particle volume size distribution

Figure 6 shows contour diagrams of the ambient and refractory particle volume size distributions, and the ratios between AMS/MAAP-based and TDMPS-based refractory

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particle mass concentrations. The basic effect is that the overall particulate volume decreases, and the particle diameters shrink after passage through the TD. This is consistent with earlier observations (Birmili et al., 2010; Ehn et al., 2007; Engler et al., 2007). However, for certain periods, the refractory volume size distribution increases in concentration above 400 nm. This effect is visible in Fig. 6, and even better in Fig. 7. Refractory particles bigger than 400 nm can occasionally dominate refractory volume size distribution, during events that occurred more frequent in February/March 2009 than in May/June 2008. Prominent examples are 13 and 18 March 2009.

What is the origin of these refractory particles bigger than 400 nm? Most of these particles do not appear in the ambient particle volume distribution (Figs. 6 and 7). We can therefore only think of particles originating in the particle size range above 800 nm, i.e. outside of the measurement range of the TDMPS. The entrance of such particles into the V-TDMPS system is principally possible via the  $PM_{10}$  inlet. It is therefore our conclusion that the high value of measured RMC can be influenced by marine super- $\mu$ m particles which shrink during passage through the TD and move into the sub- $\mu$ m measurement range of the TDMPS. In some sense, this is a measurement artifact because these particles can only be detected by the TDMPS downstream of the thermodenuder, not upstream.

It was a conspicuous observation that the events on 13 and 18 March 2009 were connected with maritime air masses, as indicated by 96 h back trajectories from the NOAA HYSPLIT trajectory model (Draxler and Hess, 2004). For example, on 18 March 2009, the air mass originated over the Atlantic, spending only the last 15–16 h over the continent before reaching Melpitz. By crossing polluted areas, the marine aerosol aged quickly either by mixing and/or condensation with other aerosols or by heterogeneous reactions (e.g. conversion of NaCl into  $NaNO_3$  and/or  $Na_2SO_4$ ) as well as by in-cloud processes. Therefore, the air mass reaching Melpitz needs to be considered as processed marine air mass rather than fresh marine air mass. Analyses of 5-stages Berner impactor samples for this day revealed unusually high contributions of sulfate, nitrate,

chloride and sodium in the coarse mode (stage 4), which are indicators of sea spray origin particles (Fig. SI-4).

Similar events took place on 13 March 2009, compared to 11 March 2009, which was more under continental influence (Fig. SI-4). The nitrate mass concentration on stage 4 has to be related to the presence of sodium nitrate, a result of the reaction of NaCl and HNO<sub>3</sub> (e.g. Dasgupta et al., 2007). Contrary to ammonium nitrate, which is a semi-volatile compound, sodium nitrate is a low-volatile compound (volatilization temperature > 300 °C, Pinnick et al., 1987), considered to represent a permanent removal pathway for atmospheric nitrate. A similar mechanism can also lead to the formation of sodium sulfate (e.g. Sievering et al., 1995). Contrary to sodium nitrate, the hydrated salt of sodium sulfate is a semi-volatile compound (melting point 32 °C) which could easily evaporate when crossing the TD.

Moreover, it is known that organic acids can contribute to the chloride depletion on marine aerosol, leading to the formation of sodium salts (e.g. Kerminen et al., 1999; Zhao and Gao, 2008). Consequently, an interesting parallel can be drawn to volatility measurements of succinic acid and its disodium salts made by Wu et al. (2009). Although succinic acid is a semi-volatile compound that fully evaporates at 65 °C, in similar sampling conditions than the present study, Wu et al. (2009) demonstrated that its disodium salt shows a mass fraction remaining of 40 % after being heated at 300 °C. Consequently, regarding the strong marine air mass influence, the presence of such compounds in the coarse mode and after crossing the TD is highly possible and should strongly influence the refractory organic mass fractions. Although a strong influence of the particles larger than 1 µm on the measured refractory particle mass fraction downstream to the TD was clearly identified, it is not possible to confirm or reject the presence of sodium nitrate and/or other organic salts in the refractory particle mass fraction, since no direct measurements of the aerosol chemical composition downstream to the TD were performed.

As mentioned above, effects of super-µm particles seem to be limited to the refractory particle size range above 400 nm (dotted lines in Figs. 6 and 7). Therefore, we

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recalculated RMC for a new size range corresponding to 3–400 nm mobility diameter (Figs. 3 to 6). This alternative approach reveals that most of the time the VFR is not particularly sensitive to the choice of the upper integration limit ( $VFR_{(400\text{ nm})} = 8 \pm 4\%$  and  $16 \pm 6\%$  for 2008 and 2009, respectively). A direct consequence is the enhancement of the BC contribution of total refractory to 54 % and 58 % of the measured refractory mass for 2008 and 2009, respectively (Fig. 3b and d) and the refractory mass concentration for February/March 2009 can be fully explained by the model now (Figs. 4 and 5e). Based on the reconstructed refractory mass, it suggests that refractory aerosol at 300 °C was made, in averaged, for  $59 \pm 16\%$  of BC and  $41 \pm 13\%$  of ROA during this period. However, the reconstructed refractory mass fraction for May/June 2008 strongly over-estimates the measured one (Fig. 5b). This is mainly due to the fact that ROA already overestimates the measured refractory mass (Fig. SI-2b). Nevertheless, no significant change on the correlation coefficient ( $R^2$ ) was observed for this period, indicating that only the absolute refractory mass concentration was affected by the adjustment of the upper size range and not the time series itself in opposite to the February/March 2009 campaign. Consequently, larger particles seem to have a lower influence in this period than during February/March 2009.

### 3.4.2 Influence of the chemical composition

Estimation of the refractory aerosol mass was only based on the chemical composition measured by the AMS, and the BC concentration, measured by the MAAP. Therefore, the presence of non-detected compounds like crustal material and/or sea-salts has to be considered. As previously mentioned, the contribution of non-measured inorganic ions represents 13 % of the total  $PM_{2.5}$  mass concentration in May/June 2008 and 4 % of the total  $PM_1$  mass concentration in February/March 2009. Additionally, identified species of daily  $PM_1$  filter explain on average  $80 \pm 12\%$  of the total filter mass in February/March 2009. Consequently, it is reasonable to consider that chemical particle composition was usually fully explained and that, finally, the non-considered compounds might have a small influence on the reconstruction of the refractory fraction. However,

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ple, e.g., by a pre-impactor. It might be desirable in the future to extend the V-TDMPS with an aerodynamic particles sizer (APS), or alternatively remove particles by a pre-impactor.

Comparing the two periods, our results suggest a possible change on the LV-OOA volatility with a highest volatility in May/June 2008 (MFR = 30 %) than in February/March 2009 (MFR = 52 %). Possible reason might be change on oxidation states and/or LV-OOA origins. Nevertheless, our results emphasize a significant contribution of OA to the refractory particle mass fraction (53 % and 41 % in May/June 2008 and February/March 2009, respectively) and also suggest a possible change on their volatility properties during the run of a year. More direct measurements using aerosol mass spectrometer downstream of the thermodenuder are needed (for example with AMS during intensive period or with ToF-ACSM for longer period). Because OA do not completely evaporate at 300 °C, the refractory OA particle mass fraction would remain in the particle phase. An influence of the thermodynamic properties of atmospheric particles might be responsible for the current underestimation of SOA particle mass concentrations in the atmospheric models.

**Supplementary material related to this article is available online at <http://www.atmos-chem-phys-discuss.net/13/26981/2013/acpd-13-26981-2013-supplement.pdf>.**

*Acknowledgements.* We gratefully acknowledge support by the German Federal Environment Agency (Umweltbundesamt), grants No. 351 03 031 and 351 01 038, and UFOPLAN grant 3703 43 200 (title “Erfassung der Zahl feiner und ultrafeiner Partikel in der Außenluft”). We acknowledge support by the European Integrated Project on Aerosol Cloud Climate and Air Quality Interaction (EUCAARI). We further appreciate extensive instrumental support by Joachim Grüner and Thomas Tuch at the TROPOS Melpitz field site.

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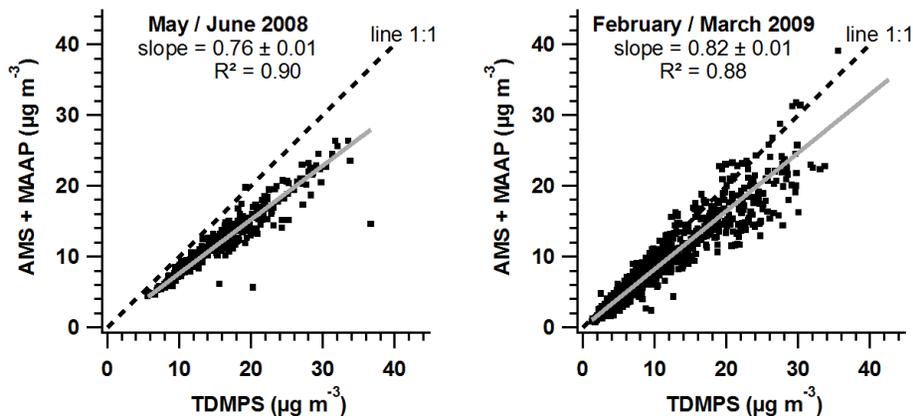
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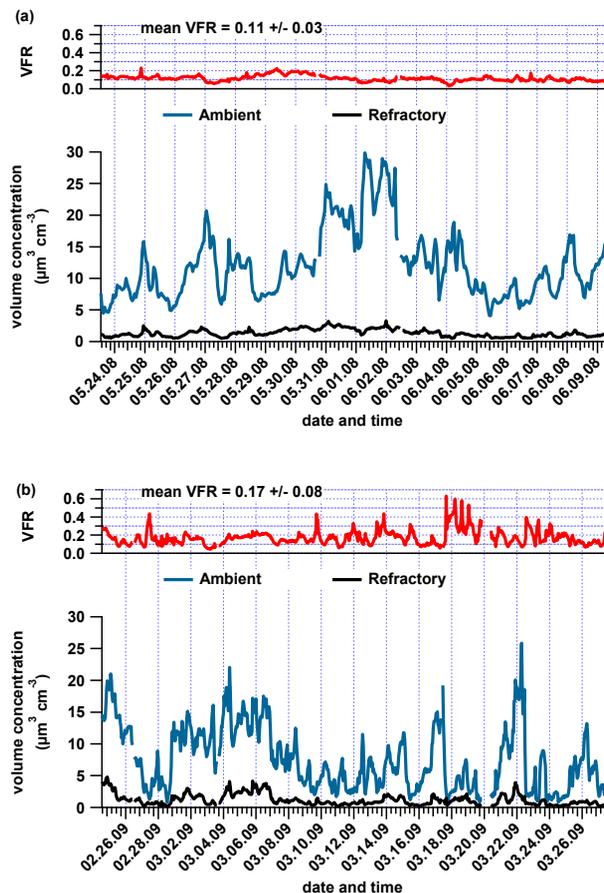


**Fig. 1.** Measured AMS+MAAP mass concentration vs. TDMPS estimated mass concentration for May/June 2008 (left) and February/March 2009 (right) periods. Estimation of the TDMPS mass concentration was made using Eq. (1). Correlation curves were calculated using the least orthogonal distance fit method.

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**Fig. 2.** Time series of the ambient and refractory volume concentration measured during May/June 2008 **(a)** and February/March 2009 **(b)** periods. The volume fraction remaining (VFR) for each time period is also presented on the top panel of each plot, including the mean value ( $\pm 1\sigma$ ) for each measurement period.

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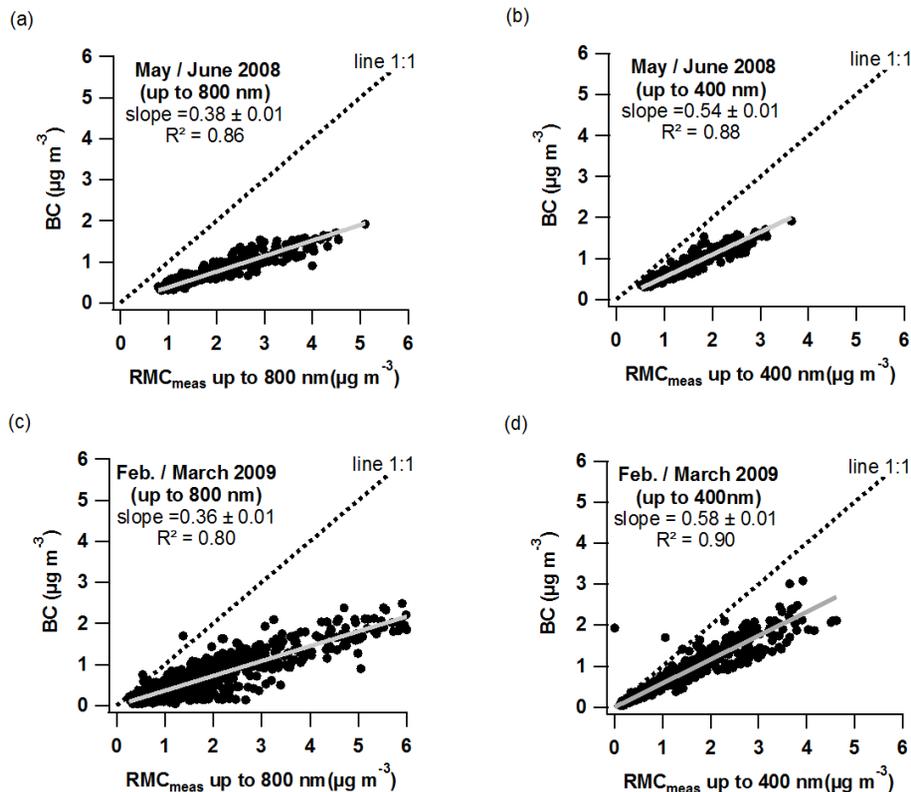
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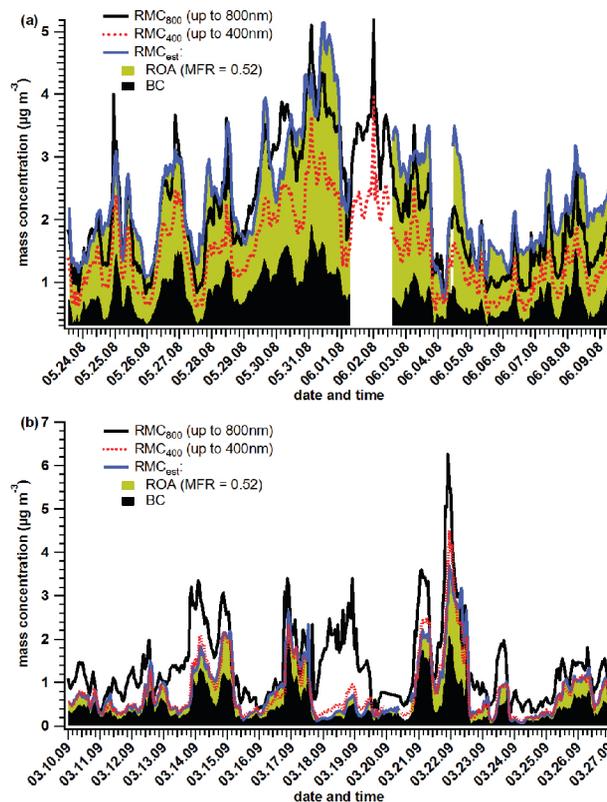
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**Fig. 3.** Black carbon (BC) vs. the refractory mass concentration (RMC) estimated from the TDMPMS for May/June 2008 and February/March 2009 periods. Estimation of the refractory mass concentration was made assuming a density of  $1.6\text{ g cm}^{-3}$ . The left panels correspond to the total V-TDMPMS size range (up to 800 nm) while the right panels refer to a size cutting of 400 nm (up to 400 nm). Correlation curves were calculated using the least orthogonal distance fit method.

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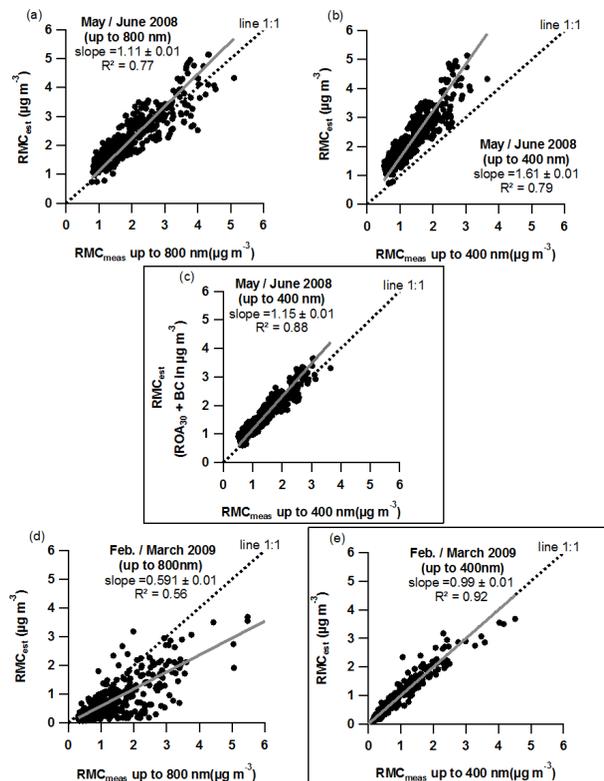
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**Fig. 4.** Time series of the estimated refractory OA (ROA) and BC for May/June 2008 **(a)** and February/March 2009 **(b)**. Time series of the resulting estimated and measured refractory particle mass concentration (RMC) are included as blue and black solid lines, respectively. The V-TDMPS results were converted in mass concentration assuming a constant density of  $1.6\text{ g cm}^{-3}$ . The red dotted lines correspond to RMC measured with upper size cutting of 400 nm (see discussion in Sect. 3.4.1).

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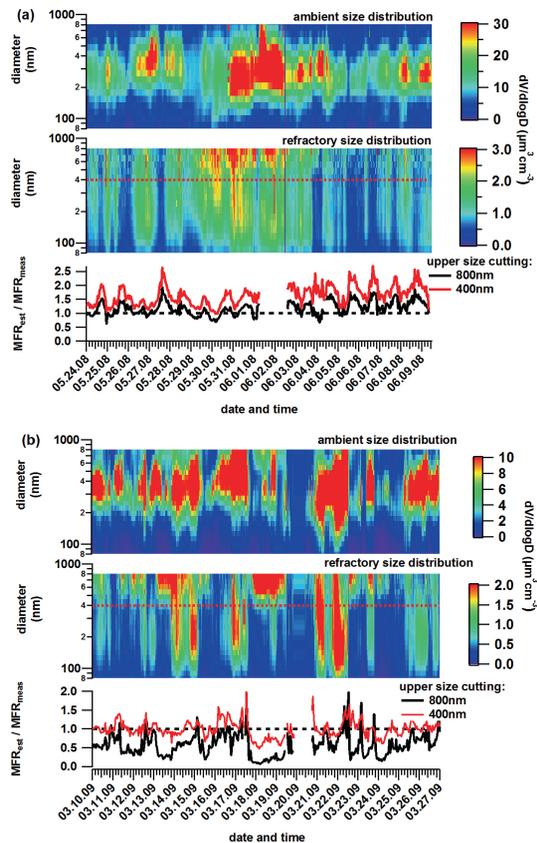
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**Fig. 5.** Comparison of the estimated ( $RMC_{est}$ ) with the measured ( $RMC_{meas}$ ) refractory particle mass concentration (RMC). Three different approaches were used to estimate the refractory particle mass fraction; using the full V-TDMPS size range, (up to 800 nm) or size cutting of 400 nm (up to 400 nm) and finally for May/June 2008, the refractory organic aerosol (ROA) was also estimated based on only 30 % of the measured LV-OOA ( $ROA_{30}$ ). The two encased scatter plots correspond to the better solution obtained for each periods (see text for discussion).

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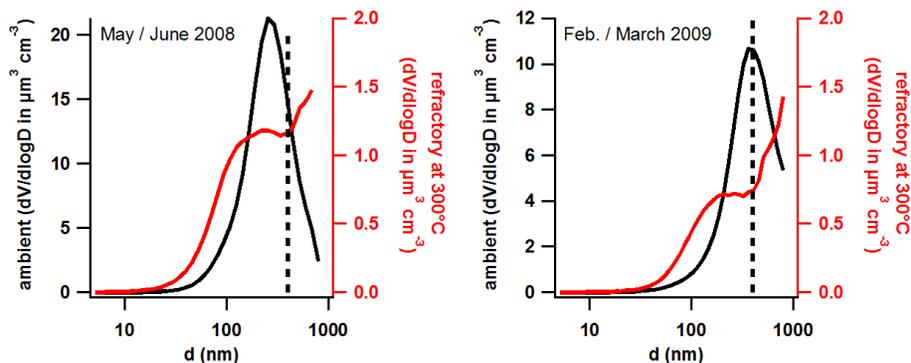
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**Fig. 6.** Cross-sensitivity effects of the sea-spray source: particle volume size distributions upstream and downstream of the thermodenuder, and the ratios of the mass fraction remaining (MFR) estimated to measure at the 2 upper size cutting (800 nm and 400 nm) for **(a)** May/June 2008, **(b)** February/March 2009. The red dotted lines mark the cut-off of 400 nm (see Sect. 3.4.1).

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**Fig. 7.** Average particle volume size distribution measured at ambient temperature (black) and after crossing the TD (red) for the 2 campaigns. The dotted lines mark the cut-off diameter of 400 nm.

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