



Supplement of

Trends, composition, and sources of carbonaceous aerosol at the Birkenes Observatory, northern Europe, 2001–2018

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1 **S1. Quality assurance**

2 The OC/EC data are not field blank corrected, in accordance with the standard operating procedure
3 provided by EMEP (Yttri et al., 2007a; EMEP, 2014). The positive sampling artefact of OC for weekly
4 samples collected at Birkenes has been quantified on a campaign basis using the QBQ (Quartz fibre
5 filter Behind Quartz fibre filter) approach (McDow and Huntzicker, 1990; Turpin et al., 1994) in summer
6 ($18\pm 4\%$; Yttri et al., 2011b), fall ($19\pm 7\%$; Yttri et al., 2019), and winter/spring ($24\pm 13\%$; Yttri et al.,
7 2019) but only for PM_{10} . For OC in $PM_{2.5}$, which at Birkenes is obtained from an identical and co-
8 located sampler, operating at the same filter face velocity as the PM_{10} sampler, the positive sampling
9 artefact is considered equally large, whereas its relative importance is slightly higher. The negative
10 sampling artefact has not been addressed.

11 OC/EC analysis was performed within 2 months after the filter samples were collected and
12 according to the Quartz (2001–2008) and the EUSAAR-2 (from 2008) temperature programs.
13 EUSAAR-2 is designed to reduce the inherited uncertainties associated with splitting of OC and EC,
14 e.g. by preventing premature burn-off of EC (Cavalli et al., 2010). The uncertainty associated with
15 repeated OC/EC analyzes of a filter sample is typically $<10\%$, which includes both analytical uncertainty
16 and heterogenic distribution of the deposited aerosol particles on the filter sample.

17 The laser's ability to detect changes in the transmittance of a filter sample high in initial EC is
18 crucial to obtain a correct value for EC (and OC). $15 \mu\text{g EC cm}^{-2}$ has been suggested as an upper limit
19 (Subramanian et al., 2004; Wallén et al., 2010) but this value is likely to vary. The nine filter samples
20 (out of nearly 1800) with an EC content exceeding $15 \mu\text{g C cm}^{-2}$ in the current dataset were considered
21 valid. Further, a non-biased separation between OC and EC requires that either pyrolytic carbon (PC)
22 evolves before EC during analysis or that PC and EC have the same light absorption coefficient. It is
23 well known that this is not always the case (Yang and Yu, 2002) and there is a lack of information on
24 the magnitude of this imperfection.

25 Deviation from the protocol-defined temperature steps will affect the analysis results of the TOA
26 instrument (Chow et al., 2005; Panteliadis et al., 2015) and temperature offsets ranging from $-93 \text{ }^\circ\text{C}$ to
27 $+100 \text{ }^\circ\text{C}$ per temperature step have been reported (Panteliadis et al., 2015). Thus, calibration by the
28 temperature calibration kit available from the instrument manufacturer (Sunset laboratory Inc) since
29 2012 is strongly recommended. Temperature calibration was implemented as part of the regular QA/QC
30 procedures for thermal-optical analysis in 2013.

31 A comparison of the two temperature programmes used for the Birkenes time series was
32 performed for $PM_{2.5}$ filter samples collected at Birkenes in 2014, using temperature calibrated versions
33 of both Quartz and EUSAAR-2. There was a good agreement between the two temperature programs
34 for TC and OC, i.e. close to the expected uncertainty associated with analysis and sampling, whereas
35 for EC the difference was pronounced (Table S 17), although in close correspondence with that
36 previously reported by Panteliadis et al. (2015). Note that OC and EC data for the period 2001–2007
37 discussed in the main are text not corrected according to Eq. (S 18–20) (Table S 17), except for the

38 purpose of trend calculations.

39 Field blanks did not contain monosaccharide anhydrides, sugars, sugar-alcohols or 2-
40 methyltetrols in noticeable amounts. Filter samples for which the content was below the limit of
41 detection (LOD) but > 0 , were considered valid and included when calculating the annual and seasonal
42 means. Organic tracers were analyzed within 1 year after collection of the aerosol filter samples. The
43 uncertainty (analytical and sampling uncertainty) associated with measurements of monosaccharide
44 anhydrides is within 10 – 15 % (Yttri et al., 2015). A similar range of uncertainty is expected for the
45 other organic tracers.

46 Mass concentrations of PM_{10} and $PM_{2.5}$ were field blank corrected. The overall uncertainty
47 associated with determination of the PM_{10} and $PM_{2.5}$ mass concentration is $< 5\%$. The monitoring of
48 major ions and trace elements follows the guidelines by EMEP (EMEP, 2014) and are within the data
49 quality objective of the network: 15–25% uncertainty for the combined sampling and analysis of major
50 ions and 30% for heavy metals.

51

52 **S2. Calculation of trends - Statistical approach**

53 The Mann-Kendall test (Mann, 1945; Kendall, 1975; Gilbert, 1987) was used for calculating the
54 significance of the trend and if a significant trend was found, the Theil-Sen slope (Theil, 1950; Sen,
55 1968; Gilbert, 1987) was calculated. This procedure has been widely used in atmospheric science, like
56 in the recent TOAR project analysing global surface ozone trends (e.g. Fleming et al., 2018; Lefohn et
57 al., 2018), in the review of the EMEP observations (Tørseth et al., 2012) and in
58 numerous other observation based papers (Aas et al. 2019; Ciarelli et al., 2019; Theobald et al., 2019;
59 Masiol et al., 2019; Collaud Coen et al., 2020).

60 The Mann-Kendall test is a non-parametric test that does not rely on any assumptions of
61 distribution and is therefore well suited for atmospheric data that often deviate from normality and
62 contain outliers that would hamper a standard linear regression. The basics of the Mann-Kendall test is
63 to count the signs of all forward concentration differences in time, and if there is a sufficient overweight
64 of positive or negative differences, the 0-hypothesis (H_0) of no trend could be rejected. The S statistic
65 given below contains the sum of all the signs based on the observed values y_i at time i :

66

$$67 \quad S = \sum_{i=1}^{n-1} \sum_{j=i+1}^n \text{sign}(y_j - y_i) \quad \text{Eq. S1}$$

68

69 This statistic together with the number of samples and the number of ties in the data were used to
70 calculate the p value as given by Gilbert (1987). In our work, we assumed significant trends when $p <$
71 0.05.

72 With $p < 0.05$ H_0 was rejected and the value of the trend was estimated by the Theil-Sen slope estimator:

73

$$74 \quad \beta = \text{median} \left(\frac{y_j - y_i}{t_j - t_i} \right), \quad j > i \quad \text{Eq. S2}$$

75

76 where t_i denotes the time i of the observed value y_i .

77 The Theil-Sen slope is simply the median of all the forward concentration gradients. In addition
 78 to the slope, the 2σ confidence intervals were calculated according to Gilbert (1987), providing the 95
 79 % confidence range of the slopes.

80 The Mann-Kendall test and Theil-Sen slope estimation were applied to all species and ratios
 81 discussed in this work. These calculations were based on the seasonal and annual mean values,
 82 separately, as presented below. For the ratios, $r = x/y$ (e.g. the fraction of NO_3^- in PM_{10}), we based the
 83 calculations on the ratios of the seasonal means and not on the seasonal means of the ratios, i.e.:

84

$$85 \quad r = \frac{x}{y}, \text{ where } x = \frac{1}{n} \sum(x_i) \text{ and } y = \frac{1}{n} \sum(y_i) \quad \text{Eq. S3}$$

86

87 For all cases where the 0-hypothesis (H_0) could be rejected, the Theil-Sen slopes were calculated, and
 88 this slope was further transferred into the relative trend by dividing the trend (β) by the mean of the
 89 observed values:

90

$$91 \quad \beta_{rel} = \frac{\beta}{\left[\frac{1}{n} \sum(y_i) \right]}, \text{ where } y_i = \text{observed concentration or ratio at time } i \quad \text{Eq. S4}$$

92

93 **S3. Absorption coefficient measurements and source apportionment**

94 The absorption coefficient (B_{Abs}) was measured using the multi wavelength ($\lambda=370; 470; 520; 590; 660;$
 95 $880; 950$ nm) aethalometer (AE33, Magee Scientific), operating behind a PM_{10} inlet. We calculate
 96 absorption coefficients (B_{Abs}) according to Drinovec et al. (2015):

97

$$98 \quad B_{Abs}(\lambda) = \frac{A \cdot \left(\frac{ATN_{t2}(\lambda) - ATN_{t1}(\lambda)}{100} \right)}{Q \cdot C \cdot (1 - \zeta) \cdot \left(1 - k(\lambda) \cdot (ATN_{t2}(\lambda) - ATN_{ref}(\lambda)) \right) \cdot (t_2 - t_1)} \quad \text{Eq. S5}$$

99 where ATN = attenuation at time $t = 1$ and $t = 2$, and of the reference spot ref , Q is the instrument flow
 100 rate on spot 1, A is the filter spot area, k is the loading compensation parameter from the 2 spot
 101 compensation algorithm. Here we neglect lateral air flow losses (ζ) and the scattering compensation C
 102 since these are not wavelength dependent in Eq. (S5) and hence do not affect source apportionment
 103 based on wavelength dependence, while conversion to eBC via co-located filter measurements of EC
 104 also results in compensation of these parameters using:

105

106 $eBC(\lambda) = B_{Abs}(\lambda) / \alpha_{effective}(\lambda)$ Eq. S6

107 where $\alpha_{effective}$ is an effective mass absorption cross section (α) incorporating scattering and lateral flow
 108 losses:

109 $\alpha_{effective}(\lambda) = \alpha(\lambda) \times c \times (1 - \zeta)$ Eq. S7

110 Hence $\alpha_{effective}$ is a conversion factor between B_{Abs} and eBC and has no physical meaning beyond
 111 this.

112 The AE33 of this study automatically generates $B_{Abs}(\lambda)$ at 1-minute resolution. However, as
 113 discussed by Springston et al. (2007) and Backman et al. (2017), the time interval ($t_2 - t_1$) Eq.(S5) can
 114 be adjusted to any integer multiple of the base resolution in post-processing. Here we adopt the approach
 115 of Backman et al. (2017), fixing the time interval to 1 hour and calculating $B_{Abs}(\lambda)$ according to Eq.
 116 (S5). In case one or more filter advances occurred within the one-hour interval, data from each individual
 117 filter spot falling within the interval were treated separately and a time-weighted average recorded for
 118 that hour. The advantage of this technique is enhanced noise reduction, i.e. using the one-hour interval
 119 approach the noise reduction is proportional to as much as $1/n$ (where n are the measurement points),
 120 rather than $1/\sqrt{n}$, attainable via signal averaging.

121 Here we performed source apportionment of aethalometer data using the *aethalometer model*
 122 (Sandradewi et al., 2008). Assuming two sources contribute to total Babs ($B_{Abs,Tot}$), i.e. fossil fuel
 123 combustion ($B_{Abs,ff}$) and biomass burning ($B_{Abs,bb}$):

124
 125 $B_{Abs,Tot} = B_{Abs,ff} + B_{Abs,bb}$ Eq. S8

126 Then, using a wavelength pair, here $\lambda_1=470$ nm and $\lambda_2=880$ nm,

127 $B_{Abs,bb}(\lambda_2) = \frac{B_{Abs}(\lambda_1) - B_{Abs}(\lambda_2) \cdot \left(\frac{\lambda_1}{\lambda_2}\right)^{-\alpha_{ff}}}{\left(\frac{\lambda_1}{\lambda_2}\right)^{-\alpha_{bb}} - \left(\frac{\lambda_1}{\lambda_2}\right)^{-\alpha_{ff}}}$ Eq. S9 and

128 $B_{Abs,ff}(\lambda_2) = \frac{B_{Abs}(\lambda_1) - B_{Abs}(\lambda_2) \cdot \left(\frac{\lambda_1}{\lambda_2}\right)^{-\alpha_{bb}}}{\left(\frac{\lambda_1}{\lambda_2}\right)^{-\alpha_{ff}} - \left(\frac{\lambda_1}{\lambda_2}\right)^{-\alpha_{bb}}}$ Eq. S10

129 where α_{ff} and α_{bb} are the absorption Ångström exponents (AAE) for fossil fuel and biomass burning,
 130 respectively. Note that when using this approach, the AAEs must be assumed *a priori*, while the data
 131 are not fitted or error weighted, which can lead to negative values in the resulting time series of the
 132 factors due to uncertainty in the AAEs e.g. Grange et al. (2020).

133 Here we also used positive matrix factorisation (PMF) to distinguish between the two sources
 134 in Eq. (S8). The theory of PMF is detailed elsewhere (Paatero and Tapper, 1994) Briefly, a matrix of
 135 measurement data X is represented by a bilinear model comprising factor profiles F (rows), factor time
 136 series G (columns) and a residual matrix E :

137
 138 $X = G \cdot F + E$ Eq. S11

139

140 In PMF factors are found using a least-squares fitting routine in which the object function Q , i.e. the
 141 square of residuals e weighted to uncertainty σ , is mimimised across all cells (rows i - m , columns j - n)
 142

$$143 \quad Q^m = \sum_{i=1}^m \sum_{j=1}^n \left(\frac{e_{ij}}{\sigma_{ij}} \right)^2 \quad \text{Eq. S12}$$

144 Here, we use the source finder (SoFi, (Canonaco et al., 2013)) toolkit ref, to call PMF (To model the
 145 error matrix σ_{ij} we use the clean air test function of the AE33 to determine the standard deviation of the
 146 attenuation of the blank $\delta_{ATN_{air}}$, calculating σ_{ij} , using:

$$148 \quad \sigma_{ij} = \sqrt{f_A^2 + f_Q^2 + 2 \left(\frac{\delta_{ATN_{air}}(\lambda_j)}{ATN_i(\lambda_j)} \right)^2 + \left(\frac{\delta_{ATN_{air}}(\lambda_j)}{ATN_{i-1}(\lambda_j)} \right)^2 + \left(\frac{\delta_{ATN_{air}}(\lambda_j)}{ATN_{ref}(\lambda_j)} \right)^2} \cdot B_{Abs,i}(\lambda_j) \quad \text{Eq. S13}$$

149
 150 where f_A and f_Q are the fractional uncertainties in the spot area and the flow rate, respectively (both
 151 0.015 according to Backman et al., 2017). Clean air tests were performed only periodically. Therefore,
 152 to generate an error estimate for all time points, we interpolated (bilinear interpolation) between the
 153 clean air tests to generate the full error matrix, accounting for drift in $\delta_{ATN_{air}}$. Points before and after
 154 the last clean air test were calculated using the first and last values of $\delta_{ATN_{air}}$, respectively.

155 According to Eq. (S11), X could be represented by any combination of G and F , i.e. the PMF
 156 model has *rotational ambiguity*. In practice, many rotations produce negative values and are thus
 157 forbidden. Nevertheless, many rotations and local minima in Eq. (S11) are likely to exist. To assess this,
 158 we generated multiple ($n=2000$) bootstrap replacement matrices (block size 24 to conserve diurnal
 159 variation if present), running PMF on each matrix 5 times for a total of 10000 runs. PMF settings are
 160 shown in Table S 2.

161 We import all 2000 files generated using SoFi for each factor solution. To map the factors, we
 162 calculated an effective AAE from the factor profiles α_F , using

$$163 \quad \alpha_F$$

$$164 \quad = - \frac{\log \left(\frac{F_{j=2}}{F_{j=6}} \right)}{\log(470/880)} \quad \text{Eq. S14}$$

166 sorting factors and time series from each run from low to high with respect to α_F . Binning the effective
 167 AAEs from each factor also provides a convenient means to investigate the solution space for rotational
 168 ambiguity.

169

170 **S4. Positive matrix factorisation applied to filter data**

171 We performed PMF for samples collected in 2016-2018 (151 samples), with the following as input
172 data: OC (in PM_{2.5} and PM_{10-2.5}), EC (in PM₁₀), levoglucosan, mannosan, galactosan, arabinol,
173 mannitol, trehalose, glucose, V, Mn, Ti, Fe, Co, Ni, Cu, Zn, As, Cd, and Pb (all in PM₁₀), SO₄²⁻, NO₃⁻,
174 NH₄⁺, Ca²⁺, Mg²⁺, K⁺, Na⁺, Cl⁻ (open filter face).

175 Table S 3 shows miscellaneous settings of the PMF analysis of these data. The input data and error
176 estimates were prepared using the procedure suggested by Polissar et al. (1998) and Norris et al.
177 (2014), see also Table S 3 for miscellaneous settings including missing data treatment and assessment
178 of the PMF performance.

179 If the concentration was greater than the LOD, the calculation was based on a user provided
180 fraction of the concentration and LOD:

$$181 \quad Unc = \sqrt{(Error\ Fraction \times Concentration)^2 + \left(\frac{1}{2} \times LOD\right)^2} \quad Eq. S15$$

182
183 The analytical uncertainties (20%) as error fraction of OC, EC, organic tracers, ions, and elements
184 were used to determine the corresponding error estimates. Based on given understanding of OC sources,
185 2–10 factors with random seeds were examined, and 7 factors were determined based on: 1) The
186 decrease in Q/Q_{exp} was larger than the relative change in number of factors up to 7; 2) All factors could
187 be interpreted; 3) All factors were distinct.

188 To assess the statistical uncertainty in the model we performed repeated analyses on bootstrap-
189 resampled matrices. A base profile was generated from a manually mapped average of 50 runs. From
190 each bootstrap run, we fitted all 7 bootstrap factors vs all 7 factors from the base run profile (representing
191 a 7×7 matrix of r² values). We then mapped the bootstrap factors in order of the r² value: The highest
192 value was assumed to be a match, then then the next highest value excluding both previously mapped
193 factors to any other factor (representing a 6×6 matrix of r² values), and so on. This was to avoid any
194 factors being mapped twice.

195 The minimal robust and true Q values of the base run were 5507.9 and 5580.8, respectively. All the
196 (error) scaled residuals were within ±5 and > 97.8% within ± 3, normally distributed and centred around
197 zero. The average Q/Q_{exp} was 1.2. We also observe no structure in the residuals, which were evenly
198 distributed between measurements from different instruments (i.e. we did not observe factors
199 representing groups of compounds by instrument type, Figure S 3).

200

201 **S5. Emission ratios used to calculate OC and EC from biomass burning**

202 Emission ratios derived from ambient data are a good alternative to direct emission measurements,
203 accounting for the aggregate effects of fuel type and combustion conditions, but results will nevertheless
204 vary from region to region (e.g. Zotter et al., 2014). Here, we used ratios from our PMF analysis
205 (Table 1) to calculate carbonaceous aerosol from biomass burning for 2008–2018. The levoglucosan to

206 mannosan ratio is rather consistent between seasons, with the values for summer (5.1 ± 0.9) and fall
207 (5.2 ± 0.7) being slightly lower than for winter (5.4 ± 0.8) and spring (6.0 ± 0.7). This might indicate that
208 emissions from one source of biomass burning (wood burning for residential heating) dominate for all
209 seasons, supporting the use of one levoglucosan to OC (and EC) ratio for calculations. The lower
210 levoglucosan to mannosan ratio observed in summer and fall might indicate increased influence of wild
211 and agricultural fires, but the magnitude of these sources remains speculative, except during severe
212 episodes, e.g. in August 2002, May and September 2006, and June 2008.

213

214 **S6. Levels of PBAP and BSOA organic tracers**

215 The annual mean concentration of the PBAP tracers ranged from 2.8–3.4 ng m⁻³ (trehalose) to 4.8–5.8
216 ng m⁻³ (arabitol) (2016–2018) (Figure 6, Table S 15). Levels were elevated in the vegetative season,
217 particularly in summer and fall. Mannitol and arabitol were highly correlated ($R^2=0.85$), underlining
218 their common origin, and the mannitol to arabitol ratio (0.9 ± 0.2) corresponds well with previously
219 reported results for these fungal spore tracers (e.g. Bauer et al., 2008; Yttri et al., 2007b; Yttri et al. 2011
220 a, b).

221 The annual mean concentration of 2-methylerythritol ($0.365\text{--}0.441$ ng m⁻³) (2016–2018) was
222 higher than that of 2-methylthreitol ($0.105\text{--}162$ ng m⁻³), and the two isomers were highly correlated
223 ($R^2=0.915$), which is consistent with other studies (e.g., Ion et al., 2005; Kourtchev et al., 2005; Edney
224 et al., 2005; El Haddad et al., 2011; Alier et al., 2013). 2-methyltetrols were elevated in the period when
225 deciduous trees have leaves (transition May/June to early October).

226

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