

## Source apportionment of the summer time carbonaceous aerosol at Nordic rural background sites

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**Abstract.** In the present study, natural and anthropogenic sources of particulate organic carbon (OC<sub>p</sub>) and elemental carbon (EC) have been quantified based on weekly filter samples of PM<sub>10</sub> (particles with aerodynamic diameter <10 μm) collected at four Nordic rural background sites [Birkenes (Norway), Hyytiälä (Finland), Vavihill (Sweden), Lille Valby, (Denmark)] during late summer (5 August–2 September 2009). Levels of source specific tracers, i.e. cellulose, levoglucosan, mannitol and the <sup>14</sup>C/<sup>12</sup>C ratio of total carbon (TC), have been used as input for source apportionment of the carbonaceous aerosol, whereas Latin Hypercube Sampling (LHS) was used to statistically treat the multitude of possible combinations resulting from this approach.

The carbonaceous aerosol (here: TC<sub>p</sub>; i.e. particulate TC) was totally dominated by natural sources (69–86%), with biogenic secondary organic aerosol (BSOA) being the single most important source (48–57%). Interestingly, primary

biological aerosol particles (PBAP) were the second most important source (20–32%). The anthropogenic contribution was mainly attributed to fossil fuel sources (OC<sub>ff</sub> and EC<sub>ff</sub>) (10–24%), whereas no more than 3–7% was explained by combustion of biomass (OC<sub>bb</sub> and EC<sub>bb</sub>) in this late summer campaign i.e. emissions from residential wood burning and/or wild/agricultural fires. Fossil fuel sources totally dominated the ambient EC loading, which accounted for 4–12% of TC<sub>p</sub>, whereas <1.5% of EC was attributed to combustion of biomass. The carbonaceous aerosol source apportionment showed only minor variation between the four selected sites. However, Hyytiälä and Birkenes showed greater resemblance to each other, as did Lille Valby and Vavihill, the two latter being somewhat more influenced by anthropogenic sources.

Ambient levels of organosulphates and nitrooxy-organosulphates in the Nordic rural background environment are reported for the first time in the present study. The most abundant organosulphate compounds were an organosulphate of isoprene and nitrooxy-organosulphates of α- and β-pinene and limonene.



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## 1 Introduction

The ambient air carbonaceous aerosol (here: particulate carbonaceous matter (PCM) = organic matter (OM) + elemental carbon (EC)) is found to be abundant in the European rural background environment, accounting for 10–40% (mean 30%) of PM<sub>10</sub> (Yttri et al., 2007a; Putaud et al., 2004). The carbonaceous aerosol is believed to have an important impact on the global climate (e.g. Kanakidou et al., 2005), as well as causing adverse effects on human health (e.g. Metzger et al., 2004; Bell et al., 2009). Both anthropogenic (e.g. fossil fuel combustion) and biogenic sources (mainly biogenic secondary organic aerosol, BSOA, and primary biological aerosol particles, PBAP, such as degraded plant material and fungal spores) contribute to the carbonaceous aerosol loading, and its complexity in terms of composition, formation mechanisms and sources has been the topic of a number of recent studies (e.g. Donahue et al., 2005, 2009; Kanakidou et al., 2005; Hallquist et al., 2009). The carbonaceous aerosol can be either primary, i.e. from direct emissions, or secondary, i.e. low volatility products following from reactions between volatile organic compounds (VOC) or oxidants in the atmosphere. In particular, the reactions of unsaturated biogenic VOCs with ozone (O<sub>3</sub>), nitrate radicals (NO<sub>3</sub>) and hydroxyl radicals (OH) have been extensively studied to evaluate the chemical speciation and aerosol yield (Hallquist et al., 2009; Hoffmann et al., 1997; Kavouras and Stephanou, 2002). The products range from volatile to non-volatile species capable of forming new particles, and include a variety of oxygenated carbon compounds (Atkinson and Arey, 2003).

During the last few years a number of studies have become available which point towards natural sources as particularly important contributors to the carbonaceous aerosol loading in Europe, during summertime, including both the rural and the urban environment (e.g. Gelencsér et al., 2007; Szidat et al., 2006, 2009; Yttri et al., 2011). Common for these studies is that they have used <sup>14</sup>C analysis along with source specific organic tracers to distinguish between and quantify carbonaceous aerosol from anthropogenic and natural sources. Carbon from fossil fuel sources is devoid of <sup>14</sup>C due to radioactive decay, while carbon in most living materials has the same <sup>14</sup>C/<sup>12</sup>C ratios similar to that of atmospheric carbon dioxide. The organic tracers are used to further distinguish between the sources emitting contemporary carbon; e.g. the biomass burning tracer levoglucosan is used to apportion carbonaceous aerosol from biomass burning.

The carbonaceous aerosol observed in the Nordic countries (represented in the current study by Denmark, Finland, Norway and Sweden) are likely substantially influenced by natural sources, particularly in summer. The northern part of the study area in the present study is located within the Boreal region where large forested areas emit PBAP and biogenic VOCs forming secondary

organic aerosol (SOA) (Anderson-Sköld and Simpson, 2001; Tunved et al., 2006; Saarikoski et al., 2008; Yttri et al., 2007a, b, 2011). Particle-phase oxidation products of biogenic VOCs have been used as chemical markers to evaluate the contribution from SOA to the carbonaceous aerosol (Kourtchev et al., 2008a; Kleindienst et al., 2007). Such oxidation products have been identified in laboratory studies involving isoprene, monoterpenes and sesquiterpenes (Hallquist et al., 2009 and references therein). A widely used marker is *cis*-pinic acid, which is formed during oxidation of the abundant monoterpenes  $\alpha$ -pinene and  $\beta$ -pinene by O<sub>3</sub> and OH (Christoffersen et al., 1997; Larsen et al., 2001; Yu et al., 1999). *Cis*-pinic acid has been detected in a number of locations, and recently in Hyttälä, with concentrations ranging from 2–30 ng m<sup>-3</sup> (Kourtchev et al., 2008b). Organosulphates and nitrooxy organosulphates of isoprene and monoterpenes were recently identified as products of acid-catalyzed uptake of their VOC precursors in the aerosol phase (e.g. Surratt et al., 2007, 2010; Iinuma et al., 2007). Organosulphates and nitrooxy organosulfates are formed by processes involving both biogenic and anthropogenic emissions, and can thus be regarded as tracers of ageing of aerosols in mixed air masses.

Cellulose is used as a quantitative tracer of plant debris (Puxbaum and Tenze Kunit, 2003; Gelencsér et al., 2007; Sánchez-Ochoa et al., 2007), whereas mannitol and arabitol are tracers used to account for the contribution of Asco- and Basidio-mycetes fungal spores (Bauer et al., 2008). Plant debris and fungal spores are likely the major contributors to the atmospheric mass concentration of PBAP (Bauer et al., 2002, 2008; Puxbaum and Tenze-Kunit, 2003; Yttri et al., 2011) and its abundance in the Nordic rural background environment has been demonstrated by Yttri et al. (2011).

Residential wood burning is common in the Nordic countries, particularly during the cold season, and contributes to the carbonaceous aerosol loading both in the urban and the rural background environment (Yttri et al., 2005, 2009; Glasius et al., 2006, 2008; Krecl et al., 2007; Saarikoski et al., 2008). Levoglucosan is a thermal degradation product of cellulose emitted in high concentrations during combustion of biomass and which is widely used as a tracer for carbonaceous aerosol emissions, including emissions both from residential heating and wild/agricultural fires (Simoneit et al., 1999; Puxbaum et al., 2007). Recent studies have indicated that levoglucosan can be prone to degradation in the atmosphere and particularly by OH (Hoffmann et al., 2010; Hennigan et al., 2010). Thus, its stability during long-range transport and during summer in particular, can be questioned.

It is well documented that the Nordic countries are subject to long-range transport (LRT) of particulate matter air pollution, in particular from the more densely populated areas of continental Europe, but also as a result of distant wild and agricultural fires (Stohl et al., 2007; Yttri et al., 2007a; Saarikoski et al., 2008). During the EMEP (European

Monitoring and Evaluation Programme) EC/OC campaign (2002–2003), organic matter (OM) accounted for 36–38 % of PM<sub>10</sub> at Nordic rural background sites in summer, whereas the corresponding range for EC was 1.8–2.9 %. In contrast to continental European rural background sites, the Nordic ones experienced 30 % higher levels of organic carbon (OC) in summer compared to winter (Yttri et al., 2007a). This distinct pattern likely reflects a seasonal increase in (B)SOA and PBAP, as well as low influence of anthropogenic sources. This is in accordance with observations of high aerosol loadings over boreal forests, which can be explained by the relationship between monoterpene emissions and gas to particle conversion following atmospheric oxidation (Tunved et al., 2006). Saarikoski et al. (2008) nicely demonstrated that 17–29 % of OC in the Helsinki urban background environment was attributed to LRT, and that the relative contribution of LRT peaked in spring. The LRT OC was found to be a mixture of components originating from both primary and secondary sources.

The objective of the SONORA (Secondary Organic aerosol in the NOrdic RurAl Environment) study was to provide quantitative estimates of the most abundant sources contributing to the carbonaceous aerosol in the Nordic rural background environment in summer. The source apportionment of the carbonaceous aerosol was based on the content of selected source specific organic tracers, EC, OC, and the fraction of modern carbon (F<sup>14</sup>C) of TC in particle filter samples collected at four sites in four different countries. The dataset benefits from the use of centralized laboratories for the various species analyzed and that sampling artifacts have been accounted for. By using Latin Hypercube Sampling for statistical treatment (similar to Gelenscer et al., 2007; Yttri et al., 2011), seven subcategories/sources of the carbonaceous aerosol have been apportioned. In the current paper we present the main findings from the SONORA study.

## 2 Experimental

### 2.1 Site description and measurement period

Aerosol filter samples were collected at four Nordic rural background sites (Table 1, Fig. 1), all representative for various environmental types encountered in Northern Europe. The samples were collected during the period 5 August to 9 September 2009.

The Birkenes atmospheric research station (58°23' N, 8°15' E, 190 m a.s.l.) is a joint supersite for EMEP and GAW (Global Atmospheric Watch) and is situated approximately 20 km from the Skagerrak coast in southern Norway. The station is located in the boreal forest with mixed conifer and deciduous trees accounting for 65 % of the land use in the vicinity of the site; the remaining 35 % is attributed to meadow (10 %), low intensity agricultural areas (10 %), and

freshwater lakes (15 %). The nearest local emission source is the city of Kristiansand (65 000 inhabitants), located 25 km south/south-west of the station, which is known to have minor or even negligible influence on the air quality at the site.

The SMEAR-II (Station for Measuring Forest Ecosystem-Atmosphere Relations) station Hyytiälä (61°51' N, 24°17' E, 181 m a.s.l.) is located in a rather homogeneous Scots pine (*Pinus sylvestris*) stand on a flat terrain at Hyytiälä Forestry Field Station of the University of Helsinki, 220 km northwest from Helsinki. The site represents the rural background area of Southern Finland. Occasionally measurements can be affected by the station buildings (0.5 km away) and the city of Tampere (population of 200 000, 60 km away) both located west to south-west of the site.

Lille Valby (55°41' N, 12°07' E, 12 m a.s.l.) is a semi-rural monitoring station in the Sjælland region of Denmark, which is situated in the boreal zone. The surrounding area is characterized by agricultural land, small villages and the Roskilde Fjord (1 km west of the monitoring site). The station is located 30 km to the west of Copenhagen (1.2 million inhabitants), and 7 km North-East of central Roskilde (46 000 inhabitants). The nearest road (A6 with about 15 800 vehicles day<sup>-1</sup>) is located about 0.8 km west of the station.

Vavihill is a EUSAAR (European Supersites for Atmospheric Aerosol Research) and EMEP site situated in Southern Sweden (56°01' N, 13°09' E, 172 m a.s.l.). The surrounding area is dominated by grassland (49 %) deciduous trees (40 %) and farmland (10 %). The site is situated 25–45 km north-east to east of the densely populated areas of Greater Malmö (630 000 inhabitants), Copenhagen and Helsingborg (100 000 inhabitants) and continental air masses passing over these areas are typically more polluted than air masses originating from other directions.

### 2.2 Aerosol sampling

Ambient aerosol filter samples were obtained using the Klein-filtergerät low volume sampler equipped with a PM<sub>10</sub> inlet, collecting aerosols on prefired (850 °C; 3 h) quartz fibre filters (Whatman QMA; 47 mm in diameter, batch number 11415138). The filter samples were collected according to the Quartz fibre filter behind Quartz fibre filter (QBQ) approach to provide a quantitative estimate of the positive sampling artefact of organic carbon (OC). The instruments were operated at a flow rate of 38 l min<sup>-1</sup>, corresponding to a filter face velocity ranging between 50 and 54 cm s<sup>-1</sup> (see Table 1), depending on the actual exposed filter area. The sampling time was 1 week, and a total of 4 samples were collected at each site. The sampling inlets were installed approximately 4 m above ground level. Post exposure the filter samples were placed in petrislides, and stored in a freezer at -18 °C in order to prevent any form of degradation or evaporation of the analytes.

**Table 1.** Location of the four Nordic rural background sites participating in the SONORA sampling campaign and the duration of the sampling period. The inlet cut-off size, volumetric flow rate, and filter face velocity of the aerosol samplers applied is also provided.

Sampling site	Location	Height (m a.s.l.)	Sampling period	Cut-off size	Flow rate (l min <sup>-1</sup> )	Filter face velocity (cm s <sup>-1</sup> )
Birkenes (Norway)	58°23' N, 8°15' E	190	05.08.2009–02.09.2009	PM <sub>10</sub>	38	54
Hyytiälä (Finland)	61°51' N, 24°17' E	181	12.08.2009–09.09.2009	PM <sub>10</sub>	38	50
Lille Valby (Denmark)	55°41' N, 12°08' E	10	05.08.2009–02.09.2009	PM <sub>10</sub>	38	56
Vavihill (Sweden)	56°01' N, 13°09' E	172	05.08.2009–02.09.2009	PM <sub>10</sub>	38	53



**Fig. 1.** Map of Northern Europe including the location of the sampling sites Birkenes (Norway), Hyytiälä (Finland), Lille Valby (Denmark) and Vavihill (Sweden) in the Nordic countries.

### 2.3 Thermal-optical analysis

Three of the four partners used the thermal-optical instrument from Sunset laboratories Inc. to quantify the samples content of total carbon (TC), elemental carbon (EC), and organic carbon (OC), whereas the fourth partner used the OC/EC Thermal Optical Carbon Analyzer from DRI (Desert Research Institute). Both instrument types corrected for charring of OC during analysis using transmission and operated according to the EUSAAR 2 thermal program

(Cavalli et al., 2010). The analytical detection limit of the EC/OC analyses is  $0.2 \mu\text{g C cm}^{-2}$ .

### 2.4 <sup>14</sup>C-analysis

80–200  $\mu\text{g}$  of carbon was extracted from each filter prior to <sup>14</sup>C analysis, corresponding to a filter area of 1–4 cm<sup>2</sup> for front filters and 11 cm<sup>2</sup> for backup filters. In the first step of the analysis, the sample was combusted in the presence of pre-cleaned CuO needles (1 g; Merck pro analysis, 0.65 × 6 mm) in a vacuum system to yield CO<sub>2</sub> (Genberg et al., 2010). Solid graphite targets were then produced by reducing the formed CO<sub>2</sub> using H<sub>2</sub> and a heated (600 °C) metal catalyst (1 mg Fe, Merck, pro analysis, reduced, diameter 10  $\mu\text{m}$ ). Mg(ClO<sub>4</sub>)<sub>2</sub> (Merck, diameter 1–4 mm) was used as a drying agent. The time for complete reduction of each sample was less than 4 h. After complete graphitization, the carbon and iron catalyst were pressed into an aluminum sample holder. The sample holders containing the carbon from the aerosol samples were placed on a 40 position sample wheel together with graphitized standards (4 OxI as primary standard; 2 IAEA-C6 and 2 IAEA-C7 as secondary standards) and blanks (made from bottled, commercial fossil CO<sub>2</sub> which was combusted and graphitized as the rest of the samples and standards). The <sup>14</sup>C analysis was performed using the single stage accelerator mass spectrometry (SSAMS) facility at Lund University (Skog, 2007; Skog et al., 2010).

### 2.5 Measurement of levoglucosan, mannosan and galactosan

Quantification of the monosaccharide anhydrides (MA) levoglucosan, mannosan and galactosan was performed according to the method by Dye and Yttri (2005), and is only briefly described here. One punch (1.5 cm<sup>2</sup>) of the quartz fibre filter was soaked in tetrahydrofuran (2 ml) and subjected to ultrasonic agitation (30 min). The filter extract was filtered through a syringe filter (0.45  $\mu\text{m}$ ) to remove PM and filter parts. Each filter was extracted twice. The extracted volumes were pooled and evaporated to a total volume of 1 ml in an N<sub>2</sub> atmosphere. Before analysis the sample solvent elution strength was adapted to the mobile

phase by adding Milli-Q water (0.8 ml). The concentrations of MAs were determined using High Performance Liquid Chromatography (HPLC) (Agilent model 1100) in combination with HRMS-TOF (High Resolution Mass spectrometry Time-of-Flight) (Micromass model LCT) operated in the negative electrospray mode. The compound separation was performed with two series-connected reversed-phase C18 columns (Atlantis dC18, Waters). Levoglucosan, mannosan, and galactosan were identified on the basis of retention time and mass spectra of authentic standards. Quantification was performed using isotope labeled ( $^{13}\text{C}$ ) standards of levoglucosan and galactosan. The limit of quantification for the method at a signal to noise ratio of ten is approximately 30 ng injected of the individual MAs. The limit of detection for the method at a signal to noise ratio of three ranged from 1.2–3.0 ng  $\text{cm}^{-2}$  for the individual MAs.

## 2.6 Measurement of arabitol, mannitol and trehalose

The sugar-alcohols arabitol, mannitol and trehalose were quantified according to the method described by Yttri et al. (2007b), with a few modifications. Briefly, one punch (1.0  $\text{cm}^2$ ) from the quartz fibre filter was soaked in 50/50 acetonitrile/methanol (1.5 ml) and subjected to ultrasonic agitation (30 min). Each filter was extracted twice. The extracted volumes were pooled, filtered through a syringe filter (0.45  $\mu\text{m}$ ) to remove particulates and filter debris, and evaporated to dryness under an  $\text{N}_2$  atmosphere. The dry extract was redissolved in Milli-Q water (100  $\mu\text{l}$ ) and isopropanol (300  $\mu\text{l}$ ) prior to analysis. The analysis was performed by HPLC/HRMS-TOF analysis operated in the negative electrospray mode. The compounds were identified by comparison of retention time obtained by separation on a carbohydrate column (Prevail Carb ES Column-W, 250 mm  $\times$  4.6 mm, 5  $\mu\text{m}$ ). The limit of quantification of the method at a signal to noise ratio of ten is approximately 30 ng injected of the individual sugar-alcohols. Isotope labeled standard of glucose, purchased from Cambridge Isotope Laboratories, was used as internal standard for quantification of the sugar-alcohols. The limit of detection of the method at a signal to noise ratio of three ranged from 15–29 ng  $\text{cm}^{-2}$  for the individual sugar-alcohols.

## 2.7 Measurement of pinic acid, organosulphates and nitrooxy-organosulphates

The analysis generally followed the procedure described by Kristensen and Glasius (2011). Filter punches (1  $\text{cm}^2$ ) were extracted in acetonitrile by ultra sonication for 20 minutes. Extracts were filtered through a Teflon filter (0.45  $\mu\text{m}$ ) and evaporated to dryness in a flow of  $\text{N}_2$ . The residue was re-dissolved in 200  $\mu\text{l}$  0.1 % acetic acid containing 3 % acetonitrile. Sample extracts were analyzed by HPLC coupled through an electrospray ionization inlet (operated in negative mode) to a quadrupole time-of-flight

mass spectrometer (microTOFq, Bruker Daltonics). The HPLC stationary phase was a Waters Atlantis T3 C18 column (2.1  $\times$  150 mm; 3  $\mu\text{m}$  particle size). The mobile phase consisted of acetic acid (0.1 % v/v) and acetonitrile with an overall gradient from 3 % to 95 % acetonitrile in 50 min. The injection volume was 40  $\mu\text{l}$  and the flow rate was 0.2  $\text{ml min}^{-1}$ . Camphor sulphonic acid was used as recovery standard and deuterated adipic acid as injection standard. *cis*-Pinic acid was quantified using a commercial standard, while camphor sulphonic acid was used as a surrogate standard for organosulphate and nitrooxy organosulphate compounds. The limit of detection of the method was 2 ng  $\text{cm}^{-2}$  for pinic acid, organosulphates and nitrooxy-organosulphates.

## 2.8 Measurement of cellulose

Free cellulose was determined based on the enzymatic method described by Kunit and Puxbaum (1996). Free cellulose was assumed to be 72 % of total cellulose. Filter aliquots of 2  $\text{cm}^2$  were subjected to ultrasonic agitation (45 min) in a citric acid solution (2.2 ml, 0.05 M, pH = 4.8) containing Thymol (0.05 %) to prevent bacterial growth. The cellulose was saccharified by two enzymes, *Trichoderma reesei* cellulase (80  $\mu\text{l}$ , 10 %) and *Aspergillus Niger* cellobiase (80  $\mu\text{l}$ , 1 %) for 24 h at 45  $^\circ\text{C}$ . The saccharification was stopped by denaturing the enzymes at 80  $^\circ\text{C}$ . After centrifuging (4000 rpm, 20 min) the supernatant was collected for determination of D-glucose using a modified test-combination (D-Glucose-HK, Megazyme, Ireland). Glucose was phosphorylated to glucose-6-phosphate, and subsequently oxidized by NADP to gluconate-6-phosphate (G-6-P), with the formation of NADPH, which is stoichiometrically proportional to the initial amount of D-glucose in the sample. NADPH was quantified by UV photometry at 340 nm, read against distilled water. The samples content of free glucose was subtracted from the result. The limit of detection is 160 ng  $\text{cm}^{-2}$ .

## 2.9 Precursor specific SOA tracers

A composited sample from the Birkenes site, including all four weeks of sampling, was analyzed for selected SOA tracers using the technique of Kleindienst et al., (2007). Samples were Soxhlet-extracted using dichloromethane/methanol (1:1). Prior to the extraction, 20  $\mu\text{g}$  each of *cis*-ketopininc acid and  $\text{d}_{50}$ -tetracosane were added. Extracts were evaporated to dryness then derivatized with *bis*-(trimethylsilyl)-trifluoroacetimidate (250  $\mu\text{l}$ , with 1 % TMCS) and pyridine (100  $\mu\text{l}$ ). Samples were injected onto the ThermoQuest GC (Austin, TX) without reduction in volume. Separation was performed on a 60 m, 0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness  $\text{RT}_x$ -5MS column (Restek, Inc., Bellefonte, PA), using conditions described in detail by Jaoui et al. (2006).

Mass spectral analysis of the actual tracer compounds has been described by Jaoui et al. (2005) and Kleindienst et al. (2007). Compounds used as tracers are the following:

1. Isoprene tracers: 2,3-dihydroxymethacrylic acid, 2-methylthreitol, 2-methylerythritol,
2.  $\alpha$ -pinene tracers: 3-acetyl pentanedioic acid, 3-acetyl hexanedioic acid, 3-carboxy heptanedioic acid, 3-hydroxy glutaric acid, 4-isopropyl-1-,2-dihydroxy hexanol, 3-(2-hydroxy-ethyl)-2,2-dimethylcyclobutane-carboxylic acid, pinic acid, pinonic acid,
3. toluene tracer: 2,3-dihydroxy-4-oxopentanoic acid.

Since no standards exist for many of these compounds, the concentrations of all tracers were estimated assuming unity response relative to ketopinic acid (Jaoui et al., 2004). Analysis for the tracer compounds was conducted using a selected ion technique described earlier by Kleindienst et al. (2007). The limits of detection range from 6 to 30 ng cm<sup>-2</sup> for the precursor specific SOA tracers.

## 2.10 Quality assurance

The filter samples were collected according to the QBQ (Quartz fibre filter Behind Quartz fibre filter) approach, which provides a quantitative estimate of the positive sampling artefact of OC (McDow and Huntzicker, 1990; Turpin et al., 1994). The rather high filter face velocity (50–54 cm s<sup>-1</sup>), and the fact that negative artifacts are not accounted for by this approach suggests that the corrected levels of OC (OC<sub>p</sub>) should be considered conservative. In the present study, the mean positive sampling artifact of OC ranged from 11 ± 2 % at the Finnish site Hyytiälä to 18 ± 4 % at the Birkenes site in Norway, which is in accordance with what has been reported previously (see Yttri et al., 2007 and references therein). The identical filter face velocity of the four samplers further increases the comparability, in particular with respect to OC and TC.

All analyses were performed within 6 months after the samples had been collected.

Thermal-optical analysis of EC and OC were performed according to the EUSAAR 2 thermal program, which is designed to reduce the inherited uncertainties associated with splitting of EC and OC, e.g. by preventing premature burn-off of EC (Cavalli et al., 2010). While all other chemical analysis was performed at centralized laboratories, the EC/OC analysis was performed at four different laboratories. To ensure comparability, an inter comparison was conducted, distributing four aliquots cut from the same filter amongst the four laboratories. The samples' contents of TC were reproduced within an accuracy of 5 % amongst the four laboratories. For OC (9 %), and in particular for EC (23 %), the deviation was larger. It is found that this

deviation was attributed solely to the DRI (Desert Research Institute) instrument at one of the participating laboratories, which gave lower EC than the SUNSET lab instruments used elsewhere. For the three other laboratories, the consistency in determining EC was within <4 %. The EC level of the samples analyzed at the actual laboratory has been adjusted according to the finding of the inter comparison; i.e. to be comparable to the results obtained by the three SUNSET lab instruments.

The extended uncertainty associated with measurements of monosaccharide anhydrides and sugar-alcohols is found to range within 10–15 %, while for measurements of pinic acid the uncertainty is <25 %.

Quantification of organosulphates and nitrooxy organosulphates was done using a surrogate standard. This adds uncertainty to the absolute concentrations of the various organosulphates and nitrooxy organosulphates, but it will not affect the relative concentrations. An inter comparison of organosulphates and nitrooxy organosulphates involving Aarhus University and CalTech (USA) (J. Surratt, personal communication, 2011) showed good agreement with respect to identification and linearity, but a 5–10 times underestimation of absolute concentrations at Aarhus University due to the use of a surrogate standard instead of authentic standards (Kristensen and Glasius, 2011). Authentic standards are not commercially available for organosulphates and nitrooxy organosulphates. The detection limit for the surrogate standard camphor sulfonic acid was 0.51 ng injected (Kristensen and Glasius, 2011), which corresponds to about 0.015 ng m<sup>-3</sup> for organosulphates and nitrooxy organosulphates in the present study.

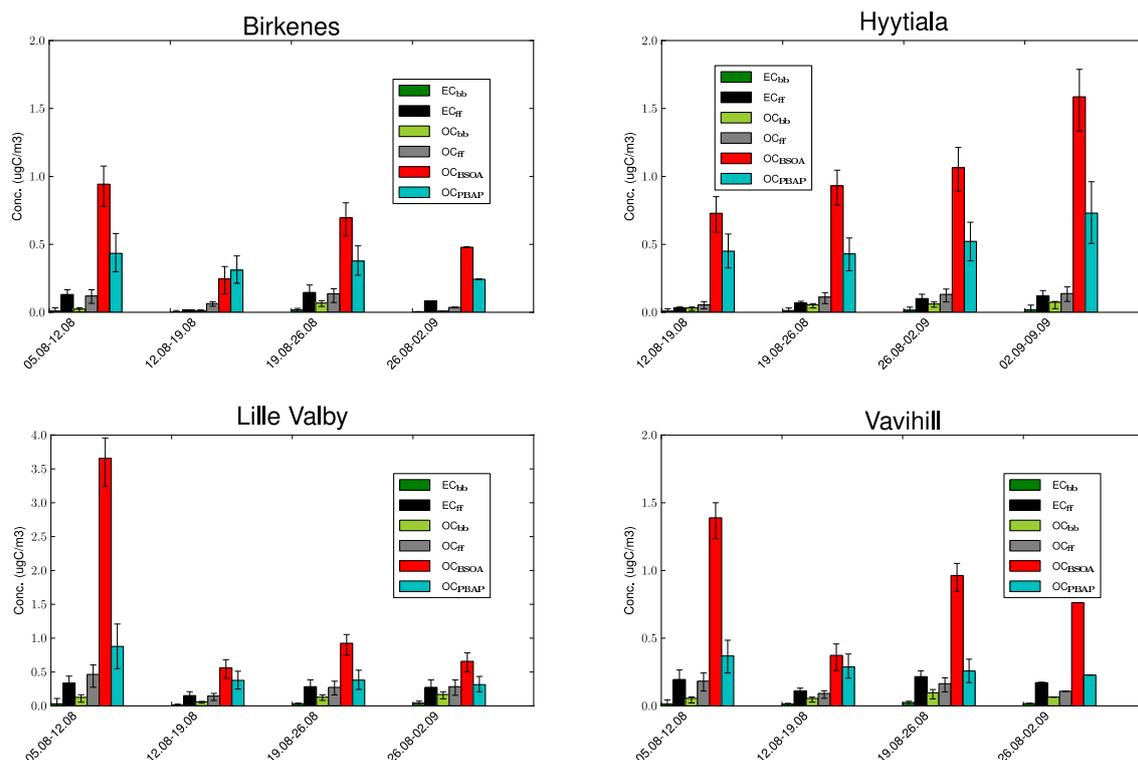
The secondary standards (2 IAEA-C6 and 2 IAEA-C7) analyzed along with the ambient samples during <sup>14</sup>C analyses were all within 1 standard deviation of the consensus values.

## 3 Meteorology and surface types

### 3.1 Meteorological conditions

The month of August was chosen due to our focus on the natural sources of the carbonaceous aerosol. As illustrated by Andersson-Sköld and Simpson (2001), this is the month likely to produce the highest emissions of biogenic volatile organic compounds which subsequently provide the highest levels of biogenic secondary organic aerosols (BSOA) for Nordic areas. Certain sources of primary biological aerosol particles, e.g. release of fungal spores, are also likely to be particularly active in late summer/early fall (Yttri et al., 2007b).

The weather pattern at the start of the campaign was characterized by an anticyclone located over Scandinavia. Largely stagnant conditions and slight advection from the east or south-east led to accumulation of aerosols for the



**Fig. 2.** Best estimate, i.e. 50 percentile, concentrations ( $\mu\text{g m}^{-3}$ ) of different carbonaceous particle fractions for the Birkenes, Hyttiälä, Lille Valby, and Vavihill filter samples,  $\text{PM}_{10}$ . Uncertainty bars represent 10 and 90 percentiles from LHS calculations (not given when LHS solution rate  $< 10\%$ ). Note the different scale on the y-axis for the Lille Valby site; and that sampling started one week later at the Hyttiälä site.

stations Birkenes, Lille Valby and Vavihill. Sampling at Hyttiälä started a week later and so did not include this period. On 10 August, the anticyclone weakened and retreated to the south, and from 11 August, the air sampled at the three western stations arrived from the west, with cyclones passing mainly north of the stations. This circulation pattern prevailed throughout the time period of the second sample (12–19 August), explaining the drop in concentrations between the first and second sampling period (see Fig. 2). At Hyttiälä, the westerly flow started a day later, on 12 August, when also the first sampling period began. During the third week of sampling (19–26 August), the anticyclone over Central Europe started extending towards the north again and carbonaceous aerosol concentrations increased at all four sites. The advection, however, was still mainly from the west, thus, concentrations did not reach the high levels of the first sampling week. Passing cyclones and westerly winds also influenced the stations from 26 August to 2 September when low concentrations were observed again at the three western stations. Hyttiälä still received air from the south (Eastern Europe) from the beginning of the sampling until 28 August, which seems to explain the higher measured concentrations at this station. During the final week of sampling at Hyttiälä, cyclonic influence was still predominant. However, air flow was on two occasions from

the south ahead of passing cyclones, advecting air masses from Eastern Europe to the site.

Meteorological data from the four measurement sites showed that the ambient temperature, the relative humidity and precipitation amount during the sampling period was comparable to preceding years, hence the sampling period is likely to be representative for this time of the year.

### 3.2 Surface type

The surface type and land use is likely to play a crucial role for the ambient aerosol concentration, its chemical composition and physical properties. With output from the FLEXPART model (Stohl et al., 2005) we are able to define footprint sensitivities to various surface types and land use categories. For this analysis we have developed a new set of FLEXPART output products that utilize The Community Noah Land-Surface Model (Noah LSM; Mitchell, 2005). The Noah LSM provides land surface classifications gridded at 0.5 deg. resolution. The thirteen land surface types are based on the Vegetation Types (“SiB-1”) after Dorman and Sellers (1989). Of the thirteen types, we have only included the seven largest contributors, whereas the rest are included as Other.

To generate surface-type specific information, the FLEX-PART global footprint emission sensitivity product is folded with the globally gridded surface types, i.e. emission sensitivities are considered only for the specific surface type considered and set to zero for all other surface types. In Fig. 3 we show the surface type sensitivity time series. This figure shows the relative air mass exposure to each of the surface types for the period of measurement observation. It should be noted that the NOAA LSM land use categories, used to define the surface types, are static and thus do not include seasonality nor changes over time.

The marine footprint totally dominated at all four sites but was more pronounced for the Birkenes, Lille Valby and Vavihill sites ( $92 \pm 1.7\%$ ), which are all situated less than 25 km from the coast, than for the more continental site Hyytiälä ( $89\%$ ), 65 km from the coast (Fig. 3). The major terrestrial surface types were Needleleaf evergreen (e.g. pine and spruce), Agricultural and Tundra. For the three sites situated less than 25 km from the coast there were only minor differences in the relative contribution of the three major terrestrial categories; i.e. Agricultural ( $33 \pm 3.5\%$ ; Mean  $\pm$  SD), Needleleaf evergreen ( $29 \pm 1.5\%$ ), and Tundra ( $24 \pm 2.6\%$ ). The Needleleaf evergreen category ( $58\%$ ) totally dominated at the more continental site Hyytiälä, followed by Tundra ( $16\%$ ) and Agricultural ( $12\%$ ). The Mixed forest and Needleleaf evergreen categories were found to be increased at the three sites located less than 25 km from the coast during the first week of sampling. This was particularly pronounced for the mixed forest category accounting for  $14 \pm 2.4\%$  during week 1 compared to  $3.2 \pm 1.7\%$  for the rest of the period. The corresponding percentages for the Needleleaf evergreen category was  $43 \pm 6.1\%$  (week 1) and  $25 \pm 5.8\%$  (week 2–4).

#### 4 Source apportionment using Latin Hypercube Sampling (LHS)

A tracer methodology is used to provide source apportionment of the total carbon into different source categories. This methodology, originally developed for the CARBOSOL project (Gelencsér et al., 2007), has been refined for new measurements and Nordic conditions, and previously applied by Szidat et al. (2009) for Gothenburg, Sweden, and Yttri et al. (2011) for two sites in Norway. Indeed, the methodology used here is identical to that used by Yttri et al. (2011), and so only a brief description is given here.

In summary, measurements of levoglucosan are used as a tracer of wood-burning emissions ( $TC_{bb} = OC_{bb} + EC_{bb}$ ;  $OC_{bb}$  includes primary and secondary OC), mannitol and cellulose are used as tracers of primary biological aerosol particles ( $OC_{PBAP}$ ) derived from fungal spores ( $OC_{pbs}$ ) and plant debris ( $OC_{pbc}$ ), respectively. The  $^{14}C$  isotopic ratios ( $F^{14}C$ ) are used along with the measured OC and EC and assumed emission ratios (e.g.  $TC_{bb}/levoglucosan$

and  $OC_{bb}/TC_{bb}$  from wood combustion, or OC/EC ratios from fossil-fuel combustion), to assign the remaining carbon between fossil-fuel sources and secondary organic aerosol sources. Total carbon is in this way split into  $TC_{bb}$ ,  $OC_{PBAP}$ ,  $TC_{ff}$  ( $= OC_{ff} + EC_{ff}$ , from fossil-fuel sources;  $OC_{ff}$  includes primary and secondary OC), and finally any remaining modern-carbon is assumed to be  $OC_{BSOA}$  (biogenic secondary organic aerosol).

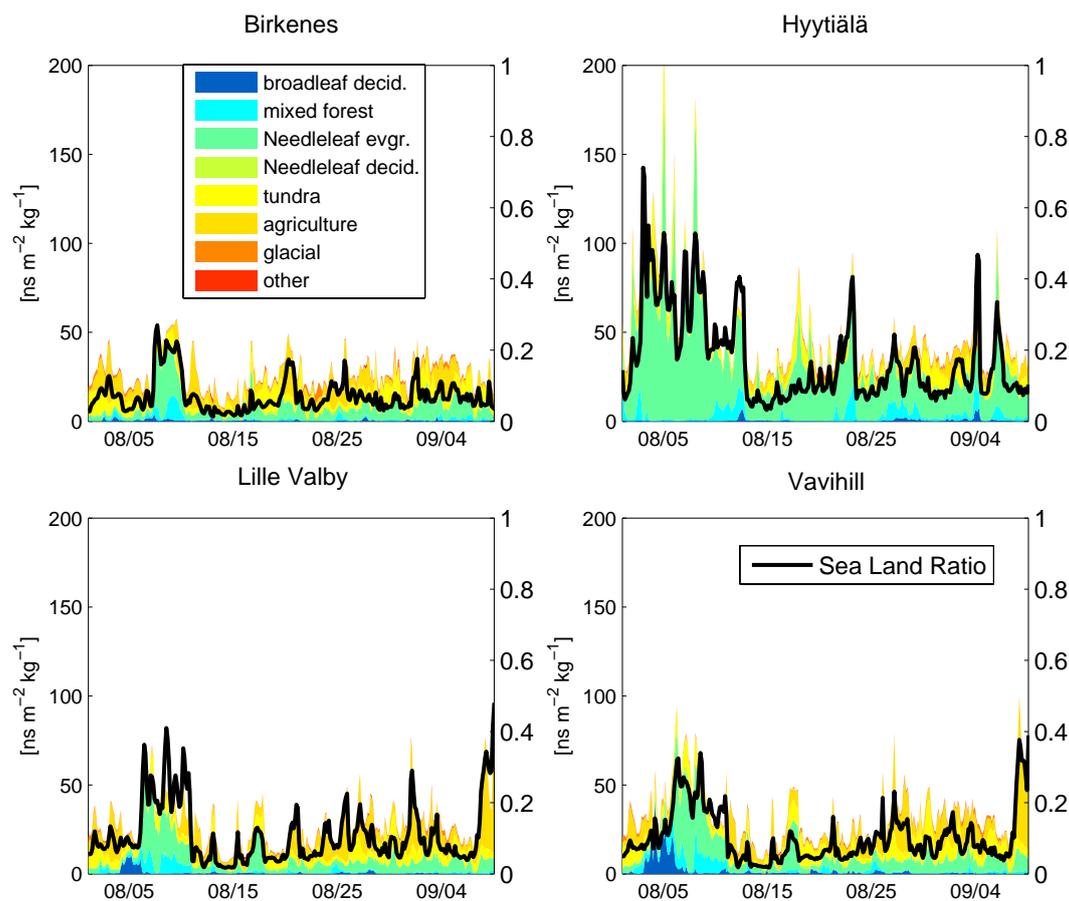
The relationship between any tracer and its derived TC component is very uncertain, and so we have assigned an uncertainty distribution of allowed parameter values for all important emission ratios or measurement inputs. In order to solve the system of equations, allowing for the multitude of possible combinations of parameters, an effective statistical approach known as Latin-hypercube sampling (LHS) is used, which is comparable to Monte Carlo calculations. Details of this procedure were first given by Gelencsér et al. (2007), and the procedure as used here is described in detail in Yttri et al. (2011). In brief, central values with low and high limits are associated to all uncertain input parameters. These factors are combined using a simplified approach of LHS in order to generate thousands of solutions for the source-apportionment. All valid combinations of parameters (i.e. excluding those producing negative solutions) are condensed in frequency distributions of possible solutions. Extensive discussion of the choices behind the factors used, and their uncertainties, can be found in earlier related studies: Szidat et al. (2009), Gelencsér et al. (2007) and, for wood-burning emissions, Simpson et al. (2007).

The result of this analysis consist of so-called best-estimates of the TC components (i.e. the 50th percentile), as well as the range of possibilities allowed by the LHS calculation, usually expressed as the 5th and 95th percentiles of the solutions.

## 5 Results

### 5.1 Ambient concentrations of EC and $OC_p$

Mean concentrations of elemental carbon (EC), positive-artifact-corrected particulate organic carbon ( $OC_p$ ), organic carbon on backup filters ( $OC_B$ ), particulate total carbon ( $TC_p$ ), and EC/ $TC_p$  ratios for  $PM_{10}$  are presented in Table 2. The levels appear to be in the lower range of that previously reported for the Nordic rural background environment during summer (Yttri et al., 2007a), however different sampling-times and techniques are likely to contribute at least partly to the observed differences. Within Europe, the Nordic countries typically experience the lowest carbonaceous aerosol loading (Yttri et al., 2007a). The rather low mean EC/ $TC_p$  ratio ( $14 \pm 8.2\%$ ; for all four sites) is consistent with a modest anthropogenic influence. The EC/ $TC_p$  ratio was particularly low at the Finnish site



**Fig. 3.** Time series plots showing the footprint emissions sensitivity to the Noah LSM vegetation types for the sites Birkenes (Norway), Hyytiälä (Finland), Lille Valby (Denmark) and Vavihill (Sweden) for the period 5 August–9 September 2009. Note that of the thirteen land surface types we only plot the seven largest contributors and include the rest as Other. The black line is the ratio of land to ocean contribution, showing that the bulk of the measured air mass at these sites is of Marine origin.

Hyytiälä ( $5.6 \pm 1.5\%$ ) compared to the ratio observed at Vavihill ( $23 \pm 6.0\%$ ) and Lille Valby ( $17 \pm 6.6\%$ ).

## 5.2 Ambient concentrations of organic tracers

Ambient mean concentrations of levoglucosan, mannosan, galactosan, mannitol, arabitol, trehalose, cellulose, pinic acid and selected organo-sulphates in  $PM_{10}$  are reported in Table 2. The mean concentration of levoglucosan was low,  $<10 \text{ ng m}^{-3}$  at all sites, suggesting that emissions from wood burning was a minor contributor to the carbonaceous aerosol loading during the study period. Levoglucosan was the major monosaccharide anhydride (MA), accounting for  $83 \pm 4\%$  of the sum of the three MA quantified (i.e. levoglucosan, mannosan and galactosan). Levels of the fungal spore tracers mannitol, arabitol, and trehalose were within the range reported previously for the Scandinavian (Yttri et al., 2007b; Carvalho et al., 2003) and the continental European (Ion et al., 2005) rural background environment, however only a very few studies have reported such measurements. A

high correlation ( $r^2 > 0.93$ ) between the three sugar alcohols emphasises their common origin and thus their suitability as fungal spore tracers. Pinic acid concentrations were all less than  $10 \text{ ng m}^{-3}$ , which are similar to concentrations reported by Zhang et al. (2010, and references therein) for measurements conducted in Europe.

The content of cellulose in the ambient aerosol has only been reported in a very few studies (Kunit and Puxbaum, 1996; Puxbaum and Tenze-Kunit, 2003; Sanchez-Ochoa et al., 2007). The mean cellulose concentrations observed in the present study, ranging from  $89\text{--}342 \text{ ng mm}^{-3}$ , are comparable to those observed for the European rural background environment by Sanchez-Ochoa et al. (2007).

A number of the selected SOA tracers sought for as described in Sect. 2.9 (see Table 3) were identified in a composited sample from the Birkenes site, confirming their presence also in the Nordic rural background environment. The sum of the three isoprene tracers was found at a concentration of  $1.5 \text{ ng m}^{-3}$ , whereas the toluene tracer and the  $\beta$ -caryophyllene tracer were not observed above limits

**Table 2.** Mean ( $\pm$ SD) concentrations of carbonaceous sub-fractions and selected organic compounds in PM<sub>10</sub>. The EC-to-TC<sub>p</sub> ratio and the fraction modern carbon (F<sup>14</sup>C) of TC, based on <sup>14</sup>C/<sup>12</sup>C – analysis, are also listed. b.d. means below detection limit.

	Birkenes (Norway)	Hyytiälä (Finland)	Lille Valby (Denmark)	Vavihill (Sweden)
Unit: ( $\mu\text{g C m}^{-3}$ )				
TC <sub>p</sub>	0.96 $\pm$ 0.38	1.7 $\pm$ 0.54	2.4 $\pm$ 1.9	1.4 $\pm$ 0.48
OC <sub>p</sub>	0.84 $\pm$ 0.32	1.6 $\pm$ 0.49	2.1 $\pm$ 1.8	1.1 $\pm$ 0.45
OC <sub>B</sub>	0.19 $\pm$ 0.10	0.20 $\pm$ 0.05	0.24 $\pm$ 0.05	0.17 $\pm$ 0.05
EC	0.12 $\pm$ 0.07	0.10 $\pm$ 0.05	0.32 $\pm$ 0.09	0.30 $\pm$ 0.08
Unit: (%)				
EC/TC <sub>p</sub>	12 $\pm$ 6.9	5.6 $\pm$ 1.5	17 $\pm$ 6.6	23 $\pm$ 6.0
F <sup>14</sup> C TC	0.93 $\pm$ 0.03	0.99 $\pm$ 0.03	0.83 $\pm$ 0.08	0.8 $\pm$ 0.02
Unit: ( $\text{ng m}^{-3}$ )				
Levogluconan	2.1 $\pm$ 2.1	4.6 $\pm$ 1.5	9.8 $\pm$ 3.7	5.6 $\pm$ 1.7
Mannosan	0.39 $\pm$ 0.42	0.81 $\pm$ 0.17	1.3 $\pm$ 1.1	0.71 $\pm$ 0.29
Galactosan	0.06 $\pm$ 0.09	0.18 $\pm$ 0.06	0.35 $\pm$ 0.13	0.24 $\pm$ 0.22
Arabitol	16 $\pm$ 3.2	24 $\pm$ 5.8	12 $\pm$ 0.82	10 $\pm$ 3.3
Mannitol	16 $\pm$ 4.7	30 $\pm$ 8.2	17 $\pm$ 7.3	13 $\pm$ 3.5
Trehalose	5.8 $\pm$ 2.6	13 $\pm$ 4.1	4.8 $\pm$ 2.7	6.4 $\pm$ 3.6
Cellulose	89 $\pm$ 20	133 $\pm$ 43	172 $\pm$ 113	86 $\pm$ 16
Pinic Acid	3.2 $\pm$ 1.5	6.2 $\pm$ 2.7	2.4 $\pm$ 0.61	2.8 $\pm$ 1.3
Organo-sulphate (MW = 216)	0.80 $\pm$ 1.2	1.2 $\pm$ 1.6	0.27 $\pm$ 0.14	0.24 $\pm$ 0.14
Organo-sulphate (MW = 250)	0.05 $\pm$ 0.09	0.08 $\pm$ 0.15	b.d.	b.d.
Organo-sulphate (MW = 264)	b.d.	0.05 $\pm$ 0.03	0.05 $\pm$ 0.06	b.d.
Organo-sulphate (MW = 280)	b.d.	0.10 $\pm$ 0.13	b.d.	b.d.
Nitrooxy-organo-sulphate (MW = 295)	0.38 $\pm$ 0.42	0.75 $\pm$ 0.35	0.85 $\pm$ 0.74	0.74 $\pm$ 0.58
Nitrooxy-organo-sulphate (MW = 297)	0.52 $\pm$ 0.59	1.2 $\pm$ 0.68	1.5 $\pm$ 2.4	1.2 $\pm$ 1.6

of detection of approximately 0.1  $\text{ng m}^{-3}$ . The sum of eight  $\alpha$ -pinene tracers was 14  $\text{ng m}^{-3}$ , which is significantly lower than the levels previously reported by this technique in the US and in Hong Kong (Offenberg et al., 2011; Kleindienst et al., 2007; Lewandowski et al., 2008; Hu et al., 2008), as well as in France (El Haddad et al., 2011).

### 5.3 Ambient concentrations of organosulphates and nitrooxy organosulphates

Only three studies have reported ambient aerosol concentrations of speciated organosulphates and nitrooxy-organosulphates in Europe (Gómez-Gonzalez et al., 2008; Iinuma et al., 2007; Kristensen and Glasius, 2011), of which two reported concentrations for the rural background environment, i.e. at K-Puszta (Hungary) and in Waldstein (Fichtelgebirge, Germany). Thus, the present study substantially expands the knowledge of speciated organosulphates and nitrooxy organosulphates in Europe, reporting results from four sites which represent various subcategories of the Nordic rural background environment. In addition, the

current study covers one of the longest measurement periods reported so far.

Only four organosulphates and two nitrooxy organosulphates were identified in the samples, which probably reflects the rather small filter punch available for each type of analysis. The organosulphate resulting from oxidation of isoprene (MW = 216) was found at higher concentrations (0.24–1.2  $\text{ng m}^{-3}$ ) than previously reported for a study conducted in Denmark during spring ( $\sim$ 0.01  $\text{ng m}^{-3}$ ) (Kristensen and Glasius, 2011), but still much lower compared to levels reported for the Southeastern USA; e.g. 64  $\text{ng m}^{-3}$  reported by Chan et al. (2010). Three organosulphates from monoterpenes (MW = 250, 264 and 280) were identified, of which those with a molecular weight of 250 and 280 were present at concentrations comparable to that reported by Kristensen and Glasius (2011). In contrast, concentrations of nitrooxy organosulphates originating from  $\alpha$ -pinene and  $\beta$ -pinene (MW = 295) and from limonene (MW = 297) were several times higher in the present study compared to the previous study by Kristensen and Glasius (2011).

**Table 3.** Concentrations of SOA tracers in a four week composited PM<sub>10</sub> filter sample at the Birkenes site (Norway). Unit: ng m<sup>-3</sup>. b.d. means below detection limit.

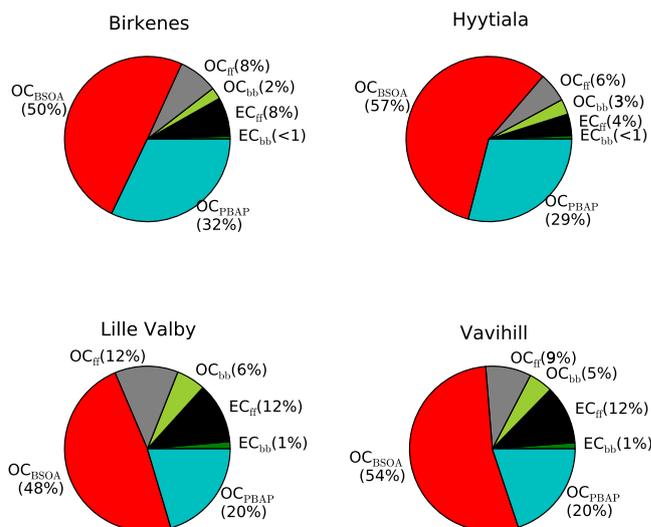
Birkenes (Norway)	
Isoprene tracers	
2,3-dihydroxymethacrylic acid	0.70
2-methylthreitol	0.28
2-methylerythritol	0.49
$\alpha$ -pinene tracers	
3-acetyl pentanedioic acid	b.d.
3-acetyl hexanedioic acid	0.96
3-carboxy heptanedioic acid	5.2
3-hydroxy glutaric acid	4.9
4-isopropyl-1,2-dihydroxy hexanol	2.5
3-(2-Hydroxy-ethyl)-2,2-dimethyl-cyclobutane-carboxylic acid	b.d.
Pinic acid	0.33
Pinonic acid	b.d.
Toluene tracer	
2,3-dihydroxy-4-oxopentanoic acid	b.d.
$\beta$ -caryophyllene tracer	
$\beta$ -caryophyllinic acid	b.d.

## 5.4 F<sup>14</sup>C TC

The results from the <sup>14</sup>C measurements of TC in PM<sub>10</sub> are presented in Table 2 as F<sup>14</sup>C values (Reimer et al., 2004). The F<sup>14</sup>C values at the Danish site Lille Valby (0.83) and the Swedish site Vavihill (0.87) are similar to the levels reported from rural sites in continental Europe (Gelencsér et al., 2007; May et al., 2009). The Finnish and Norwegian sites (Hyytiälä and Birkenes) display slightly higher <sup>14</sup>C concentrations (F<sup>14</sup>C values of 0.99 and 0.93, respectively) compared to the other two sites, and are comparable to the upper range of F<sup>14</sup>C values reported by Yttri et al. (2011) for the Norwegian rural background environment. Reported values from urban sites in Europe show significantly higher fossil impact (F<sup>14</sup>C values of 0.60–0.73,  $p < 0.01$ ) (Szidat et al., 2004, 2006 and 2009; Yttri et al., 2011).

## 6 Discussion

The results of the source-apportionment analysis, presented in Figs. 2 and 4 (and Tables S1–S8), show that natural sources, and BSOA in particular, totally dominated the carbonaceous aerosol loading in the Nordic rural background environment during summer. The various carbonaceous components are discussed in detail in Sects. 6.1–6.5. In Sect. 6.6 we present a brief overview of the biogenic oxidation products.



**Fig. 4.** Best estimate, i.e. 50 percentile, percentage contributions of different carbonaceous particle fractions to TC<sub>p</sub> for Birkenes, Hyytiälä, Lille Valby, and Vavihill filter samples (PM<sub>10</sub>) from LHS analysis.

### 6.1 Carbonaceous aerosol from fossil-fuel sources and biomass burning

The mean concentration of OC from fossil-fuel sources (OC<sub>ff</sub>; 0.1–0.3  $\mu\text{g C m}^{-3}$ ) was higher than OC from wood burning (OC<sub>bb</sub>;  $\leq 0.1 \mu\text{g C m}^{-3}$ ) at all sites throughout the sampling period. The highest mean concentrations were observed in Lille Valby both with respect to OC<sub>ff</sub> and OC<sub>bb</sub>, being a factor 2–3 higher compared to the three other sites. On a weekly basis, OC<sub>ff</sub> did not exceed 0.5  $\mu\text{g C m}^{-3}$  at any of the sites, whereas OC<sub>bb</sub> stayed below 0.2  $\mu\text{g C m}^{-3}$ . The mean relative contribution of OC<sub>ff</sub> to TC<sub>p</sub> ranged from 6% in Hyytiälä to 12% at Lille Valby, whereas the corresponding range for OC<sub>bb</sub> was 2% (Birkenes) to 6% (Lille Valby). These low percentages clearly demonstrate that OC from combustion of biomass and fossil-fuel sources are minor contributors to the carbonaceous aerosol loading in the Scandinavian rural background environment in summer. Fossil fuel sources were the major contributor to EC at all four sites. The mean EC<sub>ff</sub> concentration ranged from approximately 0.1  $\mu\text{g C m}^{-3}$  to 0.3  $\mu\text{g C m}^{-3}$ , whereas for EC<sub>bb</sub> the mean concentrations was  $< 0.03 \mu\text{g C m}^{-3}$ . The highest mean concentrations of EC<sub>bb</sub> and EC<sub>ff</sub> were both observed at Lille Valby. For EC<sub>ff</sub> the mean relative contribution to TC<sub>p</sub> ranged from 4–12%, whereas for EC<sub>bb</sub> it was  $< 1.5\%$  at all sites.

A moderately high correlation coefficient ( $r^2 = 0.5$ ) observed between the EC/TC<sub>p</sub> ratio and the Agricultural land use category could suggest that late summer agricultural activity, e.g. harvesting, agricultural waste burning, has an impact on the EC levels observed in the Nordic rural

background environment. The very low  $EC_{bb}$  levels observed indicated that agricultural waste burning is of minor importance, though, suggesting that e.g. tractors and off-road machinery is the source of high EC fractions.

### 6.1.1 Wild fire contribution to $OC_{ff}$ and $EC_{ff}$

Measurements of levoglucosan alone cannot differentiate between emissions from residential wood burning and wild/agricultural fires. Thus, we have applied the FLEXPART carbon monoxide CO passive fire tracer (Stohl et al., 2007) to address the influence of wild/agricultural fires, and find that all sites have a certain influence from this source, although the CO passive fire tracer levels are quite low (i.e. peak levels below 30 ppb). Elevated CO passive fire tracer levels were typically the results of fire emissions more than 10 days prior to arrival of the air mass at the measurement site, thus wet and dry deposition were likely to have depleted the aerosol particle concentration substantially. Further, the aerosol particle concentration of levoglucosan might be selectively depleted by OH during long range transport, particularly during summer, thus underestimating levels of  $EC_{bb}$  and  $OC_{bb}$ . Although levoglucosan containing aerosol from wild/agricultural fires is deposited during atmospheric transport, co-emitted semi-volatile organic compounds (SVOCs) can be present at the receptor point. This will cause an underestimation of the  $EC_{bb}$  and  $OC_{bb}$  levels, as well as adding to the level of  $OC_{BSOA}$ , according to the approach described in section 4. Nevertheless, there appears to be an association between CO passive fire tracer levels associated with more recent air masses (atmospheric residence time <5 days) influenced by wild/agricultural fires and levoglucosan. This becomes apparent when superimposing the weekly time resolution time series of levoglucosan on that of the CO passive fire tracer, as seen in Fig. 5. Further, the negative correlation observed between the biomass burning tracer levoglucosan and  $F^{14}C$ , suggest that other sources than biomass burning were driving the  $F^{14}C$  values (here:  $OC_{BSOA}$  and  $OC_{PBAP}$ ).

### 6.2 Biogenic secondary organic aerosol, $OC_{BSOA}$

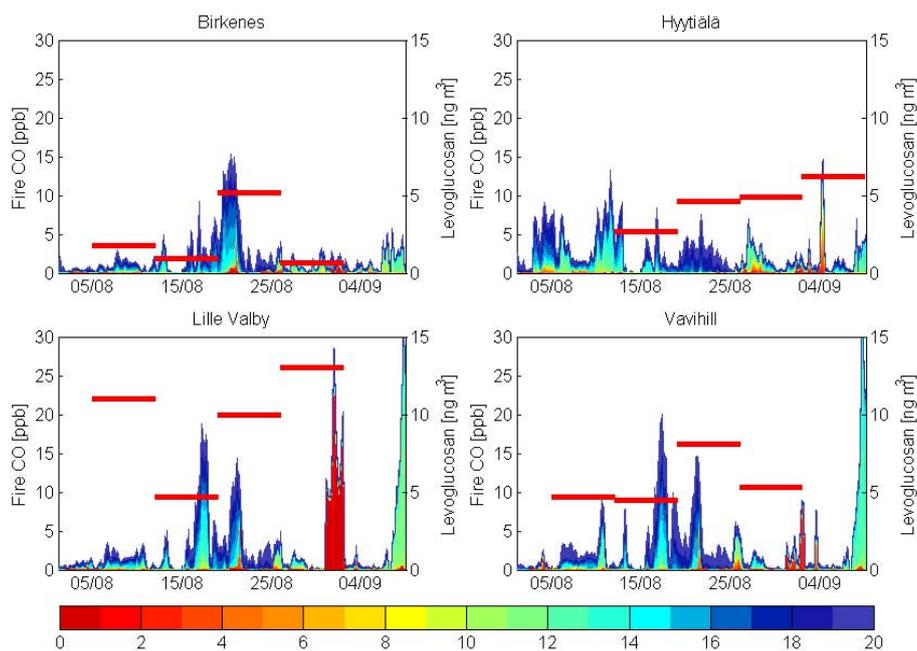
$OC_{BSOA}$  was the major contributor to the carbonaceous aerosol at all four sites, accounting for 48–57% of  $TC_p$  on average during the one month sampling period. The highest relative contribution was observed for the Finnish site Hyttiälä and the lowest for the Danish site Lille Valby. The relative contribution of  $OC_{BSOA}$  to  $TC_p$  was remarkably stable in Hyttiälä, differing no more than 3% between the highest (59%) and lowest (56%) on a weekly basis, whereas the corresponding range was 20–30% for the other three sites. The monthly mean  $OC_{BSOA}$  concentration ranged from  $0.6 \mu\text{g C m}^{-3}$  at the Norwegian site Birkenes to  $1.5 \mu\text{g C m}^{-3}$  at Lille Valby. Substantial week-to-week variation in the  $OC_{BSOA}$  concentration was

observed; e.g. by a factor of 7 at Lille Valby. The higher  $OC_{BSOA}$  concentrations at Lille Valby could possibly be a result of the higher  $OC_p$  concentrations observed (Table 2), favouring condensation (Donahue et al., 2009), as otherwise we would expect similar source strength of BSOA as at Vavihill. The  $OC_{BSOA}$  concentration range reported here corresponds well with that reported by Yttri et al. (2011) (i.e.  $OC_{BSOA} = 2.0\text{--}2.3 \mu\text{g C m}^{-3}$ ) for the Norwegian rural background environment during summer.

### 6.3 Primary biological aerosol particles, $OC_{PBAP}$

In the present study,  $OC_{PBAP}$  was accounted for by the sum of OC associated with fungal spores ( $OC_{pbs}$ ) and plant debris ( $OC_{pbc}$ ). The results show that  $OC_{PBAP}$  comprised on average 20–32% of  $TC_p$  during the actual sampling period, confirming that PBAP is an important source of the summer time carbonaceous aerosol in the Scandinavian rural background environment. The relative contribution of  $OC_{PBAP}$  to  $TC_p$  was noticeably higher at Birkenes (32%) and in Hyttiälä (29%) compared to Lille Valby and Vavihill (both 20%). Consequently, PBAP was the second largest source of  $TC_p$  next to BSOA at Birkenes, Hyttiälä and Vavihill, whereas it was slightly less than the joint contribution of EC and OC from fossil fuel sources at Lille Valby. In fact,  $OC_{PBAP}$  accounted for twice the contribution made up by anthropogenic sources; i.e. the sum of EC and OC originating from combustion of biomass and fossil fuel sources at Birkenes and in Hyttiälä. With the exception of the second sampling week, the relative contribution of  $OC_{PBAP}$  to  $TC_p$  showed almost no variation for the four sites.  $OC_{pbc}$  (12–18%) made a larger contribution to  $TC_p$  than  $OC_{pbs}$  (7–15%), except for Hyttiälä where their contributions were equally large. The monthly mean concentration level ranged from  $0.3 \mu\text{g C m}^{-3}$  at Birkenes and Vavihill to  $0.5 \mu\text{g C m}^{-3}$  at Hyttiälä and Lille Valby, whereas the highest weekly mean was close to  $0.9 \mu\text{g C m}^{-3}$ . These concentration levels are comparable to the levels reported by Yttri et al. (2011; i.e.  $OC_{PBAP} = 0.9 \mu\text{g C m}^{-3}$ ) for the Norwegian rural background environment. A correlation of  $r^2 = 0.72$  was observed between  $OC_{BSOA}$  and  $OC_{PBAP}$  which mainly was attributed to the  $OC_{pbc}$  fraction ( $r^2 = 0.87$ ) of  $OC_{PBAP}$ . This finding could support the suggestion made by Yttri et al. (2011) that PBAP might act as a condensational sink in areas where the carbonaceous aerosol from anthropogenic sources are scarce. However, PBAP was not found to be associated with BSOA to any particular degree in the Amazon, a region less perturbed by anthropogenic sources than the Nordic countries (Pöschl et al., 2010).

A pronounced correlation was observed between  $OC_{pbs}$  and the Needleleaf evergreen surface category ( $r^2 = 0.64$ ), suggesting that areas with coniferous trees were important for the ambient aerosol concentration of fungal spores during late summer in the Nordic rural background environment.



**Fig. 5.** Time series of observed levoglucosan concentrations (red horizontal bars) and CO wild/agricultural fire tracer mixing ratios (ppb) obtained from the FLEXPART backward simulations for Birkenes (Norway), Hyttiälä (Finland), Lille Valby (Denmark) and Vavihill (Sweden) for the period 5 August–9 September 2009. The colored bars correspond to the time (days) passed since emission at the fire locations.

For  $OC_{pbc}$  no pronounced correlation for any land use category was observed.

#### 6.4 Natural versus anthropogenic sources of the carbonaceous aerosol

BSOA and PBAP are defined as natural sources, although anthropogenic emissions and activity may influence their levels. This includes air pollution enhancement of BSOA formation (Tsigaridis and Kanakidou, 2003; Carlton et al., 2010; Donahue et al., 2009; Hoyle et al., 2011), as well as increased levels of PBAP have been found to be associated with e.g. agricultural activities, sewage plants and building demolition (Matthias-Maser, 1998, and references therein). We define carbonaceous aerosol arising from fossil-fuel sources and biomass combustion ( $EC_{bb}$ ,  $EC_{ff}$ ,  $OC_{bb}$  and  $OC_{ff}$ ) as anthropogenic emissions. Obviously, wild fires emissions can be categorized as natural in cases when ignited by lightning, as is the case for the major Boreal fires in Canada and Siberia (Stocks et al., 2002), but most incidences when natural vegetation catches fire in Europe is likely due to human activity (Winiwarter et al., 1999). In the present study, we found that increased levels of levoglucosan were associated with nearby wild fires (i.e. atmospheric residence time <5 days; see Fig. 5). Thus, for the sake of simplicity we categorize all emissions from wild fires as anthropogenic in the current study. Carbonaceous aerosol from natural sources was the major contributor to  $TC_p$  by a fair margin

at all four sites. The highest mean relative contribution was observed for the Finnish site Hyttiälä (86 %) and the lowest for the Danish site Lille Valby (69 %). The monthly mean concentration ranged from  $0.9 \mu\text{g C m}^{-3}$  at Birkenes to  $1.9 \mu\text{g C m}^{-3}$  at Lille Valby. On a weekly basis the natural contribution even reached 90 % of  $TC_p$  for the Hyttiälä site. The natural contribution was always dominated by  $OC_{BSOA}$ , except for one week at Birkenes during which  $OC_{PBAP}$  prevailed. The highest relative contribution of carbonaceous aerosol from anthropogenic sources to  $TC_p$  on a weekly basis was observed at Lille Valby, reaching 44 %, of which 32 % was from fossil sources and 12 % due to biomass burning. The monthly mean concentration of carbonaceous aerosol from anthropogenic sources ranged from  $0.2 \mu\text{g C m}^{-3}$  at Birkenes to  $0.7 \mu\text{g C m}^{-3}$  at Lille Valby, thus showing somewhat greater variation between the sites than the contribution from natural sources.

#### 6.5 Consistency of results from LHS calculations

The challenges associated with splitting  $OC_{PBAP}$ ,  $OC_{bb}$  and  $OC_{BSOA}$  have been discussed in the literature (e.g. Yttri et al., 2011; Grieshop et al., 2009a, b). Grieshop et al. (2009a, b) showed that SOA from wood-burning actually may equal levels of POA, while a SOA/POA ratio of about 3.1 can be derived from the results of Heringa et al. (2011). The ratios used in the present study were derived from wintertime ambient measurements (Yttri et al., 2009), thus they may

also include condensed vapors. By calculating  $OC_{pbc}$  and  $OC_{pbs}$ , we have likely accounted for the two most important terrestrial PBAP sources that would otherwise introduce uncertainty into the calculation of  $OC_{BSOA}$ . On the other hand, Ceburnis et al. (2011) recently suggested a major impact of fine mode PBAP derived from plankton from the marine environment at Mace Head on the West coast of Ireland, which is not accounted for by the PBAP tracers used in the present study. In Sect. 3.2 it is shown that the marine footprint dominates at all four sites and that it is most pronounced at the Birkenes, Lille Valby and Vavihill sites which are all situated less than 25 km from the coastline. Thus, one cannot exclude the possibility that a certain fraction of the apportioned BSOA in fact is PBAP. Such a finding would however not affect the magnitude of the natural source contribution.

Tire debris is also a source of coarse mode contemporary carbon which we have not accounted for in our source apportionment. Tire treads have a natural rubber content of 0.5–3.5% (Edeskär, 2004), thus we expect the contribution to be minor for the Scandinavian rural background environment. Emissions from cooking could make a significant contribution to contemporary carbon in urban areas, while we find this less likely for the rural background environment. The current study does not consider the increased use of biofuels in vehicle engines as we are trying to adapt to a carbon neutral society. Bennet et al. (2008) showed that the fraction modern ( $F^{14}C$ ) value in  $PM_{10}$  increased linearly with the percentage of biodiesel in the fuel. Consequently, any source apportionment attempting to separate biogenic from anthropogenic carbonaceous aerosol emissions involving  $^{14}C$  will be affected.

Following an identical approach, i.e. using the same tracers as input to LHS statistical analysis as in the present study, Yttri et al. (2011) demonstrated that  $OC_{BSOA}$  was successfully separated from other sources of contemporary carbon based on its seasonality, diurnal variation, and regional character.

### 6.6 Biogenic oxidation products – pinic acid, organosulphates and nitrooxy organosulphates

The highest mean concentration of biogenic oxidation products in aerosols was observed in Hyytiälä; e.g. the mean concentration of pinic acid was 2–3 times higher compared to the three other sites in the study. Hyytiälä is a continental site situated in the Boreal forest and thus likely experiences higher local and regional emissions of monoterpenes, as well as of isoprene compared to the other three sites. This is supported by the results obtained from the FLEXPART model which shows that the land surface categories involving trees (i.e. Broadleaved deciduous Trees; Mixed Forest; Needleleaf evergreen, Needleleaf deciduous; e.g. larch) was relatively more important for the Hyytiälä site (69%) than for the three other sites ( $40 \pm 3.5\%$ ) during the

sampling period (see Fig. 3). Levels and temporal variation of biogenic oxidation products were comparable for Lille Valby and Vavihill, which is likely due to the relatively short distance (<70 km) between the two sites.

Organosulphates and nitrooxy organosulphates from isoprene and monoterpenes are formed through acid-catalyzed ring-opening of epoxides (Iinuma et al., 2009; Surratt et al., 2010) and through sulphate radical processes in the aerosol aqueous-phase (Nozière et al., 2010), while the previously suggested sulphate esterification mechanism (Liggio et al., 2005; Liggio and Li, 2006; Surratt et al., 2007) is not feasible at the pH of the atmospheric aerosol (Minerath et al., 2008). Formation of organosulphates and nitrooxy organosulphates thus occur during ageing of the aerosol and their concentrations depend on both the level of precursor compounds, as well as rate and conditions for the ageing processes. The concentration of first-generation biogenic oxidation products, such as pinic acid, is thus not necessarily correlated with levels of organosulphates and nitrooxy-organosulphates.

The concentration of the two nitrooxy organosulphates (denoted MW 295 and MW 297) measured (see Table 2) showed a noticeable dependency upon the land surface category mixed forest ( $r^2 = 0.6–0.7$ ), which did not account for more than 5–8% on average of the total terrestrial footprint during the sampling period. For the other land surface categories involving trees, i.e. Broadleaf deciduous ( $r^2 = 0.4–0.5$ ), Needleleaf evergreen and broadleaved deciduous trees ( $r^2 = 0.3–0.4$ ) the correlation was low or not existing. According to Surratt et al., 2008, limonene is the precursor of the nitrooxy organosulphate MW 297, while MW 295 originates from oxidation of  $\alpha$ -pinene. In the European Boreal forest (Lindfors et al., 2000), as well as on the global scale (Griffin et al., 1999), emissions of  $\alpha$ -pinene is substantially higher than that of limonene, nevertheless, the concentrations of MW 297 is 1.4–1.8 times higher than that of MW 295, suggesting different formation pathways and/or reactions rates. Indeed, Kristensen and Glasius (2010) showed that concentrations of MW 297 peaked during night, suggesting involvement of the  $NO_3$  radical, whereas MW 295 peaked in the morning, thus pointing towards another formation pathway. Further, Andersson-Sköld and Simpson (2001) showed that with its higher yields, limonene can contribute more to the Nordic aerosol than species with higher emissions but lower yields, notably  $\alpha$ -pinene.

The concentration of MW 297 was 6–17 times higher during week one compared to the rest of the sampling period (i.e. week 2–4) at Birkenes, Lille Valby and Vavihill, whereas the relative contribution of MW 297 to  $TC_p$  was increased by a factor of 4–5. The concentration of MW 295 was also increased during week one (by a factor of 3–5), but the relative contribution of MW 295 to  $TC_p$  was less pronounced (increased by a factor 1.1–3.5) than seen for MW 297. These findings compare well with the increased Mixed forest footprint during week one, which was

11–15 % compared to 3–4 % for week 2–4. The stagnant meteorological conditions observed during the first week of sampling at the three sites (see Sect. 3.1) probably provided favourable conditions for aging, explaining the increased levels of nitrooxy organosulphates observed, however, we find it difficult to explain the strong dependency on the mixed forest category and suggest that this might be a proxy for e.g. a defined geographical region, transport time.

### 6.7 Estimating BSOA by BSOA tracers

The contribution of each precursor to secondary organic carbon (SOC) could be determined by dividing the total tracer concentrations for each precursor in an ambient sample by the respective photochemical reaction chamber-derived SOC mass fraction given in Kleindienst et al. (2007; isoprene:  $0.155 \pm 0.039$ ,  $\alpha$ -pinene:  $0.231 \pm 0.111$ , toluene:  $0.0079 \pm 0.0026$ , and  $\beta$ -caryophyllene:  $0.023 \pm 0.0046$ ). The results indicate  $\alpha$ -pinene as the precursor with the largest contribution to measured levels of  $TC_p$ . The nine  $\alpha$ -pinene tracer compounds led to SOC contributions of  $0.06 \mu\text{g C m}^{-3}$ . The three isoprene tracer compounds represent a SOC contribution of  $0.01 \mu\text{g C m}^{-3}$ . Using the same procedure, the SOC contributions for toluene and  $\beta$ -caryophyllene were lower than  $0.006 \mu\text{g C m}^{-3}$ , and  $0.002 \mu\text{g C m}^{-3}$ , respectively. The sum of this estimate constitutes 8 % of the  $TC_p$  concentration, which is substantially less than the 50 % mean contribution resulting from the Latin Hypercube Sampling approach (see Fig. 4). This observed deviation suggests there are BSOA precursor compounds which are not included in this estimation technique, and that those compounds may have significant contributions at the Birkenes location. Other BSOA formation pathways such as polymerization and ageing processes may also contribute to BSOA not accounted for by the tracer approach (El Haddad et al., 2011). On the other hand, the Tracer:SOA ratios used by Kleindienst et al. (2007) were extrapolated from experimental conditions very far from ambient conditions and were never claimed to be of general validity. In addition, the low ambient OC concentrations make our Nordic application of the technique even further removed from the experimental data than the ambient data analyzed by Kleindienst et al. (2007). Our conclusion from this pilot study is that factors used to convert BSOA tracers into SOC cannot be applied for the Nordic rural background environment without experimental verification and further insights into the chemical speciation of the ambient carbonaceous aerosol.

## 7 Conclusions

The combined effort of measuring organic tracers, thermal-optical- and  $F^{14}\text{C}$ -analyses, and Latin Hypercube Sampling in the present study has clearly demonstrated the abundance of carbonaceous aerosol originating from natural sources

in the Nordic rural background environment in summer, accounting for 69–86 % of  $TC_p$ . The biogenic secondary organic aerosol was the single most important source (48–57 %), followed by primary biological aerosol particles (20–32 %). The anthropogenic contribution was mainly attributed to fossil fuel sources (10–24 %), whereas no more than 3–7 % was explained by combustion of biomass; i.e. emissions from residential wood burning and/or wild/agricultural fires. Fossil fuel sources totally dominated the ambient EC loading, accounting for 4–12 % of  $TC_p$ , whereas <1.5 % was attributed to combustion of biomass.

The carbonaceous aerosol source apportionment showed only minor variation between the four selected sites. However, the Finnish site Hyttiälä and the Norwegian site Birkenes showed greater resemblance to each other, as did the Danish site Lille Valby and the Swedish site Vavihill. Compared to Lille Valby and Vavihill, Hyttiälä and Birkenes had slightly higher contributions from natural sources; i.e. 82–86 % for Birkenes and Hyttiälä and 69–74 % for Lille Valby and Vavihill. This difference was mainly attributed to PBAP, which had a relative contribution of 29–32 % at Birkenes/Hyttiälä compared to 20 % at Lille Valby/Vavihill. The presence of organosulphates and nitrooxy organosulphates in the Nordic rural background environment is demonstrated for the first time in the present study. The most abundant organosulphate compounds were an organosulphate of isoprene and nitrooxy-organosulphates of  $\alpha$ - and  $\beta$ -pinene and limonene.

### Supplementary material related to this article is available online at:

<http://www.atmos-chem-phys.net/11/13339/2011/acp-11-13339-2011-supplement.pdf>.

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