



Measurement of nonvolatile particle number size distribution

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Received: 30 March 2015 – Published in Atmos. Meas. Tech. Discuss.: 25 June 2015

Revised: 21 November 2015 – Accepted: 1 December 2015 – Published: 18 January 2016

Abstract. An experimental methodology was developed to measure the nonvolatile particle number concentration using a thermodenuder (TD). The TD was coupled with a high-resolution time-of-flight aerosol mass spectrometer, measuring the chemical composition and mass size distribution of the submicrometer aerosol and a scanning mobility particle sizer (SMPS) that provided the number size distribution of the aerosol in the range from 10 to 500 nm. The method was evaluated with a set of smog chamber experiments and achieved almost complete evaporation (> 98 %) of secondary organic as well as freshly nucleated particles, using a TD temperature of 400 °C and a centerline residence time of 15 s.

This experimental approach was applied in a winter field campaign in Athens and provided a direct measurement of number concentration and size distribution for particles emitted from major pollution sources. During periods in which the contribution of biomass burning sources was dominant, more than 80 % of particle number concentration remained after passing through the thermodenuder, suggesting that nearly all biomass burning particles had a nonvolatile core. These remaining particles consisted mostly of black carbon (60 % mass contribution) and organic aerosol (OA; 40 %). Organics that had not evaporated through the TD were mostly biomass burning OA (BBOA) and oxygenated OA (OOA) as determined from AMS source apportionment analysis. For periods during which traffic contribution was dominant 50–60 % of the particles had a nonvolatile core while the rest evaporated at 400 °C. The remaining particle mass consisted mostly of black carbon with an 80 % contribution, while OA was responsible for another 15–20 %. Organics were mostly hydrocarbon-like OA (HOA) and OOA. These results suggest that even at 400 °C some fraction of the OA does not evaporate from particles emitted from com-

mon combustion processes, such as biomass burning and car engines, indicating that a fraction of this type of OA is of extremely low volatility.

1 Introduction

Atmospheric aerosols, also known as particulate matter (PM), are defined as a suspension of fine solid or liquid particles in a gaseous medium. These particles range in size from a few nanometers in diameter to as much as 100 µm. Aerosols consist of inorganic ions, organic compounds, oxides of most metals, elemental carbon, and water with organic compounds often being the dominant fraction of submicrometer PM, with a contribution of 20–90 % depending on the location (Kanakidou et al., 2005).

Fine particles (PM_{2.5} defined as the dry mass of particles collected after a particle separator with a 50 % cut point of 2.5 µm aerodynamic diameter) can affect human health by penetrating into the respiratory tract and reaching deep into the lungs (Miller et al., 1979; Dockery et al., 1993; Künzli et al., 2005; Wyler et al., 2000; Cohen et al., 2005). Toxicological data suggest that ultrafine particles, the diameter of which is < 100 nm, can have adverse pulmonary and cardiovascular effects (Donaldson and MacNee, 2001). Ultrafine particles soluble in water and lipids have a minor contribution to the total aerosol mass and are believed to have minor effects on human health (Kreyling and Scheuch, 2000) but insoluble components, like black carbon (BC), could have more significant contribution (Fuzzi et al., 2015; Terzano et al., 2010). The impacts of these ultrafine insoluble particles cannot be easily determined with mass measurements but require studies of the number concentration.

Atmospheric particulate matter can also affect the Earth's radiative budget and global climate. Particles act as cloud condensation nuclei, form cloud droplets, and scatter light, leading to cooling of the planet. Absorbing aerosol components, such as BC, contribute to warming by strongly absorbing light. BC containing particles, mostly emitted by combustion sources, evolve due to coagulation or condensation of vapors (Scheer et al., 2005). This coating of BC particles can increase not only their light absorption up to a factor of 3 (Andreae and Gelencsér, 2006; Saleh et al., 2014) but also their hygroscopicity (Kuwata et al., 2008). The number concentration, size distribution, and mixing state of BC particles are essential in understanding their effect on climate (Bond et al., 2013).

Since the number concentration of ultrafine atmospheric particles, especially of the nonvolatile BC particles, plays a key role in both their health and climate effects, ways to measure these particles have been proposed. Nonvolatile particles have been indirectly measured by heating up the aerosol through laminar flow reactors designed to remove semi-volatile components from particles, called thermodenuders (TDs) (Wehner et al., 2002; Burtscher et al., 2001). These have been used to quantify the volatility of particles at low and intermediate temperatures (An et al., 2007; Kim et al., 2010) as well as their nonvolatile fraction at higher temperatures ($> 250^{\circ}\text{C}$). Wehner et al. (2004) suggested that by heating up the particles at 280°C for residence times up to 9 s, sulfates, nitrates, and most organics evaporate, and only nonvolatile particle cores remain. To measure the number particle size distribution in this size range, scanning mobility particle sizers (SMPS) have been used after the TD (Wehner et al., 2004; Kim et al., 2010; Saleh et al., 2012). For the determination of the chemical composition of these particles, aerosol mass spectrometers (AMSs) have been increasingly applied (Lee et al., 2010; Poulain et al., 2010; Cappa and Jimenez, 2010).

Despite the increasing focus on nonvolatile particles their contribution to the total number size distribution remains uncertain and strongly depends on the different pollution sources. Chemical characterization of these nonvolatile particles can provide insights about their chemical composition, information about the contribution of BC to the total number concentration and improve the characterization of different emission sources.

In this work an experimental methodology is developed and evaluated to measure the nonvolatile particle number concentration. The method is tested with a set of chamber experiments to investigate its ability to evaporate particles formed from traditional biogenic and anthropogenic secondary organic aerosol (SOA) precursors and, most importantly, particles coming from nucleation. This experimental approach was applied during the Athens 2013 winter campaign to examine the number concentration of nonvolatile particles in an urban environment, their chemical composi-

tion and size distribution, as well as the contribution of different pollution sources.

2 Instrumentation

2.1 Thermodenuder description

The TD setup used in this study was based on the design of An et al. (2007). A detailed schematic of the TD apparatus is shown in Fig. S1 in the Supplement. The TD consists of the bypass (BP) line, which operates at ambient temperature and the TD line, which was set at 400°C in this study. Automatically operated three-way valves placed on the aerosol inlet and outlet (Fig. S1) allow rapid switching between the BP and TD lines and a comparison of the two, essential for particle evaporation and volatility measurements. The TD line includes two main parts: (i) the TD heating section and (ii) the TD cooling section. The TD heating section has a length of 0.5 m and an inner diameter of 36.4 mm. Fine sand is used to cover the inner stainless steel tube to avoid temperature fluctuations. A PID controller (model CNi, I/32, Omega) controls the TD temperature through a heating tape wrapped around the outer cylinder (diameter of 100 mm) of the TD, based on readings of a thermocouple (TJ36 Series, Omega) placed in the center of the heating tube. The heating section is insulated to minimize losses to the surroundings. The cooling section has the same dimensions as the heating section and consists of cylindrical stainless steel gauze with an inner diameter of 36.4 mm. The stainless steel gauze is covered with an activated carbon jacket which is used to remove organic and inorganic vapors that evaporated from the particle phase avoiding thus re-condensation during the cooling stage.

The residence time inside the TD has been shown to be a critical parameter for particle evaporation (Riipinen et al., 2010). In this study, a sample flow rate of 1 L min^{-1} was used. The flow in the system is laminar and results in different residence times, based on radial position. The average travel time of the particles in the heating section at 400°C (operating temperature of the TD in this study) was 13 s, significantly longer than most commercial and research TDs. In the cooling section the average residence time was approximately 30 s. The cooling section was cooled by convection and the temperature of the sample exiting the TD was within 5°C of the room temperature for all conditions.

The temperature profile of the TD when set at 400°C was measured by a stainless steel thermocouple (50 cm length, Omega) in the center of the TD tube (Fig. S2). The temperature difference between the center of the TD tube and the walls was less than 10°C . The walls of the TD were warm even before the heating section, due to conduction, resulting in preheating of the particles before entering the heating tube. The aerosol sample already has a temperature of 150°C when introduced in the heating section, which increases to the set temperature of 400°C 20 cm from the TD inlet. Sim-

ilar results were reported by Wehner et al. (2002) using a similar TD setup.

During the Athens 2013 winter campaign the TD was operating at different temperatures, ranging from 40 to 400 °C (Fig. S4). More specifically, seven temperature steps were chosen for the campaign (40, 70, 100, 120, 200, and 400 °C). One cycle, from 40 to 400 °C and back, required 10 h, which resulted in roughly two temperature cycles per day. The starting time of each cycle changed from day to day, to early morning (02:30–05:00 LT), morning (07:00–10:00 LT), afternoon (16:00–18:00 LT), and midnight (21:00–00:00 LT), so that measurements at each temperature were performed during different periods of the day. The temperature of interest for the present work is 400 °C and during the campaign there were 32 periods of measurements at this temperature, resulting in 20 h of data. It should be noted that throughout this work, nonvolatile particles are defined as the particles that did not evaporate completely under the conditions of these measurement (TD set at 400 °C) and therefore had diameters above the detection limit of the used SMPS system (approximately 10 nm). According to Riipinen et al. (2010) the saturation concentration of the corresponding compounds at room temperature should be less than $10^{-5} \mu\text{g m}^{-3}$ which, based on the terminology of Murphy et al. (2014) for atmospheric organics, should be categorized as extremely low volatility organic compounds. If these particles consist of BC or other material they should be categorized as practically nonvolatile.

2.2 SMPS

A scanning mobility particle sizer (model 3936, TSI Classifier model 3080, TSI DMA 3081, TSI Water CPC 3787) was coupled to the TD to provide the number size distribution of the aerosol in the diameter range from 10 to 500 nm. The SMPS was operated with a sheath air flow of 5 L min^{-1} . The CPC was modified with the addition of a clean air line with a HEPA filter and operated at an effective sample flow rate of 1 L min^{-1} . The aerosol number size distribution (10 to 500 nm) was measured every 3 min (SMPS scanning time). Measurements of both the TD and the BP line were achieved by automatic switching (every 3 min, synchronized with the SMPS) of the three-way valves (Fig. S1).

2.3 Aerosol mass spectrometer

The AMS (Jayne et al., 2000) is commonly used for measurement of submicron non-refractory aerosol particles, which includes organics and most inorganic salts but not black carbon. The high-resolution time-of-flight AMS (HR-ToF-AMS) instrument used here and its data analysis procedures have been already described in depth in previous works (Drewnick et al. 2005; DeCarlo et al., 2006; Canagaratna et al., 2007). In brief, aerosol particles are introduced into the AMS through a critical orifice and an aerodynamic lens fo-

cuses the particles into a narrow beam. Then, the particles are flash-vaporized (impaction on a resistively heated tungsten surface, at 600 °C) and ionized (electron impact ionization by 70 eV electrons). The HR-ToF-AMS can be operated in two ion optical modes (V or W). In this work it was operated in the V mode. The AMS data analysis software packages SQUIRREL (v1.53) and PIKA (v1.10C) were used for the analysis of the high-resolution mass spectra.

In all measurements in this work, the AMS was coupled to the TD measuring the chemical composition and mass size distribution of the non-refractory components of particles with vacuum aerodynamic diameters less than approximately $1 \mu\text{m}$. This corresponds roughly to a physical diameter of $0.7 \mu\text{m}$ assuming a density of 1.4 g cm^{-3} . A time-dependent AMS collection efficiency was calculated using the Kostenidou et al. (2007) algorithm combining the AMS and SMPS size distributions. The average collection efficiency was 0.85 ± 0.23 . The AMS data were corrected for losses in the thermodenuder as described in Sect. 3.1 below.

During the Athens 2013 winter campaign, positive matrix factorization (PMF) was applied to the ambient measurements of the AMS organic spectra, following the approach of Ulbrich et al. (2009), to estimate the contributions of the various sources to the organic aerosol (OA) levels.

2.4 Multi-angle absorption photometer (MAAP)

To estimate the $\text{PM}_{2.5}$ black carbon mass concentration a MAAP (model 5012, Thermo-Scientific) was used. The MAAP applies a constant mass absorption coefficient of $6.6 \text{ m}^2 \text{ g}^{-1}$ to internally convert the absorption coefficient measured at a wavelength of 637 nm to the soot mass concentration (Petzold and Schönlinner, 2014). The absolute value of the mass absorption coefficient depends, however, on the morphology of the carbon particles and their interactions with other compounds (Fuller et al., 1999), implying a systematic uncertainty of the BC derived from the MAAP.

During the Athens 2013 winter campaign the MAAP was characterizing the $\text{PM}_{2.5}$ fraction. To estimate the particulate mass (PM_1) BC concentration a correction factor of 0.9 was used following Poulain et al. (2014). The measurement accuracy of an individual MAAP yields a variability of less than 5 % around the mean value (Müller et al., 2011). Taking into account uncertainties of the mass absorption coefficient, the different particle cut size, and instrumentation accuracy, a total uncertainty of approximately 30 % is expected for the estimated BC mass concentrations. It should be noted though that these BC concentrations are used in a relative sense throughout this work and therefore the corresponding uncertainties do not affect our conclusions.

3 Thermodenuder characterization

3.1 Particle wall losses

Aerosol losses inside the TD at 400 °C were determined in a separate set of experiments, using NaCl particles, since their evaporation is negligible even at high temperatures (Burtscher et al., 2001). NaCl aerosol was produced by atomizing (constant output atomizer, aerosol generator 3076, TSI) aqueous NaCl solutions of known concentration in the range between 0.5 and 3 g L⁻¹ (NaCl purity ≥ 99.5 %, Sigma). The produced NaCl droplets flowed through a silica dryer (RH < 20 %) and then the dry particles passed through the TD. Experiments were conducted in a wide range of particle mass and number concentrations ranging from 50 to 300 μg m⁻³ and 10⁴ to 10⁵ cm⁻³, respectively. Particle wall loss inside the TD line was determined relative to the BP line using

$$\text{Loss}(D_p) = 1 - \frac{\left[\frac{dN}{d \log D_p} \right]_{\text{TD}}}{\left[\frac{dN}{d \log D_p} \right]_{\text{BP}}}, \quad (1)$$

where $dN/d \log D_p$ is the number concentration for the TD and BP measurements, and D_p is the mobility diameter of the particles.

Particle wall loss was determined at 400 °C and the average result from all nine experiments indicates that up to 70 % of the particles smaller than 30 nm are lost on the walls while for particles larger than 50 nm the losses are around 50 % (Fig. S3). Small particles are lost to the walls mostly due to Brownian diffusion, while for larger particles thermophoretic losses prevail (Burtscher et al., 2001). The precision of the measurements ($\pm 2\sigma$) for particles smaller than 100 nm is < 10 % while for larger particles increases up to around 20 %. The focus of this work is on particles smaller than 100 nm so the corresponding losses have been determined quite precisely.

The average determined particle wall loss function was fitted with a triple exponential function:

$$\begin{aligned} (\%) \text{Loss}(D_p) = & 1.28 \exp(-0.1 D_p) + 0.47 \\ & \exp(2 \times 10^{-4} D_p) - 0.64 \exp(-0.11 D_p), \quad (2) \end{aligned}$$

where D_p is in nm. The resulting fit parameters (Fig. S3) were used to correct all the measurements (SMPS and AMS) throughout this work.

3.2 Evaporation of SOA

The TD methodology was tested in a set of laboratory experiments performed using the indoor smog chamber facility at ICE-HT/FORTH, Patras. The chamber is a 10 m³ Teflon reactor suspended in a 30 m³ temperature-controlled room with aluminum-coated walls. The room walls are covered with

UV/vis lamps (320–450 nm wavelength range). The photolytic rate of NO₂ was measured using the well-established chemical actinometry method (Bohn et al., 2005), resulting in $J_{\text{NO}_2} = 0.59 \text{ min}^{-1}$. In all experiments the temperature and the RH inside the chamber were kept constant at 25 °C and < 30 %, respectively.

3.2.1 Biogenic SOA

For the generation of biogenic SOA, a set of experiments utilizing the dark ozonolysis of α -pinene was conducted following the experimental conditions given by Pathak et al. (2007), shown in Table 1. First, O₃ was introduced inside the chamber and then an injection of α -pinene initiated the production of SOA. The experiment took place at NO_x mixing ratio < 2 ppb in the absence of particle seeds. The SOA mass concentration was determined from the measured SMPS size distribution using a density of 1.4 g cm⁻³ (Kostenidou et al., 2007).

The particle number distributions of SOA particles formed from α -pinene ozonolysis at ambient temperature (BP) and 400 °C (TD) for experiment 1 (Table 1) are shown in Fig. 1. After the introduction of O₃ at 00:45 and injection of α -pinene at 01:20, new particles were formed and grew rapidly up to 100 nm in less than 1 h, reaching a concentration of around 2000 cm⁻³. These fresh SOA particles evaporated almost completely (2 % by number remained) after passing through the TD line at 400 °C (Fig. 1). It should be noted that the TD removal efficiency reported in this work corresponds to particles that either evaporated completely or had a residue no larger than the minimum detectable size of 10 nm.

The particle number size distribution in the chamber at the end of the experiment is shown in Fig. 1c. A significant decrease of total particle number concentration, from 1700 to 35 cm⁻³ (number fraction remaining ~ 2.2 %), after sampling through the TD line was observed. After new particle formation occurred the number fraction remaining (NFR) immediately dropped to 2 %, indicating that 98 % of the particles evaporated in the TD line. This shows that fresh SOA formed from α -pinene ozonolysis evaporates almost completely after heated at 400 °C. The few remaining particles after the TD were mainly preexisting particles in the chamber. Background particle number concentration after the TD was around 20 cm⁻³ before the reactions started and this value was relatively stable during the experiment.

3.2.2 Anthropogenic SOA

As a typical example of anthropogenic SOA, the photooxidation of toluene was examined to test the ability of the proposed TD methodology to completely evaporate anthropogenic SOA. H₂O₂ and toluene were injected in the chamber and after reactants were mixed, the UV lights were turned on, initiating the photochemistry. OH radicals were produced from H₂O₂ photolysis and OH concentration inside

Table 1. Experimental conditions used in α -pinene dark ozonolysis and toluene photooxidation experiments.

| α -Pinene experiments | Temperature (°C) | RH (%) | Initial α -pinene (ppb) | Initial O ₃ (ppb) | SOA Mass ^a (μm^{-3}) |
|------------------------------|------------------|--------|--------------------------------|------------------------------|--|
| 1 | 25 | 30 | 5.5 | 280 | 3.1 |
| 2 | 25 | 30 | 10 | 300 | 8.7 |

| Toluene experiments | Temperature (°C) | RH (%) | Initial Toluene (ppb) | Initial NO _x (ppb) | Initial H ₂ O ₂ (ppb) | [OH] ^b (molecules cm ⁻³) | SOA Mass ^a (μm^{-3}) |
|---------------------|------------------|--------|-----------------------|-------------------------------|---|---|--|
| 1 | 25 | 30 | 50 | 2 | 2 | 2.4×10^6 | 1.7 |
| 2 | 25 | 30 | 50 | 7 | 2.1 | 3.1×10^6 | 2.2 |

^a Determined from the SMPS measurements using a density of 1.4 g cm^{-3} (Kostenidou et al., 2007). ^b Initial [OH] after UV lights were turned on, as measured by the decay of toluene.

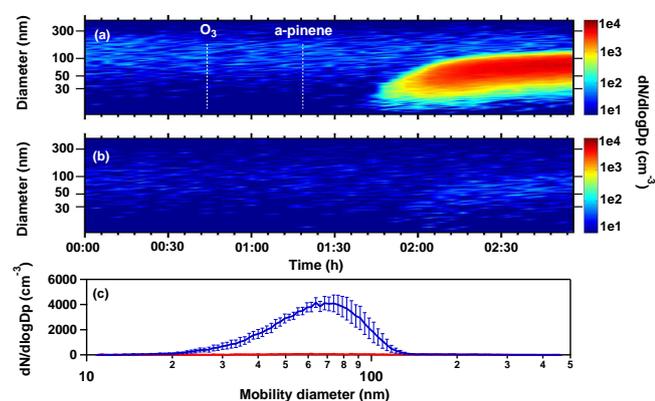


Figure 1. Time evolution of particle number size distribution during the dark ozonolysis of α -pinene, measured after (a) the bypass line at 25 °C and (b) the TD set at 400 °C. The color scale represents particle number concentration. (c) Average particle number size distribution of α -pinene SOA (15 scans, 3 min time span), for chamber measurements, at 25 °C (blue), and loss-corrected TD measurements, at 400 °C (red), for Exp. 1 (see Table 1 for details). Vertical lines correspond to confidence intervals.

the chamber was determined following the decay of toluene. The experiments were conducted at NO_x mixing ratio of < 10 ppb in the absence of particle seeds. A summary of the experimental conditions is given in Table 1.

The time evolution of the number size distribution of experiment 1 is shown in Fig. 2. After injecting toluene and H₂O₂ at 00:30, UV lights were turned on (00:45), forming fresh particles at 25 °C. The growth of these particles up to 100 nm took place in less than 1 h, reaching a concentration of 1300 cm^{-3} . When heated at 400 °C these fresh particles evaporated practically completely (NFR of 2 to 4 %).

The average number size distributions from 07:00 to 09:00 are shown in Fig. 2c. Again, a significant decrease of the particle number concentration was observed from 1350 to 60 cm^{-3} (NFR = 4 %). After new particle formation NFR

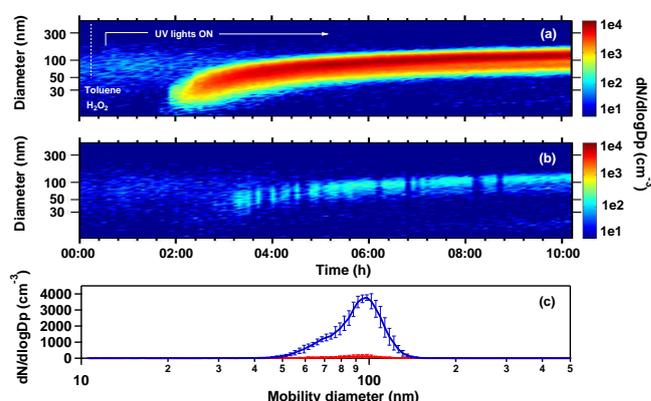


Figure 2. Time evolution of particle number size distribution during the photooxidation of toluene, measured after (a) the bypass line set at 25 °C and (b) the TD set at 400 °C. The color scale represents particle number concentration. (c) Average particle number size distribution (from 07:00 to 09:00; 40 scans, 3 min time span) of toluene SOA for chamber measurements, at 25 °C (blue), and TD loss-corrected measurements at 400 °C (red) (Exp. 1, Table 1). Vertical lines correspond to confidence intervals.

was less than 5 % and as particle number concentration increased NFR decreased to 2 %, suggesting that 98 % of the particles evaporated at 400 °C. Background particle number concentration after the TD was around 30 cm^{-3} before the reactions started. This concentration increased during the experiment to 70 cm^{-3} , suggesting that a small fraction (1–2 %) of the newly formed particles did not evaporate through the TD. This shows that fresh SOA particles formed from toluene photooxidation evaporate almost completely after heating at 400 °C.

3.3 Evaporation of freshly nucleated particles

A set of measurements was conducted to explore the ability of the TD to evaporate freshly nucleated particles that originate from photo-oxidation of ambient air mixtures enclosed in a chamber. Experiments were performed in a 10 m^3 Teflon chamber, while OH radicals were generated from H_2O_2 photolysis ($J_{\text{NO}_2} \sim 0.59\text{ min}^{-1}$). Ambient air present in typical summer days in Patras (Kostenidou et al., 2015) was introduced inside the chamber and characterized under dark conditions with the full suite of instruments as given in Table 2. After the initial characterization, the ambient air was exposed to UV light, initiating photochemistry. OH levels ranged from 3.1 to $4.2 \times 10^6\text{ molecules cm}^{-3}$, as determined by the decay of a suitable tracer (n-butanol, d9) detected by proton transfer reaction/mass spectrometry (Barnet et al., 2012).

The time series for particle number size distribution for a typical experiment is shown in Fig. 3. After the chamber background measurement, ambient air was introduced inside the chamber and characterized. In most experiments the initial total particle number ranged from 300 to 500 cm^{-3} , about half of what was measured in the atmosphere outside the chamber facility during the chamber filling stage, mostly due to dilution and losses through the transfer setup. PM_{10} ranged from 2 to $5\text{ }\mu\text{g m}^{-3}$ and as determined from AMS its chemical composition was organics (55 %), sulfate (30 %), ammonium (10 %), and nitrate (5 %), while its O : C ratio was about 0.6. A large fraction (40–45 %) of these aged particles was persistent at $400\text{ }^\circ\text{C}$ (Fig. 3b), indicating that they contained some extremely low volatility components.

After the initiation of photochemistry, significant new particle formation occurred ($\sim 4000\text{ cm}^{-3}$ new particles formed), followed by significant particle growth. AMS measurements showed that these new particles mainly consisted of organics, however, a small contribution of particulate sulfate and ammonium cannot be excluded. Figure 3c shows the number size distributions a little after the nucleation event occurred. Although a significant increase in the number of nucleation mode particles ($< 20\text{ nm}$) was observed during the nucleation phase, these particles were completely evaporated after passing through the TD line at $400\text{ }^\circ\text{C}$.

In the last phase of the experiment, nucleated particles grew up to 100 nm , growing for more than 10 h. After the nucleation event particle number concentration was stabilized and then started decreasing due to wall losses inside the smog chamber. Particles reached a maximum concentration of 6000 cm^{-3} and during aging decreased to 1000 cm^{-3} inside the chamber. The particle number concentration decreased again significantly ($\text{NFR} = 2\%$) after the TD, suggesting that more than 98 % of the particles evaporated at $400\text{ }^\circ\text{C}$. This is an indication that fresh SOA particles produced from the complex ambient organic mixture in a suburban area of Patras evaporate completely after passing through the TD.

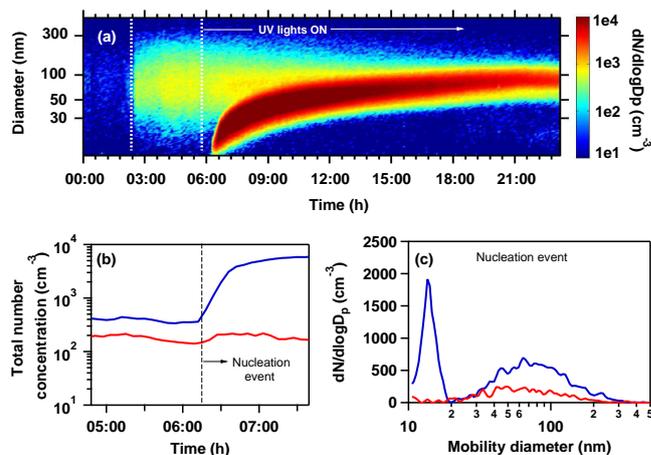


Figure 3. (a) Time evolution of particle number size distribution during the induced ambient nucleation experiment, measured after the BP line at $25\text{ }^\circ\text{C}$. The stages of the experiment were measurement of chamber background (00:00 to 02:30), introduction of ambient air in the chamber (02:00 to 06:00), nucleation event (06:00 to 09:00), and fresh SOA formation (09:00 to 23:00). (b) Total number concentration of ambient particles introduced in the chamber (04:45 to 06:15) and of particles after nucleation occurs (06:15 to 07:45) as a function of time. (c) the number size distribution during the nucleation event (at 06:15) at $25\text{ }^\circ\text{C}$ (blue) and $400\text{ }^\circ\text{C}$ (red). The Aitken mode (30–300 nm) consists mainly of ambient particles.

Overall, from this set of chamber experiments, the experimental method proposed was able to evaporate almost completely ($> 97\%$) particles formed from traditional biogenic and anthropogenic SOA precursors and most important, particles coming from a nucleation event.

4 Ambient measurements

During the winter of 2013 (7 January to 5 February) an intensive field campaign was conducted at the premises of the National Observatory of Athens, located in the center of the city ($37^\circ 58' 21.37''\text{ N}$, $23^\circ 42' 59.94''\text{ E}$). The major objective of this campaign was to determine local and regional air pollution sources in the Greek capital (3.8 million people) during wintertime with a main focus on air pollutants originating from the increasing burning of biomass for residential heating. The measurement site was in the center of Athens, 200 m from the nearest road, and is considered an urban background site. The measurements took place on top of a rocky cliff, opposite from the temple of Thissio. Details of instrumentation and operation are given in Sect. 2.

4.1 Chemical characterization of ambient and thermodenuded aerosol

During the campaign there were 32 periods of measurements at $400\text{ }^\circ\text{C}$, resulting in 20 h of data. These 32 measurement

Table 2. Initial species concentration for the induced ambient nucleation experiment.

| Gas phase | | | | | | |
|--------------------------------------|-------------------------------------|--|--------------------------------------|-------------------------------|---|--|
| O ₃ (ppb) | NO _x (ppb) | H ₂ O ₂ (ppm) | Isoprene (ppt) | Toluene (ppt) | C8 and C9 aromatics (ppt) | OH ^a (molecules cm ⁻³) |
| 34 | 6.4 | 1.34 | 100 | 400 | 900 | 3.7×10^6 |
| Aerosol phase | | | | | | |
| AMS | | | | SMPS | | |
| Organics ($\mu\text{g m}^{-3}$) | Sulfate ($\mu\text{g m}^{-3}$) | Nitrate ($\mu\text{g m}^{-3}$) | Ammonium ($\mu\text{g m}^{-3}$) | Number (cm ⁻³) | Mass ^b ($\mu\text{g m}^{-3}$) | |
| 0.45 | 0.27 | < 0.1 | 0.1 | 400 | 0.6 | |

^a Average [OH] during the experiment as measured by the decay of n-butanol(d9). ^b Assumed density of 1.5 g cm^{-3} .

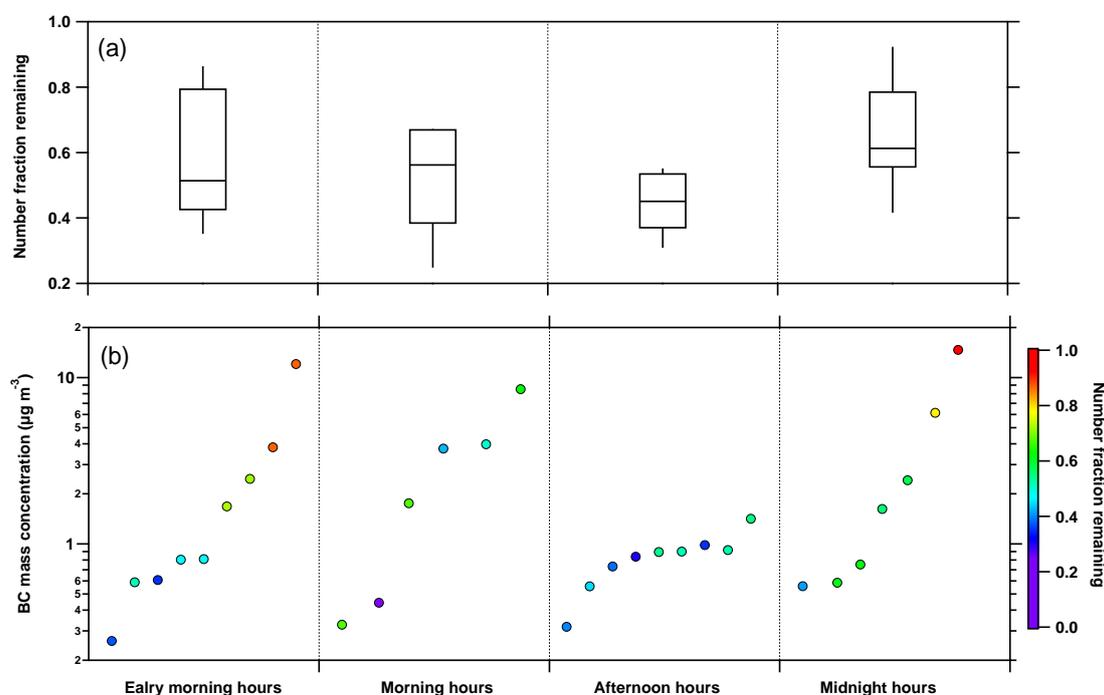


Figure 4. (a) Box-and-whisker plot showing median and 25th and 75th percentile levels for NFR during the Athens 2013 campaign when the TD was set at 400°C for the different periods of the day. Vertical lines represent range from 0 to 100%. (b) BC mass concentration measured with MAAP. The color scale represents number fraction remaining. The different periods of the day were early morning hours (02:30–05:00), morning hours (07:00–10:00), afternoon hours (16:00–18:00), and midnight hours (21:00–00:00).

periods were analyzed with a focus on number concentration and size distribution of particles with a nonvolatile core. A summary of the particle NFR after passing through the TD is shown in Fig. 4. NFR for all time periods measured, was highly variable, especially during midnight and early morning hours with values ranging from 0.3 to 0.9. The morning NFR ranged from 0.2 to 0.7 while the afternoon values were more stable, giving a NFR ranging from 0.3 to 0.5. A correlation of the NFR with BC mass concentration was evident as

shown in Fig. 4b. The higher the BC mass concentration the higher the NFR measured. During certain morning periods BC mass concentration reached values more than $3 \mu\text{g m}^{-3}$ while the NFR was < 0.65 . During these periods particles were mostly originating from traffic emissions and are discussed in detail in Sect. 4.3.

The average mass concentration of the major PM₁ species during the time that TD was set at 400°C , combined with the PMF analysis of the organics for ambient (BP line) and ther-

Table 3. Average mass concentration of major species when the TD was set at 400 °C (given for ambient conditions and after 400 °C) during the Athens 2013 campaign.

| Temperature | Organics ($\mu\text{g m}^{-3}$) | | | | Sulfate ($\mu\text{g m}^{-3}$) | Nitrate ($\mu\text{g m}^{-3}$) | Ammonium ($\mu\text{g m}^{-3}$) | BC ($\mu\text{g m}^{-3}$) |
|-------------|--------------------------------------|------|------|------|-------------------------------------|-------------------------------------|--------------------------------------|--------------------------------|
| Ambient | 10 | | | | 0.74 | 0.55 | 0.36 | 2.5 |
| | ^a BBOA | HOA | OOA | COA | | | | |
| | 31 % | 23 % | 29 % | 17 % | | | | |
| 400 °C | 2.1 | | | | 0.18 | 0.1 | 0.04 | 2.5 ^b |
| | BBOA | HOA | OOA | COA | | | | |
| | 13 % | 23 % | 58 % | 6 % | | | | |

^a Source contribution in (%) for the organic aerosol fraction estimated by PMF analysis. ^b Assuming zero evaporation of BC at 400 °C.

modenuded conditions (TD line), is given in Table 3. During ambient measurements, organics dominated the PM₁ mass concentration with a 70 % contribution, while BC was responsible for another 17 %. The remaining 13 % consisted of sulfate, nitrate, and ammonium.

Since organics dominated the total mass, further characterization was performed using PMF analysis. Organics were separated in four categories: hydrocarbon-like OA (HOA) coming from traffic, biomass burning OA (BBOA) due to fireplace and wood stove use for residential heating, oxygenated organic aerosol (OOA) corresponding to long range transport OA, and organic aerosol related to cooking activity (COA). During ambient measurements, biomass burning aerosol contributed 30 % of the organic mass due to increased burning of wood for domestic heating. BBOA had high levels mostly during the night. A high contribution of aged organic aerosol (28 %) was observed during low concentration periods. During these periods, mostly rainy days, most of the OA is transported to Athens from other areas. Aerosol emitted by traffic was 25 % of the total organic mass, occurring mostly during the morning and afternoon weekday rush-hour traffic. Finally, cooking organic aerosol contributed 17 %. These high levels could be due to the restaurants close to the sampling site.

The aerosol composition changed when particles passed through the TD. BC dominated the remaining PM₁ mass with a contribution of 51 % of the total particulate mass while organics were responsible for another 45 % (fractions were estimated assuming negligible BC evaporation through the TD at 400 °C). The remaining < 5 % consisted mainly of sulfate. The organic mass fraction remaining (MFR) was 20 %, suggesting that part of the organics was of extremely low volatility. Sulfate had a MFR of 10 %, which is a low volatility response seen also in other field studies (Huffman et al., 2009). The MFR of ammonium and nitrate is subject to a larger relative error since the corresponding concentration values after the TD were close to the detection limit of the instrument (MFR 0.03 to 0.05).

From PMF analysis, organics after 400 °C were mostly OOA, around 60 %, an expected result, since usually the more oxygenated organic compounds in the aerosol tend to have lower volatility (Florou, 2014). HOA coming from traffic sources (23 %), biomass burning (13 %), and COA (6 %) were responsible for the rest of the remaining OA. The increased OOA contribution to the TD organic mass could also be due to oxidation of the organic particles when passing through the TD at 400 °C. This could lead to artifacts in the measurement of the contribution of nonvolatile particles with TD systems. These artifacts could include (1) pyrolysis of lower volatility organic species at 400 °C potentially leading to an overestimation of the nonvolatile number and mass concentration and (2) oxidation of BC and nonvolatile particles leading to a possible underestimation. These processes have been examined in detail by Novakov and Corrigan (1995). Their work suggested that constituents such as potassium can act as catalysts for the combustion processes and therefore lower the combustion temperature of BC and organics by as much as 100 °C. Applying these to our measurements, for high concentrations of potassium (5 % of total mass) we estimated a < 5 % overestimation of the nonvolatile particle mass concentration due to pyrolysis and < 10 % underestimation due to oxidation. To further investigate whether these processes highly contribute during our campaign measurements, PMF analysis was performed twice: once using only the ambient AMS measurements and the second time combining the ambient and thermodenuded measurements at all temperatures. The resulting factor spectra were all practically identical to each other (the angles between the corresponding vectors were less than 2 °) except for OOA, for which the theta angle was 6 °. However, this discrepancy is considered within the uncertainty of the PMF analysis, suggesting that if there is chemical change during the processing of the organic aerosol by the thermodenuder then it is minor. A similar conclusion has been reached in other studies (Huffman et al., 2009). These results suggest that although oxidation processes might introduce errors in our measurements, their magnitude is probably small, thus increasing our confidence

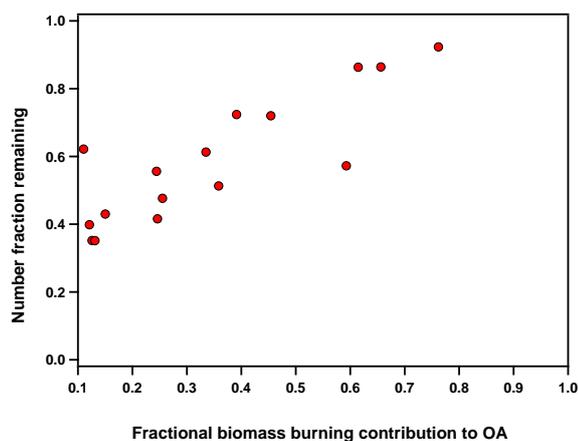


Figure 5. The number fraction remaining as a function of the fractional contribution of biomass burning to the organic aerosol mass. Each point corresponds to 0.5–1.2 h.

on the resulting nonvolatile particle number concentration. Further work is needed in order to explore these processes which might constitute a source of error for high temperature TD measurements.

Given the variability of the measured NFR, we focus next on periods when the site was dominated by aerosol from a specific source to gain insights into the behavior of the corresponding particles. When the fractional source contribution to organic aerosol was higher than 50 %, the measurement periods were considered “representative” of the emission source. Two major anthropogenic sources were investigated: (1) biomass burning and (2) traffic.

4.2 Biomass burning periods

The correlation between NFR and biomass burning contribution to OA is shown in Fig. 5. As the BBOA fraction increased the NFR increased also ($R^2 = 0.76$). For periods when the BBOA was dominant, NFR exceeded 80 %, an indication that most biomass burning particles did not evaporate completely in the TD system at 400 °C. Periods when the BBOA contribution was < 10 % were dominated by aerosol coming from other sources, mostly traffic (Fig. S6).

The average particle number size distributions during a major biomass burning period (BBOA was $50 \mu\text{g m}^{-3}$ and NFR > 90 %) at ambient conditions and at 400 °C are shown in Fig. 6. During this biomass burning event there was a significant shift of the size distribution mode during heating from 100 to 40 nm, but only a few particles evaporated completely (10 %). This is a strong indication that biomass burning particles have a nonvolatile core that survived after 400 °C and were coated with compounds that evaporated through the system and led to a decrease of particle size. Although > 90 % of the particle number concentration was in the size range from 10 to 100 nm, the chemical characterization of these particles was based on the mass concentration

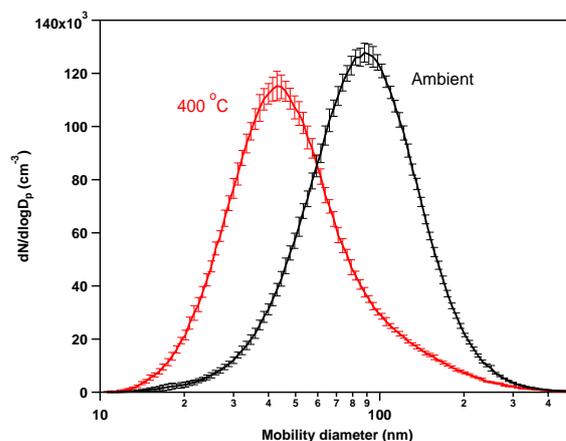


Figure 6. Average particle number size distribution (17 scans; 3 min time span) for a major biomass burning period (BBOA was around 75 % of the OA) at ambient conditions (black) and 400 °C corrected for losses (red). Vertical lines correspond to confidence intervals.

that reflects mainly particles larger than 100 nm. This asymmetry may add uncertainties to this characterization.

During ambient measurements (BP mode) organics dominated the PM_{10} mass concentration with a 70–75 % contribution, while BC was responsible for another 20 %. The remaining 5–10 % consisted of sulfate, nitrate, and ammonium. The aerosol composition changed when particles passed through the TD. BC dominated the PM_{10} mass concentration, with a contribution of 60 %, while organics were responsible for another 35–40 %. The remaining < 5 % consisted mainly of sulfate. The MFR of sulfate was 25 % after 400 °C, a low volatility response seen also in other field studies (Huffman et al., 2009). The organic mass fraction remaining was 17 %, suggesting that roughly 80 % of the organics evaporated through the TD. Detailed results are given in Table S2 in the Supplement.

The PMF analysis results for the four biomass burning events were averaged for ambient measurements (BP mode) and after 400 °C (TD mode). BBOA was dominant in the BP and TD measurements with a 75 and 50 % contribution to the organic mass, respectively. HOA and OOA mass fractions remaining were the highest with 33 and 75 %, respectively; this suggests that, although BBOA particles dominated the TD mass, HOA and OOA were the hardest to evaporate completely, while 97 % of the COA mass evaporated in the TD. Detailed results are given in Table S1.

The volatility of the organics that survived the intense heating was estimated using the TD model of Riipinen et al. (2010). Using the average size of particles, $D_p = 200 \text{ nm}$, the organic saturation mass concentration was estimated to be less than $10^{-5} \mu\text{g m}^{-3}$ at 298 K, categorizing these organics as extremely low volatility OA (ELV-OA) (Murphy et al., 2014).

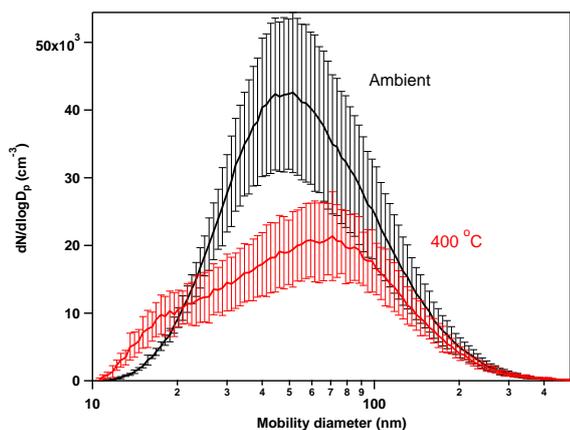


Figure 7. Average particle number size distribution (14 scans; 3 min time span) for a major traffic period (HOA was around 70 % of the OA), at ambient conditions (black) and 400 °C, corrected for losses (red). Vertical lines correspond to confidence intervals.

4.3 Traffic periods

The average particle number size distributions during a traffic period (HOA was 60 % of the OA) at ambient conditions and at 400 °C are shown in Fig. 7. During this period the ambient particle number size distribution had a peak at 45 nm. After heating at 400 °C the distribution was separated in two: one with a peak at 20 nm and one with a 70 nm peak. The NFR of 60 % indicated that 40 % of the particles evaporated completely in the TD, while the remaining 60 % had a nonvolatile core.

During the three representative traffic events when the HOA contribution was higher than 50 %, BC dominated the ambient PM₁ mass concentration with a 50 % contribution, while organics were responsible for another 35 %. The remaining 10–15 % consisted of sulfate, nitrate, and ammonium. The aerosol composition changed when particles passed through the TD. The BC contribution increased to 80 %, while organics were responsible for another 17 %. The remaining < 5 % consisted mainly of sulfate with a MFR of 18 % at 400 °C. The organic MFR was around 25 %, suggesting that a quarter of the organic mass had extremely low volatility. Detailed results are given in Table S4.

By averaging the PMF analysis from the three traffic events for ambient measurements (BP mode) and after 400 °C (TD mode), it was estimated that HOA contributed 70 % of the ambient OA. After passing through the TD, HOA and OOA were the dominant components remaining with a contribution of 55 and 40 %, respectively. BBOA and COA evaporated almost completely with < 5 % contribution to the organic mass. These organics were again categorized as ELV-OA with a saturation mass concentration estimated to be less than 10⁻⁵ μg m⁻³. Detailed results are given in Table S3.

5 Conclusions

Nonvolatile particle number concentration and size distribution were measured using a TD operating at 400 °C. The TD is based on the design of An et al. (2007), providing high residence times for the aerosol. The TD maximum temperature was set at 400 °C. The TD setup was coupled with a HR-ToF-AMS, measuring the chemical composition and mass size distribution of the PM₁ aerosol and a SMPS that provided the number size distribution of the aerosol in the range from 10 to 500 nm.

The ability of this system to measure nonvolatile particle number distributions was evaluated with a set of smog chamber experiments. It achieved almost complete evaporation (> 98 %) of biogenic and anthropogenic secondary organic aerosol derived from ozonolysis of α -pinene and OH photooxidation of toluene, respectively. In a different test, the introduction of ambient air in the chamber and exposure to OH radicals induced an ambient nucleation event. The TD was able to fully (99 %) evaporate all the particles coming from the nucleation event as well as the fresh ambient SOA that condensed on them after nucleation.

This experimental approach was applied in a winter field campaign in Athens and provided a direct measurement of nonvolatile particle levels. During periods in which the contribution of biomass burning sources was dominant (> 60 %) more than 80 % of the particles survived the intensive heating, suggesting that nearly all biomass burning particles had a nonvolatile core. The particles that did not evaporate consisted of 60 % BC and the rest was mostly organics. Organics surviving through the TD were mostly BBOA and OOA, contributing 90 % of the organic mass concentration, while 10–15 % was from HOA and COA.

For periods during which traffic contributed the majority of the OA 50–60 % of the particles had a nonvolatile core, while the rest 40–50 % evaporated at 400 °C. The remaining particles consisted mostly from BC (80 % of the mass) while organics were responsible for another 15–20 %. Organics were mostly HOA and OOA, with a contribution of > 95 % to the organic mass concentration.

These results suggest that it is very difficult or almost impossible to evaporate all organics from ambient aerosol particles using thermodenuders. Therefore, the assumption that has been used in previous studies that the particles coming from these devices are organic free is not valid. This could bias studies attempting to quantify the physical and/or chemical properties of ambient particles without including their organic content (Lack et al., 2012).

Overall, this methodology can be applied to measure the nonvolatile particle number size distribution and provide a chemical characterization of their mass. Assuming that all particles remaining after the TD have a black carbon core, the methodology also provides an indirect way of measuring the upper limit of the BC contribution to the particle number concentration.

The Supplement related to this article is available online at doi:10.5194/amt-9-103-2016-supplement.

Acknowledgements. This work was supported by the ESF-NRSF ARISTEIA grant ROMANDE, the FP7 IDEAS ATMOPACS project, and the EPA STAR program (grant RD-83503501).

Edited by: D. Toohey

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