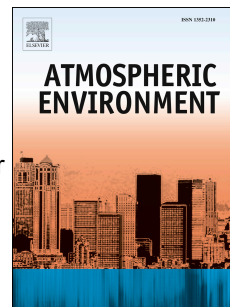


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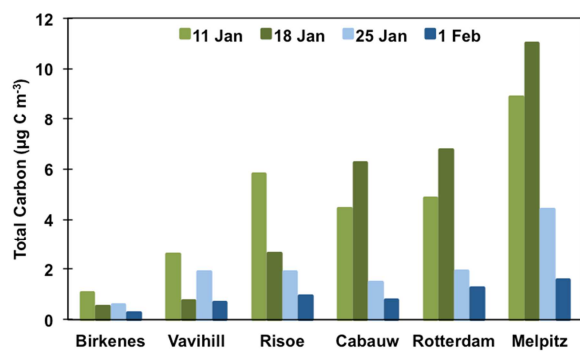
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Graphical abstract



1 **Composition and sources of carbonaceous aerosols in** 2 **Northern Europe during winter**

3

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26 Keywords: aerosol sources, source apportionment, anhydrosugars, radiocarbon analysis,
27 carboxylic acids, organosulphates.

Abstract

Sources of elemental carbon (EC) and organic carbon (OC) in atmospheric aerosols (carbonaceous aerosols) were investigated by collection of weekly aerosol filter samples at six background sites in Northern Europe (Birkenes, Norway; Vavihill, Sweden; Risoe, Denmark; Cabauw and Rotterdam in The Netherlands; Melpitz, Germany) during winter 2013. Analysis of ^{14}C and a set of molecular tracers were used to constrain the sources of EC and OC. During the four-week campaign, most sites (in particular those in Germany and The Netherlands) were affected by an episode during the first two weeks with high concentrations of aerosol, as continental air masses were transported westward. The analysis results showed a clear, increasing north to south gradient for most molecular tracers. Total carbon (TC = OC+EC) at Birkenes showed an average concentration of $0.5 \pm 0.3 \mu\text{g C m}^{-3}$, whereas the average concentration at Melpitz was $6.0 \pm 4.3 \mu\text{g C m}^{-3}$. One weekly mean TC concentration as high as $11 \mu\text{g C m}^{-3}$ was observed at Melpitz. Average levoglucosan concentrations varied by an order of magnitude from $25 \pm 13 \text{ ng m}^{-3}$ (Birkenes) to $249 \pm 13 \text{ ng m}^{-3}$ (Melpitz), while concentrations of tracers of fungal spores (arabitol and mannitol) and vegetative debris (cellulose) were very low, showing a minor influence of primary biological aerosol particles during the North European winter. The fraction of modern carbon generally varied from 0.57 (Melpitz) to 0.91 (Birkenes), showing an opposite trend compared to the molecular tracers and TC. Total concentrations of 10 biogenic and anthropogenic carboxylic acids, mainly of secondary origin, were $4\text{-}53 \text{ ng m}^{-3}$, with the lowest concentrations observed at Birkenes and the highest at Melpitz. However, the highest relative concentrations of carboxylic acids (normalized to TC) were observed at the most northern sites. Levels of organosulphates and nitrooxy organosulphates varied more than two orders of magnitude, from 2 to 414 ng m^{-3} , between individual sites and samples. The three sites Melpitz, Rotterdam and Cabauw, located closest to source regions in continental Europe, showed very high levels of organosulphates and nitrooxy organosulphates (up to 414 ng m^{-3}) during the first two weeks of the study, while low levels ($<7 \text{ ng m}^{-3}$) were found at all sites except Melpitz during the last week. The large variation in organosulphate levels probably reflects differences in the presence of acidic sulphate aerosols, known from laboratory studies to accelerate the formation of these compounds. On average, the ratio of organic sulphate to inorganic sulphate was $1.5 \pm 1.0\%$ (range 0.1-3.4%). Latin-hypercube source apportionment techniques identified biomass burning as the major source of OC for all samples at all sites (typically $>40\%$ of TC), while use and combustion of fossil fuels was the second most important source. Furthermore, EC

61 from biomass burning accounted for 7-16% of TC, whereas EC from fossil sources
62 contributed to <2-23% of TC, of which the highest percentages were observed for low-
63 concentration aerosol samples. Unresolved non-fossil sources (such as cooking and biogenic
64 secondary organic aerosols) did not account for more than 5-12% of TC. The results confirm
65 that wood combustion is a major source to OC and EC in Northern Europe during winter.

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66 1. Introduction

67 Atmospheric aerosol is of concern due to its effects on human health (Brook et al., 2010; Kelly
68 and Fussell, 2012; Cassee et al., 2013; WHO, 2013) and climate (Stocker et al., 2013). The
69 carbonaceous fraction, comprising both organic compounds and elemental carbon (EC), has
70 become increasingly important in e.g. Europe after effective abatement strategies have
71 reduced emissions of precursors to inorganic aerosol constituents, such as nitrate and sulphate.
72 Still, there is a lack of understanding of the sources, chemical composition and properties of
73 the carbonaceous aerosol (Glasius and Goldstein, 2016). The organic component is composed
74 of a multitude of compounds with a wide range of properties regarding e.g. hygroscopicity and
75 surface activity affecting cloud droplet formation, direct interactions with sun light through
76 scattering and absorption, as well as toxicity (Hallquist et al., 2009).

77 Elemental carbon is an important contributor to global warming, with an estimated total
78 radiative forcing of 1.1 W m^{-2} (90% uncertainty range $0.17\text{-}2.1 \text{ W m}^{-2}$) (Bond et al., 2013),
79 although recent studies have cast some uncertainty on these estimates (Samset et al., 2014).
80 Organic compounds (often measured as organic carbon, OC) could enhance the light-
81 absorbing capacity of EC by a factor of 2-4 when acting as a coating, known as the lensing
82 effect (Fuller et al., 1999; Jacobson, 2001; Schnaiter et al., 2005; Bond and Bergstrom, 2006),
83 though field studies have shown less absorption enhancement (Cappa et al., 2012). Increased
84 knowledge of the sources as well as physical and optical properties of EC is needed both
85 scientifically and to implement effective mitigations steps.

86 The origin of carbonaceous aerosol can be assessed by the $^{14}\text{C}/^{12}\text{C}$ ratio, as recent emissions
87 from non-fossil sources, such as vegetation, have approximately the same ratio as present-day
88 atmospheric carbon dioxide, while carbon from processing or combustion of fossil fuels are
89 devoid of ^{14}C due to radioactive decay, e.g., Heal (2014). Examples of non-fossil
90 carbonaceous aerosol in the atmosphere are primary biological aerosol particles (PBAP) (e.g.,
91 pollen, plant debris, fungal spores), biogenic secondary organic aerosol (BSOA) formed by
92 oxidation of biogenic volatile organic compounds (BVOC), particles from combustion of
93 biomass and from cooking. To separate the natural and the anthropogenic fraction of the
94 carbonaceous aerosol, source specific molecular tracers, and combinations thereof, are needed
95 to identify and constrain the contribution from the various sources.

96 In order to obtain quantitative estimates of major sources of carbonaceous aerosol in north-
97 European background areas during winter, we combined measurements of EC, OC, the
98 $^{14}\text{C}/^{12}\text{C}$ ratio and source-specific organic tracers, including levoglucosan from wood

99 combustion, mannitol and arabitol from fungal spores, and cellulose from plant debris, as well
100 as their emission ratios as input for source apportionment calculations. In addition, the
101 interpretation was supported by measurements of molecular tracers of both biogenic and
102 anthropogenic secondary organic aerosols (SOA). Table 1 lists an overview of the tracers
103 analysed in the present work.

104 During winter, episodes with elevated concentrations of carbonaceous aerosols can occur,
105 caused by stagnant weather conditions combined with high emissions from e.g. residential
106 combustion sources and long-range transport. Wood combustion for residential heating may
107 account for 20-80% of the organic aerosol in urban areas in Europe during winter (Puxbaum et
108 al., 2007; Saarikoski et al., 2008; Favez et al., 2010), and is a major, but very uncertain,
109 contributor to rural OA levels (Denier van der Gon et al., 2015). These uncertainties arise
110 largely from the available emission inventories, which are typically based upon poorly-
111 constrained information on residential wood combustion and emission factors, together with
112 problems which the issues of condensable VOC cause for even the definition of PM emissions
113 (Denier van der Gon et al., 2015; Robinson et al., 2007). Ciarelli et al. (2017) recently found
114 that residential wood combustion was a source of 52 - 76% of submicron OA in Europe during
115 winter. Even in megacities, such as Paris, residential wood combustion is a major contributor
116 to carbonaceous aerosol in winter, either from regional sources or long-range transport (Favez
117 et al., 2009; Beekmann et al., 2015).

118 The monosaccharide anhydrides levoglucosan, mannosan and galactosan are formed from
119 pyrolysis of cellulose and hemi-celluloses, and constitute specific tracers of biomass
120 combustion (Simoneit et al., 1999; Puxbaum et al., 2007), which have been applied in several
121 previous studies to investigate the influence of biomass combustion on aerosol levels in
122 Northern Europe (e.g., Yttri et al., 2005; Yttri et al., 2007b; Glasius et al., 2008; Saarikoski et
123 al., 2008; Szidat et al., 2009; Genberg et al., 2011).

124 Major sources of PBAP include plant debris and fungal spores (dry diameter typically 2-10
125 μm), in addition to pollen (up to about 30 μm) and bacteria (about 1 μm) (Deguillaume et al.,
126 2008; Despres et al., 2012). Globally, fungal spores may constitute as much as 23% of total
127 primary OC emissions (Heald and Spracklen, 2009). The contribution of fungal spores
128 (particularly from Asco- and Basidio-mycetes) to atmospheric aerosol can be traced by
129 analysis of the sugar-alcohols mannitol and arabitol, which are storage substances in fungal
130 spores (Bauer et al., 2008a; 2008b; Di Filippo et al., 2013). A previous study conducted at
131 Nordic background sites in summer showed that fungal spores organic carbon contributed 7-
132 15% of the total carbon mass in PM_{10} (Yttri et al., 2011a). Plant debris contains cellulose

133 which can be used as a source-specific tracer in aerosols (Puxbaum and Tenze-Kunit, 2003).
134 The contribution of plant debris organic carbon to total carbon in PM₁₀ was found to be 12 –
135 18% at Nordic background sites (Yttri et al., 2011a). A two-year data set of cellulose
136 concentrations in PM_{2.5} and PM₁₀ filter samples collected at six rural or background sites in
137 Europe, found that the contribution of plant debris to organic material amounted to 2 – 10%
138 (Sánchez-Ochoa et al., 2007), whereas the contribution of plant debris organic carbon to total
139 carbon was 1.5 – 6% (Gelencsér et al., 2007). Another data set covers cellulose concentrations
140 determined during periods of wildfires in Portugal (Pio et al., 2008); although absolute
141 concentrations increased slightly during the periods with intense fires, the contribution to OC
142 decreased. The differences between these studies can probably be attributed to differences in
143 studied size fractions, conversion factors from C to organic matter, and whether tracers for
144 both plant debris and fungal spores were included in the analyses. Recently, Bozzetti et al.
145 (2016) used aerosol filter sampling combined with off-line aerosol mass spectrometry (AMS)
146 and positive matrix factorization (PMF) to show that during summer, primary biological
147 organic aerosol and SOA made comparable contributions to PM₁₀ at a rural background site in
148 continental Europe.

149 Formation of SOA can be more difficult to trace by molecular tracer analysis compared to the
150 primary sources, due to the complexity of organic compounds in primary emissions and their
151 atmospheric processing (Nozière et al., 2015; Glasius and Goldstein, 2016). In the present
152 work, we analysed tracers of monoterpene SOA (e.g., pinic acid, pinonic acid and terpenylic
153 acid), as well as anthropogenic SOA from fossil fuel combustion (e.g., benzoic acid). Pinic
154 acid, pinonic acid, terpenylic acid and are formed from oxidation of α - and β -pinene
155 (Hatakeyama et al., 1989; Christoffersen et al., 1997; Hoffmann et al., 1997, 1998, Glasius et
156 al., 1999, 2000; Claeys et al., 2009), while 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA)
157 and diaterpenylic acid acetate (DTAA) are formed by further oxidation reactions of the initial
158 products (Szmigielski et al., 2007; Iinuma et al., 2008; Claeys et al., 2009; Müller et al., 2012).
159 Molecular tracers of anthropogenic SOA include benzoic acid from photochemical oxidation
160 of aromatic hydrocarbons (Kawamura et al., 1985; Rogge et al., 1993), as well as adipic acid
161 and pimelic acid from ozonolysis of cyclic olefins (Hatakeyama et al., 1985; Grosjean et al.,
162 1978). Pinene-derived SOA tracers have been measured in several field studies, which were
163 mainly performed during summer when monoterpene emissions are high (e.g., Kourtchev et
164 al., 2008, 2009; Kristensen and Glasius, 2011; Gómez-González et al., 2012; for a review, see
165 Nozière et al., 2015). The secondary OC (SOC) contribution from α -pinene was determined
166 for campaigns in summer 2003 at forested sites in Jülich, Germany (Kourtchev et al., 2008)

167 and K-puszt, Hungary (Kourtchev et al., 2009). Use was hereby made of the measured tracer
168 concentrations and the laboratory-derived tracer mass fractions reported by Kleindienst et al.
169 (2007) and Lewandowski et al. (2008). It was found that the SOC contribution to the PM_{2.5}
170 OC was, on average, 2.4% for the Jülich site and 4.8% for K-puszt. However, considering
171 that various uncertainties are associated with the approach of Kleindienst et al. (2007), as also
172 indicated by these authors, it is estimated that the uncertainty that is associated with the α -
173 pinene SOC percentage is at least a factor of 2 (Kourtchev et al., 2009).

174 We also investigated the occurrence of organosulphates (OS) and nitrooxy organosulphates
175 (NOS) formed from acid-catalysed reactions of reactive organic compounds with sulphate
176 aerosols (Surratt et al., 2008). Several precursors of the investigated OS and NOS compounds
177 are biogenic, being either isoprene or monoterpenes, while other OS and NOS have unknown
178 or anthropogenic precursors (Riva et al., 2015). OS have previously been studied in the USA,
179 Europe (Iinuma et al., 2007; Surratt et al., 2007; Gómez-González et al., 2008, 2012; Surratt et
180 al., 2008; Kristensen and Glasius, 2011; Nguyen et al., 2012; Nguyen et al., 2014; Martinsson
181 et al., 2017a) and the Arctic (Frossard et al., 2011; Hansen et al., 2014). The present study
182 comprises the geographically largest study of OS and NOS to date. In addition, we have
183 implemented a revised set of calibration standards to improve the quantification.

184 As is clear from the studies cited above, this study is not the first to investigate source-
185 apportionment of organic aerosol in Europe. However, current knowledge is patchy both in
186 terms of temporal and spatial resolution. Only very few studies have performed source
187 apportionment of the carbonaceous aerosol for the European rural background environment
188 based on organic tracers which covers the entire annual cycle (Gelencsér et al., 2007; Genberg
189 et al., 2011; Gilardoni et al., 2011). These studies all report the same major findings; OC from
190 residential wood burning emissions dominate during the heating season and SOA originating
191 from biogenic sources is the major fraction of the carbonaceous aerosol in summer. Studies
192 covering shorter time-periods (e.g., Szidat et al., 2007; Yttri et al. 2011a,b) support the major
193 findings of the long-term studies. In addition, these studies have suggested that for the
194 Northern outskirts of Europe, PBAP are the second most abundant source to carbonaceous
195 PM₁₀ during the vegetative season. Furthermore, Maenhaut et al. (2016) applied the PMF
196 technique (EPA PMF5) to a multi-species data set including a total of 29 variables (i.e., PM10
197 mass, OC, EC, levoglucosan, mannosan, galactosan, 8 water-soluble ions and 15 elements) for
198 four urban background sites in Flanders, Belgium, and found that the average contributions of
199 wood smoke were quite substantial in winter and ranged from 47 to 64% for PM₁₀ OC. The
200 contribution from wood burning to the PM₁₀ mass and OC was also assessed by using

201 levoglucosan as single marker compound and the conversion factors of Schmidl et al. (2008),
202 as done in a previous study on wood burning in Flanders (Maenhaut et al., 2012). However,
203 the apportionments were much lower than those deduced from PMF, suggesting that the
204 conversion factors of Schmidl et al. (2008) may not be applicable to all areas.

205 EC is typically dominated by fossil fuel sources regardless of season; however, the
206 contribution from residential wood burning can become equally large during the heating
207 season and even dominate in certain regions (Szidat et al., 2007; Zotter et al., 2014). A recent
208 study (Yttri et al., 2014) showed that EC from residential wood burning, derived from
209 levoglucosan measurements, could be an important source even in the remote Arctic
210 environment, accounting for 31-45% of the total EC observed in winter.

211 The increasing availability of AMS instruments allows interesting new approaches to source
212 apportionment. Crippa et al. (2014) presented results obtained by AMS measurements at 15
213 rural background sites and two urban sites during 26 field campaigns of the EU EUCAARI
214 project (Kulmala et al., 2011), including measurements during spring, fall and winter. Crippa
215 et al. (2014) used a new PMF technique (ME-2) to resolve OA into primary sources, i.e., HOA
216 (hydrocarbon-like OA), COA (cooking OA) and BBOA (biomass-burning OA), and secondary
217 sources including semi-volatile and low-volatility oxygenated OA (SV-OOA and LV-OOA).
218 For all sites and seasons, the HOA fraction accounted for $11 \pm 5\%$ of the total OA, the BBOA
219 fraction contributed $12 \pm 5\%$, and the vast majority of the OA was attributed to secondary
220 sources, i.e., SV-OOA ($34 \pm 11\%$) and LV-OOA ($50 \pm 16\%$). The COA was not retrieved at
221 any of the rural sites. Using model-based source apportionment and comparison with PMF
222 analysis of AMS data from 11 sites in Europe, Ciarelli et al. (2017) found that SOA
223 constituted a major fraction of OA (on average 62%, range 32 to 88%) during winter, HOA on
224 average 13%, while BB primary OA was as high as 25%. Although online-AMS in
225 combination with PMF techniques are very powerful, they can only address the sub-micron
226 aerosol fraction (typically <700 nm) and do not provide information on, for example, PBAP
227 sources. They also cannot distinguish modern from fossil-fuel carbon, being particularly
228 important for the secondary components (OOA). Filter-based measurements therefore remain
229 an important source of such information, and indeed the two approaches should be very
230 complementary. For both AMS and filter-based approaches, the major need now is to expand
231 the database of measurements to cover more sites, seasons and species, in order to provide
232 sufficient data for generally applicable conclusions to be drawn. Such datasets are also
233 required to serve the needs of model and emissions evaluation (Bergström et al., 2012; Denier
234 van der Gon et al., 2015).

235 In line with this need, the aim of the present study is to quantify the contribution of the most
236 abundant sources of the carbonaceous aerosol in the rural background environment in
237 Northern Europe during winter.

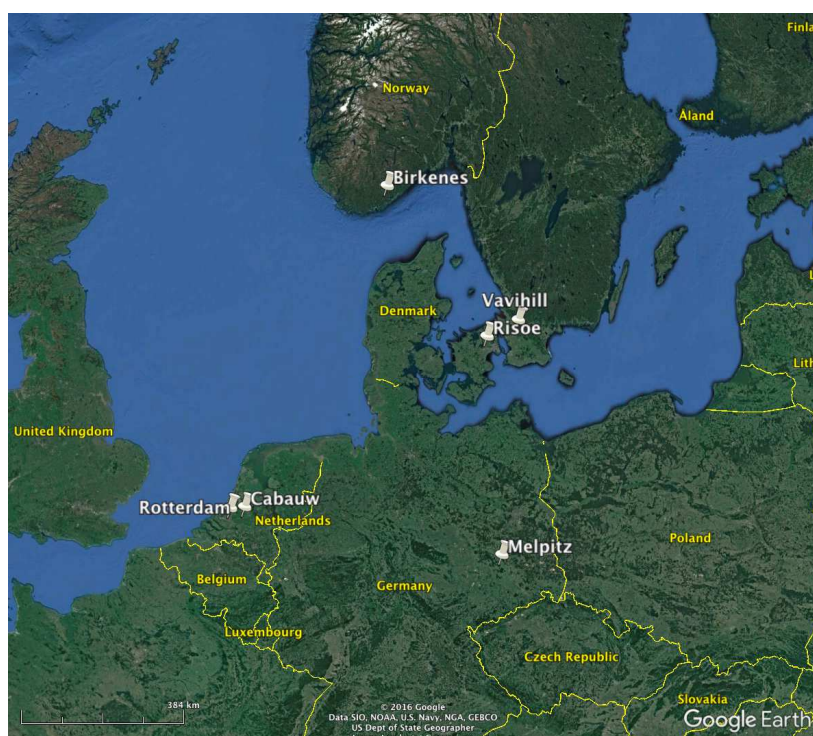
238

239 2. Experimental

240 2.1 Sampling sites

241 Aerosol samples (PM₁₀) were collected at five rural background sites and one urban
242 background site in Northern Europe (Figure 1), to represent various environments regarding
243 area type and proximity to major anthropogenic emission sources.

244



245

246 Figure 1. Map showing the location of the study sites.

247

248 The Birkenes atmospheric research station (BIR, 58° 23'N, 8° 15'E, 190 m above sea level,
249 a.s.l.) is a joint supersite for EMEP (The European Monitoring and Evaluation Programme)
250 and GAW (Global Atmospheric Watch) and is situated approximately 20 km from the
251 Skagerrak coast in southern Norway. The station is located in the boreal forest with mixed
252 conifer and deciduous trees accounting for 65% of the land use in the vicinity of the site; the
253 remaining 35% is attributed to meadow (10%), low-intensity agricultural areas (10%), and
254 freshwater lakes (15%). The nearest local emission source is the city of Kristiansand (65 000

255 inhabitants), located 25 km south/south-west of the station, which is known to have minor or
256 even negligible influence on the air quality at the site.

257
258 Risoe (RIS, 55° 41' N, 12° 07' E, 12 m a.s.l.) is a semi-rural monitoring station on the Danish
259 island Zealand, located on a small peninsula by the Roskilde fjord. The surrounding area is
260 characterized by agricultural land and small villages to the east, and the main road A6 with
261 about 15,800 vehicles per day located within a distance of one km. The Roskilde Fjord is
262 located to the west of the site and occupies 74 km². It is the longest fjord in Denmark and
263 propagates 41 km from North to South. The Risoe station is situated 30 km west of the capital
264 Copenhagen (1.2 million inhabitants) and 7 km north-east of central Roskilde (46 000
265 inhabitants). The station is part of the Danish Air Quality Monitoring Program.

266
267 Vavihill (VAV, 56° 01' N, 13° 09' E, 172 m a.s.l.) is a EUSAAR (European Supersites for
268 Atmospheric Aerosol Research) and EMEP site situated in Southern Sweden. The surrounding
269 area is dominated by grassland and pastures (49%), deciduous trees (40%) and farmland
270 (10%). The site is situated 25 – 45 km north-east to east of the densely populated areas of
271 greater Malmö (about 660 000 inhabitants), Copenhagen and Helsingborg (100 000
272 inhabitants). An earlier study by Kristensson et al. (2008) has shown that air masses passing
273 over these areas are typically more polluted than air masses originating from other directions.

274
275 The Cabauw Experimental Site for Atmospheric Research (CAB) is situated in the western
276 part of The Netherlands, 44 km from the North Sea (51° 58' N, 4° 55' E, 0.3 m a.s.l.). It is a
277 supersite that hosts several networks such as GAW, EMEP and the European project ACTRIS
278 (Aerosols, Clouds, and Trace gases Research InfraStructure Network). The agriculturally
279 dominated area is located tens of kilometers from major cities such as Amsterdam, The Hague,
280 Rotterdam, and Utrecht. A variety of air masses can be encountered, from modified clean
281 maritime to continental polluted ones.

282
283 Rotterdam (ROT), The Netherlands, is a city with a population of 570 000 inhabitants, situated
284 geographically within the Rhine–Meuse–Scheldt river delta of the North Sea. The port of
285 Rotterdam is the largest cargo port in Europe and the 10th largest in the world. The sampling
286 site is situated on Zwartewaalstraat (51° 54' N, 4° 29' E) in the south part of Rotterdam. It is
287 an urban background site with no direct influence from the port, highways or industry, and is

288 managed by the regional environmental agency. The sampling site is situated 32 km west of
289 the Cabauw rural background site.

290
291 The Melpitz (MEL) atmospheric research station (Spindler et al., 2010; 2013) operated by
292 TROPOS is a rural background site located 4 km south-west of the city of Torgau (20 000
293 inhabitants) in the glacial valley of the river Elbe in eastern Germany (12°56' E, 51°32' N, 86
294 m a.s.l.). The city of Leipzig (550 000 inhabitants) is located about 50 km to the south-west of
295 the station. The station is situated on a meadow, surrounded by agricultural land. The
296 dominating wind direction at Melpitz is south-west, whereas marine air masses reach the site
297 after crossing the western part of central Europe. Easterly air masses arriving at Melpitz
298 typically contain low relative humidity and are influenced by hot spots of anthropogenic
299 (industrial and domestic) air pollution in Eastern Europe. The Melpitz site is representative for
300 a large rural area in Saxony (East and North-East German lowlands). Melpitz is a GAW
301 regional station and integrated in EMEP and ACTRIS (Aas et al., 2012).

302

303 **2.2 Sample collection and air mass back-trajectory analysis**

304 Aerosol samples were collected on quartz fibre filters (Whatman QM-A; 47 mm), using low-
305 volume filter samplers (KleinfILTERgerät or at Vavihill Leckel SEQ47/50) equipped with a
306 PM₁₀ inlet. The filters were all from the same batch and pre-fired at 850 °C for 3 h before they
307 were distributed to the sites.

308 The study period was January 11 - February 8, 2013. Each sample was collected for one week
309 and a total of four aerosol samples were obtained at each site. After sampling, the filters were
310 placed in petri-slide dishes, and stored in a freezer at -18 °C until analysis.

311 Air mass back-trajectories were calculated for every 6 hours with the FLEXTRA trajectory
312 model (Stohl et. al., 1995; Stohl and Seibert, 1998, available at www.nilu.no/trajectories)
313 using meteorological data from European Centre for Medium Range Weather Forecasts
314 (ECMWF).

315

316 **2.3 Thermal-optical analysis of Total Carbon, OC, and EC**

317 The samples collected at Birkenes, Cabauw, Lille Valby, Melpitz and Rotterdam were
318 analysed using the Sunset laboratory OC/EC instrument, whereas the OC/EC Thermal Optical
319 Carbon Analyzer from DRI (Desert Research Institute) was used to analyse the samples from
320 Vavihill. All samples were analysed according to the EUSAAR-2 protocol (Cavalli et al.,
321 2010), using transmission to correct for charring of OC. The performance of the OC/EC

322 instruments has been subject to intercomparison, either annually as part of the joint
323 EMEP/ACTRIS quality assurance and quality control, or as part of research studies (Yttri et
324 al., 2011b).

325 In order to minimise artefacts on the determination of EC from charring of high levels of OC,
326 water-extraction of filters was performed to remove water-soluble components (Zhang et al.,
327 2012c) before a second thermal analysis. Ultrapure water with a low total organic carbon
328 content was passed through the filters, which were placed in a plastic filter holder with the
329 laden side upwards.

330

331 **2.4 ^{14}C analyses**

332 The ^{14}C content in total carbon (TC) of the collected particles was determined by accelerator
333 mass spectrometry (Hellborg and Skog, 2008), using the 250 kV single-stage instrument at
334 Lund University (Skog, 2007; Skog et al., 2010). Prior to analysis, carbon in the aerosol
335 sample was transformed into graphite according to the procedure described in Genberg et al.
336 (2010). In brief, the sample was combusted in vacuum, using CuO as an oxidation agent. The
337 evolved CO_2 was purified cryogenically and mixed with H_2 in a small-volume reduction
338 reactor and then heated to 600 °C. In this reaction, CO_2 is transformed into graphite on a
339 heated iron catalyst. The amount of carbon in the samples ranged from 23 to 150 $\mu\text{g C}$. OxI
340 was used as primary standard, IAEA-C6 and IAEA-C7 as secondary standards, and acetanilide
341 as background (Genberg et al., 2010).

342 The results of the ^{14}C measurements are presented as $F^{14}\text{C}$, fraction modern carbon (Reimer et
343 al., 2004). Fossil sources have a $F^{14}\text{C}$ value of 0 due to their large age. A $F^{14}\text{C}$ value of 1
344 represents the ^{14}C content in atmospheric CO_2 in 1950, if human influences are not taken into
345 consideration. The real atmospheric ^{14}C content has been altered because of emissions of CO_2
346 from fossil fuel combustion (the Suess effect) and new formation of ^{14}C as a result of
347 detonation of thermonuclear weapons (the bomb effect). The latter effect, which resulted in a
348 peak with an almost doubled $F^{14}\text{C}$ value in 1963, needs to be taken into account when
349 estimating the $F^{14}\text{C}$ value resulting from biogenic carbon (e.g., plant emissions), as well as
350 from combustion of biomass.

351

352 **2.5 Cellulose analysis**

353 Free cellulose was determined based on the enzymatic method described by Kunit and
354 Puxbaum (1996). Filter punches of 2 cm^2 were extracted with 1.2 mL of a citric acid buffer
355 containing thymol (0.05%) to prevent bacterial growth. Different to the method of Kunit and

356 Puxbaum (1996), the pH of the buffer was adjusted to 6.3 to obtain more suitable conditions
357 for the final enzymatic determination of glucose. Cellulose was saccharified by cellulase and
358 cellobiase for 24 hours at 45 °C. After denaturation and centrifugation, the supernatant was
359 analysed for D-glucose enzymatically using a test kit (D-glucose-HK, Magazyme). Glucose
360 was phosphorylated to glucose-6-phosphate and subsequently oxidized by nicotinamide
361 adenine dinucleotide phosphate (NADP) to gluconate-6-phosphate. The emerging NADPH
362 was quantified photometrically at 340 nm. The results were corrected for the samples content
363 of free glucose. The limit of detection of this method is 16 ng m⁻³ (calculated as three times
364 standard deviation of the blanks using an average air volume of 386 m³).

365

366 **2.6 Anhydrosugars, sugar alcohols and sugars**

367 The samples were analysed for anhydrosugars, sugars and sugar-alcohols by gas
368 chromatography/mass spectrometry (GC/MS). The anhydrosugars measured were
369 levoglucosan, mannosan and galactosan; the sugars were glucose, fructose, sucrose and
370 trehalose; and the sugar-alcohols arabitol and mannitol. The method was similar to that
371 described in Pashynska et al. (2002), but the extraction was done with methanol instead of
372 dichloromethane-methanol (80:20, v/v), a different recovery standard was used, and the GC
373 temperature program was modified.

374 A punch of the quartz fibre filter sample (usually a single 1.0 cm² punch) was used for the
375 extraction. Prior to the extraction the internal recovery standard methyl O-L-xylanopyranoside
376 was added (typically 510 ng). The filter punch was then extracted three times, each time
377 during 5 min with 10 mL methanol, using ultrasonic agitation in a 25 mL Pyrex glass flask
378 with a Teflon-lined stopper. The combined extracts were reduced with a rotary evaporator
379 (213 hPa, 35 °C) to about 1 mL. The concentrated extract was then filtered through a Teflon
380 syringe filter (0.45 µm) and completely dried under a nitrogen stream. Subsequently, a
381 derivatisation was carried out; hereto 40 µL N,O-bis(trimethylsilyl)trifluoroacetamide with 1%
382 trimethylchlorosilane was added to the dried sample, and the mixture reacted during 60 min at
383 70 °C. 1 µL of the solution obtained was then immediately analysed by GC/MS. For the
384 derivatisation of calibration mixtures with the measured compounds and the internal recovery
385 standard, the same procedure was applied with derivatisation and analysing 1 µL of the 40 µL
386 solution, but no filter punch, no extraction, and no evaporation were done.

387 The GC/MS system consists of a TRACE GC2000 gas chromatograph and a Polaris Q ion trap
388 mass spectrometer equipped with an external electron ionisation source (Thermo Scientific,
389 San Jose, CA, USA). Data acquisition and processing were done with the Xcalibur version 1.4

390 software (Thermo Scientific). The GC was provided with a deactivated silica pre-column (2 m
391 x 0.25 mm i.d.) and an ATTM-5ms “low-bleed” capillary column (95% dimethyl-, 5%
392 phenylpolysiloxane, 0.25 μm film thickness, 30 m x 0.25 mm i.d.) (Alltech, Deerfield, IL,
393 USA). The split/splitless injector was used in the splitless mode (splitless time: 0.5 min) at 250
394 $^{\circ}\text{C}$. Helium at a flow rate of 1.1 mL min^{-1} was used as carrier gas. The temperature of the
395 transfer line was 280 $^{\circ}\text{C}$. The GC temperature program was as follows: initial temperature of
396 100 $^{\circ}\text{C}$, kept for 2 min, followed by a gradient of 3 $^{\circ}\text{C min}^{-1}$ to 200 $^{\circ}\text{C}$, kept constant for 2
397 min, then a gradient of 30 $^{\circ}\text{C min}^{-1}$ to 310 $^{\circ}\text{C}$, after which the final temperature was
398 maintained for 2 min. The total GC/MS analysis time was 43 min.

399 Electron ionisation (EI) was carried out at 70 eV and an ion source temperature of 200 $^{\circ}\text{C}$. The
400 m/z values for the analytes and the recovery standard were as follows: Recovery standard,
401 levoglucosan, mannosan, galactosan: 217; arabitol, mannitol, 319; fructose, glucose: 217;
402 sucrose, trehalose: 361.

403 For the quantification of the monosaccharide anhydrides calibration curves of 8 points were
404 made in the following ranges (the quantities given are those in the 40 μL derivatisation
405 solution; of this solution 1 μL was analysed by GC/MS): levoglucosan, 20 – 2000 ng;
406 mannosan, 2 – 200 ng; galactosan, 1 – 100 ng; arabitol, 1 – 100 ng; mannitol, 1 – 100 ng;
407 fructose, 2 – 200 ng; glucose, 1 – 100 ng; sucrose, 5 – 500 ng; trehalose, 5 – 500 ng. The
408 precision of the method for the individual monosaccharide anhydrides in real aerosol filter
409 samples is estimated to be between 5 and 10%.

410

411 **2.7 Analysis for SOA tracers**

412 Each sample was analysed for three types of SOA tracers: organic acids, organosulphates, and
413 nitrooxy organosulphates, generally following previously published methods (Kristensen and
414 Glasius, 2011; Hansen et al., 2014). For this analysis between 0.75 and 1 cm^2 of the collected
415 filter samples were used. The filter punch was placed in a preparation vial and spiked with 8
416 μL of a 50 $\mu\text{g/mL}$ recovery standard (camphoric acid) to monitor the extraction efficiency.
417 The filter punch was covered with 2 mL of a 50:50 acetonitrile-methanol extraction solution
418 and extracted using a cooled ultrasonic bath for 30 min. The extract was filtered through a
419 Teflon filter with a pore size of 22 μm (Chromafil) and was evaporated to dryness under a N_2
420 flow. The sample was re-dissolved in 200 μL MilliQ water with 10% acetonitrile and 0.1%
421 acetic acid.

422 All sample extracts were analysed on an ultra-high performance liquid chromatograph
423 (UHPLC, Dionex), coupled to a quadrupole time-of-flight mass spectrometer (q-TOF-MS,
424 Bruker Daltonics) through an electrospray ionisation inlet (ESI).

425 The UHPLC stationary phase was an Acquity T3 1.8 μm (2.1×100 mm) column from Waters
426 and the mobile phase consisted of eluent A: 0.1% acetic acid and eluent B: acetonitrile with
427 0.1% acetic acid. The operational eluent flow was 0.3 mL/min and an 18 min multistep
428 gradient was applied: From 1 min to 10 min, eluent B increased from 3% to 30%. Then over 1
429 min, eluent B increased to 90% where it was held for 1 min. During the following 0.5 min,
430 eluent B increased to 95% and was held for 3.5 min before being reduced back to 3% over 0.5
431 min and held there for the remaining 0.5 min of the analysis.

432 The ESI-q-TOF-MS was operated in negative ionisation mode with a nebuliser pressure of 3.0
433 bar, a dry gas flow of 8 L/min, source voltage 3.5 kV and collision energy 6 eV. The data were
434 acquired and processed using Bruker Compass software.

435 The organic acids were identified and quantified using authentic standards. Organosulphates
436 and nitrooxy organosulphates were identified from the presence of HSO_4^- (m/z 97) and the
437 neutral loss of SO_3 (80 u) and an additional neutral loss of HNO_3 (63 u) in the case of nitrooxy
438 organosulphates (Surratt et al., 2007). Due to the lack of authentic standards, most
439 organosulphates and nitrooxy organosulphates were determined using surrogate standards of
440 an authentic β -pinene organosulphate with MW 250 (synthesised in-house according to
441 Iinuma et al., 2009), octyl sulphate sodium salt ($\geq 95\%$ Sigma-Aldrich) and D-mannose-6-
442 sulphate sodium salt ($\geq 90\%$ Sigma-Aldrich). The surrogate standard chosen for quantification
443 of the individual compounds was decided based on similar retention times in the UHPLC-q-
444 TOF-MS system, as described by Nguyen et al. (2014).

445 A linear relation between peak area and concentration was established and applied for
446 quantification of β -pinene organosulphate MW 250, D-mannose-6-sulphate, diaterpenylic acid
447 acetate (DTAA), octyl sulphate, pinic acid, and terpenylic acid. A quadratic relation between
448 peak area and concentration was established and applied for quantification of adipic acid,
449 azelaic acid, benzoic acid, camphoric acid (recovery standard), MBTCA, phthalic acid,
450 pimelic acid, pinonic acid, and suberic acid. The correlation coefficients R^2 of all calibration
451 curves were better than 0.99 ($n = 7$ data points) except for octyl sulphate, which had a
452 correlation coefficient of 0.93. The detection limits of all compounds fell within the interval of
453 0.004 – 0.016 ng m^{-3} . The results were corrected according to the response of the recovery
454 standard ($53 \pm 15\%$), and the overall uncertainty was estimated to be 30%. Supplemental

455 Information (SI) Table 1 presents an overview of detected organosulphates and nitrooxy
456 organosulphates.

457

458 **2.8 Statistical analyses**

459 The relationship between any tracer and its derived TC component is highly uncertain; hence,
460 we use a method developed in previous papers (Gelencsér et al., 2007; Szidat et al., 2009;
461 Yttri et al., 2011a; Yttri et al., 2011b) to assign an uncertainty distribution of allowed
462 parameter values for all important emission ratios or measurement inputs. In order to solve the
463 system of equations, allowing for the multitude of possible combinations of parameters, an
464 effective statistical approach known as Latin-hypercube sampling (LHS) is used, which is
465 comparable to Monte Carlo calculations. Details of this procedure were first given by
466 Gelencsér et al. (2007), and the procedure as used here is described in detail in Yttri et al.
467 (2011a). In brief, central values with low and high limits are associated to all uncertain input
468 parameters. These factors are combined using a simplified approach of LHS in order to
469 generate thousands of solutions for the source apportionment. All valid combinations of
470 parameters (i.e., excluding those producing negative solutions) are condensed in frequency
471 distributions of possible solutions. Extensive discussion of the choices behind the factors used,
472 and their uncertainties, can be found in earlier related studies (Gelencsér et al., 2007; Szidat et
473 al., 2009) and especially for wood-burning emissions in Simpson et al. (2007). The results of
474 this analysis consist of so-called central-estimates of the TC components (i.e., the 50th
475 percentile), as well as the range of possibilities allowed by the LHS calculation, usually
476 expressed as the 10th and 90th percentiles of the solutions. For example, we assign ratios for
477 TC/levoglucosan from biomass-burning with low and high limits of 11 and 17, respectively, or
478 we allow an uncertainty in the EC estimate of 25% around the measured values. In this work
479 we retain the same factors as in Yttri et al. (2011b) except that we modify the lower limit
480 values assigned to $F^{14}C$ to be 1.025 for debris and spores and 1.05 for biomass burning (Yttri
481 et al., 2011b, used 1.055 for both), reflecting the reduction in atmospheric $F^{14}C$ values
482 between the time of the Yttri et al. study (2006-2007) and the sampling conducted for this
483 work (2013).

484 Although it is impossible to give a statistical uncertainty on these LHS calculations since we
485 have no 'true' answer to compare with, each LHS estimate used here tests 8000 combinations
486 of possible contributions. One complication, for example, is that different wood-types or
487 wood-burners can give different emission profiles, but actually several studies in very
488 different parts of Europe have resulted in similar ratios for OCbb/levoglucosan (e.g. Puxbaum

489 et al., 2007 and Yttri et al, 2005). This was previously discussed extensively in Simpson et al.
490 (2007), who concluded that most studies show a levoglucosan/OC ratio of around 10-20%. In
491 the Supplementary information of Yttri et al. (2011b) we discuss the LHS scheme in more
492 detail, and also ran the LHS scheme with a wider uncertainty range for the different input
493 assumptions. This study showed that the LHS results were quite robust. In fact, the
494 supplement of Yttri et al (2011b) noted that the LHS approach is thus not primarily designed
495 to give a 'best'-estimate; it is designed to show which solutions are possible. One of the
496 encouraging and important findings of these LHS studies has been that one can allow very
497 wide ranges of emission ratios, and still end up with quite similar general findings, since the
498 impossible combinations are excluded by the requirement that all solutions are positive.

499

500 **3 Results**

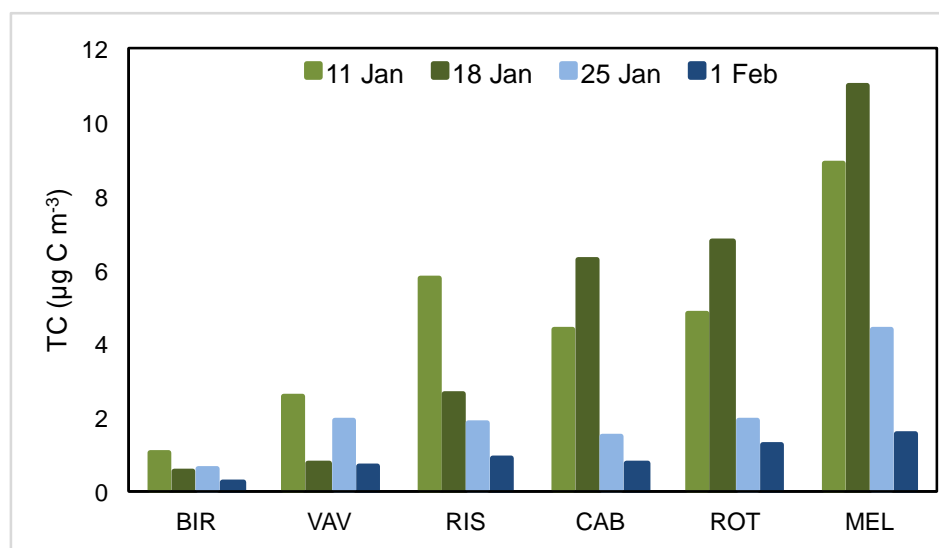
501 High carbonaceous aerosol levels were observed at most sites during the two first weeks of
502 sampling (Figure 2), when Scandinavia and parts of Northern Europe were influenced by a
503 high-pressure system transporting continental air masses towards the west (particularly during
504 13-26 January), while the remaining study period was influenced by westerly winds and lower
505 levels of aerosols.

506

507

508 **3.1 Concentrations of total carbon**

509



510

511 Figure 2. TC in aerosol samples collected at six study sites across Northern Europe as one-
 512 week samples starting on the indicated dates. BIR is Birkenes (Norway), VAV is Vavihill
 513 (Sweden), RIS is Risoe (Denmark), CAB is Cabauw (The Netherlands), ROT is Rotterdam
 514 (The Netherlands), and MEL is Melpitz (Germany).

515

516 The average TC concentration decreased one order of magnitude along a south to north
 517 transect, ranging from $6.0 \pm 4.3 \mu\text{g C m}^{-3}$ at Melpitz to $0.5 \pm 0.3 \mu\text{g C m}^{-3}$ at Birkenes. The
 518 steep gradient is partly explained by the elevated concentrations observed during the two first
 519 weeks of sampling at the continental sites, with mean weekly concentrations as high as $11 \mu\text{g C m}^{-3}$.
 520 The mean TC concentration observed at the three Nordic sites is comparable to
 521 previously reported measurements for these sites in winter (Yttri et al., 2007a; Genberg et al.,
 522 2011; Martinsson et al., 2017b) (see also ebas.nilu.no), whereas it is clearly elevated in the
 523 first two weeks especially for Melpitz (Spindler et al., 2013), for Rotterdam (see Jedynska et
 524 al., 2014), and somewhat for Cabauw (see Dusek et al., 2017). The TC concentrations at Risoe
 525 (PM_{10}) were comparable to TC concentrations at the same site ($\text{PM}_{2.5}$) available from the
 526 National Monitoring Program (Ellermann et al., 2015), which showed the same trend as TC in
 527 PM_{10} with the highest concentration in the first week and the lowest concentration in the last
 528 week (data not shown).

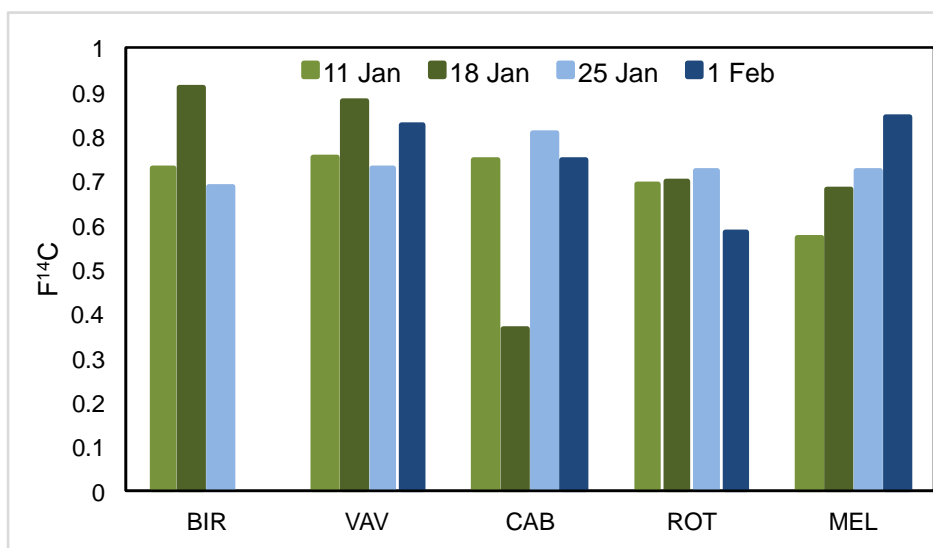
529

530

531

532 3.2 Modern carbon/fossil carbon

533 The results of the ^{14}C measurements are shown in Figure 3, excluding all samples from Risoe
 534 and one from Birkenes (see below).



535
 536 Figure 3. $F^{14}\text{C}$ in aerosols collected at five study sites across Northern Europe (start days are
 537 listed). Typical uncertainty of the measurements is $F^{14}\text{C} = 0.006$.

538
 539 The lowest $F^{14}\text{C}$ value in the current study ($F^{14}\text{C}=0.362$ at Cabauw, The Netherlands) shows a
 540 clear influence from fossil sources. Such low $F^{14}\text{C}$ values have previously been found in
 541 heavily trafficked areas in cities (Glasius et al., 2011). The samples with the two highest
 542 values are from the two northernmost sites, Birkenes and Vavihill, and were collected during
 543 the same sampling period (18 - 25 Jan 2013). A larger proportion of carbon from biomass
 544 burning results in the highest $F^{14}\text{C}$ values, as discussed later.

545 The $F^{14}\text{C}$ data sets for the various sites are not statistically significantly different from each
 546 other. The $F^{14}\text{C}$ results are very similar to those from a previous study of TC collected at
 547 Vavihill, Sweden, during January and the beginning of February 2009, where the $F^{14}\text{C}$ values
 548 ranged between 0.621 and 0.863 (Genberg et al., 2011).

549 All samples from Risoe showed a clear ^{14}C contamination ($F^{14}\text{C}$ varied between 3.9 and 42).
 550 The sampling site at Risoe is located in the vicinity of two shut-down nuclear experimental
 551 reactors presently undergoing decommissioning. The contamination most probably originates
 552 directly or indirectly from these reactors, such as from work related to decommissioning or
 553 classification of waste (Hou, personal communication). One of the Birkenes samples was also
 554 contaminated ($F^{14}\text{C}=4.6$). This may be associated with a contamination of the very small
 555 sample (only 23 μg of carbon) occurring in the ^{14}C sample preparation laboratory due to the

556 handling of the contaminated Risoe samples. However, this remains speculative as none of the
557 measured secondary standards displayed any contamination. Another possibility could be a
558 ^{14}C contamination during sampling at the Birkenes site. Buchholz et al. (2013) report that ^{14}C
559 contamination in aerosol samples is uncommon but not rare, and in their experience about
560 10% of sampling sites are affected (Buchholz et al., 2013). Buchholz et al. (2013) and Zotter
561 et al. (2014) identify potential sources as laboratories using ^{14}C as a tracer, as well as
562 incinerators combusting ^{14}C -labelled medical or biological material. These authors further
563 point out that the very high surface area of PM readily provides absorption of volatile ^{14}C -
564 labelled compounds as well as of $^{14}\text{CO}_2$. ^{14}C is also commonly used as a tracer in various
565 research disciplines, not only in laboratories but also in field experiments, see e.g. Rasmussen
566 et al. (2008). Influence from such activities in the vicinity of air monitoring stations may
567 obscure ^{14}C -based source apportionment of aerosols, and it is thus important to consider
568 potential local ^{14}C -contamination in future studies.

569

570 **3.3 Organic tracers from primary sources**

571 **Levoglucosan**

572 The mean concentrations of levoglucosan ranged from $25 \pm 13 \text{ ng m}^{-3}$ (Birkenes) to 249 ± 13
573 ng m^{-3} (Melpitz), and increased along a north to south transect (see Supplemental Information
574 Table 2). The levels are comparable to those previously reported for the European rural
575 background environment, as is the North to South gradient, and the observed levoglucosan to
576 sum monosaccharide anhydrides (levoglucosan, mannosan, galactosan) ratio ($85 \pm 2\%$)
577 (Puxbaum et al., 2007; Yttri et al., 2011a). Increased levels were observed during the first half
578 of the sampling period compared to the last one, and were attributed to meteorological
579 conditions with stagnant air and low temperatures, causing poor dispersion. High levoglucosan
580 to TC ratios (from 0.04 to 0.05) observed for all sites (SI Table 2), indicate a pronounced
581 influence of biomass combustion emissions, which with a high level of confidence can be
582 attributed to residential heating, given the geographical region and time period studied. A very
583 high correlation coefficient ($R^2 = 0.94$) for levoglucosan and TC during the sampling period
584 supports the statement of biomass combustion being a major source of the carbonaceous
585 aerosol.

586

587 **Sugars and sugar alcohols**

588 Sugars and sugar alcohols were present in all samples, demonstrating the presence of PBAP
589 even during the middle of winter in Northern Europe. The concentrations were however low,

590 in particular for the sugar alcohols arabitol and mannitol used to trace fungal spores (see SI
591 Table 2). The highest total concentrations of sugars and sugar alcohols were observed during
592 the two first weeks of sampling, except for Vavihill, whereas their relative share of TC was
593 higher for the two last weeks. There was a pronounced correlation of levoglucosan with
594 fructose ($R^2 = 0.88$) and glucose ($R^2 = 0.74$), suggesting that these species are co-emitted
595 during residential wood burning. No correlation with levoglucosan was observed for the
596 fungal spore tracers (arabitol and mannitol).

597 A correlation between glucose and levoglucosan in plumes from forest fires was observed by
598 Medeiros et al. (2006) and also for emission measurements from combustion of different types
599 of wood or biomass (Kistler et al., unpublished data), although the ratio between glucose and
600 levoglucosan was markedly lower in the emission study compared to the ambient data
601 presented here.

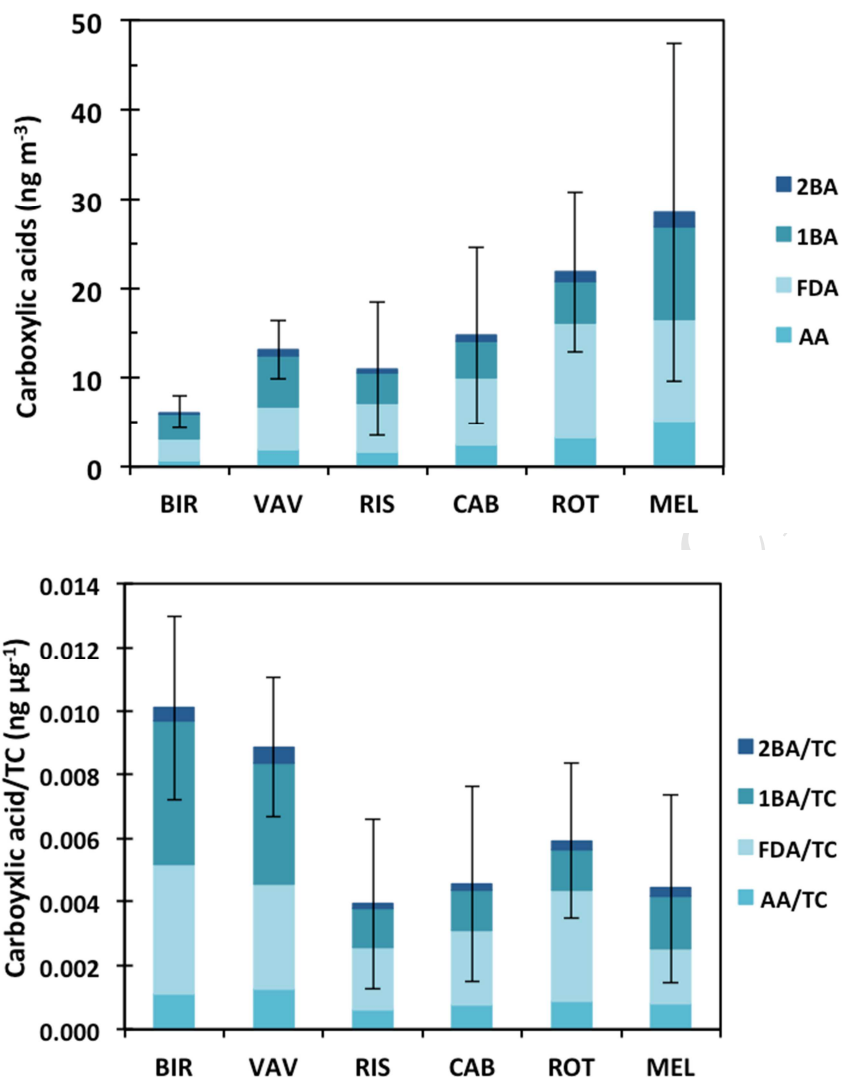
602

603 **Cellulose**

604 Free cellulose concentrations were only above the detection limit (of 16 ng m^{-3}) in the aerosol
605 samples from Rotterdam, where concentrations ranged from 24 to 43 ng m^{-3} . Summer to
606 winter ratios between 2 and 4 have been reported previously for average concentration values
607 at continental background sites (Sánchez-Ochoa et al., 2007). Summer concentrations are
608 available from measurements conducted at Birkenes and Vavihill, where averages were close
609 to 90 ng m^{-3} (Yttri et al., 2011b). Assuming the limit of detection as an upper limit of
610 wintertime cellulose concentrations, the seasonality at Birkenes and Vavihill seems to be
611 slightly more pronounced than reported by Sanchez-Ochoa et al. (2007).

612

613 **3.4 Organic tracers from secondary sources: carboxylic acids, organosulphates, and** 614 **nitrooxy organosulphates**



615

616

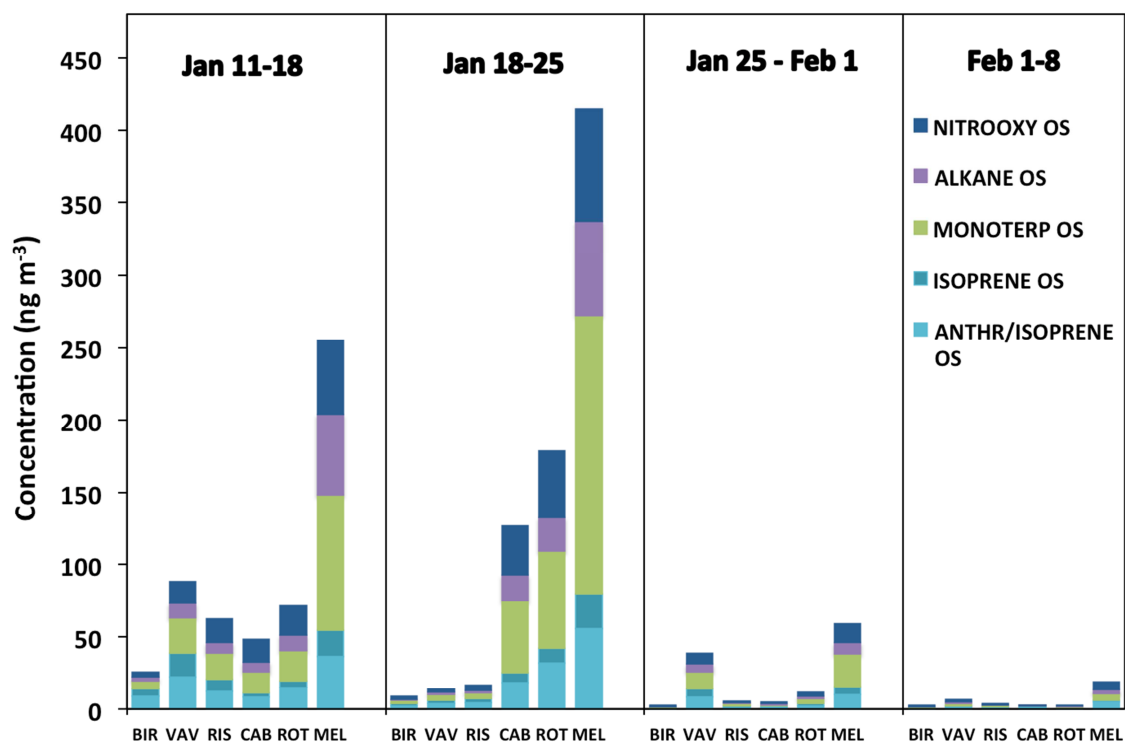
617 Figure 4. Average concentrations of carboxylic acids summarised as anthropogenic acids (AA,
 618 i.e., adipic acid, benzoic acid and pimelic acid), fatty acid-derived carboxylic acids (FDA, i.e.,
 619 azelaic acid and suberic acid), first-generation biogenic acids (1BA, i.e., pinic acid, pinonic
 620 acid, and terpenylic acid) and second-generation biogenic acids (2BA, i.e., MBTCA and
 621 DTAA). In the lower panel, the concentrations are normalised to TC concentrations. The error
 622 bars show the standard deviation of the four sampling periods.

623

624 Carboxylic acids were grouped into anthropogenic acids (adipic acid, benzoic acid and pimelic
 625 acid), fatty acid-derived carboxylic acids (azelaic acid and suberic acid), first-generation
 626 biogenic acids from oxidation of α - and β -pinene (pinic acid, pinonic acid, and terpenylic acid)
 627 and second-generation biogenic acids from oxidation of e.g. pinonic acid (MBTCA and
 628 DTAA). Figure 4 shows the average concentrations of these groups of carboxylic acids for
 629 each site during the study period. The mean total concentrations of the carboxylic acids were

630 4-53 ng m⁻³, with the lowest concentrations observed at Birkenes and the highest at Melpitz,
 631 showing a pronounced north-south gradient.

632 The concentrations of the carboxylic acids were normalised to TC, in order to reduce the
 633 influence of particle mass on partitioning of semi-volatile components (Kroll and Seinfeld,
 634 2008), and the lower panel of Figure 4 shows the results. Here the two most remote or rural
 635 sites, Birkenes and Vavihill, have higher relative contributions from biogenic acids compared
 636 to the other sites, where the fatty acid-derived acids dominate the relative contribution. The
 637 relative contribution of the biogenic acids was particularly high at Birkenes and Vavihill for
 638 week 2 and 4, whereas quite similar relative contributions were observed at the other sites
 639 during the study period (data not shown). Sources to biogenic acids at Birkenes and Vavihill
 640 could include regional monoterpene emissions and possible wood combustion. The biogenic
 641 acids from these sources together with the other carboxylic acids, which were at low
 642 concentrations, could contribute to the higher relative levels of biogenic acids at these sites.
 643 Generally, the concentrations of the biogenic acids (especially pinic acid and terpenylic acid)
 644 and the fatty acid-derived acids (in particular azelaic acid) were larger than the levels of the
 645 anthropogenic acids. The concentrations of pinic acid (0.3-9.7 ng m⁻³), terpenylic acid (0.2-
 646 10.6 ng m⁻³) and pinonic acid (below the detection limit of 1.9 ng m⁻³) were within previously
 647 observed levels in Northern and Central Europe (Kourtchev et al., 2009; Zhang et al., 2010;
 648 Kristensen and Glasius, 2011).



649

650 Figure 5. Concentrations of organosulphates (OS) and nitrooxy organosulphates (nitrooxy OS)
651 according to parent molecules (i.e., alkanes, monoterpenes, isoprene, anthropogenic or
652 isoprene, see text for further explanations).

653
654 We observed 23 different organosulphates (OS) and seven nitrooxy organosulphates (NOS)
655 during the study period (SI Table 1). The organosulphates of lowest molecular weight (OS
656 140, 154, 156, 168 and 182) were products of glycolaldehyde, hydroxyacetone, methylglycolic
657 acid, methacrolein and 2-methylglyceric acid (Surratt et al., 2007; Olson et al., 2011;
658 Schindelka et al., 2013; Shalamzari et al., 2013), originating from either the oxidation of
659 isoprene or anthropogenic compounds (Biesenthal and Shepson, 1997; Myriokefalitakis et al.,
660 2008; Surratt et al., 2008; Hakola et al., 2009; Zhang et al., 2012a; Hansen et al., 2014) and
661 contributed with $22 \pm 7\%$ of the sum of OS. Another group of OS originated from the
662 photochemical oxidation of isoprene, namely OS 170, 184, 200, 212, 214 and 216, of which
663 the latter one is derived from isoprene epoxydiols, IEPOX (Surratt et al., 2008; Surratt et al.,
664 2010; Shalamzari et al., 2013), and this group made up $13 \pm 5\%$ of the sum of OS. The
665 organosulphate OS 200 derived from 2-methylglyceric acid (Surratt et al., 2007; Zhang et al.,
666 2012b) was only observed at very low levels. Organosulphates originating from monoterpenes
667 (OS 248, 250, 252, 268a and 280a) (Surratt et al., 2006) contributed to 11-46% of the sum of
668 OS (on average $28 \pm 8\%$). Furthermore, organosulphates derived from oxidation of alkanes,
669 namely, OS 210, 238, 268b, 270, 280b, 280c, 296, and 298, as well as NOS 327, (Riva et al.,
670 2016b) constituted $13 \pm 3\%$ of the sum of OS. Of these, OS 210 was previously detected at
671 Svalbard and North Greenland during winter (Hansen et al., 2014). Only very low levels of
672 organosulphates derived from green-leaf volatiles (Shalamzari et al., 2014) and polycyclic
673 aromatic hydrocarbons, PAH (Riva et al., 2015) were observed.

674 Nitrooxy organosulphates contributed to $24 \pm 5\%$ of the sum of OS. Of these, NOS 295, 311
675 and 327b are derived from α - and β -pinene, while NOS 297, 313, 327 and 329 have been
676 observed in chamber oxidation experiments of *d*-limonene (Surratt et al., 2008).

677 Figure 5 shows the distribution of major groups of OS and NOS during the study period. The
678 total levels varied between 2 and 414 ng m^{-3} . The highest levels were observed at Melpitz
679 during week 1 and 2, followed by the Cabauw and Rotterdam sites during period 2, while the
680 lowest levels were observed for the last study week for all sites.

681 The levels of the organosulphates at each site varied considerably between sampling periods,
682 with a difference as high as 70 times observed at the Rotterdam site. These variations reflect

683 differences between sampling periods regarding emissions, air mass transport patterns and
684 atmospheric mixing.

685 When the data for OS and NOS are normalised to TC (SI Figure 1), the differences between
686 the sampling periods become smaller. For example at Rotterdam, the difference between the
687 highest and lowest relative concentration is only a factor of 13 (compared to 70 when
688 addressing the concentrations). The average ratio of OS and NOS to TC was 0.013 ± 0.010 ,
689 ranging from 0.002 to 0.038.

690 Organic bound sulphate in OS and NOS had a ratio of $1.5 \pm 1.0\%$ to inorganic sulphate,
691 determined by ion chromatography and obtained from the atmospheric monitoring database at
692 ebas.nilu.no for all sites except those in The Netherlands. The range was 0.1-3.4%, with a
693 tendency that the highest ratio of organosulphates to inorganic sulphate were observed in
694 continental, polluted air masses and the lowest ratio during periods with marine air masses
695 (with higher levels of sea-salt sulphate). As expected, a high correlation between sum of OS
696 and NOS with inorganic sulphate was observed ($R^2 = 0.84$, $n = 16$).

697 Organosulphates are formed in reactions between organic precursors, such as epoxides, and
698 sulphate aerosols, and the rate of formation can increase with acidity of the aerosol (Iinuma et
699 al., 2009; Surratt et al., 2010; Zhang et al., 2012b) and can be reduced by organic coating
700 (Riva et al., 2016a). This makes the formation of organosulphates especially sensitive to
701 aerosol acidity, sulphate and aging, which can contribute to explain the differences observed
702 between sites and samples in this study.

703

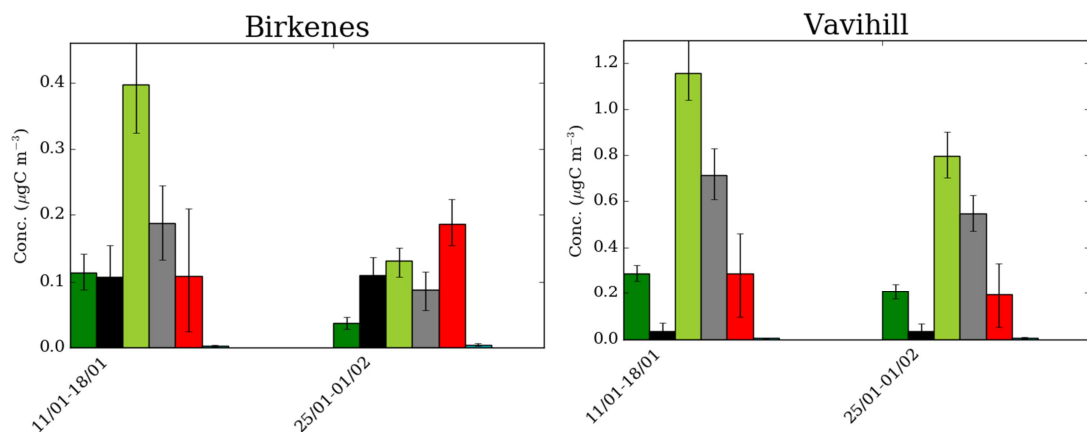
704 **3.5 Results from LHS analysis**

705 Latin hypercube sampling source apportionment (LHS SA) ascribes the carbonaceous aerosol
706 (here: TC, EC, and OC) into a number of predefined sources, as defined by a selection of
707 source-specific tracers analysed from aerosol filter samples (e.g., Gelencsér et al., 2007;
708 Genberg et al., 2011; Gilardoni et al., 2011; Yttri et al., 2011a; Yttri et al., 2011b). In the
709 present study, the tracers levoglucosan, mannitol, cellulose and ^{14}C of TC, separated the
710 carbonaceous aerosol into EC from biomass burning (EC_{bb}) (here: from residential heating)
711 and fossil fuel sources (EC_{ff}), whereas OC was attributed to biomass burning (OC_{bb}), fossil
712 fuel sources (OC_{ff}), primary biological aerosol particles (OC_{PBAP}) and OC_{mf} (remaining
713 non-fossil). The latter category has previously been considered a proxy for the biogenic
714 secondary organic aerosol (OC_{bsoa}). There are however anthropogenic sources of

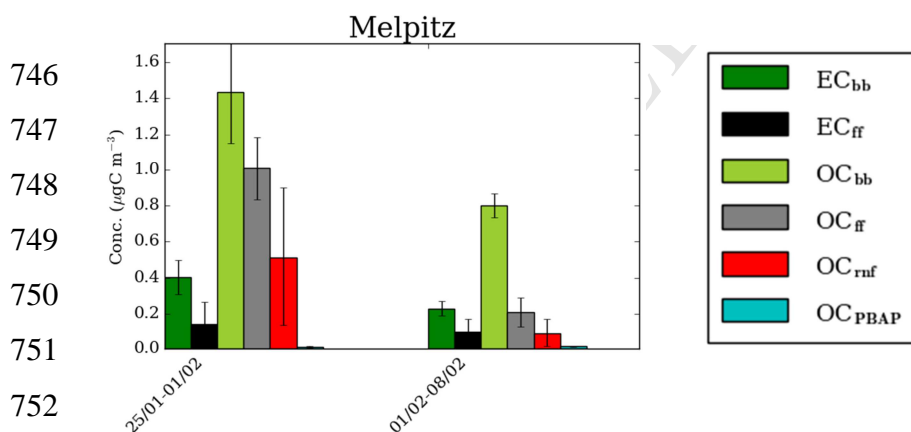
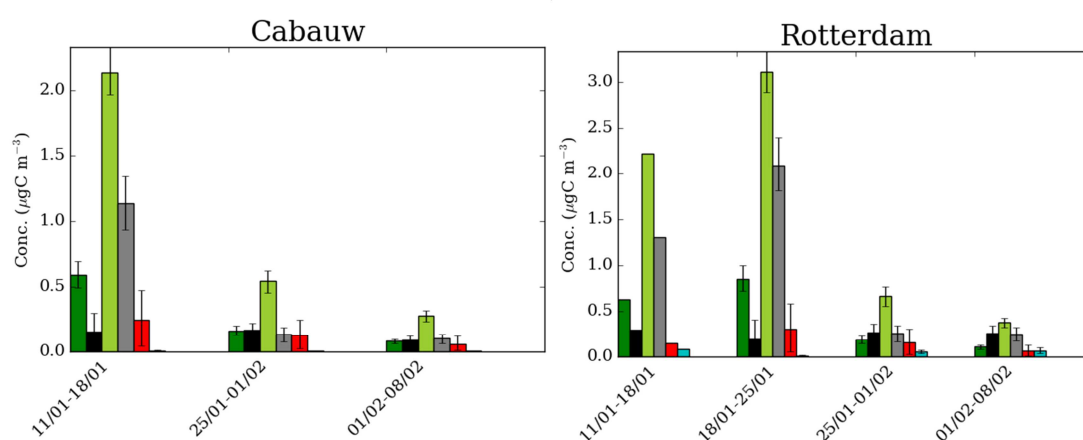
715 contemporary carbon, such as cooking and biofuel (bioethanol and biodiesel) that contribute to
716 OC_{rnf} , and there is an increasing recognition that those other sources may be included in this
717 category.

718 The exact setup of the LHS scheme used here has been described in detail in Yttri et al.
719 (2011b), and is not repeated here. The only change in parameters has been to update the values
720 for modern carbon, $F^{14}\text{C}$ to more recent years (extrapolating from Zotter et al., 2014), now
721 with the lowest values being 1.025 (e.g., for PBAP) and the wood-burning range being 1.05 -
722 1.2 (see Yttri et al. (2009) for comparison). In addition to the ^{14}C contamination mentioned
723 earlier, we also encountered problems with high levels of carbonaceous aerosols interfering
724 with the instrumental split between OC and EC for the samples of highest aerosol
725 concentrations, which limits the number of samples for which LHS source apportionment
726 could be performed. The results from the LHS SA are shown in Figure 7.

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754 Figure 7. Central estimate, i.e., 50 percentile, concentrations ($\mu\text{g C m}^{-3}$) of different
 755 carbonaceous particle fractions for sites and samples for which source apportionment was
 756 possible. Uncertainty bars represent 10 and 90 percentiles from LHS calculations (not given
 757 when the LHS solution rate $<5\%$).

758

759 Biomass burning is estimated to be the major source of OC for all analysed samples at all
 760 sites, accounting for more than 40% of TC for all but one sample at Birkenes (31%). Minor

761 variability in the relative contribution of OC_{bb} to TC was found within and between sites in
762 the other cases. Fossil fuel sources of OC are the second most important source of OC (in all
763 samples except one), accounting for typically 30% of TC. There was a general tendency (data
764 not shown) that OC from fossil fuel sources was attributed to secondary aerosol
765 (anthropogenic SOA) for samples with a high carbonaceous loading. Zotter et al. (2014)
766 reported a similar finding during winter-smog episodes in Switzerland. The OC_{mf} source
767 contributed ca. 5-12 % to TC for all samples. Exceptions were seen for the 2nd and low-
768 loading Birkenes samples, for which a noticeable 33% contribution of OC_{mf} to TC was
769 estimated. We speculate that the pronounced relative contribution is a result of low
770 anthropogenic impact for these samples, as the apportioned levels of OC_{mf} are not particularly
771 high. A dominating contribution of OC from BSOA (OC_{BSOA}) to OC_{mf} has been argued for
772 the Nordic countries (e.g., Yttri et al., 2011b), although this appears more likely in summer
773 than in winter. On the other hand, increased condensation due to lower temperatures can be an
774 important source of OC_{BSOA} in fall and winter, which could outweigh the effect of high
775 temperature and increased terpene emissions in summer (Andersson-Sköld and Simpson,
776 2001; Simpson et al., 2007). OC_{PBAP} contributed $< 5\%$ for all samples, and only Rotterdam
777 experienced a relative contribution $> 1\%$. Rotterdam was the only site for which levels of the
778 plant debris tracer (cellulose) was present above the detection limit. The part of OC_{PBAP}
779 attributed to fungal spores was less than 1% at all sites, Rotterdam included.
780 EC from biomass burning accounted for 7% to 16% of TC considering all samples, and as for
781 OC_{bb} , the variability was typically minor within and between sites. The relative contribution
782 of EC from fossil fuel sources (EC_{ff}) to TC varied more, ranging from $<2\%$ to 23%. There
783 was a tendency that the relative contribution of EC_{bb} was highest, and higher than for EC_{ff} ,
784 for high loading samples, whereas EC_{ff} dominated the low ones.

785

786 **4. General discussion**

787 The weekly concentration means at all six sites are influenced by local meteorological
788 conditions and emissions, but also by long-range transport. Backward trajectories show that
789 the source regions for long-range transport can vary over the investigated week but also for the

790 different stations, even though during this study the trajectories were relatively consistent
791 during the first two sampling periods and in contrast to the last weeks. Concentration
792 differences between the weeks and especially between the northern (more maritime) and the
793 southern (more continental) stations can be explained in this way.

794 The highest TC values in this study are observed at Melpitz (Figure 2), the easternmost of the
795 three southern sites, while the second and third highest values are obtained at the two other
796 southern sites, Rotterdam and Cabauw. For these sites, the same pattern is observed for TC,
797 with the highest values in the second week and lowest in the last week, while the three
798 northernmost stations (Birkenes, Vavihill and Risø) show a different pattern with highest TC
799 in the first week. The concentrations of the carboxylic acids, organosulphates and nitrooxy
800 organosulphates follow the pattern of TC at all six sites. A recent year-long study at Cabauw
801 observed a factor of three average increase in TC during periods of long-range transport of
802 continental air masses compared to regional pollution (Dusek et al., 2017).

803 Since local emissions near Melpitz are of minor relevance, except during strong inversions,
804 long-range transport of primary emitted species or SOA precursors is the main source of the
805 high carbonaceous aerosol levels. Daily PM₁₀ measurements during a decade show
806 considerable differences in concentrations of both organic and inorganic compounds for an
807 air-mass inflow from west versus east of Melpitz (Spindler et al., 2010; Spindler et al., 2013).
808 For example, the average concentrations of EC and sulphate in PM₁₀ during 2003-2013 are
809 about 1.1 µg EC m⁻³ and 2.2 µg SO₄²⁻ m⁻³ in winter periods with air mass inflow from west,
810 whereas there is an increase to 4.1 µg EC m⁻³ and 6.2 µg SO₄²⁻ m⁻³ during periods with air
811 masses from the east, influenced by anthropogenic combustion tracers from industry and
812 traffic, but especially from residential combustion of coal and biomass (Spindler et al., 2013).
813 The study of Ciarelli et al. (2017) also showed a major source region of POA situated east of
814 Melpitz.

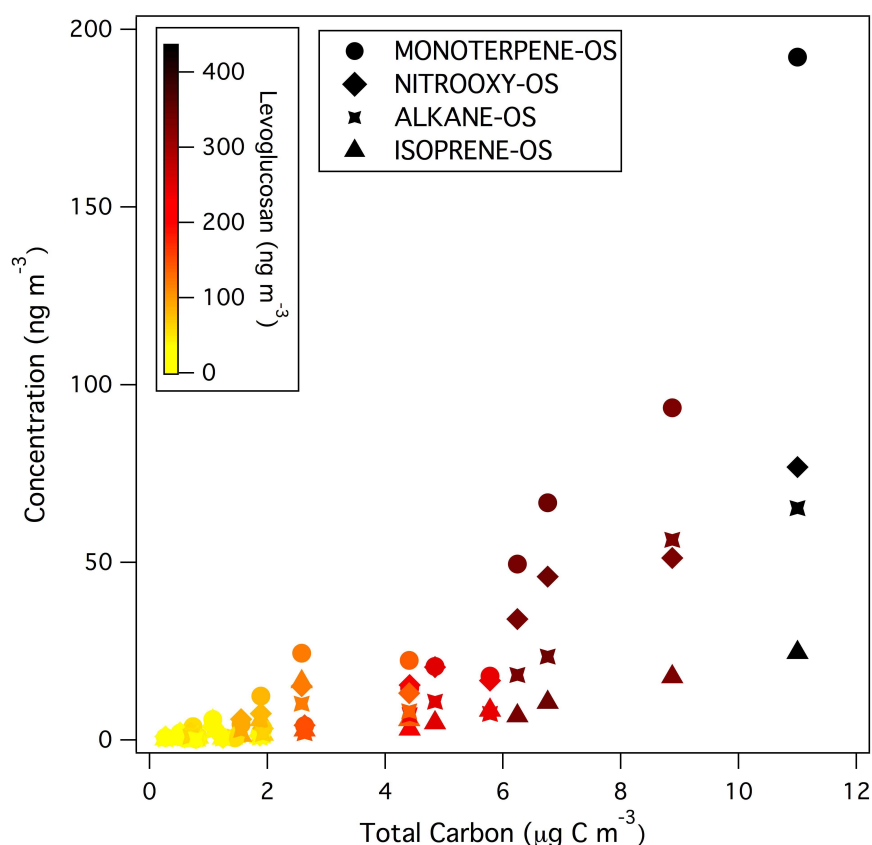
815 Solid fuels are used for heating of almost 50% of the households in Poland (situated less than
816 150 km east of Melpitz), in particular in rural areas, where anthracite coal and fuel wood are
817 combusted in single-house boilers or stoves (Central Statistical Office, 2014). Considering the
818 formation of organosulphates it is also relevant to note that Poland is the EU country with the
819 highest emission of SO₂ (840 Gg in 2013), twice the emission of the second highest emitting
820 country, Germany, and 223 Gg SO₂ of this is emitted from residential combustion sources in
821 Poland (EEA, 2015).

822 These emission patterns are reflected in our observations, as the highest concentrations of
823 levoglucosan are found in samples with intermediate or low F¹⁴C (see SI Figure 2), i.e., tracers

824 of both biomass and fossil combustion are highest in the same aerosol samples. This is also
 825 observed in the LHS SA analysis, where high contributions from fossil fuel combustion were
 826 found in samples with high concentrations of levoglucosan, supporting that combustion of
 827 coal and biomass is a significant source of carbonaceous aerosols.

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831 Figure 8. Concentrations of major groups of organosulphates as a function of TC and coloured
 832 according to levoglucosan concentration.

833

834 Emission data (mentioned above) and meteorology also contribute to explain the high
 835 concentrations of levoglucosan, TC and organosulphates observed in the particle filter samples
 836 during the first two weeks of our study period with easterly winds. Figure 8 shows that the
 837 highest levels of organosulphates, in particular the monoterpene-derived ones, are observed in
 838 samples with high concentration of the biomass-burning marker, levoglucosan (correlation
 839 coefficient $R^2 = 0.75$). Based on this, we hypothesise that combustion of coniferous wood and
 840 coal can lead to formation of organosulphates of monoterpenes from mixing of the smoke
 841 plumes. The presence of acidic sulphate aerosol surfaces can be decisive for formation of

842 organosulphates, as found e.g. in laboratory studies by Riva et al. (2016a), while coating
843 reduces the reactive uptake to form organosulphates.

844

845 **5. Conclusions**

846 In the present study, we have used a suite of molecular tracers combined with LHS source
847 apportionment to constrain the wintertime sources of carbonaceous aerosols in background
848 areas in Northern Europe.

849 The results clearly identified a strong gradient in levels of the carbonaceous aerosol (TC) and
850 molecular tracers such as levoglucosan, decreasing by as much as one order of magnitude
851 from the southernmost to northernmost site. LHS source apportionment showed that biomass
852 burning contributed more to EC than fossil fuel sources for 75% of the samples. EC
853 originating from combustion of fossil fuel was most abundant in samples with a low
854 carbonaceous aerosol loading.

855 Regarding OC, biomass burning was identified as the major source for all samples, typically
856 accounting for more than 40% of TC. Remaining sources included use and combustion of
857 fossil fuels (14-34% of TC) in addition to a low contribution (about 5-12% of TC) from
858 unresolved non-fossil sources, such as cooking and biogenic secondary organic aerosols. The
859 contribution of PBAP was negligible for all samples.

860 Overall, the results confirm that wood burning for residential heating is the major source of
861 OC and EC in Northern Europe in winter, which is in line with previous investigations.

862 In addition to the molecular tracers directly used for the LHS source apportionment, additional
863 molecular tracers including carboxylic acids, organosulphates and nitrooxy organosulphates
864 were measured to provide information on SOA sources. The organosulphates and nitrooxy
865 organosulphates showed a pronounced variation of two orders of magnitude between sites and
866 sampling periods, probably caused by differences in the levels of acidic sulphate aerosols
867 enhancing formation of organosulphates from both anthropogenic and biogenic precursors.

868 We experienced problems with the presence of so-called super modern carbon (i.e., the
869 fraction of ^{14}C is higher than the ^{14}C content in atmospheric CO_2) in some of the aerosol
870 samples. The source was identified as a nearby nuclear reactor undergoing decommissioning.

871 Other sources may include nuclear power plants and waste incinerators (processing waste
872 from laboratories and hospitals).

873 Overall, the study has provided new information to constrain the sources of OC and EC in the
874 northern part of Europe.

875

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1378 Part 1: Source apportionment and spatial variability. *Atmos. Chem. Phys.* 14, 13551-13570.

1379 Table 1. Overview of measured molecular tracers. $F^{14}C$ is fraction of modern carbon in total
 1380 carbon (TC), MW is molecular weight. SOA tracers are listed according to their origin, which
 1381 is either anthropogenic (A), fatty acid-derived carboxylic acids (FDA), first-generation
 1382 biogenic acids (1BA) or second-generation biogenic acids (2BA). Relevant references are
 1383 listed in the main text and in Table S1 regarding OS and NOS.
 1384

Source	Tracer
Biomass burning	Levoglucosan, mannosan, galactosan
Primary biological aerosol particles (PBAP)	Arabitol, mannitol, fructose, glucose, sucrose, trehalose, cellulose
Contemporary carbon	$F^{14}C$ (TC)
Secondary organic aerosol (SOA)	Adipic acid (A) ¹ , benzoic acid (A) ² , pimelic acid (A) ³ , azelaic acid (FDA) ⁴ , suberic acid (FDA) ⁴ , pinic acid (1BA) ⁵ , pinonic acid (1BA) ⁶ , terpenylic acid (1BA) ⁷ , diaterpenylic acid acetate (2BA) ⁸ , 3-methyl-1,2,3-butanetricarboxylic acid (2BA) ⁹ .
· Carboxylic acids	
· Organosulphates	Organosulphates (OS) (MW = 140, 154, 156, 168, 170, 182, 184, 200, 210, 212, 214, 216, 238, 248, 250, 252, 268, 280, 282, 296, 298)
· Nitrooxy organosulphates	Nitrooxy organosulphates (NOS) (MW = 295, 297, 311, 313, 327, 329)

1385 ¹Hatakeyama et al., 1985. ²Kawamura et al., 1985; Rogge et al., 1993. ³Grosjean et al., 1978.
 1386 ⁴Mochida et al., 2003, Rogge et al., 1991. ⁵Christoffersen et al., 1997, Hoffmann et al., 1998,
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 1388 2009. ⁸Inuma et al., 2008; Claeys et al., 2009. ⁹Szmigielski et al., 2007; Müller et al., 2012.

Highlights

- Sources of elemental carbon and organic carbon studied at six background sites
- Combination of molecular tracer analysis and latin-hypercube source apportionment
- A clear, increasing north to south gradient for most molecular tracers
- Wood combustion is a major source to OC and EC in Northern Europe during winter
- Organosulphates and nitrooxy organosulphates varied more than two orders of magnitude