COMPARISON OF CHEMICAL AND OPTICAL METHODS FOR THE MEASUREMENTS OF BLACK CARBON EMISSIONS FROM WOOD COMBUSTION

Tine Bizjak
MSc Thesis
General Toxicology and Environmental Health Risk Assessment
University of Eastern Finland, Department of Environmental and Biological Sciences
April, 2018
ABSTRACT

Atmospheric black carbon (BC) is associated with several adverse health effects and is thought to be the second most important contributor to the global warming. Atmospheric aging causes changes of the properties of aerosols. Since various methods of aerosolized BC analysis depend on the different properties of BC, they can potentially be affected differently by the aging of the aerosols.

A series of experiments using logwood stove combustion emission source, burning birch wood, was performed at the Ilmari facility of the University of Eastern Finland to compare the optical (Aethalometer), refractory (SP-AMS) and thermal-optical methods for the detection of BC and to assess how the simulated atmospheric aging in the transformation chamber affects the comparison between the selected methods.

The results of the study are in line with the results of many other studies and generally show good correlation (P < 0.01) between the different BC detection methods. The measurements of different methods differ by up to a factor of 2 in quantifying BC concentrations. Increase of the optical absorption at lower wavelengths and changes in the aerosol composition were observed during the simulated atmospheric aging. Changes in the aerosol properties caused by the atmospheric aging must be considered carefully when measuring BC by different methods.
ACKNOWLEDGMENTS

I would like to acknowledge the importance of receiving Ad Futura scholarship for studying abroad, that was awarded to me by the Public Scholarship, Development, Disability and Maintenance Fund of the Republic of Slovenia., without which I would not be able to study at the University of Eastern Finland.

Firstly my gratitude goes to both my supervisors Olli Sippula and Petri Tiitta for all the guidance and advice given during the making of this work, and especially for enabling me to finish my studies in time.

Secondly I am thanking Anni Hartikainen, Hanna Koponen, Pasi Yli-pirilä, Mika Ihalainen, Jarkko Tissari, Miika Korttelainen and other members of the Fine Particle and Aerosol Technology laboratory at the Department of Environmental and Biological Science at the University of Eastern Finland that were involved with the experiments described in this thesis and were most helpful during the analysis of the measurements results.

I would also like to thank my family, especially my dad Mirko, responsible for introducing me to BC at an early age, who advised me during the writing of this work.

My final gratitude goes to my amazing fiancée Tamara. I cannot imagine achieving all the things I have achieved so far without her. And thank you for our little Emil Olav – our ever replenishable source of motivation and joy.
ABBREVIATIONS AND DEFINITIONS

AAE  Ångström absorption exponent
AMS  Aerosol Mass Spectrometer
BB   Biomass burning
BC   Black carbon
CE   Collection efficiency
DR   Dilution ratio
eBC  Equivalent black carbon
EC   Elemental carbon
EI   Electron impact
ELPI Electrical low pressure impactor
FTIR Fourier transform infrared spectrometer
HR-TOF-AMS High-resolution time-of-flight aerosol mass spectrometer
MAC  Mass specific absorption cross section
NR-PM Nonrefractory particulate matter
OA   Organic aerosols
OC   Organic carbon
OGC  Organic gaseous carbon
PM   Particulate matter
PM$_{2.5}$ Fine particulate matter
QF   Quartz filter
rBC  Refractory black carbon
RH   Relative humidity
RIE  Relative ionization efficiency
R-PM Refractory particulate matter
SMPS Scanning mobility particle sizer
SOA  Secondary organic aerosol
SP-AMS Soot Particle Aerosol Mass Spectrometer
TC   Total carbon
TF   Teflon filter
UEF  University of Eastern Finland
UHP  Ultra-high purity
WL   Wall loses
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1. INTRODUCTION

Atmospheric black carbon (BC) can be related to several adverse health effects and is an important contributor to the global warming. Biomass burning is one of the most important sources of BC (Petzold et al. 2013, Janssen et al. 2012).

BC affects climate on local, regional and global scales. The contribution of BC to the atmospheric warming is 100 to 2000 times higher than that of the same amount of carbon dioxide (Shindell et al. 2011).

There are many instrumental methods available for the measurements of atmospheric BC. They are based on the properties of BC such as light absorption, refractory properties and chemical composition (Petzold et al. 2013). Aerosol aging can change these properties and can therefore affect the measurement methods (Tiitta et al. 2016).

Atmospheric aging of the aerosols has already been simulated and studied in different laboratory settings. Laboratory studies of atmospheric aging are usually performed in environmental chambers or flow tube reactors, which allow careful setting and regulation of experimental conditions, so they can simulate conditions in the environment as closely as possible.

Most of the aerosol aging studies did not focus primarily on the comparison of different methods of BC measurements. Moreover, they did not evaluate in detail, if there are changes in relations between the different methods, caused by the aging induced aerosol properties changes.

In this work the measurement results of different optical and chemical methods of BC analysis were compared. Furthermore the effect of aerosol aging on the inter-comparison between these methods was evaluated.
2. LITERATURE REVIEW

2.1. Definition and sources of Black carbon

Carbon (C) is a non-metallic element, with four known allotropes, which is critical to all living. While it is abundant in the living organisms it also moves through the oceans, atmosphere and earth’s crust (E. Sahan, H.M. ten Brink & E.P. Weijers 2008). Carbonaceous matter part of the atmospheric aerosols, which is the least understood and most challenging to characterize (Baltensperger et al. 2003), can consist of extremely variable mixture of different carbonaceous species with different properties. Total aerosol carbon mass (TC) can be divided into inorganic carbonates (i.e. CaCO$_3$ and other carbonate salts), organic carbon (OC) (all organic compounds found in the particle phase), and a third fraction referred to by different terms: elemental carbon (EC), black carbon (BC), soot or refractory carbon (rBC). Black carbon, elemental carbon and refractory carbon all refer to the most refractory and light absorbing part of the carbonaceous particles originating from combustion processes, even though their definition and corresponding measurement methods are different (Petzold et al. 2013).

- Black carbon (BC) has been defined as a substance made of carbon with the property of ideally absorbing light. BC is defined by its microstructure, morphology, thermal stability, solubility, light absorption and its properties, that make BC relevant for climate change research, air chemistry, ambient air quality, biogeochemistry and paleoclimatology. The prevalent source of BC is incomplete combustion of carbonaceous matter (Petzold et al. 2013).

- Elemental carbon (EC) is a substance that only consists of carbon, that is not bound to other elements, but can exist in several different allotropic forms (Schwartz, Lewis 2012).

- Refractory black carbon (rBC) is describing insoluble carbonaceous part of the particulate matter that vaporizes at 4000 K (Petzold et al. 2013).

Emissions of BC and OC are closely related, as both can be found in combustion emission products. Depending on the fuel type used and the type of combustion, their relative proportions can be different (Shindell et al. 2011). Less efficient combustion of biomass produces higher fraction of organic carbon particles relative to black carbon (Bachmann 2009). The term brown carbon is sometimes used to describe atmospheric aerosols of organic origin, that absorb light unevenly through the whole visible light spectra. Light absorption of brown carbon is increasing with higher rate at decreasing wavelengths compared to the absorption of black carbon (Petzold et al. 2013). Brown carbon is strongly associated with biomass burning (Feng, Ramanathan &
Kotamarthi 2013), but also contributes significantly to the absorption properties of non-wood smoke sources (Olson et al. 2015).

Historically total BC emissions have almost linearly increased by more than four times from 1850 to 2000 (Bond et al. 2007). In Asia and Africa between 60 and 80 % of BC originates from domestic solid fuel combustion (e.g. wood, coal). In Europe, Northern and Latin America 70 % of the atmospheric BC originates from the use of diesel engines (Bond et al. 2013). Actions proposed by the EU to decrease the CO₂ emissions could cause a 57 to 111 % increase of biomass use between 2010 and 2020 (Wagner et al. 2010). European Environmental Agency predicted that the inclusion of BC measurements in the air quality monitoring programs will increase (EEA 2013).

Reducing the BC emissions requires good understanding of the contribution of different BC sources, which is of great importance for policy makers when introducing new air quality standards and regulations.

2.2. Black carbon and health

BC is particularly interesting as a constituent of PM, because it causes adverse health effects (Shindell et al. 2011). Three billion people worldwide are exposed to elevated air PM values, which causes major health concerns (Bachmann 2009). Atmospheric PM pollution and indoor air PM pollution, originating from the use of solid fuels, are estimated to cause between 5,5 and 8 million deaths worldwide in 2010 (Lim et al. 2012).

BC measurements and models can predict the actual exposure of individuals with similar accuracy than measurements of fine particulate matter (PM₂.₅). Studies evaluating short term health effects found that BC can be a better indicator for substances with potential to cause adverse health effects than total PM (Janssen et al. 2012).

BC itself was found to be an important environmental risk factor affecting the prevalence of cardiovascular diseases (Baumgartner et al. 2014). Finally cohort studies also provide enough evidence of an association between long-term BC exposure and all-cause and cardiopulmonary mortality (Janssen et al. 2012).

2.3. Black carbon and climate

BC can affect climate in several ways. Absorption of the solar radiation on the atmospheric BC particles increases the input of energy into the atmosphere (Ramanathan, Carmichael 2008). Settling of the BC on the snow and ice can decrease albedo of the earth surface (Clarke, Noone
BC can have a strong role in the weakening of the Indian monsoon, causing differences in precipitations patterns in Asia. Overall BC contributes to the global warming. Compared to the greenhouse gases CO$_2$ and CH$_4$, which are long-lived climate forcers, BC is a short-lived climate forcer and is thus considered important in the near-term mitigation strategies targeting the effect on the climate caused by the anthropogenic emissions (Shindell et al. 2011). Radiative forcing of BC has increased with the increased BC emissions (Figure 1), even though its atmospheric lifetime is limited by the direct surface deposition and precipitation and is estimated to be about one week (Rodhe, Persson & Akesson 1972 cited by Ramanathan, Carmichael 2008).

Regardless of high uncertainties BC is considered as the second most important anthropogenic emission causing climate forcing, with only CO$_2$ having greater climate forcing effect (Bond et al. 2013).

2.4. Black carbon measurement methods

BC measurement methods rely on its different properties. They include light absorption, refractory properties, chemical composition or carbon content, graphite-like microstructure and the morphology of the particles (Petzold et al. 2013).

2.4.1. Light absorption

Absorption photometry BC measurement techniques can give almost real time data with high resolution, which is one of the most important advantages for BC monitoring, especially in comparison with the determination of EC from filter collected samples of PM (EEA 2013).

Important measure of optical techniques, used for measuring light absorption of the particles, is the volumetric cross section for light absorption, called commonly the light absorption
coefficient ($\sigma_{ap}$). No agreed reference method for measurement of light absorption coefficient exists, due to the fact that many measuring methods suffer from cross-sensitivity to light scattering particles or other measurement artefacts (Petzold et al. 2013).

BC mass concentration is calculated by equation (1), that requires knowledge of MAC (mass specific absorption cross section) and presumes that there is no other light absorbing particulate species apart from BC (Petzold et al. 2013).

$$BC = \sigma_{ap} \times MAC^{-1}$$

Mass concentrations of BC obtained by chemical and optical methods can differ by several factors, but are usually correlated with statistical significance level of $P \leq 0.05$ (Petzold et al. 2013).

The most common instruments for real-time optical measurement of BC are Aethalometer (A. Hansen, Rosen & Novakov 1983), Multi-Angle Absorption Photometer (MAAP) and Particle Soot Absorption Photometer (PSAP). As all three instruments measure the concentration of highly light absorbing carbonaceous aerosols at certain wavelengths ($\lambda$) it would be more appropriate to refer to their results as to the concentrations of equivalent BC (eBC). Nevertheless, it is more common to only use BC (Petzold et al. 2013). Photometers that use filters are affected by nonlinearity, caused by the filter loading, that causes decreased sensitivity of measurements with the increasing amount of filtered air - increased filter loading (Weingartner et al. 2003, Virkkula et al. 2007).

In the past Aethalometer BC measurements were corrected to compensate for the nonlinearity with the models by Weingartner et al. (2003), Virkkula et al. (2007) and Backman et al. (2014). Newest Aethalometer model AE33 includes an in-built algorithm for nonlinearity compensation, caused by the filter loading, in real-time (Drinovec et al. 2015). Filter loading parameters ($k$) for each of the $\lambda$ are used for the compensation of the Aethalometer absorption data. Particle coating was found to decrease $k$ values. As a results parameters $k$ can also be used as indicators for the increased particle coating and thus enable the differentiation between fresh and aged particles (Drinovec et al. 2017).

Nonlinearity compensation algorithm in the Aethalometer AE33 also enables a real-time determination of the contributions of biomass burning and fossil fuel combustion emission sources to the total emissions with the Aethalometer model (Sandradewi et al. 2008). Aethalometer model for the determination of biomass burning and fossil fuel combustion to
total BC concentration presumes that the use of fossil fuels and biomass are the only sources of BC.

2.4.2. Aerosol mass spectroscopy
Aerosol mass spectroscopy (AMS) methods are targeting the chemical composition of the particles. Aerosols are thermally vaporized prior to ionization – using laser vaporization method for refractory material such as BC. This is followed by standard mass spectroscopy methods, which are used to analyze the chemical composition of individual aerosol particles (Petzold et al. 2013). Non-refractory aerosol components, such as the main fraction of organic aerosols (OA) are vaporized without laser using tungsten vaporized at 600 °C under vacuum conditions.

Soot particle aerosol mass spectroscopy (SP-AMS) (Onasch et al. 2012) technique can determine chemical composition of refractory aerosols. SP-AMS combines a laser induced incandescence and mass spectroscopy approaches. While the laser induced incandescence heats and vaporizes the sampled particles for refractory aerosols, mass spectroscopy is used for the detection of resulting charged clusters of carbon. Detectable particle size is controlled by the aerodynamic lens, with median diameter limits of 75 nm and 650 nm (P. Liu et al. 2007), that focuses the particles into a narrow beam, that is directed through the vacuum chambers into an ionization chamber. The lower limit of detectable particle size of SP-AMS measurements is higher than in other techniques such as electron microscopy methods (Petzold et al. 2013).

2.4.3. Evolved carbon
Chemical composition of the atmospheric aerosols can be determined by various filter based methods. Different carbon specific methods are relying on the thermal resistivity of elemental carbon part of the carbonaceous matter. In an inert atmosphere volatilization of elemental carbon only occurs at temperatures of around 4000 K, while the gasification by oxidation starts at temperatures above 340 °C (Cachier, Brémond & Buat-Ménard 1989, Jennings et al. 1994). Carbon in the sample, typically collected on the filter, is detected as CO₂ or CH₄ by different types of methods. IMPROVE (Chow et al. 2007), EUSAAR_2 (Cavalli et al. 2010) and NIOSH 5040 (The National Institute for Occupational Safety and Health 1999) protocols are three of the most commonly used analysis protocols.

Protocol that is used for the thermal-optical analysis is an essential part of the results and must always be documented (Petzold et al. 2013).
2.5. Aging of aerosols

During the aging in the atmosphere, aerosols can be affected by changes in their physical or chemical properties, such as size and chemical composition. The reasons for these changes are aerosol dynamic processes and photochemical reactions with atmospheric oxidants (Leskinen et al. 2015). Atmospheric aging of emissions causes surface coating of soot particles which can also significantly change their properties (Tiitta et al. 2016).

Aging of the aerosols can occur in the dark conditions or under UV light. Photo-oxidation aging was shown to be faster than dark aging, although dark aging can generate similar amount of secondary organic aerosols (SOA) (Tiitta et al. 2016).

While SOA formation is important source of new aerosol mass in the atmosphere (Donahue et al. 2012), atmospheric processes does not produce any additional BC (Tasoglou et al. 2017).

Condensed coatings on the surface of BC particles were found to enhance the light absorption of the particles by 50 to 60 % in laboratory and modelling studies. Evidence from sparse real-world experiments is conflicting, suggesting absorption enhancements of between less than 5 % and up to 140 % (D. Liu et al. 2017). Absorption enhancements must be considered when interpreting results of light absorption measurements (Petzold et al. 2013). The enhancement can be caused by the semi-volatile species coating of the particles (Lack, Cappa et al. 2009). In addition, coating of the particles was shown to affect not only the optical, but also the microphysical properties of soot aggregates (Schnaiter et al. 2005).

Absorption enhancement of the aerosols is affected by relative humidity (RH). Compared to the absorption at lower relative humidity, it was found to be enhanced more in higher RH conditions (Lack, Quinn et al. 2009), although RH increase of over 70 % led to systematical decrease of light absorption (Arnott et al. 2003).

Observed absorption enhancements and other changes, due to transformation during atmospheric aging, can affect the results obtained by different methods of BC detection. A study performed in the Vienna area found large discrepancies between obtained EC values by thermal/optical methods and BC values obtained by optical methods (Reisinger et al. 2008). Discrepancies were largest when the contribution of brown carbon to the total light absorbing carbon was the largest. Especially in winter, when there are higher amounts of brown carbon in the aerosols, measurement methods tend to overestimate both EC or BC concentrations. Thermal-optical method for the determination of EC gave 33 % lower values compared to BC concentration (Reisinger et al. 2008).
Particle coating, changing the morphology of the particles, was also found to narrow the width of the particle beam, which affected the collection efficiency and increased the sensitivity for highly coated particles when measuring them with the SP-AMS (Willis et al. 2014).

Transformation processes during atmospheric aging have a significant effect on the properties of the combustion emissions, that are of high concern because of their effects on health and climate (Tiitta et al. 2016). Aging of aerosol can modify toxicological properties of combustion emissions. For example, it has been observed that dark aging increases genotoxic properties of PM in an in vitro mouse macrophage model (Nordin et al. 2015).

Aerosol aging studies in the laboratory are typically performed with environmental chambers or with flow reactors, which are both convenient and inexpensive way for the investigation of the aerosols aging. Moreover, they enable control of aging conditions by controlling humidity, oxidants, temperature or other relevant factors.

Results of several chamber experiments, investigating changing aerosol properties due to their aging, are already published (C. J. Hennigan et al. 2011, Grieshop et al. 2009, Tiitta et al. 2016, Tasoglou et al. 2017). For example smog chamber experiment was conducted to study the changes of physical and chemical properties of particles originating from biomass burning that occur in the atmosphere. Biomass burning smoke was exposed to UV light, ozone or OH radicals and as it aged, organic material was found to condense on the existing particles. This particle coating caused a two-fold increase in absorption of BC containing particles originating from pine wood burning, and an increase of the mass concentration of the organic aerosols (Tasoglou et al. 2017). In contrast, another study observed no absorption enhancement with particles originating from traffic sources (D. Liu et al. 2017).

Smog chamber at UEF’s Ilmari research facility, used in this study, was shown to have reasonable formations of SOA and gaseous first and second generation reaction products, that are comparable to those in other laboratories with similar setups (Leskinen et al. 2015). Results of the experiments performed in the same chamber already proved that logwood burning emissions undergo intensive transformation processes in the atmosphere in relatively short timescales (Tiitta et al. 2016).
3. AIM OF THE WORK

To successfully approach the various issues concerning impacts of aerosolized BC, it is of utmost importance that the results of different measurement methods are comparable and that the measurement methods are not affected by external factors such as aerosol aging. This is especially important, since it is currently impossible to unambiguously determine conversion parameters between different BC measurements (Petzold et al. 2013).

Several studies (Petzold et al. 2013, Lack, Cappa et al. 2009, D. Liu et al. 2017) suggest that surface coating of the aerosols causes light absorption enhancements, which can have an effect on the quantitative results of optical methods of BC analysis.

Present study aims at comparison of chemical (filter sampling for thermal-optical analysis of EC and OC), refractory (SP-AMS) and optical (Aethalometer) measurement methods for BC emissions from logwood stove, using birch logwood as fuel. Furthermore, it aims to evaluate the effect of the changing of the aerosol properties, caused by aging, on the above mentioned different measurement methods.
4. MATERIALS AND METHODS

Experiments took place in Ilmari research facility of the University of Eastern Finland (UEF) on the 23rd, 28th and 29th of November 2017. Ilmari facility enables studies on emissions from different combustion sources, including the determination of toxicological properties of fresh and aged aerosols, with all the necessary experimental setup parts side by side under the same roof. 6 kW domestic type wood stove Aduro 9-3 burning birch (*Betula pubescens*) wood logs was chosen as the source of emissions. Birch logwood was selected as one of the most commonly used wood types for residential heating in Finland. Besides it was found to have the highest total emissions and largest rBC mass fractions in an experiment, that included beech, birch and spruce wood (Tiitta et al. 2016).

One batch of wood used (Figure 2) weighed a total of 1,85 kg. It included three logs of 300 g, five logs of 140 g, four pieces with combined weight of 150 g and 100 g of wood chips including some bark. Additionally, two wooden sticks were used below the batch to elevate it. In each experiment second batch of wood was added approximately 35 min after the ignition of the first batch. The moisture content of the used birch logs was 17 % (analyzed on 13th of November 2017).

![Figure 2: Batch of birch logs before the experiment on the 23.11.2017](image)

4.1. Experimental design

Experimental setup (Figure 3) consisted of wood stove and stack, sampling systems smog chamber and aerosol and gas analyzers.
Fresh emissions were analyzed with Fourier transform infrared spectrometer (FTIR; Gasmet DX4000). Sampling of the emissions from the wood stove exhaust pipe was done with the heated sampling probe with PM10 pre-cut cyclone, followed by the porous tube diluter developed by UEF spin-off company Venacontra (http://www.venacontra.com/). Before the sample was filled into the environmental chamber (Leskinen et al. 2015) used for the aging of the aerosols, it was again diluted with the DI-1000 Dekati ejector diluter (Lyyränen et al. 2004). After the Dekati diluter separate sensors measured the content of CO2, O2, NOx, CO and organic gaseous carbon (OGC) (ABB AO2040). Nominal volume of the chamber was 29,4 m³, with the surface area of 58,1 m². Obtained surface-to volume ratio of the chamber was 2,0, which is of importance when evaluating the degree of wall effects. Higher values of the ratio indicate that there is more contact between the aerosols and chamber walls (Leskinen et al. 2015).

Total dilution ratio (DR) of the sample was calculated according to equation (2) (Tissari 2008),

$$DR = \frac{CO_2(\text{flue gas}) - CO_2(BG)}{CO_2(\text{chamber}) - CO_2(BG)}$$  (2)

where CO2 (flue gas) is average CO2 concentration of the undiluted fresh exhaust before the sampling probe in the exhaust pipe, CO2 (chamber) is average concentration of CO2 of the fully diluted sample in the chamber and CO2 (BG) is concentration of CO2 in the air used for dilution and in the air that was pre-fed into the chamber.
CO₂ in fresh exhaust was measured with FTIR and CO₂ in the chamber was measured with Vaisala CARBOCAP® Carbon Dioxide Probe GMP343 and with Siemens detector. Linear interpolation of FTIR CO₂ values was performed to get CO₂ values with the time base of 1 s, as was the time base of the CO₂ measurements with the other instruments. CO₂ (BG) value was determined from the average CO₂ in the chamber before the start of the sample feeding.

Diluted exhaust in the chamber was analyzed with several on-line instruments: O₃ (UV photometric analyzer Thermo 49i); NO, NO₂, NOₓ (trace-level chemiluminescence analyzer Thermo 42i-TL); CO₂ detectors; proton transfer reaction time of flight mass spectrometer (PTR-TOFMS); scanning mobility particle sizer (SMPS; TSI 3081 DMA + 3776 CPC); electrical low pressure impactor (ELPI); soot particle aerosol mass spectrometer (SP-AMS) and Aethalometer (AE33). In addition, filter samples were collected for OC/EC analysis. Aerosol aging evaluation was performed according to method using butanol-d9, that determines the OH exposure of the sample and the photochemical age during the experiment (Barmet et al. 2011). The decay of the butanol-d9 was measured by the PTR-TOFMS (PTR-TOF 8000, Ionicon Analytik, Innsbruck, Austria). On each of the experimental days O₃ was added to almost fully convert NO into NO₂ in the chamber.

Figure 4 shows the timeline of all three experiments. Every day, before the starting of the experiment, chamber was flushed and pre-filled with clean air as described in detail by (Leskinen et al. 2015).

![Figure 4: Timelines of the experiments](image-url)
Sample feeding started at the time of birch wood logs ignition, after which a part of the wood stove emissions was sampled, diluted and fed into the chamber (red line in Figure 4). Filling of the chamber was followed by stabilization and addition of 3 µl (30 ppb) of butanol-d9 (yellow line in Figure 4). After the butanol-d9 addition filter sample of fresh emissions was collected for an hour. After the filter sampling ozone was fed into the chamber (blue line in Figure 4) and after the ozone feeding UV lights (λ= 340 and 350 nm) were switched on to start the UV-light induced photochemical aerosols aging process (purple line on Figure 4). UV lights used imitated the UV irradiance in Central Finland at midday on a midsummer sunny day (Leskinen et al. 2015). On the 23rd of November all of the UV lights were switched on, while on the 28th and 29th of November only 2/3 were switched on, to decrease the heating of the chamber during the aging observed on the 23rd of November. O₃ addition caused all of the NO in the chamber to be transformed into NO₂ during the aging process. During the aerosol aging 50, 55 or 60 min filter samples were collected (green lines in Figure 4) and stored in the freezer for further analysis. Different duration of the filter sample collection time was affected by the simultaneous cell exposure tests for the evaluation of the toxicity of emissions, which is not covered in this work. Experiment ended after 4 hours of aging in the chamber.

Atmospheric aging equivalence was evaluated based on the OH exposure of the selected tracer, which is applicable in cases where OH radicals are the main oxidant species. Butanol-d9, that was used as OH tracer, is known to only react with OH and has little or no interference with other compounds evaluated by the PTR-MS (Barmet et al. 2011). Total OH exposure for each experimental day was calculated according to equation (3) (Lambe et al. 2011),

$$\text{OH}_{\text{exposure}} = \left[ \frac{1}{k_{\text{OH, butanol-d9}}} \right] \times \left[ -\ln \left( \frac{\text{butanol-d9}_{\text{final}}}{\text{butanol-d9}_{\text{initial}}} \right) \right]$$

where butanol-d9_{final} is the constant final concentration of butanol-d9 tracer, butanol-d9_{initial} the constant initial concentration of butanol-d9 (after the stabilization and before the aging) and k_{OH, butanol-d9} the bimolecular rate constant between OH and butanol-d9. Value of k_{OH, butanol-d9} used in the calculation of OH exposure was 3.4 x 10⁻¹² cm³ molecule⁻¹ s⁻¹ (Barmet et al. 2011). Obtained value of OH exposure in the chamber was compared with the assumed value of 1 x 10⁶ molecule cm⁻³ for the equivalent atmospheric aging at typical boundary layer OH concentrations (Tiitta et al. 2016), to estimate the equivalent photochemical age achieved during the experiments.
The measurements on the 28th and 29th of November included additional ozone scrubber in the sampling line before the filter sampling and the line for cell exposure experiments (ALI). Ozone scrubber was not used on the 23rd of November (Figure 3).

4.2. Instruments

4.2.1. Aethalometer

Optical measurement of BC was performed with Aethalometer model AE33 (Magee Scientific). Aethalometer continuously collects aerosol particles on the filter tape. Attenuation of light was measured at seven $\lambda$ (370, 470, 520, 590, 660, 880 and 950 nm) on two spots of the filter containing the sample and on the unloaded reference part of the filter tape. BC mass concentration is usually defined from the measurements of optical attenuation at 880 nm using the mass absorption cross section (MAC) value of 7.77 m$^2$g$^{-1}$ (Drinovec et al. 2015). MAC values used for the measurements at all $\lambda$ are shown in Table 1. Measurements were performed with time resolution of 1 s and with the flow set to 2 lpm.

<table>
<thead>
<tr>
<th>Channel</th>
<th>$\lambda$ (nm)</th>
<th>MAC (m$^2$g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>370</td>
<td>18.47</td>
</tr>
<tr>
<td>2</td>
<td>470</td>
<td>14.54</td>
</tr>
<tr>
<td>3</td>
<td>520</td>
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<td>5</td>
<td>660</td>
<td>10.35</td>
</tr>
<tr>
<td>6</td>
<td>880</td>
<td>7.77</td>
</tr>
<tr>
<td>7</td>
<td>950</td>
<td>7.19</td>
</tr>
</tbody>
</table>

BC concentration from the Aethalometer measurements is calculated by equation (4),

$$BC = \frac{S \times (\frac{\Delta ATN_1}{100})}{Q_1 \times (1 - \zeta) \times MAC \times C \times (1 - k \times ATN_1(\lambda)) \times \Delta t}$$

(4)

where S is the filter area, ATN$_1$ the attenuation of light at the measurement spot 1, Q$_1$ volume flow at measurement spot 1, $\zeta$ parameter for correction of side air flow in the filter, MAC mass absorption cross section, C absorption enhancement in the filter due to multiple scattering of light, t time and k loading parameter used for the filter loading effect compensation (Drinovec et al. 2015).
Aethalometer automatically estimates biomass burning contribution using measurements at 470 and 950 nm and calculations based on the Aethalometer model presented by (Sandradewi et al. 2008). Aethalometer model utilized most commonly used Ångström absorption exponent (AAE) values of 1 for fossil fuel combustion and 2 for biomass burning (Favez et al. 2010, Harrison et al. 2013), which have been shown to give adequate results in case of long term BC measurements, when comparing the BC contribution of biomass to the biomass tracer levoglucosan (Bizjak 2016) and when evaluating the contribution of traffic emissions (Ježek 2015). On the contrary, a study from India showed that AAE cannot be used to identify the fuels used and is consequently not suitable as generic tracer for source contribution apportionment (Garg et al. 2016).

The uncertainty of the Aethalometer AE33 measurements is expected to be lower than that of the Aethalometer model AE31 measurements which is about ± 5 % (A. D. A. Hansen 2005, Titos et al. 2015).

4.2.2. Soot Particle Aerosol Mass Spectrometer (SP-AMS)

Measurements with SP-AMS were performed to get online chemically speciated mass and sizing measurements of particles with aerodynamic diameter roughly between 50 and 600 nm. SP-AMS used was a standard Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS), containing an intracavity continuous wave laser vaporizer (Onasch et al. 2012).

SP-AMS measurements were performed using thermal and laser vaporization modes in order to obtain data for nonrefractory (NR-PM) and the refractory (R-PM) components of particles. Sampled particles were focused into a narrow beam and vaporized with a laser vaporizer (1064 nm). Heating of these particles vaporizes refractory light-absorbing submicron aerosol particles (R-PM, i.e. rBC) as well as the species attached to the refractory black carbon (rBC). The attached species were vaporized at species specific vaporization temperatures. Alternatively, in the standard AMS configuration, particles are vaporized thermally at the center of ionization chamber on the porous tungsten surface heated to 600 °C (NR-PM). After ionization vaporized molecules were ionized by electron impact (EI, 70 eV) and detected with high-resolution time-of-flight mass spectrometer (Onasch et al. 2012, Tiitta et al. 2016).

SP-AMS sampled with the time resolution of 2 minutes and switched between tungsten vaporizer and dual laser + tungsten vaporization modes every 2 minutes. rBC and organic species mass concentration was obtained from SP-AMS mass spectra using standard AMS data
analysis methods (Jimenez et al. 2003, Onasch et al. 2012). Ionization efficiency mass-based calibrations in the AMS were performed using dried and size selected (300 nm) ammonium nitrate (NH₄NO₃) particles. Relative ionization efficiency (RIE) for rBC was evaluated with Regal Black particles (Regal 400R Pigment Black, Cabot Corp.). RIE for rBC of 0.24 was used together with laser vaporizer collection efficiency (CE) value of 0.6 to account for incomplete particle and laser beam overlap and for the shape and size of the particles (Willis et al. 2014, Tiitta et al. 2016). Results were corrected, by taking into account the influence of the background CO₂, and adjusted to standard temperature and pressure.

Due to technical issues only thermal vaporization mode was used on the 23rd of November, while on the 28th and 29th of November both vaporization configurations were used alternatingly every 2 min.(Onasch et al. 2012)

4.2.3. OC/EC analysis

Setup for the collection of filter samples for particulate carbon content analysis is shown on Figure 3 (in the bottom). Sample collection was done by using a constant flow of 5 lpm in each filter sampling line (combined flow of 10 lpm), that was adjusted with the Brooks 4800 Series Thermal Mass Flow controller. First, an impactor (Dekati PM₁₀ impactor) was used to remove larger particles. Downstream of the impactor the sampling line split into two parallel lines. First line consisted of two quartz filters (QF) in a sequence and the second line consisted of a Teflon filter (TF) that was followed by QF. 47 mm quartz fiber filters were used. As TF only captures the particles the analysis of the QF following the TF enables the estimation of gas phase organic vapors that get absorbed into the QF (Sippula et al. 2009, Sippula et al. 2007). Particulate organic carbon can be calculated by subtracting the amount of organic vapors (OC value obtained from the QF placed after the TF) from the OC value obtained from the front QF of the other parallel sampling line (Turpin, Saxena & Andrews 2000). Laboratory blank sample was collected on 20th of November 2017.

Analysis of the organic carbon (OC) and elemental carbon (EC) content in the filter samples was done with the Thermal-Optical Carbon Aerosol Analyzer (Sunset Laboratory Inc.). A punch of 1.5 cm² from the QF was placed into the thermal-optical analyzer, where it was first heated in helium atmosphere to volatilize organic carbon. After the temperature reduction, oxygen was added to the helium carrier gas. Organic compounds desorbed from the filter are oxidized to CO₂, reduced to methane and measured in the flame ionization detector. Then another heating in several steps was used for the oxidation of the elemental carbon. To determine the split between OC and EC He-Ne laser is used to monitor sample reflectance.
Some OC is pyrolytically transformed to EC during its volatilization. The split between OC and EC is determined at the point where the reflectance returns to the pre-pyrolysis value (Turpin, Saxena & Andrews 2000). Each sample was analyzed twice according to two different procedures: National Institute for Occupational Safety (NIOSH) procedure 5040 (The National Institute for Occupational Safety and Health 1999) and EUSAAR_2 (Cavalli et al. 2010). NIOSH thermal-optical protocol is one of the most widely used in the atmospheric research and the EUSAAR_2 is optimized for analysis of carbonaceous aerosols at European regional background sites. The protocols differed in the duration and values of temperature set points (Table 2) (Cavalli et al. 2010).

Table 2: Temperature and duration of the steps in NIOSH 5040 and EUSAAR_2 protocols for OC/EC analysis (Cavalli et al. 2010)

<table>
<thead>
<tr>
<th>Step</th>
<th>NIOSH 5040 T (°C), duration (s)</th>
<th>EUSAAR_2 T (°C), duration (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He1</td>
<td>250, 60</td>
<td>200, 120</td>
</tr>
<tr>
<td>He2</td>
<td>500, 60</td>
<td>300, 150</td>
</tr>
<tr>
<td>He3</td>
<td>650, 60</td>
<td>450, 180</td>
</tr>
<tr>
<td>He4</td>
<td>850, 90</td>
<td>650, 180</td>
</tr>
<tr>
<td>He/O₂ 1*</td>
<td>650, 30</td>
<td>500, 120</td>
</tr>
<tr>
<td>He/O₂ 2</td>
<td>750, 30</td>
<td>550, 120</td>
</tr>
<tr>
<td>He/O₂ 3</td>
<td>850, 30</td>
<td>700, 70</td>
</tr>
<tr>
<td>He/O₂ 4</td>
<td>940, 120</td>
<td>850, 80</td>
</tr>
</tbody>
</table>

* 2 % oxygen in UHP helium

The results of the thermal-optical analysis were the amounts of OC, EC and TC in μg/cm². This value was multiplied by the total sampling area on the filter (12 cm²) and divided by the volume of air sampled through the filter. Volume was calculated from the set flow in the filter sampling lines and the time of the filter sample collection. The final result was the amount of OC, EC and TC in μg/m³ of sampled air.

4.3. Data analysis

Wall loses (WL) affected the measured concentrations in all of the three methods used after the feeding of the chamber ended, which can be observed by the decreasing values of BC, rBC and EC in all the experiments (Results sections 5.1.2, 5.1.3 and 5.1.4). Although WL rates of
aerosols particles observed in the chamber were small, due to the low surface to volume ratio, in the previous experimental campaigns (Leskinen et al. 2015) it is important to estimate WL for reliable estimation of SOA formation (Tiitta et al. 2016). During the blank experiments with pure air, performed in the same chamber, the WL corrected particle mass concentrations 4 hours after the irradiation was 0.5 - 2.5 μg m⁻³ (Leskinen et al. 2015). The purpose of this work is the comparison of different methods of BC measurements and not the exact quantification of the BC, rBC or EC emission factors obtained with every method. No WL corrections were therefore applied, since all three methods sampled from the same medium and were therefore assumed to be equally affected by the WL.

Statistical analysis of the data obtained by the measurements was performed with MS Excel and IBM SPSS 24. In order to compare the results of Aethalometer (BC) and SP-AMS (rBC), time series results of both were transformed to 1 min time base. In case of Aethalometer, data with the time base of 1 s was averaged to obtain average minute concentrations of BC. Time base of rBC measurements was 4 min, 1 min values of rBC were obtained by linear extrapolation method. The comparison of EC with BC and rBC was performed by averaging BC and rBC values during the time period, that matched the time period of filter sample collection for the OC/EC analysis. The comparison of the different methods was done by Pearson correlation and ordinary least squares linear regression analysis.

Pearson correlation was performed based on the null hypotheses that there is no correlation between the results of the two measurement methods compared in each case:

a) H₀: There is no correlation between BC and rBC measurement results,
b) H₀: There is no correlation between BC and EC measurement results,
c) H₀: There is no correlation between rBC and EC measurement results and
d) H₀: There is no correlation between EC results obtained with the NIOSH 5040 protocol and the EC results obtained with the EUSAAR_2 protocol.

Two-tailed significance level of 0.01 was selected. \( R^2 \) value of the linear regression is the same as squared value of the Pearson correlation coefficient (R), therefore both statistical methods give similar conclusions about the correlation of the two methods analyzed. Results of both are shown to provide additional information about the significance of the correlation, in case of Pearson correlation results, and to better illustrate the relation between the methods, in case of the linear regression plots.
Linear regression analysis was done since it is commonly applied in such cases. The choice of the parameter on the x-axis is arbitrary, even though it should theoretically be without any statistical error – the condition that cannot be met when comparing different analysis methods (Hitzenberger et al. 2006).
RESULTS

The Results of the thesis are divided into five sections. The first section (5.1) has four sub-sections: presenting dilution ratios, temperature, relative humidity and atmospheric aging equivalence for each experiment (5.1.1), results of the Aethalometer measurements of BC (5.1.2), results of the SP-AMS measurements of rBC (5.1.3) and results of the OC and EC analysis with both thermal-optical protocols (5.1.4).

The second section (5.2) is evaluating the effect of aerosol aging on the Aethalometer measurements of BC, followed by third section (5.3) comparing the results of the NIOSH 5040 and EUSAAR_2 protocols used for the thermal-optical analysis. The fourth section (5.4) compares the BC and rBC measurements and the final section (5.5) inter-compares all the methods used, with the time base set by the filter samples (about one hour averaged data values). Effect of the aerosol aging is considered within the sections comparing different methods.

5.1. Measurements

5.1.1. Experimental conditions

DRs, average temperature, relative humidity and atmospheric aging equivalent for each of the experiments are shown in Table 3.

Table 3: Dilution ratios (DR), average temperature (T), relative humidity (RH) and atmospheric aging equivalence (T and RH with standard deviations from the start of the sample feeding until the end of the experiment)

<table>
<thead>
<tr>
<th>Date of experiment</th>
<th>DR</th>
<th>T chamber (°C)</th>
<th>RH (%)</th>
<th>Age (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.11.2017</td>
<td>440</td>
<td>22,5 ± 4,5</td>
<td>33,5 ± 11,2</td>
<td>1,65</td>
</tr>
<tr>
<td>28.11.2017</td>
<td>408</td>
<td>21,0 ± 1,9</td>
<td>30,6 ± 4,2</td>
<td>1,30</td>
</tr>
<tr>
<td>29.11.2017</td>
<td>402</td>
<td>18,6 ± 1,1</td>
<td>53,5 ± 5,4</td>
<td>1,23</td>
</tr>
</tbody>
</table>

Temperature and relative humidity values show, that the experimental conditions were slightly different between all three experimental days. The temperature was not as stable and was slightly higher on the 23rd of November (22,5 ± 4,5 °C) compared to the other two experimental days (21,0 ± 1,9 °C and 18,6 ± 1,1 °C). The average relative humidity was highest on the 29th of November (53,5 ± 5,4 %). On the 23rd and 28th of November the relative humidity was about 30 % (33,5 % and 30,6 %). Atmospheric aging equivalence in days ranged from 1,23 to 1,65.

The average DR in Table 3 are calculated with Vaisala CO2 chamber values on the 23rd and 29th, since the Siemens detector measurements on these two days showed some anomalies.
Average DR on the 28th is calculated from CO$_2$ measurements with Siemens detector. Final calculation of average DR could be affected by the results from different instruments used for the CO$_2$ measurements in the chamber. Detailed time series charts of temperature and relative humidity are shown in APPENDIX I, time series of CO$_2$ measurements, during the sample feeding, are shown in APPENDIX II and time series charts of dilution ratios are shown in APPENDIX III.

5.1.2. Aethalometer

BC concentrations from all seven wavelength channels for all three measuring days are shown in Figure 5, Figure 6 and Figure 7. These figures also include the calculated estimate of the proportion of biomass burning (BB) throughout each experiment, based on the Aethalometer model (Sandradewi et al. 2008) using AAE values of 1 and 2 for fossil fuel and biomass burning.

![Graph showing BC concentrations from Aethalometer measurements](image)

**Figure 5: Results of the Aethalometer measurements from 23rd of November 2017**

BC6 values obtained from the measurements at 880 nm are the defining standard used for BC concentration reporting (Aerosol d.o.o. 2016) and were used when comparing BC concentrations of Aethalometer with the EC and rBC concentrations of the other two methods. Data obtained from the other channels at different $\lambda$ was used to check the validity of the Aethalometer source apportionment model and for the evaluation of the aging effect on the Aethalometer measurements.
The BB contribution shown on all three figures (Figure 5, Figure 6 and Figure 7), based on the pre-set AAE values, was not meant to show exact contribution of the biomass burning. In addition, this thesis did not focus on the determination of the most appropriate values of AAE.
for fossil fuel and biomass burning for the selected fuel type and experimental conditions. Since only biomass burning (birch wood) source of emissions was used in all three experiments the biomass contribution was 100 %. Aethalometer model for the source attribution was therefore not needed, nor did it give accurate information from the determined BB value. Nevertheless, BB values are shown, because they indicate relative absorption enhancement (with increasing BB) between the measurements at two $\lambda$ (470 nm and 950 nm) used in the model. Increasing BB contribution therefore indicates increased absorption measured at 470 nm relative to that measured at 950 nm.

5.1.3. SP-AMS

Time series results of linearly extrapolated rBC concentrations (as Regal Black equivalent) are presented in Figure 8 and Figure 9 for the experiments on the 28th of November and 29th of November. Misalignment of the rBC peak with the end of the sample feeding on the 28th is probably caused by the 4 min time base of the rBC measurements.

![Figure 8: Times series of the linearly extrapolated SP-AMS rBC values from the measurements on the 28th of November](image-url)
Results of the other AMS analysis except rBC for all three experimental days are shown and discussed in APPENDIX IV. Although they are not discussed in detail in this thesis, that focuses primarily on the measurements of the rBC, they provide additional information about the changing properties (i.e. chemical composition) of soot agglomerates during each experiment. They show that the aging increased the organic content of the soot particles and changed the organic aerosols (OA) elemental ratios by increasing O:C ratio and decreasing H:C ratio and furthermore by increasing OA oxidation state (OS). SOA formation was also observed in a smog chamber experiment using longleaf pine wood and white birch bark (Tasoglou et al. 2017).

5.1.4. OC and EC
Results of the OC, EC and TC values obtained by NIOSH 5040 and EUSAAR_2 procedures of thermal-optical analysis are shown in Figure 10, Figure 11 and Figure 12. Detailed numerical values of OC/EC analysis of both protocols are shown in the APPENDIX V.

Some of the results of the OC and EC analysis, especially performed with the EUSAAR_2 protocol, were negative (Figure 11, Figure 12). All the EUSAAR_2 analysis was done after the NIOSH 5040 analysis which could potentially increase the possibility of contamination of the samples during the handling or storage of the samples, although all the necessary precautions were done. Additionally, high dilution ratios could also affect the reliability of the performed analyses, as the concentrations determined during the analysis were close to the lower detection limits of the method used.
Figure 10: OC, EC and TC values obtained by NIOSH 5040 (in blue) and EUSAAR_2 (in green) procedures from samples collected on 23.11.2017

Figure 11: OC, EC and TC values obtained by NIOSH 5040 (in blue) and EUSAAR_2 (in green) procedures from samples collected on 28.11.2017

Figure 12: OC, EC and TC values obtained by NIOSH 5040 (in blue) and EUSAAR_2 (in green) procedures from samples collected on 29.11.2017
5.2. Aerosol aging and Aethalometer results

Measurements from all three days (Figure 13, Figure 14 and Figure 15) demonstrate that values of BC concentration measured at the lowest $\lambda$ (370, 470 nm) do not follow the measurements at the highest $\lambda$ (880, 950 nm) as much as they follow each other throughout the experiment. The same can be observed vice-versa for the measurements at the highest $\lambda$, compared to those at the lowest $\lambda$. The measurements at 370 and 470 nm initially showed higher BC concentrations, which changed after the sample feeding stopped. After that and during the aging their measured BC values were more similar to the values of BC measured at 880 and 950 nm or even lower on the 23$\text{rd}$ of November (Figure 13). Despite this, it can also be observed that during the aging, the variation of absorption at 370 and 470 nm started to increase. The variation of the measurements at 880 and 950 nm stayed similar throughout the experiment.

Figure 13: Results of the Aethalometer measurements at two highest and two lowest $\lambda$ (370, 470, 880, 950 nm) and ratio between the measurements at 470 and 950 nm from the 23$\text{rd}$ of November 2017
Figure 14: Results of the Aethalometer measurements at two highest and two lowest λ (370, 470, 880, 950 nm) and ratio between the measurements at 470 and 950 nm from the 28th of November 2017.

Figure 15: Results of the Aethalometer measurements at two highest and two lowest λ (370, 470, 880, 950 nm) and ratio between the measurements at 470 and 950 nm from the 29th of November 2017.
Plotted ratio of BC measured at 470 nm and 950 nm (Figure 13, Figure 14 and Figure 15; 470/950) is also affected by the higher variation of measurements at 470 nm. Measurements at this two λ were used because the Aethalometer model for source apportionment (Sandradewi et al. 2008) uses results from these two channels. Overall slightly increasing trend of the ratio can be observed in all three experiments during the aging processes. Slight absorption enhancement at lower λ is more obvious on the 23rd of November, which can be explained with slightly higher RH during the aging (APPENDIX I). Findings of two published studies also show that there is more absorption enhancements at higher RH values (Lack, Quinn et al. 2009, Arnott et al. 2003). Another study showed that absorption enhancements of primary organic aerosols were larger at 404 nm than at 532 nm (Lack et al. 2012).

Although slight increase of the absorption at lower λ was observed, it was not as large as the absorption enhancement of BC particles by as much as a factor of 1.9, that was observed in a smog chamber aging study with pine wood (Tasoglou et al. 2017).

5.2.1. Filter loading effect compensation parameter

Figure 16, Figure 17 and Figure 18 are showing the time series of the filter loading parameters k (for all seven channels) used for the calculation of the filter loading compensation, during all three experiments. The results show that parameter k is decreasing during the aerosol aging as was also found in the study published by (Drinovec et al. 2017). Values of k started to decrease shortly after the end of the sample feeding. Based on these findings, parameter k may be used as an indicator for the increasing coating of the particles and for the increasing atmospheric age of the aerosols.
Figure 16: Time trends of the compensation parameters $k$, for all channels, during the Aethalometer measurements on the 23rd of November 2017

Figure 17: Time trends of the compensation parameters $k$, for all channels, during the Aethalometer measurements on the 28th of November 2017
5.3. NIOSH 5040 and EUSAAR_2

Figure 10, Figure 11 and Figure 12 show that both protocols used for the OC/EC analysis gave similar values in some cases, while in several cases their results were quite different. Use of the NIOSH 5040 protocol showed higher concentrations of OC in 13 samples, while higher EC concentrations were only found in 9 samples analyzed by the EUSAAR_2 protocol.

Comparison between the measurements of the EC, OC and TC by both thermal-optical protocols, was done by the linear regression analysis. Values from the NIOSH 5040 were chosen as independent variables and values from the EUSAAR_2 as dependent variables, because NIOSH 5040 protocol was used before the EUSAAR_2 protocol (Cavalli et al. 2010) and because it is one of the most commonly used protocols.

Figure 19 shows the linear regression analysis results for EC, OC and TC values obtained with NIOSH 5040 and EUSAAR_2 procedures. The figure shows that both protocols are correlated well in case of EC values, having the \( R^2 \) value of 0.94, meaning that nearly 94 % of variation of values obtained by the EUSAAR_2 procedure can predict the variation of values obtained by the NIOSH 5040 procedure. On the contrary the \( R^2 \) value of 0.044 from the linear regression of the OC values suggests that the procedures are not correlated and that only about 4 % of the OC variation of EUSAAR_2 procedure can explain the variation of the NIOSH 5040 OC
values. Lower $R^2$ value for the OC is also reflected in the $R^2$ value of 0.65 from the linear regression analysis of TC values from both procedures.

![Graph showing linear regression analysis](image)

Figure 19: Linear regression analysis between EC (a), OC (b) and TC (c) values obtained with NIOSH 5040 and EUSAAR_2 protocols

5.3.1. OC/EC ratio and aging

Figure 20 shows the ratios of OC/EC for all three experimental days, obtained by both thermal optical protocols. Numerical values of the OC/EC ratios are presented in the table of OC/EC results in APPENDIX V. Low and negative values of OC (Figure 11 and Figure 12), caused by the high dilution ratios or possible OC loses during handling and storage, are possible reasons for low OC/EC ratios. Negative values of particulate OC was also caused by higher content of OC determined in the backup filters, which could be due to the higher abundance of VOCs such as small carboxylic acids that can be captured in the backup QF, especially since slightly more
oxidized organics were detected by FTIR in undiluted emissions during the measurements on the 28th and 29th of November 2017 (APPENDIX VI).

From the results of the OC/EC analysis by both protocols it is not possible to conclude if the aging of the aerosols had big effect on the OC/EC ratio. The presence of the O3 scrubber during the measurements on the 28th and 29th of November could potentially be the reason for the different results on these two days compared with the results of the 23rd of November, since the presence of the O3 could cause additional chemical changes of the aerosols collected on the filters on the 23rd of November.

Figure 20: Ratios of OC/EC for all three experimental days obtained by NIOSH 5040 and EUSAAR_2 protocols: (a) from the 23rd of November, (b) from the 28th of November and (c) from the 29th of November
5.4. Black carbon and refractory black carbon

Figure 21 and Figure 22 are showing the comparison of the Aethalometer measurements of BC (at 880 nm) and SP-AMS rBC time series data. Due to the linear extrapolation of SP-AMS data, to get one minute values from the values from every four minutes, the rBC concentrations are smoother. During both experiments the ratio BC/rBC became constant quickly after the start of the sample feeding and settled at around 2 (average value of 1.9 after the initial 5 minutes on the 28th and 2.2 after 5 min on the 29th). Initial higher BC/rBC ratio, observed on both experimental days, may be caused by the smaller time base of the original Aethalometer measurements, which enabled faster BC detection response after the start of the sample feeding.

![Figure 21: BC and rBC data – 28.11.2017](image)

The ratio of BC/rBC did not change a lot during the aging of the aerosols on the 28th of November (Figure 21). Only a very slight decrease may be observed during the aging. In contrast, the increase of the BC/rBC ratio was more obvious during the aging on the 29th of November (Figure 22). It increased from about 2 to 2.4.
Table 4 and Table 5 are presenting the results of the Pearson correlation analysis between the values of BC (880 nm) and rBC on the 28th and 29th of November 2017.

Table 4: Results of the Pearson correlation between the rBC and BC measurements on the 28th of November for the entire time period of the measurements, during fresh emissions and during the emissions aging

<table>
<thead>
<tr>
<th></th>
<th>Pearson correlation (R)</th>
<th>Sig. (2-tailed)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>all</td>
<td>0.992**</td>
<td>0.000</td>
<td>395</td>
</tr>
<tr>
<td>fresh</td>
<td>0.970**</td>
<td>0.000</td>
<td>154</td>
</tr>
<tr>
<td>aged</td>
<td>0.997**</td>
<td>0.000</td>
<td>241</td>
</tr>
</tbody>
</table>

**. Correlation is significant at the 0.01 level (2-tailed).

Table 5: Results of the Pearson correlation between the rBC and BC measurements on the 29th of November for the entire time period of the measurements, during fresh emissions and during the emissions aging

<table>
<thead>
<tr>
<th></th>
<th>Pearson correlation (R)</th>
<th>Sig. (2-tailed)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>all</td>
<td>0.991**</td>
<td>0.000</td>
<td>384</td>
</tr>
<tr>
<td>fresh</td>
<td>0.977**</td>
<td>0.000</td>
<td>145</td>
</tr>
<tr>
<td>aged</td>
<td>0.996**</td>
<td>0.000</td>
<td>239</td>
</tr>
</tbody>
</table>

**. Correlation is significant at the 0.01 level (2-tailed).

Separate correlation analyses were performed for the whole period of the measurements and separately for the time period before aging in the chamber started (fresh) and during the
chamber aging (aged). The null hypotheses that there is no correlation between rBC and BC values can be rejected in all cases with high significance levels (P < 0.01). Furthermore high values of Pearson correlation coefficient (R) between 0.97 and 0.99 are suggesting strong correlation between the values of BC, measured with the Aethalometer, and rBC, measured with SP-AMS. Slightly higher R values for aged emissions can be explained by more data points (N) during the aging and by the different initial responses between the two methods due to the different measurement time bases (observed in Figure 21 and Figure 22). Good agreement between the Aethalometer measurements of BC and SP-AMS measurements of rBC is also reflected in high $R^2$ values of the linear regression analysis shown in Figure 23 and Figure 24. On both days more than 98 % of the BC variance can be explained with the rBC variance.

![Figure 23: Linear regression of BC and rBC values from the measurements on the 28th of November 2017](image)

Relative stability of the BC/rBC ratios throughout the measurements on both experimental days, especially on the 28th of November, and high degree of correlation, before and after the start of the aging in the chamber, suggest that aerosol aging did have a large effect on the measurements of BC and rBC or that both methods were similarly affected by the aging of the aerosols.
5.4.1. The effect of particle size

Light absorption BC measurements (i.e. Aethalometer) are not affected by the lowest detectable particle size, because they are not referring to the properties of a single particle (Petzold et al. 2013). Aethalometer measurements were performed without the use of a pre-impactor at the sample inlet, that would cut-off particles of certain size. Aethalometer measurements were therefore not affected by the detectable particle size limits. In contrast, the SP-AMS technique is limited by the size of the particles that can be focused by the aerodynamic lens (Tiitta et al. 2016, P. Liu et al. 2007). Aerodynamic focusing lens system evaluated by P. Liu et al. (2007) had 90 % transmission efficiency for the particles with the median diameter of roughly between 70 - 350 nm.

Results of the SMPS measurements throughout each experiment were used to determine if particle size could affect the results obtained by the Aethalometer and SP-AMS. Size distribution of the particles was measured, based on their electrical mobility with the time resolution of 5 min. The lowest detection limit of the particles was 14,3 nm and the upper size limit of detectable particles was 697,8 nm.

Figure 25, Figure 26 and Figure 27 are showing the results obtained by SMPS on each measuring day. Grey areas show the range of particle sizes (from the geometric mean divided by the geometric standard deviation factor to the geometric mean multiplied by geometric standard deviation factor) that contains about two thirds of all the values (if lognormal distribution of the data is assumed).
Figure 25: Geometric mean of the particle size during the experiment on the 23rd of November (upper limit of grey area obtained by multiplying geometric mean by geometric standard deviation factor, lower limit of grey area obtained by dividing geometric mean by geometric standard deviation factor)

Figure 26: Geometric mean of the particle size during the experiment on the 28th of November (upper limit of grey area obtained by multiplying geometric mean by geometric standard deviation factor, lower limit of grey area obtained by dividing geometric mean by geometric standard deviation factor)

Figure 27: Geometric mean of the particle size during the experiment on the 29th of November (upper limit of grey area obtained by multiplying geometric mean by geometric standard deviation factor, lower limit of grey area obtained by dividing geometric mean by geometric standard deviation factor)
In previous study performed in the same chamber the median diameter of soot agglomerates changed from 70 - 120 to 150 - 220 nm during aging (Tiitta et al. 2016). Similar increase was only observed on the 23rd, while the geometric mean of the particle sizes stayed more or less unchanged during the remaining two experiments. Nevertheless, the results of the SMPS particle size distribution analysis suggest that particle size should not have any considerable effect on the measurements performed with the Aethalometer and SP-AMS, since the majority of the particles is within the 100 % detection efficiency particle size interval of the SP-AMS.

5.5. Comparison between all methods

Simultaneous comparison between all methods of BC detection used on each experimental day was done by calculating the average BC and rBC concentrations during the time of the filter sample collection for the thermal-optical analysis. The value of the statistical analysis for each experiment is consequently highly limited by the low number of data points.

Correlation analysis was performed to determine correlation coefficients with significance levels between different pairs of measurement methods for each experiment (Table 6, Table 7 and Table 8). Linear regression analysis was used for all three pairs of measurement methods, including the two protocols of the thermal-optical analysis, to check if the variation of rBC values could predict the variation of BC and EC (Figure 29 and Figure 30) or if the BC variation could predict the variation of EC values (Figure 28). To easily compare the findings with the results obtained by (Nielsen et al. 2017) rBC was chosen as independent variable for the analysis of results from 28th and 29th of November (BC and EC were dependent variables). Linear regression between BC and EC, from the 23rd of November, was done by selecting BC as independent variable.

Table 6 shows the results of the correlation analysis between the Aethalometer measurements of BC and EC values determined by the thermal-optical method using two different protocol of analysis from the measurements on the 23rd of November 2017. The null hypothesis that there is no correlation between the different measurement methods for EC and BC can be rejected with high significance (P < 0.01). The highest Pearson correlation coefficient (R = 0.995) was determined between the EC concentrations determined with the NIOSH 5040 protocol and Aethalometer BC concentrations. The lowest value of correlation (R = 0.964) was determined between the EC values determined by NIOSH 5040 and EUSAAR_2 protocols.
Table 6: Correlation analysis of the results from the 23rd of November

<table>
<thead>
<tr>
<th></th>
<th>EC NIOSH 5040</th>
<th>EC EUSAAR_2</th>
<th>BC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>EC NIOSH 5040</strong></td>
<td>Pearson Correlation</td>
<td>1</td>
<td>0,964**</td>
</tr>
<tr>
<td></td>
<td>Sig. (2-tailed)</td>
<td>0,008</td>
<td>0,000</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td><strong>EC EUSAAR_2</strong></td>
<td>Pearson Correlation</td>
<td>0,964**</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Sig. (2-tailed)</td>
<td>0,008</td>
<td>0,005</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td><strong>BC</strong></td>
<td>Pearson Correlation</td>
<td>0,995**</td>
<td>0,975**</td>
</tr>
<tr>
<td></td>
<td>Sig. (2-tailed)</td>
<td>0,000</td>
<td>0,005</td>
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<tr>
<td></td>
<td>N</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

**. Correlation is significant at the 0.01 level (2-tailed).

Figure 28 shows the linear regression analysis of BC and EC values obtained by the measurements on the 23rd of November 2017. High R² values confirm that high degree of the BC variation can be explained by the variation of the EC values determined by both protocols.

Figure 28: Linear regression analysis of the results from the 23rd of November

Table 7 is showing the results of the Pearson correlation between the results of the BC measurement methods used on the 28th of November. The null hypothesis that there is no correlation between the selected measurement methods can be rejected in all cases with high
degree of significance (P < 0,01). The highest Pearson correlation (R = 1) coefficient can be observed between the BC and rBC measurements.

Table 7: Correlation analysis of the results from the 28th of November

<table>
<thead>
<tr>
<th>Method</th>
<th>Pearson Correlation</th>
<th>EC NIOSH</th>
<th>EC EUSAAR_2</th>
<th>BC</th>
<th>rBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC NIOSH 5040</td>
<td>Sig. (2-tailed)</td>
<td>1</td>
<td>0,997**</td>
<td>0,997**</td>
<td>0,996**</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>EC EUSAAR_2</td>
<td>Pearson Correlation</td>
<td>0,997**</td>
<td>1</td>
<td>0,988**</td>
<td>0,986**</td>
</tr>
<tr>
<td></td>
<td>Sig. (2-tailed)</td>
<td>0,000</td>
<td>0,002</td>
<td>0,002</td>
<td></td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>BC</td>
<td>Pearson Correlation</td>
<td>0,997**</td>
<td>0,988**</td>
<td>1</td>
<td>1,000**</td>
</tr>
<tr>
<td></td>
<td>Sig. (2-tailed)</td>
<td>0,000</td>
<td>0,002</td>
<td>0,000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>rBC</td>
<td>Pearson Correlation</td>
<td>0,996**</td>
<td>0,986**</td>
<td>1,000**</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Sig. (2-tailed)</td>
<td>0,000</td>
<td>0,002</td>
<td>0,000</td>
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<tr>
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<td>N</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

**. Correlation is significant at the 0,01 level (2-tailed).

The degree of correlation between the results of the two methods increased when correlating averaged data from longer time period (Table 7) compared to the correlation of the measurements with the time base of 1 min (Table 4). The lowest degree of correlation was determined to be between EC EUSAAR_2 and both other analysis methods: rBC (R = 0,986) and BC (R = 0,988). The degree of correlation was still high.

Figure 29 presents the linear regression analysis between the BC measurement methods from the 28th of November 2017. The highest R² value of 0,9996 can be seen between the rBC and BC values, which differed roughly by a factor of 2.
Figure 29: Linear regression analysis of the results from the 28th of November

Table 8 shows the results of the correlation analysis between the BC methods used on the 29th of November 2017.

Table 8: Correlation analysis of the results from the 29th of November

<table>
<thead>
<tr>
<th></th>
<th>EC NIOSH</th>
<th>EC EUSAAR_2</th>
<th>BC</th>
<th>rBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC NIOSH 5040</td>
<td>Pearson Correlation</td>
<td>1</td>
<td>0.762</td>
<td>0.997**</td>
</tr>
<tr>
<td></td>
<td>Sig. (2-tailed)</td>
<td>0.134</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>EC EUSAAR_2</td>
<td>Pearson Correlation</td>
<td>0.762</td>
<td>1</td>
<td>0.779</td>
</tr>
<tr>
<td></td>
<td>Sig. (2-tailed)</td>
<td>0.134</td>
<td>0.120</td>
<td>0.119</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>BC</td>
<td>Pearson Correlation</td>
<td>0.997**</td>
<td>0.779</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Sig. (2-tailed)</td>
<td>0.000</td>
<td>0.120</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>rBC</td>
<td>Pearson Correlation</td>
<td>0.999**</td>
<td>0.781</td>
<td>0.999**</td>
</tr>
<tr>
<td></td>
<td>Sig. (2-tailed)</td>
<td>0.000</td>
<td>0.119</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

** Correlation is significant at the 0.01 level (2-tailed).

The null hypothesis that there is no correlation can be rejected (with P < 0.01) when correlating EC NIOSH 5040, BC and rBC values. Pearson correlation coefficient between BC and rBC and
EC NIOSH 5040 and rBC was 0.999. In case of EC EUSAAR_2 correlation with EC NIOSH 5040, BC and rBC the null hypothesis that there is no correlation cannot be rejected (P values of 0.134, 0.12 and 0.119 all higher than 0.01) (Table 8).

Figure 30 shows the linear regression analysis between the methods used on the 29th of November 2017. The lowest value of $R^2$ is explained by highly scattered values of EC EUSAAR_2.

Overall there is better correlation between the EC values of NIOSH 5040 protocol with the BC and rBC values on all three experimental days (Table 6, Table 7 and Table 8), although EUSAAR_2 protocol analyzed higher EC concentrations in more samples than the NIOSH 5040 protocol (Figure 10, Figure 11 and Figure 12).

5.5.1. Aerosol aging and ratios between different methods

Figure 31 illustrates how the ratio between all measurement methods changed during the aging in all three experiments. During the aging on the 23rd of November the ratio of EC/BC clearly increased, while it is hard to conclude anything from the changing ratios, obtained by the measurements on the 28th and 29th of November.
Figure 31: Comparison of all three BC measurement methods (23rd of November (a), 28th of November (b) and 29th of November (c))
6. DISCUSSION

The results of Pearson correlation analysis (Table 4, Table 5) and linear regression (Figure 23, Figure 24) between the BC and rBC concentrations are in accordance with the findings that BC mass concentrations from chemical and optical methods can differ by several factors, but are usually correlated with statistical significance level of $P \leq 0.05$ (Petzold et al. 2013).

Moreover, the high degree of correlation observed between all compared methods (Table 6, Table 7, Table 8) is also in accordance with several other studies. Comparison between BC measurements (Aethalometer AE16) and EC values obtained from the filter samples by the NIOSH 5040 method was also done for diesel exhaust aerosols. Good agreement between BC and EC values was observed (Ng et al. 2007). The average BC and EC values also agreed within their standard deviations in a study performed in Vienna area (Hitzenberger et al. 2006). Equivalent BC obtained by Aethalometer measurements and EC values were also found to be comparable in a study performed in the Ny-Ålesund station in the Arctic (Eleftheriadis, Vratolis & Nyeki 2009). Comparison between Aethalometer obtained BC values and NIOSH 5040 method obtained EC and OC values was performed in a study focusing on diesel particulate matter inside school buses. A correlation between BC and results from the open-faced cassettes was observed, but historically derived conversion factors to relate EC and BC were inappropriate (Borak et al. 2003). Good correlation between the EC (determined with EUSAAR-2 protocol), eBC and rBC values was also confirmed in another study focusing on the residential biomass combustion emissions (Nielsen et al. 2017).

Measurements of EC and rBC are relying on different measurement principles. While rBC is examined at the refractory end (4000 K), EC represents the residual part of the carbon mass during thermal-optical carbon analysis, which is evolved during the analysis at temperatures close to 900 °C, in the presence of $O_2$. EC includes rBC and possibly other non-BC carbonaceous components, mistakenly interpreted as BC (Sharma et al. 2017, Andreae, Gelenesér 2006). EC may overestimate BC and BC relative to rBC (Sharma et al. 2017). The results of the experiments on the 28th and 29th of November (Figure 29, Figure 30 and Figure 31) indeed show that EC values were higher than related rBC, while the values of BC were even higher than EC. These results are similar than the results from the comparison of long-term averaged monthly values of BC, rBC and EC measured in the high Arctic, that showed that rBC concentrations were the lowest and BC the highest with EC concentration in between (Sharma et al. 2017).
Equivalent BC, measured by Aethalometer, and EC concentrations from filter samples analyzed by thermal technique EnCan-total-900 (Huang et al. 2006, Chan et al. 2010) were 2.7 and 3.1 times higher than the values of rBC, obtained by single particle soot photometer (SP2) in a study performed at the Global Atmosphere Watch baseline observatory in Alert, Nunavut (82.5°N) (Sharma et al. 2017). Although Aethalometer BC concentrations were the highest in all experiments (Figure 28, Figure 29 and Figure 30) they were only up to about 2 times higher compared to the determined rBC and EC values.

Considering the results shown in Figure 10, Figure 11 and Figure 12, the results of the linear regression analysis between the two thermal-optical protocols (Figure 19) and all the correlation analyses (Table 6, Table 7 and Table 8), it could be concluded that NIOSH 5040 gave better results than EUSAAR_2. In contrast, a study performed in the Philippines concluded that EUSAAR_2 protocol seems to be the most accurate, while it still was not the best one for resolving the individual OC values (Bautista et al. 2015).

The ratios between the different methods (Figure 31) in this study are of the same order of magnitude than those identified in the study that focused on the comparison of thermal and optical methods for EC and BC detection in Vienna (Hitzenberger et al. 2006), that did not consider any effect of the aerosol aging.

On the 23rd of November a slight increase of OC/EC ratios, determined by EUSAAR_2 protocol; is observed during the chamber aging (Figure 20). Higher analyzed fraction of OC could cause a higher response in the Aethalometer measurements (Ng et al. 2007) and can have a high impact on the overall absorption intensity, especially at lower λ (Olson et al. 2015), which could be observed in Figure 5 and Figure 13. In all the other cases, the increasing of the OC/EC ratio during the aging was not observed as clearly.
7. CONCLUSIONS AND SUMMARY

Comparison of the chemical, refractory and optical methods, that was the main objective of this study, shows that there is in general good correlation between the methods. Values of EC, rBC and BC determined by the different methods differed between each other similarly than in the previously published and herewith cited studies. BC (880 nm) and rBC mass concentrations differed by a factor of 2.

Different time base of the methods must be considered when selecting one for a specific purpose. Methods with larger time base, such as the ones relying on the filter collection (thermal-optical analysis), are not able to show variations of measured parameters within smaller time periods and are therefore not as appropriate for precise following of the high variability of combustion emissions near the source. In addition, filter collection methods are not suitable for the emissions monitoring in real-time.

There were some differences between the OC and EC concentrations determined by the NIOSH 5040 and EUSAAR_2 protocols. While the EC results were similar, the OC values differed more. Uncertainty of the thermal-optical analysis results in this study could be affected by the relatively high DR and consequent low sample amount on filters. Aerosol aging should affect the ratio of OC/EC, even though it was not clearly observed in this study.

During the aging, the ratio between the BC and rBC was found to change. Possible absorption enhancement in the optical methods must be considered carefully especially considering that the aging equivalent in this study (roughly 1,5 days) was much lower than the estimated BC lifetime in the atmosphere of about one week. Longer aging time could potentially cause different results and affect the comparison between the methods more. To understand the effects of aging on the aerosol properties, it is important to consider changes of the chemical and physical properties that are not evaluated directly with optical methods.

Chamber aging experiments, where the conditions can be carefully adjusted and monitored, are an effective way of studying the effects of the atmospheric aging on the properties of the aerosols. More studies could be performed to evaluate the effect of the longer atmospheric aging on the measurements of BC and to determine the most appropriate method for aerosolized BC analysis, that could potentially be used as a reference method.
8. REFERENCES


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Ježek, I. 2015, Contribution of traffic and biomass burning to air pollution discriminated with Aethalometer measurements of black carbon, Doctoral dissertation, University of Ljubljana Faculty of Mathematics and Physics Department of Physics Chair of Meteorology, Ljubljana.


APPENDICES

APPENDIX I  Time series of temperature and relative humidity
APPENDIX II  Time series of CO₂ measurements
APPENDIX III  Time series of dilution ratios
APPENDIX IV  Time series of the AMS results of the major compounds condensed on the soot agglomerates
APPENDIX V  Results of the thermal-optical OC/EC analysis with NIOSH 5040 and EUSAAR_2 protocols
APPENDIX VI  Gas-phase organic emissions during the sample feeding
APPENDIX I

Time series of temperature (T; °C) and relative humidity (RH) during all three experiments.

23.11.2017 - Temperature and relative humidity

28.11.2017 - Temperature and relative humidity
29.11.2017 - Temperature and relative humidity

- **RH (%)**
- **T (°C)**

Sample feeding stops
UV lights on
APPENDIX II

Time series of CO\textsubscript{2} values for raw emissions (FTIR), first dilution (ABB) and fully diluted sample in the chamber (Vaisala, Siemens) during the sample feeding of all three experiments. The second peak of the CO\textsubscript{2} comes after the introduction of the second batch of birch wood into the stove.

![23.11.2017 - CO\textsubscript{2} values](image-url)
APPENDIX II

**28.11.2017 - CO₂ values**

**29.11.2017 - CO₂ values**
APPENDIX III

Time series of dilution ratios (DR) during the sample feeding of the chamber, based on the FTIR CO₂ measurements and CO₂ measurements in the chamber, measured by Vaisala and Siemens detectors. On the 28th only Siemens CO₂ detector was working. Scale of the charts is adjusted to only show the DR towards the end of the chamber filling, since initial calculated DR are much larger.
28.11.2017 - DR time series

29.11.2017 - DR time series
AMS results from the 23rd of November 2017, without the WL corrections:

Oxidation state (OS) at the end of experiment on the 23rd of November 2017 was around 0.22-0.28 (H:C=1.3, O:C=0.8). In the previous experiment in the same chamber the OS was 0.08-0.14 (H:C=1.4, O:C=0.7) (Tiitta et al. 2016)
AMS results from the 28th of November 2017, without the WL corrections:
At the end of experiment on the 28th of November 2017 OS was around 0.31-0.32 (H:C=1.2, O:C=0.8)
AMS results from the measurements on the 29th of November 2017, without the WL corrections:

At the end of experiment on the 29th of November 2017 the OS was around 0,5 (H:C=1,18, O:C=0,86).
Despite no WL corrections were applied the AMS results of all three experimental days show that the organic mass in the aerosol particles increased during the aging in the chamber, nitrates content decreased, H:C elemental ratio increased and O:C ratio decreased.
APPENDIX V

Results of the thermal-optical OC/EC analysis with NIOSH 5040 and EUSAAR_2 protocols

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>OC (µg/filter)</th>
<th>EC (µg/filter)</th>
<th>TC (µg/filter)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NIOSH 5040</td>
<td>EUSAAR_2</td>
<td>NIOSH 5040</td>
</tr>
<tr>
<td>Lab Blank</td>
<td>1,22</td>
<td>1,80</td>
<td>0</td>
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</table>

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>OC (µg/m³)</th>
<th>EC (µg/m³)</th>
<th>TC (µg/m³)</th>
<th>OC/EC</th>
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</thead>
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<td>82,42</td>
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<td>37,56</td>
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<td>9</td>
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<td>21,74</td>
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</table>
Average values of gas-phase organic emissions, measured with FTIR, during the sample feeding for each experiment. Non-methane alkanes include: ethane, propane, butane, pentane, hexane, heptane and octane. Unsaturated aliphatics include: acetylene, ethylene, propene and 1,3-butadiene. Aromatics include: benzene, toluene, m-xylene, o-xylene, p-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene. Oxidized organics include: formic acid, acetic acid, formaldehyde, acetaldehyde, methanol, ethanol, propanol and methyl tertiary butyl ether.