On the Relationship of Biogenic Primary and Secondary Organic Aerosol Tracer Compounds on the Aethalometer Model Parameters

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ABSTRACT

The aethalometer model has shown to offer a fast, inexpensive and robust method for source apportionment. The method relies on aerosol light absorption attribution, mass balance of the total carbon and results in a fraction of unaccounted, residual carbon that has been associated to biogenic carbon due to its presumably non-light absorbing properties. This residual carbon and its relation to tracers of biogenic primary and secondary organic aerosol was investigated at a rural measurement station in Sweden. Special focus is devoted to 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), a second-generation oxidation compound in biogenic secondary organic aerosols. The results show that the residual carbon and the biogenic tracers show a high degree of correlation and that the tracers were highly seasonally dependent with largest carbon contributions during summer. MBTCA showed positive correlation with the aethalometer model derived absorption coefficients from fossil fuel carbonaceous aerosol, stressing the suspicion that biogenic aerosol might be falsely apportioned to fossil fuel carbon in the aethalometer model. MBTCA showed an increasing degree of correlation with higher aethalometer absorption coefficient wavelengths. However, spectrophotometric analysis revealed that the ambient concentrations of MBTCA are most likely to low to give a significant response in the aethalometer. These results support the application of MBTCA as a molecular tracer for biogenic secondary organic aerosol and indicates that a large fraction of the aethalometer model residual carbon is of biogenic origin. Future studies should investigate the light absorbing properties of precursor monoterpenes such as α-pinene, their oxidation products and eventual influence on the aethalometer model.

Keywords: Aethalometer; Source apportionment; Biogenic aerosol.

INTRODUCTION

The carbonaceous aerosol contributes to approximately 20–50% to the total aerosol mass in Europe (Kanakidou et al., 2005; Putaud et al., 2010; Fuzzi et al., 2015). Its high abundance, detrimental health effects and climate impact makes the carbonaceous aerosol crucial to study as an environmental stressor. The ambient carbonaceous aerosol mainly originates from three distinguished sources: fossil fuel combustion, biomass burning and biogenic emissions (Lioussse et al., 1996). Due to the detrimental effects of combustion generated aerosol particles, fossil fuel combustion and biomass burning aerosol physicochemical properties and related source apportionment have gained large attention in the past (Barregard et al., 2006; Naeher et al., 2007; Bolling et al., 2009; Schlestedt et al., 2010; Janssen et al., 2011; Bond et al., 2013). However, there are only a few source apportionment studies focusing on the biogenic carbonaceous aerosol fraction (Yttri et al., 2011).

Biogenic aerosols are comprised of biogenic primary organic aerosols (BPOA) and biogenic secondary organic aerosols (BSOA). BPOA can be found as pollen, bacteria, fungal spores and plant debris. BSOA is the product of biogenic volatile organic compound (BVOC) oxidation in the atmosphere. BVOCs are used as communicative tool as well as to handle abiotic and biotic stress and is emitted globally in large quantities from terrestrial and aquatic plants (Gabrić et al., 2001; Penuelas and Lušia, 2003; Sharkey et al., 2008; Monson et al., 2013; Glasius and Goldstein, 2016; Steinke et al., 2018). Emissions of BPOA and BVOCs have been shown to increase with increasing photosynthetically active radiation (PAR) and temperature (Guenther et al., 1993; Guenther et al., 1995; Hakola et al., 2003), which explains the dominance of the biogenic mass fraction in carbonaceous aerosol during summer (Gelencser et al., 2007; Genberg et al., 2011; Yttri et al., 2011; Martinsson et al., 2017a, b). The main BVOC is isoprene, which is emitted...
mostly from deciduous forests with an annual emission rate of 400-600 Tg y⁻¹ (Laathawornkitkul et al., 2009). Coniferous forest emits large quantities (30–500 Tg y⁻¹) of monoterpenes such as α-pinene, β-pinene, Δ²-carene and limonene (Räisänen et al., 2008; Laathawornkitkul et al., 2009; Hakola et al., 2012). The α-pinene contributes to approximately 40% of the global monoterpene emissions (Guenther et al., 2012). Landmasses at northern latitudes are largely covered by coniferous forests. Global climate modeling has shown that these areas are the most susceptible for global warming in terms of temperature increment (IPCC, 2013). Hence, following an increase in temperature may cause a significant increase in monoterpene emission at these latitudes (Sporre et al., 2019). Consequently, global BSOA production may increase due to increased BVOC emissions.

Andersson-Sköld and Simpson (2001) showed that monoterpene BSOA may contribute to 50% of the total organic aerosol mass over the Nordic countries with α-pinene being the dominant precursor compound. Atmospheric oxidation of α-pinene can result in the production of first-generation oxidation products including pinic acid, pinonic acid and pinonaldehyde (Larsen et al., 2001; Jaoui and Kamens, 2002; Lee et al., 2006). The 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) is produced by gas-phase oxidation of pinonic acid ( Muller et al., 2012), and is thus a second-generation oxidation product from α-pinene. MBTCA has been suggested and used as a tracer for BSOA originating from OH-initiated oxidation of monoterpene emissions (Szmacielski et al., 2007; Zhang et al., 2010). MBTCA has low volatility (1.8 ± 1.3·10⁻³ µg m⁻³) and an atmospheric lifetime of 3–5 days assuming an average daily OH radical concentration of 10⁶ molecules cm⁻³ (Donahue et al., 2013; Kostenidou et al., 2018), and has been detected and measured in various terrestrial locations on Earth (Kubatova et al., 2000; Kubatova et al., 2002; Gao et al., 2006; Lewandowski et al., 2007; Kourchnev et al., 2008a, b; Fu et al., 2009; Kourchnev et al., 2009; Yasmeen et al., 2011; Vogel et al., 2013; Martinsson et al., 2017c). Recently, Kostenidou et al. (2018) presented a high-resolution aerosol mass spectrometry (HR-AMS) spectra of MBTCA and suggested to use the m/z 141 as a signature for MBTCA in AMS measurements. Hence, MBTCA has great potential acting as a high time resolution tracer for BSOA emissions.

Source apportionment as a concept offers a basis for decision making in order to mitigate health and climate effects of carbonaceous aerosol. Low cost, low maintenance and high time resolution are desirable attributes of an auspicious source apportionment method. The aethalometer model, originally presented by Sandradewi et al. (2008a), utilizes differences in the spectral light absorption of fossil fuel combustion and wood burning aerosol to apportion the organic aerosol mass to these two sources. All non-light absorbing carbon present are, through mass balance of the total carbon apportioned as residual carbon, which is thought to contain large portions of the biogenic carbon as BSOA or BPOA. The aethalometer model has been proven to deliver a robust source apportionment with high time resolution to a low cost (Martinsson et al., 2017b). In a recent study by Martinsson et al. (2017b) it was shown that the wood burning parameter from the aethalometer model correlated satisfactorily with the chemical tracer for wood burning, levoglucosan. This result can be viewed as a strong indicator of the method working correctly for wood burning apportionment. Hence, the aethalometer model combustion components, wood burning and fossil fuel combustion, has been evaluated against strong source indicators, tracers, such as levoglucosan and radiocarbon (¹⁴C). BSOA compounds have been shown to have low or negligible light absorption due to absence of conjugated molecular systems (Nakayama et al., 2010; Henry and Donahue, 2012; Laskin et al., 2014). However, whether increased mass concentrations of non-light absorbing carbon have effect on filter based light absorption techniques for source apportionment purposes remains unexplored. In this study we want to investigate the aethalometer model and the presumably non-light absorbing residual carbon and its possible strong association to biogenic carbon through measurement of a biogenic tracers and in particular a tracer for monoterpene oxidation, MBTCA.

METHODOLOGY

Measurement Site and Sampling

Ambient aerosol sampling was conducted at the aerosol, clouds and trace gases research infrastructure (ACTRIS) and European Monitoring and Evaluation Programme (EMEP) Vavilh measurement station. Vavilh measurement station was located on a ridge at an altitude of 172 m.a.s.l. (56°01' N, 13°09' E) in southern Sweden. The surrounding landscape consists of mixed deciduous and coniferous forests. The measurement station itself was in the middle of a small pasture that is occasionally visited by grazing cattle from May to September. The cities closest to Vavilh are Helsingborg, Malmö and Copenhagen located at distances of 20, 50 and 65 km, respectively, in the west, south-west direction. Aerosols were sampled through a PM₁₀ inlet at 38 L min⁻¹ on pre-heated (900°C for four hours) 47 mm quartz fiber filters (Pallflex 2500QAT-UP) during 72 h using an automatic low volume sampler (Leckel SEQ46/50). Active carbon denuders were installed in the sampling line together with double filters in order to correct for sampling artifacts caused by VOCs, the denuders were replaced once every year. Following sampling, the filters were placed in petri dishes, wrapped in aluminum foil and stored in a -18°C freezer until analysis. Sampling was conducted continuously from 2007 until 2017. In this paper we used filters that were sampled during April 2013 to August 2013 (N = 47) and September 2015 to March 2016 (N = 61). The reason for two incoherent sampling periods was the purpose to cover all months in a year together with varying instrument availability and functioning during the operation of the measurement station. The Vavilh measurement station was decommissioned during 2018 and all measurement activity has been moved to the ACTRIS, EMEP and Integrated Carbon Observation System in Sweden (ICOS), Hyltemossa measurement station 20 km east of Vavilh.

Thermo-optical Analysis

Organic carbon (OC), elemental carbon (EC) and total
carbon (TC) was derived from thermo-optical analysis of the filters using a DRI carbon analyzer (model 2001) with the EUSAAR_2 analytic protocol (Cavalli et al., 2010). The method utilizes the refractive properties of the carbonaceous aerosol to evolve and quantify the carbon at different temperatures in different atmospheres. In short, the EUSAAR_2 protocol initiate the analysis by allowing OC from a 0.5 cm² filter to evolve in an inert He-atmosphere to a maximum temperature of 570°C. During the heating process a 633 nm He/Ne laser is continuously irradiating the filter, a photodetector is mounted 180° from the laser light path to measure the light transmission through the filter. When the laser transmission signal reaches its baseline value the remaining carbon is defined to be EC. The EC is then heated from 500 to 850°C in a 2% O₂ atmosphere, allowing refractory carbon to be combusted. All carbon that are evolved from the filter are oxidized to CO₂. The CO₂ is further reduced to methane by passing hydrogen gas over a zinc catalyst. Finally, the methane is quantified using a flame ionization detector (FID). A recent study by Cavalli et al. (2016) estimated the thermo-optical analysis uncertainty of TC from Vavilh filter samples to 17% relative standard deviations (RSD).

**Light Absorption Measurements**

The light absorption of ambient aerosols was measured with an aethalometer (AE33, Magee Scientific). Aerosols were sampled with a flow of 5 L min⁻¹ through a PM₁₀ inlet to the aethalometer where the aerosol were deposited on a filter spot. The aethalometer filter spot is continuously irradiated by seven LEDs with wavelengths from 370 nm to 950 nm. The light attenuation was measured with photodetectors with a time resolution of 1 min. The aethalometer, model AE33, was developed to correct for the artefacts common in filter-based light absorption techniques, the shadowing effect and the filter matrix scattering effect (Drinovec et al., 2015). These artefacts are described in detailed by Weingartner et al. (2003).

The aethalometer output parameter is attenuation coefficients which, after automatic artefact corrections, are transformed to absorption coefficients for each wavelength, \( b_{abs}(\lambda) \), with the unit of m⁻¹. Further, the \( b_{abs}(\lambda) \) can be converted to mass concentration of BC (µg m⁻³) by division of the specific mass absorption coefficients (\( \sigma_{abs}(\lambda) \), MAC), with the unit m² g⁻¹.

**The Aethalometer Model**

For the source apportionment of carbon mass the aethalometer model originally presented by Sandradewi et al. (2008a) with modifications by Martinsson et al. (2017b) was used. In the aethalometer model the total aerosol light absorption are attributed to light absorbing carbon from fossil fuel combustion (FF) or wood burning (WB) according to Eqs. (1)–(3):

\[
b_{abs}(\lambda) = b_{absFF}(\lambda) + b_{absWB}(\lambda)
\]

\[
b_{absFF}(370 \text{nm}) = \frac{370}{950} AAE_{FF}
\]

\[
b_{absFF}(950 \text{nm}) = \frac{370}{950} AAE_{FF}
\]

In these equations, the AAE is the absorption Ångström exponent that describes the spectral absorption dependence of the source specific aerosols. These parameters need to be accurately pre-defined and this is commonly achieved by using reference values from laboratory or field experiments. In this study we used AAE_{WB} = 1.81 and AAE_{FF} = 1.0, values that were used and motivated in the study by Martinsson et al. (2017b). From the derived aethalometer model absorption coefficients, \( b_{absFF} \) and \( b_{absWB} \), it is now possible to calculate the source apportioned carbonaceous aerosol mass (CM). CM is thought to consist of three components, where CM_{FF} and CM_{WB} are the source apportioned carbon mass concentrations, and CM_{Bio} is a residual non-light absorbing component:

\[
TC = CM_{FF} + CM_{WB} + CM_{Bio} = C_1 b_{absFF}(950 \text{nm}) + C_2 b_{absWB}(370 \text{nm}) + CM_{Bio}
\]

In this study we want to compare the residual carbon, CM_{Bio}, to biogenic aerosol tracer compounds. Hence, solving Eq. (4) as a multilinear regression, leaving CM_{Bio} as a fixed intercept as originally proposed by Sandradewi et al. (2008a) is not convenient when aiming to study potential variation in CM_{Bio}. Hence, we use the alternative solution where CM_{Bio} is allowed to vary outside the Eqs. (5)–(6) that are used to calculate \( C_1 \) and \( C_2 \):

\[
\frac{TC}{b_{absWB}(370 \text{nm})} = C_1 b_{absFF}(950 \text{nm}) + C_2 + \frac{CM_{Bio}}{b_{absWB}(370 \text{nm})}
\]

\[
\frac{TC}{b_{absFF}(950 \text{nm})} = C_1 b_{absWB}(370 \text{nm}) + C_2 + \frac{CM_{Bio}}{b_{absFF}(950 \text{nm})}
\]

\( C_1 \) and \( C_2 \) can be calculated as the slope of the linear regression of Eqs. (5)–(6) as in Martinsson et al. (2017b). The calculations for deriving \( C_1 \) and \( C_2 \) are made exclusively for samples collected during winter (December–February), in this way the presumed non-light absorbing biogenic carbon (CM_{Bio}) are minimized as a factor of interference. As opposed to Sandradewi et al. (2008), CM_{Bio} is here allowed to vary outside the linear regressions:

\[
CM_{Bio} = TC - CM_{FF} - CM_{WB}
\]

The linear slopes representing \( C_1 \) and \( C_2 \) was estimated to 446 853 and 96 272 µg m⁻², respectively, based on 30 data points obtained during the winter (December–February). The coefficient of determination, \( R^2 \), was 0.39 for the \( C_1 \) parameter and 0.31 for the \( C_2 \) parameter, these numbers are in similar range to the parameter statistics found in Martinsson et al. (2017b). Further, since CM_{Bio} is expected to be suppressed during winter, the last division term in Eqs. (5)–(6) should result in a small number relative to the estimated C parameters.
Hence, the intercept of the linear fit of Eq. (5) (i.e., $C_2 + CM_{bio}/D_{abs/Whit(370nm)}$) should be very close to the estimated $C_2$ parameter through the linear fit of Eq. (6). The same concept is applicable for quality control of the $C_1$ parameter. The intercept of the linear regression of Eq. (5) was estimated to 82.57 which is deviating by 14% to the estimated $C_2$ parameter. The intercept of the linear regression of Eq. (6) was estimated to 396.936 which is deviating by 11% to the estimated $C_1$ parameter. These deviations are smaller than the ones estimated in Martinsson et al. (2017b) who found deviations of 22 and 15% of the $C_1$ and $C_2$ parameters to their intercepts, respectively. The linear regressions plots are displayed in Figs. S1 and S2 in the supplement.

As mentioned earlier it is also possible to solve Eq. (4) as a multilinear regression as originally proposed by Sandradewi et al. (2008a). However, in such case the $CM_{bio}$ would be fixed as a residual as a constant and not be allowed to vary in time. Further, this was examined in Martinsson et al. (2017b) and gave unrealistic high $C_1$ parameter. Hence, for the purpose of this study the originally proposed solution to Eq. (4) will not be considered here.

**Analysis of Biogenic Aerosol Tracers**

Analysis of six emission markers including levoglucosan, arabitol, fructose, sucrose, cis-pinonic acid and 3-methyl-1,2,3-butane tricarboxylic acid was performed according to the method of Pietrogrande et al. (2014). Briefly, filter punches were divided into small pieces using a sterile surgical blade. Extractions were performed in ultrasonic bath for 15 min using 10 mL of methanol and dichloromethane mixture (9:1). Extractions were filtered prior to analysis using a 25 mm (pore size 0.45 µm) polypropylene syringe filter.

Extracts were analyzed by supercritical fluid chromatography (SFC, Agilent 1260 Infinity II) coupled to Triple Quadrupole Mass Spectrometer (Agilent 6460 system) using the following conditions. Initially a mobile phase (CO$_2$/methanol) with composition of 93:7% was used for 5 min followed by a composition of 80:20% for 6.5 min and returning back to 93:7% at 7.5 minutes. Mobile phase and make-up (methanol) flow rates were maintained at 2.5 mL and 0.5 mL, respectively. Injection volume of 2 µL was used for all samples while column temperature was maintained at 50°C. The back-pressure regulator was programmed for 135 bars and 50°C throughout the analysis. Mass spectrometric analysis was performed using gas temperature of 80°C, gas flow of 20 L min$^{-1}$ and nebulizer pressure of 30 psi. Sheath gas temperature and flow were 250°C and 12 L min$^{-1}$, respectively. Capillary and nozzle voltages were set to 3000 V and 0.5 mL, respectively. An electron multiplier voltage of 400 V was used. Identification and quantification of emission markers was performed using retention times and SIM using m/z 161, 151, 179, 341, 183, 203 for levoglucosan, arabitol, fructose, sucrose, cis-pinonic acid and 3-methyl-1,2,3-butane tricarboxylic acid, respectively.

**Spectrophotometric Analysis**

A standard of 3-methyl-1,2,3-butane tricarboxylic acid (MBTCA) was purchased from Toronto Research Chemicals Inc., Toronto, Canada. Five 25 mL solutions of 10, 20, 100, 250 and 500 mmol L$^{-1}$ was produced by dissolving weighed MBTCA powder in ultrapure water (MilliQ). Spectrophotometric analyses were carried out using a portable spectrophotometer (USB-650, Red Tide Spectrometer, OceanOptics) using a wavelength range of 200–850 nm. 2 mL of ultrapure water was placed in a quartz cuvette and used as background measurement. The cuvette was then rinsed with ultrapure water before adding any MBTCA solution. Output data from the spectrophotometer was absorbance (A). Absorbance was then transformed to absorption per density ($\alpha\rho^{-1}$) according to Chen and Bond (2010):

$$\alpha\rho^{-1} = \frac{A}{c \cdot L} \cdot \ln(10)$$

$L$ is the optical path length, which in this case was 1 cm and $c$ is the concentration of the MBTCA solutions expressed as mass per volume.

**Trajectory Analysis**

The Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYPLIT) (Draxler and Hess, 1998; Stein et al., 2015) was used to study the history of the air mass carrying the particles sampled on the filters and measured by the aethalometer. Gridded meteorological data from the Centre of Environmental Predictions (NCEP) Global Data Assimilation System (GDAS) were used as input to trajectory model. Back-trajectories were calculated at an hourly frequency 120 h backward in time and the trajectories started 100 m above ground at the Vavihill measurement site. For each filter sample, 72 trajectories were used since the sampling time was 72 h. Four regions of origin were defined (Northeast = 0–90°; Southeast = 90–180°; Southwest = 180–270°; Northwest = 270–360°) and for each sample the fraction of time that the air-mass spent over each of the regions of origin was calculated.

**Meteorological Observations**

Temperature and precipitation data were obtained through the website of the Swedish Meteorological and Hydrological Institute (SMHI). The closest observation points for temperature and precipitation to the Vavihill measurement station was found in the city of Helsingborg (56'03"N, 12'77"E) and Gillastig (56°01’N, 13°23’E), respectively. Helsingborg is located 20 km west of Vavihill while Gillastig is located 3 km southeast of Vavihill.

**RESULTS AND DISCUSSION**

**Temporal Variation of Measured Parameters**

Fig. 1(a) shows the temporal variations of OC and EC for the measurement period. Spring and summer showed similar concentrations levels for OC (OC$_{\text{meanSpring}} = 1.17$ µg m$^{-3}$; OC$_{\text{meanSummer}} = 1.28$ µg m$^{-3}$) and EC (EC$_{\text{meanSpring}} = 0.20$ µg m$^{-3}$; EC$_{\text{meanSummer}} = 0.15$ µg m$^{-3}$). Both OC and EC were elevated in the autumn (OC$_{\text{mean}} = 1.68$ µg m$^{-3}$; EC$_{\text{meanAutumn}} = 0.38$ µg m$^{-3}$) which is mainly caused by the two peaks during 2015-10-18 and 2015-11-02, these two periods had slightly lower temperature (7.9 and 8.8°C) than the average temperature of
the whole autumn ($T_{\text{mean Autumn}} = 9.3^\circ \text{C}$). Hence, it can be expected that the higher carbonaceous aerosol concentrations during these periods was caused by and increased activity of residential wood burning. As expected, the levoglucosan concentrations was also elevated during these periods (0.35 and 0.25 $\mu$g m$^{-3}$ compared to the autumn mean of 0.08 $\mu$g m$^{-3}$). Winter data display $OC_{\text{mean Winter}}$ and $EC_{\text{mean Winter}}$ of 0.96 and 0.21 $\mu$g m$^{-3}$, respectively. As observed during the autumn, suppressed temperature during 2016-01-04 and 2016-01-13 ($-3.2$ and 0.0$^\circ \text{C}; T_{\text{mean Winter}} = 2.3^\circ \text{C}$) resulted in two distinct peaks in OC and EC and was associated with increased levoglucosan concentrations (0.15 and 0.15 $\mu$g m$^{-3}$ compared to winter mean of 0.10 $\mu$g m$^{-3}$) and also increased AAE (1.58 and 1.52 compared to winter mean of 1.39, Fig. 1(b)). The transition from the 2013 to the 2015–2016 measurement period did not result in any abrupt and significant change in the carbonaceous aerosol concentration.

The absorption Ångström exponent (AAE) experience low levels during the spring and summer of 2013 and rapidly increases with the transition to the 2015 and 2016 measurement period. The increase from summer to autumn and winter is expected due to increased wood burning as the temperature decreases, however this rapid shift in AAE could be worth investigating more in depth. This transition is actually followed by a rather steep decrease in ambient temperature, from a quite stable summer temperature during

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**Fig. 1.** (a) OC and EC during the measurement period. The dotted line in the transition between summer and autumn displays the junction between the measurement period of 2013 and 2015–2016. N = 111. (b) Temporal variation of the absorption Ångström exponent (AAE) during the measurement period. The AAE was calculated by a linear fit using absorption coefficient in all seven available wavelengths (370–950 nm). N = 106. (c) Temporal variation of the measured biogenic tracer compounds. $N_{\text{Arabitol}} = 103; N_{\text{Sucrose}} = 115; N_{\text{Fructose}} = 72; N_{\text{MBTCA}} = 81.$
2013 with a mean and standard deviation of 16.9 ± 2.1°C to around 7°C within a month (i.e., from 2015-09-12 to 2015-10-12), presumably leading to a rapid increase in residential wood combustion. During this month of rapidly increasing AAE we can also see a fivefold increase in levoglucosan concentrations (i.e., from 0.01 to 0.05 µg m⁻³). Hence, the steep increase in AAE during the transition between measurement periods can be explained by decreasing temperatures and increased wood burning rather than any operational changes within the aethalometer instrument. The overall trend is although clear with low values during the cold season and the opposite during summer. AAE and temperature display a strong relationship (R² = 0.76). The seasonal AAE values are comparable to the levels found in Martinsson et al. (2017b).

Temporal variations of measured biogenic tracers are displayed in Fig. 1(c) and in Table 1. The concentrations of all tracers are, as expected, elevated during summer and suppressed during winter. MBTCA was during spring and summer on similar concentration levels to what has been found in previous European studies (Kourtchev et al., 2009; Kristensen and Glasius, 2011; Maenhaut et al., 2017; Martinsson et al., 2017c). Elevated MBTCA concentrations was further associated to raising temperatures (R² = 0.23, p < 0.01), an effect that was peculiarly prominent during spring (R² = 0.56, p < 0.01) and summer (R² = 0.27, p < 0.01). MBTCA showed a positive, although weak, whole-year correlation to air masses from southeast (R² = 0.09, p = 0.03). The correlation was stronger during spring and summer (R² = 0.20, p = 0.04; R² = 0.35, p < 0.01). The remaining air mass directions (NW, NE and SW) had a negative impact on the MBTCA concentration, this was particularly pronounced for air masses arriving from the northwestern sector (R² = 0.08, p < 0.01), a sector dominated by the North Sea and vascular plant debris (Cowie and Hedges, 1984; Speranza et al., 1997). The fructose concentration followed similar temporal pattern as sucrose but was a factor 5–15 lower, similar observations has been made by others (Yttri et al., 2007; Verma et al., 2018). Both sucrose and fructose showed weak relationships to temperature (R² = 0.11, for both), although analyzing the seasonal temperature correlation displayed stronger relationship during spring (R² = 0.55 for sucrose; R² = 0.60 for fructose) underlining the importance of the springtime pollen bursts. Further, both sugars showed no correlation with any air mass origin.

**Source Apportionment by the Aethalometer Model**

The temporal behavior of the aethalometer model output parameters is showed in Fig. 2(a). The carbon concentration reflects the carbonaceous content, as displayed in Fig. 1(a), while the distribution between the sources reflects the AAE and the aethalometer model. CMFB show low variation in mass concentration throughout the year (mean = 0.86 ± 9.5 ng m⁻³) as found in Yttri et al. (2011) who measured biogenic tracers at four Scandinavian measurement stations during summer, Vavilh included. As MBTCA, arabitol also showed a strong positive temperature dependence (R² = 0.54), with a maximum concentration around 18–21°C which is a pattern that also have been observed by others (Burstein et al., 2011). Arabitol showed no trends of variability with different air mass origins. Sucrose is a tracer of mainly pollen, but also soil biota and lichens (Caseiro et al., 2007; Yttri et al., 2007), and were highest during spring and summer. Pollen emissions by plants usually peaks in the beginning of the annual vegetation cycle (Siljamo et al., 2008; Yli-Panula et al., 2009; Manninen et al., 2014) which may be the explanation for finding the seasonal maximum of sucrose during spring, a phenomenon already observed by Yttri et al. (2007). Fructose found in aerosol can originate from the fruits of terrestrial plants but is also a tracer of pollen and vascular plant debris (Cowie and Hedges, 1984; Speranza et al., 1997). The fructose concentration followed similar temporal pattern as sucrose but was a factor 5–15 lower, similar observations has been made by others (Yttri et al., 2007; Verma et al., 2018). Both sucrose and fructose showed weak relationships to temperature (R² = 0.11, for both), although analyzing the seasonal temperature correlation displayed stronger relationship during spring (R² = 0.55 for sucrose; R² = 0.60 for fructose) underlining the importance of the springtime pollen bursts. Further, both sugars showed no correlation with any air mass origin.

**Table 1.** Seasonal means and standard deviations of the main measured and calculated parameters as well as meteorological data on temperature and precipitation.

| Parameter                  | Winter       | Spring       | Summer       | Autumn       |
|----------------------------|--------------|--------------|--------------|--------------|
| TC (µg m⁻³)                | 1.17 ± 0.87  | 1.36 ± 0.80  | 1.42 ± 0.56  | 2.06 ± 2.00  |
| OC (µg m⁻³)                | 0.96 ± 0.70  | 1.17 ± 0.70  | 1.28 ± 0.50  | 1.68 ± 1.66  |
| EC (µg m⁻³)                | 0.21 ± 0.17  | 0.20 ± 0.12  | 0.15 ± 0.07  | 0.38 ± 0.39  |
| AAE                        | 1.39 ± 0.09  | 1.20 ± 0.12  | 1.07 ± 0.06  | 1.31 ± 0.09  |
| Levoglucosan (ng m⁻³)      | 104.76 ± 58.66 | 55.65 ± 36.65 | 13.19 ± 7.07 | 77.22 ± 78.41 |
| MBTCA (ng m⁻³)             | 1.03 ± 1.31  | 14.95 ± 24.58 | 19.00 ± 23.84 | 12.58 ± 12.07 |
| Arabitol (ng m⁻³)          | 7.77 ± 6.96  | 16.49 ± 16.15 | 39.52 ± 19.27 | 27.17 ± 15.05 |
| Sucrose (ng m⁻³)           | 15.84 ± 21.90 | 84.90 ± 111.28 | 65.52 ± 99.34 | 16.29 ± 8.61  |
| Fructose (ng m⁻³)          | 0.88 ± 0.35  | 16.06 ± 24.14 | 10.22 ± 8.55  | 3.29 ± 2.28  |
| cis-Pinonic acid           | 2.86 ± 0.96  | 4.18 ± 3.28  | 5.67 ± 7.87  | 3.52 ± 2.64  |
| CM_FB (µg m⁻³)             | 0.68 ± 0.42  | 0.97 ± 0.57  | 0.81 ± 0.31  | 1.02 ± 0.85  |
| CM_WB (µg m⁻³)             | 0.64 ± 0.73  | 0.23 ± 0.21  | 0.05 ± 0.05  | 0.62 ± 0.76  |
| CM_BIO (µg m⁻³)            | -0.14 ± 0.55 | 0.17 ± 0.81  | 0.56 ± 0.46  | 0.43 ± 0.92  |
| Temperature (°C)           | 2.28 ± 4.32  | 7.98 ± 4.93  | 16.89 ± 2.07 | 9.27 ± 3.49  |
| Precipitation (mm)         | 3.28 ± 3.33  | 1.19 ± 1.64  | 1.88 ± 2.69  | 3.03 ± 3.60  |
0.57 µg m⁻³), contributing in average with 68% to the TC mass concentration. This is a factor 2.4 higher than the contribution to TC found at Vavihill in Martinsson et al. (2017b) (mean contribution = 28%) and could be an indicator of an erroneous C₁ parameter. CM_WB show a distinct seasonal pattern with elevated concentrations during winter (mean = 0.64 ± 0.73 µg m⁻³) compared to summer (mean = 0.05 ± 0.05 µg m⁻³). The CM_WB contribution to TC was maximized during winter with 55%, this number is in line with previous findings from Vavihill (Martinsson et al., 2017b). CM_Bio peaked during summer with a mean mass concentration of 0.57 ± 0.46 µg m⁻³, leading to a TC contribution of 35%. The carbon contribution of CM_Bio to TC is here a factor two lower than the value found in Martinsson et al. (2017b). Due to the aethalometer model setup in Eq. (7) it is possible for CM_Bio to adopt negative values if the sum of CM_FF and CM_WB exceeds TC. Negative values of CM_Bio was frequently observed during winter, thus leading to a winter average mass concentration of −0.14 ± 0.55 µg m⁻³. It can be feasible to allow some exceedances by the sum of CM_FF and CM_WB to the TC concentration, leading to negative CM_Bio values. However, with the current estimated C-parameters there are cases where CM_FF and CM_WB are in the range of 2–4 times higher than TC, which obstruct any endeavor to accomplish a sound source apportionment. It is indeed a non-trivial task to explain the highly elevated C₁ parameter found in this study. By studying the linear regression that was used to obtain the C₁ parameter (Fig. S1), it is evident that there are no clear outliers that could explain the elevated slope of the regression line. Hence, from a statistical point of view, it seems like the slope is correct, and that the issue is instead systematic. Another bias might occur when organic aerosol coats a soot core and hence increases the MAC value of the aerosol (Bond and Bergstrom, 2006). This means higher aerosol light absorption per unit mass. If there would be a high extent of organic coating (i.e., high MAC) during the C parameter calibration period (winter) lower C parameters would be obtained, compared to higher C parameters which would be the case if only fresh soot were detected (i.e., lower MAC). If the coating (or MAC value) during the measurement period will differ greatly from the mean MAC value during the calibration period a bias will be introduced which then might lead to over- or underestimation of either parameter (CM_FF, CM_WB or CM_Bio).

Sensitivity Analysis and Optimization of C₁ and C₂ Parameters

Unrealistically high C₁ parameter results in an unrealistic
apportionment of carbon to fossil sources. In this case, the
C1 parameter is that high that it generates CMWF values
which exceeds TC during 14 occasions. CMWB contribution
to TC is similar to what was found in Martinsson et al.
(2017b), however the sum of unrealistically high CMWF and
realistic CMWB still creates a large deficit in CMBio. Hence,
the C1 parameter, and consequently the CMWF, needs to be
adjusted to lower values in order to proceed with the
analysis. Hence, we performed a sensitivity analysis in order
to optimize the selection of C-parameters.

Averaging the C-parameters from this study with the
respective values from Martinsson et al. (2017b) seems rational
since the studies are conducted at the same measurement site,
under similar circumstances and the performed measurements
were conducted close in time to each other (i.e., 2013 and
2015–2016 vs. 2014–2015). Hence, combining the estimated
C1 parameter from this study with the C1 parameter from
Martinsson et al. (2017b) to a mean value will only decrease
the C1 parameter from 446 853 µg m⁻² to 330 660 µg m⁻²,
i.e., a decrease by 26%. Another possibility is to use the C1
parameter found in Martinsson et al. (2017b), 214 467 µg m⁻².
This procedure would result in a decrease of the C1 parameter
by 52%. However, the validity of this value is still challenged
by the results presented in Martinsson et al. (2017b) who
found that the aethalometer model apportioned fossil fuel
carbonaceous aerosol was a factor 1.3 higher than fossil fuel
carbon apportioned by radiocarbon and levoglucosan. Hence,
as a final step, we embrace the results from Martinsson et al.
(2017b) and divide the C1 parameter by a factor of 1.3 and
get a final value of the C1 parameter of 164 974 µg m⁻².

Since the contribution of CMWB to TC is similar to the
study by Martinsson et al. (2017b), we will only fine-tune
the C2 parameter by using the average from the current study
and from Martinsson et al. (2017b). The averaged C2
parameter is 105 076 µg m⁻², which is only 9% higher than
the original value estimated in this study (C2 = 96 272 µg m⁻²),
therefore leading to small differences in the apportionment
of wood burning carbonaceous aerosol.

It should be noted that using C parameters from other
studies during different time periods might, even if the
measurement location is constant, introduce bias into the
source apportionment. However, with the more comparable
results to previous conducted studies where radiocarbon and
levoglucosan were used in the source apportionment it is
likely that this methodology makes the source apportionment
more realistic. Ideally, one should use high time resolved
measurements (i.e., aerosol mass spectrometer and
aethalometer measurements) during several winters in order
to estimate more robust C parameters.

With the new C-parameters (C1 = 164 974 µg m⁻²; C2 =
105 076 µg m⁻²) in place it is possible to evaluate the
improvement of the apportionment through comparisons
and correlations with source specific tracer compounds. The
modified apportionment parameters are denoted CMWF(Mod),
CMWB(Mod) and CMBio(Mod). A quick comparison of the source
contributions from this study to the study by Martinsson et
al. (2017b) show a clear improvement. The CMWF(Mod) is now
contributing with 25% to TC over the measurement period
which is in line with Martinsson et al. (2017b) who found
CMWF to be in the range of 21–35%. In this range we find the
CMWF(Mod) in the lower end due to the use of the 1.3 factor as
explained above. CMWB(Mod) show agreement with the
contribution levels found in Martinsson et al. (2017b), with
low contribution during summer (4% to reference of 6%)
and high contributions during winter (60% to reference of
57%). Further, CMWB(Mod) shows a significant correlation with
levoglucosan (Fig. 3, R² = 0.462, p < 0.01), with a slightly
higher coefficient of determination compared to the original
CMWB (R² = 0.458). CMBio(Mod) shows excellent conformity
in TC contribution when compared to Martinsson et al.
(2017b) with high contribution in summer (74% to reference
of 72%) and low during winter (14% to reference of 8%).
The contribution during autumn (49% to reference of 49%)
and spring (42% to 42%) was on a significant level, as also
showed in Martinsson et al. (2017b). Again, higher values of
CMBio(Mod) during summer and winter compared to the
reference values obtained in Martinsson et al. (2017b) may
depend on the 1.3 reduction factor of the C1 parameter.
CMBio displayed a rather poor correlation to MBTCA (R² =
0.14, p < 0.01), however this correlation was improved when
compared MBTCA to the modified apportioned biogenic
carbon, CMBio(Mod) (Fig. 4, R² = 0.27, p < 0.01). The correlation
was further slightly improved for arabitol (R² = 0.13 vs. R²
= 0.12) and for fructose (R² = 0.06 vs. R² = 0.03), while the
correlation with sucrose was unaffected (R² = 0.10 vs. R²
= 0.10). Even though the correlation improved for most
biogenic tracers, it still can seem low. This is because the
whole-year correlation is presented which also accounts for
winter data where the concentration of both the biogenic
carbons and CMBio(Mod) is in general low, with high variability,
resulting in very poor correlations (R² = 0.03; R² = 0.10;
R² = 0.05, p < 0.01; R² = 0.03). Seasonal correlation
analysis of the biogenic tracers and CMBio(Mod) show that the
correlation is strong during spring for MBTCA (R² = 0.70, p
< 0.01), arabitol (R² = 0.64, p < 0.01), sucrose (R² = 0.56, p
< 0.01) and fructose (R² = 0.42, p < 0.01). The correlation
during summer exhibit more straggling numbers where
MBTCA still has a fairly high coefficient of determination to
CMBio(Mod) (R² = 0.33, p < 0.01) while the three other
biogenic tracers display very low coefficients (R² = 0.03;
R² = 0.034; R² = 0.05, p < 0.01; R² = 0.05, p = 0.25; R² = 0.05,
p = 0.25). It is possible that this discrepancy can be explained
by continued photooxidation of α-pinene, hence MBTCA
formation, during summer while the activity in pollen and
fungi spore production is reduced. Manninen et al. (2014)
analyzed pollen and other BPOA from the Hyytiäälä
measurement station in Finland and found that the pollen
concentration peaked in May while the other BPOA
(including fungal spores) peaked in August or September.
This finding is consistent with the temporal concentration
variation for arabitol, sucrose and fructose as displayed in
Fig. 1(c) and Table 1.

MBTCA and the other measured biogenic aerosol
parameters presented here do unfortunately not act as a broad
biogenic activity index. With the current selected chemical
compounds, it is mainly possible to get an indication of the
coniferous plant activity (i.e., large emitters of α-pinene).
Oxidation products from deciduous plant VOC emissions
Fig. 3. Scatter plot displaying the relation between levoglucosan and CM_{WB(Mod)}. N = 106; R^2 = 0.46.

Fig. 4. Scatter plot displaying the relation between MBTCA and CM_{Bio(Mod)}. N = 81; R^2 = 0.27.

(i.e., mainly isoprene) should be included in future studies when investigating the residual carbon of the aethalometer model.

All three sources displayed positive correlation between their calculated carbon mass concentrations and air masses from the southeastern sector (R^2_{CM_FF(Mod)} = 0.37, p < 0.01; R^2_{CM_{WB(Mod)}} = 0.38, p < 0.01; R^2_{CM_{Bio(Mod)}} = 0.14, p < 0.01). On the other hand, air masses from the northwestern sector (i.e., the North sea and Atlantic ocean) seemed to have a negative effect on the mass concentration from the three sources (R^2_{CM_FF(Mod)} = 0.17, p < 0.01; R^2_{CM_{WB(Mod)}} = 0.12, p < 0.01; R^2_{CM_{Bio(Mod)}} = 0.07, p < 0.01).

Relationship between MBTCA and Aethalometer Model Parameters

Surprisingly we found that the MBTCA concentration show a significant correlation with the aethalometer model light absorption for fossil fuel carbon (b_{absFF(950nm)}) (Fig. 5, R^2 = 0.20, p < 0.01). Although the whole year correlation is low, there is a clear covariance during spring (R^2 = 0.47, p < 0.01) and fall (R^2 = 0.58, p < 0.01). During the winter, the MBTCA concentrations are greatly suppressed and hence are unable to show any relationship to b_{absFF(950nm)}. Similar correlation is lacking when studying the whole-year relationship between MBTCA and b_{absWB(370nm)} (R^2 = 0.01, p = 0.39). Further, no significant relationships could be established between the other biogenic tracers and b_{absFF(950nm)}. The Pearson correlation coefficient between MBTCA and the absorption coefficients derived from the seven wavelengths of the aethalometer show an increasing trend with higher wavelengths, and thus we find the highest correlation coefficient for 950 nm (0.23, Fig. S3). This finding leads to several speculations. To the authors’ knowledge, no studies exist on the investigation on the light absorption properties of the MBTCA molecule, hence one option is that MBTCA itself display light absorptive properties in the infrared region of the UV-IR spectra. Another option might be co-transport of biogenic aerosols containing MBTCA and aerosols with high absorption in 950 nm (i.e., soot) from similar geographical regions. As mentioned above, air masses from the southeastern sector are more polluted than air masses from other regions, this has been seen in previous publications from the Vavilov...
measurement station (Kristensson et al., 2008; Martinsson et al., 2017b). Air masses from the southeastern sector of the Vavilov measurement station may originate from central Europe (eastern Germany, Czech Republic, Hungary, Slovakia and Poland) as well as major parts of eastern Europe (Ukraine, Belarus, Lithuania and Russia). We find large forests in parts of this sector, especially in Belarus, northern Ukraine northwestern Poland and Slovakia. With these facts in mind it is very possible that the co-variation between MBTCA and \( b_{abs(950nm)} \) is explained by a co-transport rather than measurement detection of MBTCA in \( b_{abs(950nm)} \). However, this speculation is contradicted by the low abundance of air masses from the southeastern sector which is only 13% for the whole measurement period. As stated above the correlation between \( b_{abs(950nm)} \) and MBTCA was the highest during spring and fall, however the southeasterly air masses only occurred around 17% of the time during these seasons.

We investigated the light absorption of MBTCA through spectrophotometric analysis, the results are presented in Fig. 6. Regardless of the concentration, MBTCA showed distinct absorption peaks around 200–250 nm and 350–450 nm. In the wavelength region of interest for this discussion (> 800 nm) there is a small increase in absorption. Unfortunately, due to the upper wavelength range of the instrument (850 nm) we are not able to study the absorption up to 950 nm. Despite the absorption increase above 800 nm it is unlikely that this increase would explain any covariation between MBTCA and \( b_{abs(950nm)} \) for three reasons. First, the MBTCA mass used in the liquid solutions for the spectrophotometric analysis exceeds the ambient aerosol mass concentrations during summer (mean of 19 ng m\(^{-3}\)) by 8–10 orders of magnitude. As an example, a MBTCA solution of 10 mmol L\(^{-1}\) corresponds to approximately 0.05 g MBTCA in 25 mL ultrapure water. Hence it is likely that a realistic ambient aerosol MBTCA concentration used in spectrophotometric analysis would give results below the detection limit. Second, brown carbon (BrC), a term for organic chemical compounds with enhanced light absorption in the UV-blue range that are produced in large quantities through biomass combustion, but can also be found in humic-like substances (HULIS) derived from biogenic oxidation products, is detectable in the aethalometer (Sandradewi et al., 2008b; Laskin et al., 2015) but has a light absorption per mass (\( \alpha \rho \)) that is 4–5 orders of magnitude higher than the results from the spectrophotometric analysis (Chen and Bond, 2010). Third, if the experimental concentrations used in the spectrophotometric analysis would have had a significant impact in the aethalometer data, the 370 nm channel, i.e., \( b_{absWB(370nm)} \), would also have correlated with MBTCA due to the absorption peak observed around 400 nm (Fig. 6).

Liu et al. (2016) presented a spectrum for mass absorption coefficients (MAC) for the MBTCA precursor \( \alpha \)-pinene. It was evident that the MAC value for \( \alpha \)-pinene in 370 nm is negligible while it is elevated at wavelengths above 600 nm. Hence, it is possible that the observed correlation between MBTCA and \( b_{abs(950nm)} \) is explained by presence of the weak IR absorber, and MBTCA precursor, \( \alpha \)-pinene. Another option is that MBTCA are formed or co-emitted together with BC, originating from fossil fuel or biomass combustion. However, this option is highly doubtful and emission of MBTCA from fossil fuel combustion has to the author’s knowledge never been proved or seen earlier. Although, it should be noted that both MBTCA and \( b_{abs(950nm)} \) show increasing trends with a higher fraction of southeasterly air masses (\( R^2 = 0.09, \ p = 0.03 \) and \( R^2 = 0.38, \ p < 0.01 \) respectively), a geographic sector that has been shown to contribute with anthropogenic air pollutants (Kristensson et al., 2008; Martinsson et al., 2017b). The three remaining air mass sectors (NE, NW, SW) contribute with declining
Fig. 6. Absorption per mass (α/ρ) for MBTCA. The wavelength section between 200–249 nm has been removed due to very high α/ρ values (> 6).

concentrations of MBTCA and b_{absFF(950mm)}. An in depth investigation of the causes of this finding goes beyond the scope of this paper, however the suspicion from Martinsson et al. (2017b) that biogenic carbon might interfere and possibly obstruct the CM_{FF} quantification in the aethalometer model is still unclear and demands further investigation. However, in this study the MBTCA concentrations was very low and in many cases below detection limit during winter, which is the period used for deriving the C parameters in the aethalometer model. Hence, in this study the C parameters should be spared the interference of the possible IR absorbing MBTCA molecule.

CONCLUSIONS

In this study, we demonstrated that four common biogenic tracers showed positive correlation with the aethalometer model residual carbon, apportioned as biogenic carbon, CM_{Bio}. We also illustrated the need and performance to modify and optimize the C parameters, in this case the C_1 parameter. It should be noted that such a modification demands a thorough comparison between the aethalometer model output parameters and a tracer-based source apportionment that includes radiocarbon, levoglucosan and biogenic tracer measurement. In this study we used radiocarbon and levoglucosan source apportionment data generated from a previous study conducted at the same measurement station. To conclude, several years of measurements may be needed in order to establish stable C parameters for a particular measurement station, an aethalometer instrument and a thermo-optical instrument.

Surprisingly, we also found that MBTCA displayed a positive correlation with the derived absorption coefficients from fossil fuel carbonaceous aerosol, stressing the suspicion that biogenic aerosol might be falsely apportioned to this fraction. Hence, future studies should be directed towards experimental investigations with the aim of studying the light absorption properties of artificially produced biogenic secondary organic aerosol. The experimental investigation should be parallel to further ambient aerosol studies utilizing high time resolved instrumentation such as the aerosol mass spectrometer as a complement to wet chemistry filter analysis.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at https://doi.org/10.4209/aaqr.2020.01.0035

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