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*Published in:*  
Atmospheric Chemistry and Physics

*DOI:*  
[10.5194/acp-11-9375-2011](https://doi.org/10.5194/acp-11-9375-2011)

2011

[Link to publication](#)

*Citation for published version (APA):*  
Yttri, K. E., Simpson, D., Stenström, K., Puxbaum, H., & Svendby, T. (2011). Source apportionment of the carbonaceous aerosol in Norway - quantitative estimates based on C-14, thermal-optical and organic tracer analysis. *Atmospheric Chemistry and Physics*, 11(17), 9375-9394. <https://doi.org/10.5194/acp-11-9375-2011>

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5

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# Source apportionment of the carbonaceous aerosol in Norway – quantitative estimates based on $^{14}\text{C}$ , thermal-optical and organic tracer analysis

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Received: 2 February 2011 – Published in Atmos. Chem. Phys. Discuss.: 3 March 2011

Revised: 1 September 2011 – Accepted: 5 September 2011 – Published: 9 September 2011

**Abstract.** In the present study, source apportionment of the ambient summer and winter time particulate carbonaceous matter (PCM) in aerosol particles ( $\text{PM}_1$  and  $\text{PM}_{10}$ ) has been conducted for the Norwegian urban and rural background environment. Statistical treatment of data from thermal-optical,  $^{14}\text{C}$  and organic tracer analysis using Latin Hypercube Sampling has allowed for quantitative estimates of seven different sources contributing to the ambient carbonaceous aerosol. These are: elemental carbon from combustion of biomass ( $\text{EC}_{\text{bb}}$ ) and fossil fuel ( $\text{EC}_{\text{ff}}$ ), primary and secondary organic carbon arising from combustion of biomass ( $\text{OC}_{\text{bb}}$ ) and fossil fuel ( $\text{OC}_{\text{ff}}$ ), primary biological aerosol particles ( $\text{OC}_{\text{PBAP}}$ , which includes plant debris,  $\text{OC}_{\text{pbc}}$ , and fungal spores,  $\text{OC}_{\text{pbs}}$ ), and secondary organic aerosol from biogenic precursors ( $\text{OC}_{\text{BSOA}}$ ).

Our results show that emissions from natural sources were particularly abundant in summer, and with a more pronounced influence at the rural compared to the urban background site. 80 % of total carbon ( $\text{TC}_p$ , corrected for the positive artefact) in  $\text{PM}_{10}$  and ca. 70 % of  $\text{TC}_p$  in  $\text{PM}_1$  could be attributed to natural sources at the rural background site in summer. Natural sources account for about 50 % of  $\text{TC}_p$  in  $\text{PM}_{10}$  at the urban background site as well. The natural source contribution was always dominated by  $\text{OC}_{\text{BSOA}}$ , regardless of season, site and size fraction. During winter anthropogenic sources totally dominated the carbonaceous

aerosol (80–90 %). Combustion of biomass contributed slightly more than fossil-fuel sources in winter, whereas emissions from fossil-fuel sources were more abundant in summer.

Mass closure calculations show that PCM made significant contributions to the mass concentration of the ambient PM regardless of size fraction, season, and site. A larger fraction of  $\text{PM}_1$  (ca. 40–60 %) was accounted for by carbonaceous matter compared to  $\text{PM}_{10}$  (ca. 40–50 %), but only by a small margin. In general, there were no pronounced differences in the relative contribution of carbonaceous matter to PM with respect to season or between the two sites.

## 1 Introduction

Particulate carbonaceous matter (PCM) is found to constitute 10–40 % (mean 30 %) of  $\text{PM}_{10}$  levels at rural and natural background sites in Europe (Yttri et al., 2007a; Putaud et al., 2004). PCM is believed to have important impacts on global climate (Novakov and Penner, 1993; Kanakidou et al., 2005), and on human health (McDonald et al., 2004; Bell et al., 2009). PCM consists largely of organic matter (OM), and usually smaller quantities of so-called elemental or black carbon (EC or BC). OM is dominated by its carbon content (OC), but with associated oxygen, hydrogen, nitrogen, and sulphur. The sum of EC and OC is referred to as total carbon (TC). (Table 1 summarizes the notation used in the present study.) Recent reviews have highlighted the complexity of the carbonaceous aerosol both in terms of composition and



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**Table 1.** Notation used in this study.

OC <sub>F</sub>	Measured organic carbon on front filter
OC <sub>B</sub>	Measured organic carbon on back filter
OC <sub>p</sub>	Organic carbon after correction for positive artefact, OC <sub>p</sub> = OC <sub>F</sub> – OC <sub>B</sub>
TC <sub>p</sub>	Total carbon after correction for positive artefact, TC <sub>p</sub> = OC <sub>p</sub> + EC
LG	Levoglucosan
OC	Organic carbon
OA	Organic aerosol (includes other elements, e.g. O, H, N)
POA	OA arising from primary emissions
ASOA	OA arising from secondary oxidation of anthropogenic precursors
BSOA	OA arising from secondary oxidation of biogenic precursors (mainly terpenes, isoprene )
PBAP	Primary biological aerosol particles, includes fungii, plant debris, virus, etc.
Cel.	Free cellulose, as measured
PCM	Particulate carbonaceous matter
subscript bb	Associated with biomass burning
subscript ff	Associated with fossil-fuels (includes POA and ASOA for OC)
subscript pbs	PBAP associated with sugars, e.g. fungii, etc.
subscript pbc	PBAP associated with cellulose, e.g. plant debris
subscript ASOA, BSOA	Associated with ASOA, BSOA
F <sup>14</sup> C	Fraction of modern carbon relative to a reference standard (Reimer et al., 2004) (without subscript, F <sup>14</sup> C refers to whole TC sample, otherwise subscript indicates origin)
Φ <sub>EC</sub>	Uncertainty factor for EC observations
Φ <sub>NA</sub>	Uncertainty factor to account for negative sampling artefact of OC
Φ <sub>F<sup>14</sup>C</sub>	Uncertainty factor for F <sup>14</sup> C observations

formation mechanisms (Baltensperger et al., 2005; Donahue et al., 2005, 2009; Kanakidou et al., 2005; Kroll and Seinfeld, 2008; Pöschl, 2005; Hallquist et al., 2009).

Over the last few years a number of studies have become available which shed light on the important sources of PCM in Europe. Szidat et al. (2006) attributed the ambient aerosol carbon content to either fossil carbon (from combustion of coal, oil) or modern carbon (from recent vegetation, either by combustion, emissions, or formation using <sup>14</sup>C-analysis). They found that fossil-fuel combustion accounted for only 30 % of OC throughout the year, even in the city center of Zürich (Switzerland). Biomass burning in wintertime and SOA in summertime seemed to account for the majority of the remaining OC. Follow-up studies in Switzerland using a variety of techniques have confirmed the basic source patterns (Szidat et al., 2007; Lanz et al., 2007, 2008). Recent results from northern Italy show similar features (Gilardoni et al., 2011).

The EU CARBOSOL project (CARBOnaceous AeroSOLs over Europe, Legrand and Puxbaum 2007) provided the first long-term assessment (2002–2004) of PCM in Europe. By using the results of <sup>14</sup>C-, thermal-optical-, and organic tracer analysis as input, Gelencsér et al. (2007) made use of a novel statistical method to calculate the likely contributions of different sources of the PCM at six sites in central/southern Europe. Wintertime residential-wood burning was found to be a significant contributor to

measured PCM levels at all the sites, whereas in summertime, biogenic SOA (BSOA) was the dominant contributor. These data enabled for the first time an evaluation of the components (primary, secondary, anthropogenic, biogenic) of chemical transport model simulations (Simpson et al., 2007). Previously, only EC or OC has been available for model comparison, and as shown by Simpson et al. (2007), this has been wholly inadequate for understanding the role of e.g. local biomass burning versus long range transport, or of primary organic aerosol (POA) versus secondary (SOA).

In Northern Europe, studies addressing the sources of PCM have been limited. In a pioneering study, Currie et al. (1986) showed that residential wood burning was the major contributor to the carbonaceous aerosol in winter in Norway. A number of recent studies have confirmed the importance of wood-burning emissions to ambient PM levels in Nordic areas in wintertime (Glasius et al., 2006; Hedberg et al., 2006; Saarikoski et al., 2008; Szidat et al., 2009; Yttri et al., 2005, 2009). Scandinavia is a particularly interesting region with respect to natural sources of PCM. Large forested areas, emitting vast amounts of VOCs during the long days of the Scandinavian summer, create a basis for BSOA formation. Using a network of Nordic sites measuring aerosol number size distributions, combined with extensive trajectory analysis, Tunved et al. (2006) has shown a very good relationship between accumulated biogenic VOC (BVOC) emissions and particle mass changes, suggesting that, in clean-air

conditions at least, the buildup of PM can be interpreted almost entirely in terms of biogenic precursors and presumably SOA formation. However, this study described very clean air conditions, and it is unclear how far this result can be generalized to typical Nordic conditions. Nevertheless, a substantial 64 % contribution of SOA to OC was reported for Helsinki, Finland, during summertime by Saarikoski et al. (2008), of which the major fraction of SOA was likely to have a biogenic origin. Szidat et al. (2009) found that the contribution of non-fossil sources (likely BSOA) (53 %) and fossil sources (47 %) to TC almost equaled each other at a site in central Gothenburg in June 2006.

Yttri et al. (2007a) showed that levels of OC in PM<sub>10</sub> were higher in summer compared to winter at rural background sites in Scandinavia, as compared to rural background sites in continental Europe. Based on results from the Norwegian site Birkenes this was attributed to coarse OC, which constituted approximately 50 % of OC in PM<sub>10</sub> on a monthly basis during summer. Further evidence that this coarse OC could be attributed to primary biological aerosol particles (OC<sub>PBAP</sub>) stems from seasonal and size distribution measurements of sugars and sugar-alcohols, which are tracers of OC<sub>PBAP</sub> (Yttri et al., 2007b).

Model studies have also suggested that BSOA formation can make a large contribution to PCM levels in Northern Europe (Andersson-Sköld and Simpson, 2001; Chung and Seinfeld, 2002; Tsigaridis and Kanakidou, 2003; Simpson et al., 2007). The study of Simpson et al. (2007) noted the possibility that BSOA formation may even be a significant contributor to PCM levels in wintertime at Nordic sites, despite low emission rates of precursor species, as a result of the higher condensation rates applicable in cold Nordic conditions. This study also stressed that a major problem in all modeling of PCM is that too many steps in the calculation process are highly uncertain, and there are too few constraints. The uncertainties cover emissions from both anthropogenic and biogenic sources, atmospheric chemistry, and the fate of the various semi volatile products involved in SOA formation. Clearly, there is a strong need for measurements which are able to test the model's abilities to predict all major components of PCM.

In the present study we present concurrent measurements of TC, EC, OC, monosaccharide anhydrides, sugars and sugar-alcohols, and cellulose, conducted at an urban background site (Oslo) and a rural background site (Hurdal), as part of the Norwegian SORGA (Secondary ORGANIC Aerosols in Urban Areas) project. These data are used to apportion the measured TC concentrations into primary, secondary, fossil-fuel, and non-fossil-fuel related sources by the aid of <sup>14</sup>C-analysis. Further, the carbonaceous aerosol emitted from these sources has been examined with respect to season, size fraction and time of day.

## 2 Experimental methods

### 2.1 Sampling sites

Aerosol filter samples were collected at an urban background site in Oslo, Norway, (Veterinary Institute, 59°56' N, 10°44' E, 77 m a.s.l.) and at a rural background site (Hurdal, 60°22' N, 11°04' E, 300 m a.s.l.) situated 70 km north east of Oslo, for a summer period (19 June–15 July 2006) and winter period (1–8 March 2007).

The Veterinary Institute measurements site is situated in the middle of the Oslo metropolitan area. Oslo is located in the innermost part of the Oslo fjord, and is largely surrounded by forested hills. The City of Oslo has a population of 0.6 million inhabitants, while the population of the greater Oslo-region is approximately 0.9 million. The Veterinary Institute measurements site is surrounded by low buildings of 2–3 storeys. The nearest major road is situated approximately 120 m from the site (25 000 cars/day).

The EMEP (European Monitoring and Evaluation Programme, [www.emep.int](http://www.emep.int)) site Hurdal is situated in the Boreal forest with mixed conifer and deciduous trees, which together with the Hurdal Lake (32 km<sup>2</sup>) account for the majority of the surrounding land use. The nearest local emission source is the local community of Hurdal (600 inhabitants), located 7 km north of the measurements site, which is known to have minor or even negligible influence on the air quality at the site. The nearest road is situated 200 m away from the site (<500 vehicles/day).

### 2.2 Aerosol sampling

#### 2.2.1 PM<sub>10</sub>, PM<sub>1</sub>, EC, OC, TC, monosaccharide anhydrides, sugars, sugar-alcohols

Aerosol (PM<sub>10</sub> and PM<sub>1</sub>) filter samples for subsequent analysis of mass concentration, EC, OC, TC, monosaccharide anhydrides, sugars and sugar-alcohols were collected on pre-fired (850 °C, 3 h) quartz fibre filters (Whatman QM-A, 47 mm), operated at ambient temperature. Tandem filter setups (McDow and Huntzicker, 1990) operating according to the QBQ-approach (quartz-fibre filter behind quartz fibre filter) were applied to account for the positive sampling artefact of OC. All quartz fibre filters were obtained from the same batch number to minimize differences in the adsorptive capacity, which otherwise would have biased the estimate of the positive artefact (Kirchstetter, 2001). After sampling, the front filters were conditioned at a temperature of 20 ± 2 °C and at a relative humidity of 50 ± 5 % for 48 h for gravimetric determination of the mass concentration. Thereafter the filters were placed in petrislides, packed in airtight plastic bags, and stored at –20 °C. The backup filters were stored immediately after sampling. Leckel LVS 3.1 samplers, operating at a flowrate of 38 l min<sup>-1</sup>, were used to collect aerosol filter samples both at the urban and the rural background site.

Two 12 h samples were collected per 24 h, approximating day (9 a.m.–9 p.m.) and night (9 p.m.–9 a.m.), respectively.

### 2.2.2 $^{14}\text{C}$ , Cellulose

Aerosol filter samples ( $\text{PM}_{10}$  and  $\text{PM}_1$ ) were collected at both sites for subsequent  $^{14}\text{C}$  and cellulose analysis. The aerosol were collected on pre-fired (850 °C, 3 h) quartz fibre filters (Whatman QM-A, 47 mm). At the rural background site, the time resolution for this sampling was 336 ( $14 \times 24$ ) h during the summer campaign and 168 ( $7 \times 24$ ) h during the winter campaign. The time resolution for the urban background site was 168 h during the summer campaign and 84 h during the winter campaign, as sampling was separated into day and night, respectively. A Leckel LVS 3.1 samplers, operating at a flow rate of  $381 \text{ min}^{-1}$  were used to collect  $\text{PM}_1$ , whereas a NILU (Norwegian Institute for Air Research) filter holder with an IVL (Swedish Environmental Research Institute) inlet, operating at a flowrate of  $16.7 \text{ l min}^{-1}$ , was used to collect  $\text{PM}_{10}$ .

The different sampling procedures (averaging times and filter face velocity) gave somewhat different estimates of  $\text{OC}_p$ , by 12 % of average, presumably due to differences in homogeneity and unavoidable differences in sampling artefacts between the systems. We have thus scaled the sampled cellulose by the  $\text{OC}_p$  ratios in order to generate compatible values of all components.

## 2.3 Thermal-optical transmission analysis

The aerosol filter samples content of EC, OC, and TC was quantified using a thermal-optical transmittance (TOT) instrument from Sunset laboratories Inc., operating according to a NIOSH derived temperature program. The '8785 Air Particulate Matter On Filter Media reference material from The National Institute of Standards and Technology (NIST) was used to test the performance of the temperature program. For further details about the temperature program and its performance see Yttri et al. (2007a).

## 2.4 Determination of organic tracers

### 2.4.1 Monosaccharide anhydrides

Levogluconan, mannosan, and galactosan (monosaccharide anhydrides, MAs) were quantified according to the method described by Dye and Yttri (2005), described briefly here. One punch ( $1.5 \text{ cm}^2$ ) from the quartz fibre filter was soaked in tetrahydrofuran (2 ml) and subjected to ultrasonic agitation (30 min). The extract was then filtered through a syringe filter ( $0.45 \mu\text{m}$ ) to remove PM and filter parts. The filter punch was extracted twice and the extracted volumes were pooled and evaporated to 1 ml by  $\text{N}_2$ . Before analysis the sample solvent elution strength was adapted to the mobile phase by adding Milli-Q water (0.8 ml). Concentrations of the individual monosaccharide anhydrides were

determined using a High-Performance Liquid Chromatography (HPLC, Agilent model 1100) instrument combined with High-Resolution Mass-Spectrometry – time-of-flight (HRMS-TOF, Micromass model LCT) operated in the negative electrospray mode. The compounds were identified by comparison of retention time and mass spectra with authentic standards. The compound separation was performed with two series-connected reversed-phase C18 columns (Atlantis dC18, Waters). The limit of quantification for the method at a signal to noise ratio of ten is approximately 20–40 ng injected of the individual MAs. An isotope labeled standard of mannosan, purchased from Cambridge Isotope Laboratories, was used as internal standard for quantification of the monosaccharide anhydrides.

### 2.4.2 Sugars and sugar-alcohols

Sugars (fructose, glucose, sucrose, trehalose), and sugar-alcohols (arabitol, erythritol, inositol, mannitol), were quantified according to the method described by Yttri et al. (2007b). Briefly, one punch ( $1.5 \text{ cm}^2$ ) from the quartz fibre filter was soaked in Milli-Q water (1.5 ml) and subjected to ultra sonic 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 an amino column (Asahipak NH2-2D, 2.0 mm id  $\times$  150 mm). The limit of quantification of the method at a signal to noise ratio of ten is approximately 30 ng injected of the individual sugars and sugar-alcohols. An isotope-labeled standard of glucose, purchased from Cambridge Isotope Laboratories, was used as internal standard for quantification of the sugars and sugar-alcohols.

### 2.4.3 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 (*Ibid.*). Filter aliquots of  $2 \text{ cm}^2$  were eluted with 2.2 ml of 0.05 M citric acid solution (pH of 4.8), containing 0.05 % of Thymol to prevent bacterial growth, during 45 min under ultrasonic agitation. The cellulose was then saccharified by two enzymes (Trichoderma reesei cellulase 80  $\mu\text{l}$  10 % and Aspergillus Niger cellobiase 80  $\mu\text{l}$  1 %) during 24 h at 45 °C. After stopping the saccharification by denaturizing the enzymes at 80 °C and centrifuging, the supernatant was collected in order to determine D-glucose using a modified test-combination (D-Glucose-HK, Megazyme, Ireland). Glucose was phosphorylated to glucose-6-phosphate, and

**Table 2.** Basis for source-apportionment.

$$EC = [EC] \times \Phi_{EC} \quad (1)$$

$$OC = [OC_p] + \Phi_{NA} \times (OC_F - OC_B) \quad (2)$$

$$TC = OC + EC \quad (3)$$

$$TC_{bb} = [LG] \times (TC/LG)_{bb} \quad (4)$$

$$OC_{bb} = TC_{bb} \times (OC/TC)_{bb} \quad (5)$$

$$EC_{bb} = TC_{bb} - OC_{bb} \quad (6)$$

$$EC_{ff} = EC - EC_{bb} \quad (7)$$

$$OC_{pbc} = [Cel.] \times (OC_{pbs}/Cel.) \quad (8)$$

$$OC_{pbs} = [Mannitol] \times (OC_{pbs}/Mannitol) \quad (9)$$

$$OC_{PBAP} = OC_{pbc} + OC_{pbs} \quad (10)$$

$$F^{14}C = [F^{14}C] \times \Phi_{F^{14}C} \quad (11)$$

$$OC_{BSOA} = ([TC] \times F^{14}C - TC_{bb} \times F^{14}C_{bb} - OC_{pbs} \times F^{14}C_{spores} - OC_{pbc} \times F^{14}C_{debris}) / F^{14}C_{bio} \quad (12)$$

$$OC_{ff} = OC - (OC_{bb} + OC_{pbs} + OC_{pbc} + OC_{BSOA}) \quad (13)$$

$$OC_{POA} = EC_{ff} \times (OC_{ff}/EC_{ff}) \quad (14)$$

$$OC_{ASOA} = OC_{ff} - OC_{POA} \quad (15)$$

Notes: Square brackets denote measured quantities. Parentheses denote emission ratios, see Table 3. See also Table 1 for notation.

subsequently oxidized by Nicotinamide adenine dinucleotide phosphate (NADP) to gluconate-6-phosphate (G-6-P), with the formation of NADPH, stoichiometrically proportional to the amount of D-glucose originally present. NADPH was quantified by UV photometry at 340 nm, read against distilled water. Free glucose was subtracted from the result. The limit of detection is 160 ng cm<sup>-2</sup>.

## 2.5 Radiocarbon analysis

Prior to the <sup>14</sup>C analysis, the carbon was extracted from filters (about 75 μg of carbon per filter). This was achieved by first combusting the sample to CO<sub>2</sub> in presence of pre-cleaned CuO (powder and needles) and Cu (needles) in a vacuum system. Elemental carbon was then produced reducing the CO<sub>2</sub> to elemental carbon using H<sub>2</sub> and a heated metal catalyst (about 2 mg of Fe powder, Merck, pro analysis reduced, diameter 10 μm, at 450 °C), and Mg(ClO<sub>4</sub>)<sub>2</sub> (Merck, diameter 1–4 mm) as a drying agent. The time for complete reduction of each sample was less than 3 h. After complete graphitization the carbon and iron catalyst were pressed into Al sample holders and put on a 40 position sample wheel together with graphitized standards (OxI, IAEA-C6 and IAEA-C7) and blanks (anthracite).

The <sup>14</sup>C analysis was performed by accelerator mass spectrometry at Lund University, using a compact, high capacity machine dedicated to radiocarbon dating, as well as to biomedical and environmental research (Skog, 2007; Skog et al., 2010).

## 3 Source-apportionment methodology

The measurements of EC, OC, TC, <sup>14</sup>C, levoglucosan, cellulose, sugars and sugar-alcohols in this study provide a set of tracers which provide information on the sources of the observed carbonaceous aerosol (c.f. Table 1). Levoglucosan is used as a tracer of TC from wood-burning (TC<sub>bb</sub>), whereas measurements of cellulose and selected sugar-alcohols (here: mannitol) can be used to determine the contribution of various primary biological aerosol particles (OC<sub>PBAP</sub>). Measurements of <sup>14</sup>C help to determine the percentage of modern carbon versus carbon from fossil-fuel sources.

Here we perform a very similar analysis as that of Gelencsér et al. (2007), in an effort to calculate the relative contributions of the main anthropogenic and natural sources of the carbonaceous aerosol. The methodology is updated with newer emissions ratios and information on the contribution of OC from fungal-spores provided by the inclusion of the sugar-alcohol mannitol. We also make an attempt to account for the negative as well as the positive artifact associated with sampling of OC. The approach used here is summarized in Eqs. 1–15, in Table 2, and the terms discussed in Sects. 3.1–3.9.

Each step of this analysis has a level of uncertainty, but a major advantage of the present study compared to those presented in e.g. Gelencsér et al. (2007) and Szidat et al. (2006, 2009) is that almost all parameters are derived from self-consistent studies from Oslo and surrounding areas. In particular, Yttri et al. (2009) reported very high correlations ( $R > \sim 0.9$ ) between levoglucosan and OC in the small town of Elverum, 120 km east of Oslo, during wintertime sampling, and that the wood-burning contribution to OC/EC/TC was estimated to be close to 100%. (This contribution likely includes both primary and secondary components, see Sect. 3.3). Further, related studies by Yttri et al. (2007b, 2005) and Dye and Yttri (2005) all provide a comprehensive background to the nature of the carbonaceous aerosol in Norway, and on the contribution of wood-burning and PBAP. These data have a number of advantages for our analysis:

- Location: Emission sources at Elverum (type of wood, appliance, etc.) are expected to be similar to those around the sampling sites in the current study.
- Consistency of analytical methodology: The analytical methodology used to quantify the samples contents of EC/OC and levoglucosan in the present study is identical to that reported by Yttri et al. (2009), thus excluding many of the problems associated with differences in analytical methods, e.g. the EC/OC split. Consequently, one does not require any assumptions about the equivalence of the ambient data with those of an emission inventory.

- Consistency of sampling: In the present study the corrections for the positive sampling artifact of OC are consistent with the procedures of Yttri et al. (2009).

Uncertainties still remain of course, and following Gelencsér et al. (2007) we define both a central best-estimate value for each factor and a plausible range of uncertainty. In order to tackle the multitude of possible combinations of uncertain parameters, we have made use of an effective statistical approach known as Latin-hypercube sampling (LHS) (Iman et al., 1981; Beachkofski and Grandhi, 2002; McKay et al., 1979). LHS approaches are somewhat similar to Monte Carlo calculations, and allow vast numbers of combinations of input variables to be computed. A Monte-Carlo simulation would involve testing all possible combinations of input parameters. LHS provides a much more effective way of sampling the data, and for our purposes provides essentially the same results as a full Monte-Carlo analysis. We used the software available at [http://people.scs.fsu.edu/~burkardt/f\\_src/ihs/ihs.html](http://people.scs.fsu.edu/~burkardt/f_src/ihs/ihs.html) for this purpose. Due to the paucity of information on the input factors, parameters are (unless otherwise noted below) assigned equally between the low limit and the central value and between the central value and the high limit. The reasoning behind some of the design-decisions behind the LHS approach as used here is expanded in the Supplement, Appendix S1. All valid combinations of parameters (i.e. excluding those producing negative contributions) are condensed in frequency distributions of possible solutions. Table 2 describes the equations that are used for the source-apportionment analysis, and Table 3 summarizes the central-estimates and range of uncertainty for each factor. The rationale for each value is provided in Sects. 3.1–3.9.

Further, in the Supplementary material (Fig. S1), we briefly present the results of an alternative set of calculations, in which even wider uncertainty ranges have been utilized for one of the key factors,  $(OC/TC)_{bb}$ . These alternative calculations are presented partly to illustrate what happens with other sets of assumptions, and partly to demonstrate the robustness of the source-apportionment methodology.

### 3.1 Estimation of EC, c.f. Eq. (1)

As discussed extensively by Schmid et al. (2001), different analytical methods give rather similar values for TC, but very different values for EC; i.e. more than a factor of 2 differences for EC concentrations measured by various techniques. Ideally, the same analytical method should be used when establishing the emission ratios including EC (e.g.  $(OC/EC)_{bb}$ ) as that used for analysis of the ambient aerosol content of EC. Since thermal-optical analysis, used in the present study, is the most accepted and widely used technique for EC measurements and also used for the emission ratio assumptions in the present study, we have adopted a narrower range of uncertainty,  $\Phi_{EC}$ , than that found by Schmid et al. (2001), with low, central and best estimates of 0.75, 1.0 and 1.25.

### 3.2 Estimation of OC, TC, c.f. Eqs. (2–3)

Collection of ambient aerosol filter samples for analysis of the particulate phase OC content is associated with both positive and negative sampling artefacts. As discussed by Chow et al. (2010), the positive artifact is usually bigger than the negative one. We assume this to be true for the Nordic countries as well, thus, the true OC should lie between the measured front and back filter values, i.e. between  $OC_F$  and  $OC_B$ . Hence, we make use of the  $\Phi_{NA}$  term in Eq. (2), and have assigned the low, central, and high value of OC to be  $OC_p$ ,  $OC_p + 0.2 \times (OC_F - OC_B)$ ,  $OC_F$ .

Given EC and OC, TC is derived simply as  $EC + OC$  Eq. (3).

### 3.3 Estimation of $TC_{bb}$ , c.f. Eq. (4)

On a mass basis, the largest source of biomass burning emission in Norway, and neighbouring countries, is wood burning in stoves and fireplaces used for residential heating. Wildfires may occasionally impact PCM in Norway (Tsyro et al., 2007; Yttri et al., 2007a), but the contribution seems to be low in general. During the summertime measurement period in the current study, no nearby fire-activity was detected by MODIS (<http://modis-fire.umd.edu>).

Levoglucosan (LG) is emitted in high concentrations from wood burning and is regarded as a highly useful tracer of wood burning emissions (e.g. Schauer et al., 2001; Simoneit, 2002). A large number of studies concerning the emission ratio  $((OC/LG)_{bb}$  or  $(TC/LG)_{bb}$ ) is available, and their suitability with respect to European conditions has been discussed by Gelencsér et al. (2007); Puxbaum et al. (2007) and Simpson et al. (2007).

Here we make use of the emission ratios estimated by Yttri et al. (2009) for Norwegian urban areas. They reported a best-fit  $(TC/LG)_{bb}$  ratio of 20 for  $PM_{10}$  and 16 for  $PM_{2.5}$ , with most data falling within 14–23 and 10–18 respectively. These data were based upon a quartz-behind-teflon (QBT) sampling protocol. In the present study, levoglucosan was collected on a quartz-behind-quartz fiber filter setup (QBQ), which have been shown to retain some levoglucosan compared to Teflon filters (Dye and Yttri, 2005). Based upon Dye and Yttri (2005), we have applied a factor of 0.76 to the ratios to account for the difference between QBT and QBQ protocols, and other corresponding central-estimate values and corresponding ranges of  $(TC/LG)_{bb}$  would then be 15 (11–17) for  $PM_{10}$  and 12 (7.6–14) for  $PM_{2.5}$ . For the LHS analysis, we allow for the possibility that the lowest ratio for  $PM_{2.5}$  (7.6) is also appropriate for  $PM_{10}$ , resulting in the ranges shown in Table 3.

It is hard to prove if modern carbon is due to biomass burning or other sources of modern carbon, e.g. BSOA, and to distinguish primary from rapidly formed secondary components. As noted in Szidat et al. (2009),  $OC_{bb}$  when derived from ambient  $(OC/LG)_{bb}$  measurements may be higher

**Table 3.** Summary of uncertainty factors used in the LHS analysis. Low, central and high values are listed.

Parameters	Low	Central*	High	Equation	Comment
$\Phi_{\text{EC}}$	0.75	1.0	1.25	1	Uncertainty in EC
$\Phi_{\text{NA}}$	0.0	0.2	1.0	2	Artefact uncertainty, Sect. 3.2
$(\text{TC/LG})_{\text{bb}}$ , $\text{PM}_{10}$	11	15	17	4	Ratio in emissions
$(\text{TC/LG})_{\text{bb}}$ , $\text{PM}_{2.5}$	7.6	12	14		Ratio in emissions
$(\text{OC/TC})_{\text{bb}}$ , $\text{PM}_{10}$	0.73	0.78	0.82	5	Ratio in emissions
$(\text{OC/TC})_{\text{bb}}$ , $\text{PM}_{2.5}$	0.66	0.71	0.76		Ratio in emissions
$(\text{OC/EC})_{\text{POA}}$	0.2	0.6	1.3	14	Ratio in emissions
$\text{OC}_{\text{pbc}}/\text{Cel.}$	0.8	1.6	3.2		See Sect. 3.5
$\text{OC}_{\text{pbs}}/\text{Mannitol}$	5.2	–	10.8	9	See section 3.6
$\Phi_{\text{F}^{14}\text{C}}$	0.95	1.0	1.05	11	Uncertainty in $\text{F}^{14}\text{C}$ , Sect. 3.7
$\text{F}^{14}\text{C}_{\text{bb}}$	1.055	–	1.25	12	See Sect. 3.7
$\text{F}^{14}\text{C}_{\text{spores}}$	1.055	–	1.25	12	See Sect. 3.7
$\text{F}^{14}\text{C}_{\text{debris}}$		1.055		12	See Sect. 3.7

\* Where no central value is given, the value used is simply the mean of the low and high values.

when compared to data derived from ratios from laboratory emission studies, as the data derived from ambient measurements include some condensed and secondary OC. Indeed, Grieshop et al. (2009b,a) demonstrated in smog chamber experiments that wood-burning SOA actually may reach up to similar levels as POA. Heringa et al. (2011) found similar results in a smog-chamber even with winter light conditions, and Lanz et al. (2010) found some evidence for secondary  $\text{OC}_{\text{bb}}$  in field data. Thus, we regard the  $\text{TC}_{\text{bb}}$  values derived here from levoglucosan as an “operational” definition. The ratios used in the present study were derived from wintertime ambient measurements (Yttri et al., 2009) and may also include condensed vapors and secondary products.

### 3.4 Estimation of $\text{OC}_{\text{bb}}$ , $\text{EC}_{\text{bb}}$ , $\text{EC}_{\text{ff}}$ , c.f. Eqs. (5–7)

Analysis of the Yttri et al. (2009) data suggests best values for  $(\text{OC/TC})_{\text{bb}}$  of 0.78 for  $\text{PM}_{10}$  and 0.71 for  $\text{PM}_{2.5}$ . In general the range of variation of this ratio was small, with the uncertainty range given in Table 3 encompassing most points. We also assume that the ratios found for  $\text{PM}_{2.5}$  in this earlier study can be applied for  $\text{PM}_1$  here, since most direct combustion emissions are in the sub-micron mode. Given  $\text{TC}_{\text{bb}}$  and  $\text{OC}_{\text{bb}}$ ,  $\text{EC}_{\text{bb}}$  is the difference, Eqs. (4–5), and  $\text{EC}_{\text{ff}}$  is derived simply as the difference between EC and  $\text{EC}_{\text{bb}}$ .

For the sensitivity analysis presented in Supplementary information, we have adopted a wider range for these  $(\text{OC/TC})_{\text{bb}}$  values, to reflect findings from other studies. For example, Gilardoni et al. (2011) used a very wide range of  $(\text{OC/EC})_{\text{bb}}$ , from 1–20, equivalent to  $(\text{OC/TC})_{\text{bb}}$  between 0.5 – 0.95. Grieshop et al. (2009b) also found a wide range, 1.1–13, in  $(\text{OC/EC})_{\text{bb}}$  ratios in fresh emissions, and demonstrated that photochemical production of SOA quickly enhanced the OC/EC ratio which would make it hard to distinguish biomass-burning POA from SOA in ambient samples.

Both of these studies make use of non-European tree data, however. Heringa et al. (2011) found very low OM/EC values ( $<0.5$ ) in some conditions in smog-chamber studies, but again the wood-types used (beech logs and pellets) are less important than birch or softwoods in Norway. Given the differences in wood-types and study methodology, we believe the extreme values in these studies are probably less relevant to SORGA than the ambient-data based Yttri et al. (2009) results. However, for the sensitivity study we allow low, central and high values of  $(\text{OC/TC})_{\text{bb}}$  of 0.66, 0.82, 0.95.

### 3.5 Estimation of $\text{OC}_{\text{pbc}}$ from plant debris, c.f. Eq. (8)

Similar to Gelencsér et al. (2007) and Sánchez-Ochoa et al. (2007) the contribution of plant debris to the carbonaceous aerosol is estimated from the measured amount of free cellulose. Free cellulose forms on average about 72 % of total cellulose. Further, for the mass balance the amount of plant debris has to be expressed in carbon equivalent, which is about 57 % of the total mass. Plant debris is assumed to be about two times the concentration of total cellulose (Puxbaum and Tenze-Kunit, 2003). Thus, measured cellulose concentrations were multiplied by a factor of 1.6 ( $=0.57 \times 2/0.72$ ) as a best-estimate of the contribution of  $\text{OC}_{\text{pbc}}$  on a carbon equivalent basis. As in Gelencsér et al. (2007), a factor of two is used in the uncertainty estimates.

### 3.6 Estimation of $\text{OC}_{\text{pbs}}$ from fungal spores, c.f. Eq. (9)

$\text{OC}_{\text{pbs}}$  is calculated from mannitol. Bauer et al. (2008a) found that mannitol accounted for 1.2–2.5  $\text{pg spore}^{-1}$  and that the spores OC content was 13  $\text{pg OC spore}^{-1}$  (Bauer et al., 2002). This indicates that  $\text{OC}_{\text{pbs}}$  to mannitol ratios are ranging from 5.2–10.8.



A mean mannitol-to-arabitol ratio of  $1.5 \pm 0.5$  can be deduced from the study of Bauer et al. (2008a). The 24 h mean mannitol-to-arabitol ratios observed for  $\text{PM}_{10}$  in summer (Oslo:  $1.4 \pm 0.3$ ; Hurdal:  $1.3 \pm 0.5$ ) in the present study (Table 5) were within the range reported by Bauer et al. (2008a), thus justifying our use of their findings. During winter the ratio was slightly lower (Oslo:  $1.1 \pm 0.3$ ; Hurdal:  $1.3 \pm 0.5$ ) and the variation greater, for unknown reasons. Further, the mannitol-to-arabitol ratio had a diurnal variation in summer, with a higher ratio during night compared to the day. This could indicate influence from various genera of fungi.

### 3.7 Estimation of $F^{14}\text{C}$ , $F^{14}\text{C}_{\text{bb}}$ , $F^{14}\text{C}_{\text{spores}}$ Eq. (11)

$F^{14}\text{C}$  is the so-called modern fraction of  $^{14}\text{C}$ , indicating of the amount of contemporary carbon in the aerosol. Fossil-fuels have  $F^{14}\text{C}$  values of zero, and recently grown vegetation has  $F^{14}\text{C}$  values close to 1. A  $F^{14}\text{C}$  value of 1.0 approximately refers to conditions before the atomic bomb tests of the 1950s (Currie et al., 2002). The average  $^{14}\text{C}$  signature of atmospheric  $\text{CO}_2$  for the two years (2006, 2007) during which the sampling campaigns of the present study was conducted gives  $F^{14}\text{C} = 1.055$  (Szidat et al., 2009). The measured value of  $F^{14}\text{C}$  in an aerosol sample, ( $F^{14}\text{C}$ ), is one of the most accurately measured quantities in these analyses, but still has a small uncertainty due to both measurement errors and heterogeneity on the filters. We allow for a small error, of  $\pm 5\%$ , and use an uncertainty factor  $\Phi_{F^{14}\text{C}}$  (0.95–1.05) and symmetrical beta(2,2) distribution (NIST/SEMATECH, 2010) to assign probabilities around the central value. The  $^{14}\text{C}$  signature of biomass burning emissions ( $F^{14}\text{C}_{\text{bb}}$ ) is generally uncertain, ranging from 1.055 for burning of agricultural residues to a maximum of 1.25 from burning of trees (Lewis et al., 2004; Szidat et al., 2006). For plant debris, we have assumed a recent biological origin,  $F^{14}\text{C}_{\text{debris}} = 1.055$ .

Asco- and Basidiomycota (ABM) are heterotrophic organisms, i.e. they require carbon for growth and energy but cannot fix carbon themselves. ABM can acquire organic molecules from dead organic material, (e.g. dead plant leaves, logs, etc.), so-called decomposers, or as symbionts. Formation of mycorrhiza, which is a symbiotic association between quite a few ABM and the root systems of plants, makes the fungus benefit from photosynthetic products produced by the tree, which has a recent origin; i.e.  $F^{14}\text{C}$  similar to plant debris (1.055). Decomposers may live on old as well as recent substrate, thus in order to account for this we allow for a wider range of  $F^{14}\text{C}_{\text{spores}}$  (1.055–1.25) than for plant debris.

### 3.8 Estimation of $\text{OC}_{\text{BSOA}}$ c.f. Eq. (12)

$\text{OC}_{\text{BSOA}}$  is calculated from the radiocarbon balance equation (Eq. 12), assuming modern origin ( $F^{14}\text{C}_{\text{bio}} = 1.055$ ) for this aerosol component. As BSOA is thought to be generated mainly from isoprene and monoterpenes (e.g. Hallquist et al.,

2009), and these originate from recent foliage, the radiocarbon signature should be well defined.

### 3.9 Estimation of $\text{OC}_{\text{ff}}$ , $\text{OC}_{\text{POA}}$ and $\text{OC}_{\text{ASOA}}$ c.f. Eqs. (13–15)

$\text{OC}_{\text{ff}}$ , the carbon associated with fossil-fuels, is calculated as the difference between OC and the sum of  $\text{OC}_{\text{BSOA}}$ ,  $\text{OC}_{\text{pbs}}$ ,  $\text{OC}_{\text{pbc}}$  and  $\text{OC}_{\text{bb}}$ , and consists of both primary emissions ( $\text{OC}_{\text{POA}}$ ) and secondary compounds ( $\text{OC}_{\text{ASOA}}$ ). In this work, we present the further breakdown of  $\text{OC}_{\text{ff}}$  into these POA and ASOA components, albeit with the strong caveat that this is probably the most uncertain split in the source-apportionment calculations. This caveat would apply for any calculations at the end of a chain of uncertain steps, but for these components the problems are exacerbated by their nature. As discussed in Robinson et al. (2007) and Donahue et al. (2006), the relationships between tailpipe emissions of POA and OA components arising from these emissions are complex, involving evaporation and condensation of emitted gases and particles, chemical processing and partitioning. Observed OC/EC ratios which have previously been used for source-apportionment (e.g. Cabada et al., 2004; Castro et al., 1999; Gelencsér et al., 2007) cannot usually distinguish true POA from ASOA.

Nevertheless, it can be useful to distinguish POA contributions from ASOA, since both components can serve to evaluate chemical transport models (e.g. Simpson et al., 2007), and as they are subject to different control measures. As shown in eqn 14,  $\text{OC}_{\text{POA}}$  is estimated using assumed primary OC/EC ratios. Such ratios have indeed been used extensively in the past, but values vary widely. Kupiainen and Klimont (2004, 2007) estimated non-biomass  $(\text{OC}/\text{EC})_{\text{POA}}$  to be 0.71 for old EU15 countries, but 1.2 for new member states. Gelencsér et al. (2007) used 0.48 (range 0.48–1.2), largely on the basis of Austrian tunnel studies. More recent studies using aerosol mass spectrometer AMS instruments found OA/BC ratios of 12–44% in fresh emissions from in-use diesel engines in a chamber (Chirico et al., 2010). Tunnel measurements with AMS instruments demonstrated important effects of partitioning on OA/BC ratios, with OA/BC ratios of ca. 0.4 at low organic loadings ( $\sim 10 \mu\text{g m}^{-3}$ ) to about 1.5 for OA of 100–200  $\mu\text{g m}^{-3}$  (Chirico et al., 2011). With an OM/OC ratio of about 1.3 (*ibid.*), this suggests OC/EC ratios of around 0.3 for ambient vehicular emission ratios. Gilardoni et al. (2011) used a range for  $(\text{OC}/\text{EC})_{\text{POA}}$  from 0.3 to 1.2. Given this variability, we have adopted the wide range of  $(\text{OC}/\text{EC})_{\text{POA}}$  ratios (from 0.2 to 1.3) shown in Table 3, using the same range for both PM size fractions.

## 4 Results

### 4.1 PM<sub>10</sub> and PM<sub>1</sub> mass concentrations

Mean concentrations of PM<sub>10</sub> and PM<sub>1</sub> are presented in Table 4. These values are similar to annual mean concentration ranges of PM<sub>10</sub> and PM<sub>2.5</sub>/PM<sub>1</sub> previously reported for Norwegian urban and rural environments (Yttri, 2007). The rather short duration of the two sampling periods conducted in the present study could influence their representativeness; e.g. summer time concentrations are found to be higher than or equal to the concentrations observed during winter, which is opposite of that commonly seen (Yttri, 2007). PM<sub>1</sub> accounted for a larger fraction of PM<sub>10</sub> at the rural background site compared to the urban background site. Also, the PM<sub>1</sub>-to-PM<sub>10</sub> ratio was higher in winter compared to summer.

### 4.2 EC and OC concentrations

The carbonaceous aerosol (here: EC, OC<sub>p</sub>, TC<sub>p</sub>) concentrations (see Table 4) observed at the urban background site is in the lower range of that previously reported for Norwegian urban areas (Yttri et al., 2005, 2009), whereas it is in the upper range of what has been observed for the rural environment (Yttri et al., 2007a). The levels of OC<sub>p</sub> and TC<sub>p</sub> should be considered as conservative estimates, as the QBQ sampling approach account for the positive but not the negative sampling artefact of OC (see Sect. 2.2). The mean positive artifact of OC ranged from  $18 \pm 8.6\%$  for the urban background site in winter to  $50 \pm 14\%$  at the rural background site in winter.

The difference between the urban- and the rural background site with respect to the OC<sub>p</sub> level is relatively small in summer (25–30% higher at the urban background site), whereas the difference was substantially larger (a factor 2.4–2.8 higher at the urban background site) in winter. EC had a similar pattern, with urban background levels being 50% higher compared to the rural background site in summer and a factor of approximately 3 higher in winter.

Levels of OC<sub>p</sub> in PM<sub>10</sub> were higher in summer than during winter at the urban background site, whereas it is opposite for PM<sub>1</sub>. For EC, levels were higher in winter for both size fractions. At the rural background site, levels of OC<sub>p</sub> were substantially higher in summer compared to winter. This seasonal variation was more pronounced for PM<sub>10</sub> than for PM<sub>1</sub>. For EC, a similar pattern as for OC<sub>p</sub> was observed for PM<sub>10</sub>, whereas for PM<sub>1</sub> the levels remained unchanged.

Only minor differences in the EC/TC<sub>p</sub> ratio were observed between the two sites, regardless of season and size fraction. The EC/TC<sub>p</sub> ratio was found to be substantially higher in winter (27–31%) compared to summer (16–21%) at both sites and for both size fraction.

### 4.3 Organic tracers concentrations

Ambient mean concentrations of the wood burning tracer levoglucosan are reported in Table 4. The mean concentration observed at the urban background site in winter ( $130 \text{ ngm}^{-3}$ ) was lower than that previously reported by Yttri et al. (2005) for Norwegian urban areas during winter time sampling (i.e.  $166\text{--}407 \text{ ngm}^{-3}$ ). At the rural background site, the winter time mean levoglucosan concentration ( $40 \text{ ngm}^{-3}$ ) was 2–3 times higher than that reported by Yttri et al. (2007b) for the rural background site Birkenes in southern Norway. The levoglucosan concentration was 3–5 times higher in winter compared to summer.

Levels of sugars and further sugar alcohols (see Table S1 of the Supplement) were within the range previously reported for Scandinavian and continental rural (Carvalho et al., 2003; Ion et al., 2005; Yttri et al., 2007b) and urban background (Yttri et al., 2007b) environments in Europe. Higher concentrations in summer compared to winter were observed for all species. In summer, the highest concentrations were seen at the rural background site (except for ribose), whereas it was the opposite way around in winter. With the exception of ribose and fructose, close to 90% of the sugars and sugar-alcohols observed in summer could be attributed to the coarse fraction of PM<sub>10</sub>. A similar calculation could not be performed for the samples collected during the winter campaign.

The content of cellulose in the ambient aerosol has been reported in a very few studies only (Kunit and Puxbaum, 1996; Puxbaum and Tenze-Kunit, 2003; Sánchez-Ochoa et al., 2007). The cellulose concentrations observed in the present study, ranging from  $5\text{--}130 \text{ ngm}^{-3}$ , are comparable to those observed for the European rural background environment by Sánchez-Ochoa et al. (2007), as is the seasonal variation with increased concentrations in summer.

### 4.4 Radiocarbon, F<sup>14</sup>C

The F<sup>14</sup>C values are reported in Table 4. We find that F<sup>14</sup>C was higher at the rural background site compared to the urban background site, regardless of season and size fraction. In addition, F<sup>14</sup>C was typically higher in summer compared to winter at both sites. The F<sup>14</sup>C values show no diurnal variation, except for PM<sub>1</sub> at the urban background site in winter; i.e. F<sup>14</sup>C was 0.70 during the night and 0.59 during the day.

F<sup>14</sup>C appears to be in the upper range of, or higher than, values reported for European and US urban and rural areas by Glasius et al. (2011); Heal et al. (2011); Hodzic et al. (2010).

### 4.5 Source apportionment analysis

The best estimate concentration, the 10th and the 90th percentile of the carbonaceous fractions in PM<sub>10</sub> and PM<sub>1</sub>, as calculated by Latin Hypercube Sampling (LHS) are presented in Fig. 1 and Tables S2–S5 of the Supplement,

**Table 4.** Measured concentrations of aerosol components.

Size	Site	Season	Period	PM $\mu\text{g m}^{-3}$	OC $\mu\text{g Cm}^{-3}$	OC <sub>p</sub> $\mu\text{g Cm}^{-3}$	EC $\mu\text{g Cm}^{-3}$	TC <sub>p</sub> $\mu\text{g Cm}^{-3}$	F <sup>14</sup> C frac	Levo. $\text{ng m}^{-3}$	Mannitol $\text{ng m}^{-3}$	Cellulose $\mu\text{g m}^{-3}$
PM <sub>10</sub>	U	S	Day	14.8	4.04	3.15	0.68	3.83	0.73	29	24	0.18
PM <sub>10</sub>	U	S	Night	16.1	3.56	2.82	0.74	3.56	0.72	53	26	0.069
PM <sub>10</sub>	U	S	24 h	15.4	3.8	2.98	0.71	3.70	0.73	40	25	0.13
PM <sub>10</sub>	R	S	Day	11.4	3.76	2.36	0.45	2.81	–	8.3	28	–
PM <sub>10</sub>	R	S	Night	11.3	3.64	2.54	0.49	3.03	–	12	64	–
PM <sub>10</sub>	R	S	24 h	11.3	3.70	2.45	0.47	2.92	0.93	10	45	0.066
PM <sub>10</sub>	U	W	Day	10.8	3.18	2.53	0.99	3.52	0.59	118	3.2	0.026
PM <sub>10</sub>	U	W	Night	9.88	2.38	1.98	0.86	2.85	0.63	142	2.6	0.034
PM <sub>10</sub>	U	W	24 h	10.3	2.78	2.26	0.93	3.18	0.61	130	2.9	0.03
PM <sub>10</sub>	R	W	Day	5.53	1.58	1.02	0.30	1.32	–	51	0.78	–
PM <sub>10</sub>	R	W	Night	4.46	1.09	0.69	0.29	0.99	–	53	0.53	–
PM <sub>10</sub>	R	W	24 h	4.99	1.34	0.86	0.30	1.15	0.68	52	0.65	0.043
PM <sub>1</sub>	U	S	Day	7.31	2.67	1.83	0.34	2.17	0.65	29	(a)	0.006
PM <sub>1</sub>	U	S	Night	7.87	2.33	1.72	0.58	2.29	0.66	53	(a)	0.005
PM <sub>1</sub>	U	S	24 h	7.60	2.50	1.77	0.46	2.23	0.65	40	1.5	0.0055
PM <sub>1</sub>	R	S	Day	7.67	2.84	1.44	0.28	1.72	–	8.3	–	–
PM <sub>1</sub>	R	S	Night	6.83	2.36	1.36	0.26	1.62	–	12	–	–
PM <sub>1</sub>	R	S	24 h	7.66	2.60	1.40	0.27	1.67	0.83	10	2.1	0.005
PM <sub>1</sub>	U	W	Day	8.04	2.33	2.02	0.81	2.83	0.59	118	(a)	0.01
PM <sub>1</sub>	U	W	Night	7.48	2.04	1.67	0.76	2.43	0.70	142	(a)	0.002
PM <sub>1</sub>	U	W	24 h	7.76	2.19	1.84	0.78	2.63	0.64	130	1.3	0.006
PM <sub>1</sub>	R	W	Day	4.50	1.67	0.79	0.23	1.04	–	51	–	–
PM <sub>1</sub>	R	W	Night	4.14	0.97	0.76	0.30	1.06	–	53	–	–
PM <sub>1</sub>	R	W	24 h	4.32	1.32	0.77	0.27	1.05	0.70	52	1.8	0.012

Notes: Sites are (U)rban: Oslo, (R)ural: Hurdal; Seasons are (S)ummer = 19 June–15 July 2006, (W)inter = 1 March–8 March, 2007; (a) day and night mannitol not measured, but assumed equal to 24 h value for LHS analysis. (Values are very small, so have little impact on the analysis).

**Table 5.** Mannitol-to-arabitol ratios for PM<sub>10</sub>.

	24 h	Day	Night
Oslo			
Summer	1.4 ± 0.3	1.3 ± 0.2	1.5 ± 0.4
Winter	1.3 ± 0.5	1.3 ± 0.5	1.3 ± 0.5
Hurdal			
Summer	1.5 ± 0.3	1.2 ± 0.2	1.7 ± 0.3
Winter	1.1 ± 0.3	1.1 ± 0.2	1.1 ± 0.5

whereas the relative contributions of these concentrations to TC<sub>p</sub> are shown in Tables 6–9. These results are discussed in detail below.

Results for the alternative calculation (with wider uncertainty ranges) are presented in Fig. S1 of the Supplement for comparison.

## 5 Discussion

The results of the source-apportionment analysis, presented in Fig. 1 and Tables 6–9 (also Tables S2–S5) show broad scale features similar to those found in previous studies: large contributions of wood-burning in winter time and large contributions of BSOA in summertime. We discuss the major components in Sects. 5.1–5.6 and in Sect. 5.7 we present an estimate of the contribution of the organic aerosol components to the total PM<sub>1</sub> and PM<sub>10</sub> mass concentrations.

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

As discussed in Sect. 3.9, the source-apportionment methodology does generate a split between the primary POA components and secondary ASOA components but this split is highly uncertain. For this reason, Fig. 1 only presents the more robust category OC<sub>ff</sub>, but the breakdown is given in the Tables.

OC originating from fossil-fuel sources (OC<sub>ff</sub>) was more abundant than OC from wood burning (OC<sub>bb</sub>) during summer, whereas it was the other way around in winter (See Tables S2–S5). Further, there was an urban background increment with respect to both OC<sub>ff</sub> and OC<sub>bb</sub> compared to the rural background site: i.e. the mean concentration of OC<sub>ff</sub> and OC<sub>bb</sub> was 2.4–4.2 times higher at the urban background site than at the rural background site, both seasons and size fractions included. The tentative POA/ASOA breakdown presented in the Tables suggests that both components are significant, but with ASOA often contributing about twice as much as POA. Smallest ASOA contributions are seen at the rural site for both PM<sub>10</sub> and PM<sub>1</sub> in summertime. In general it seems that winter conditions increase the ASOA estimate. This may be related to increased emissions of ASOA precursors, or to increased condensation mechanisms (especially for the urban site), but given the uncertainties it seems unwise to speculate further on these differences.

We find that there is almost no difference in the relative contribution of OC<sub>ff</sub> (24–33 %) and OC<sub>bb</sub> (31–38 %) to TC<sub>p</sub> in winter between the two sites, both size fractions

**Table 6.** Calculated percentage contributions to total carbon from LHS analysis, PM<sub>10</sub>, summer sampling (19 June–15 July 2006). C.E. is central estimate (50th percentile), range is 10th–90th percentiles of LHS results.

	Hurdal-24 h		Oslo-24 h		Oslo-Day		Oslo-Night	
	C.E.	Range	C.E.	Range	C.E.	Range	C.E.	Range
EC <sub>bb</sub>	1.0	(0.6–1.3)	3.2	(2.1–4.2)	2.3	(1.4–2.9)	4.5	(2–5)
EC <sub>ff</sub>	8.6	(6–10)	14	(7–18)	13	(7–18)	14	(7–19)
OC <sub>bb</sub>	3.5	(2.3–4.2)	11	(7–13)	7.9	(5–9)	16	(10–18)
OC <sub>ff</sub>	6.5	(3–9)	18	(12–24)	18	(12–23)	20	(13–26)
OC <sub>POA</sub>	4.0	(2–6)	7.7	(3–12)	7.6	(3–12)	7.9	(3–13)
OC <sub>ASOA</sub>	2.6	(0–5)	11	(2–19)	10	(2–18)	12	(2–21)
OC <sub>BSOA</sub>	56	(49–63)	38	(30–44)	43	(35–49)	32	(24–39)
OC <sub>PBAP</sub>	24	(18–30)	16	(11–20)	16	(11–21)	15	(10–18)
OC <sub>pbs</sub>	18	(13–22)	7.4	(5–9)	5.9	(4–7)	9.2	(6–11)
OC <sub>pbc</sub>	5.8	(3–9)	8.4	(4–13)	10	(5–16)	5.5	(2–8)

**Table 7.** Calculated percentage contributions to total carbon from LHS analysis, PM<sub>10</sub>, winter sampling (1–8 March 2007). C.E. is central estimate (50th percentile), range is 10th–90th percentiles of LHS results.

	Hurdal-24 h		Oslo-24 h		Oslo-Day		Oslo-Night	
	C.E.	Range	C.E.	Range	C.E.	Range	C.E.	Range
EC <sub>bb</sub>	9.7	(7–12)	9.2	(6–11)	8.9	(6–11)	10	(8–12)
EC <sub>ff</sub>	13	(4–20)	17	(7–25)	16	(7–24)	17	(6–25)
OC <sub>bb</sub>	34	(27–41)	32	(25–39)	31	(21–39)	35	(30–40)
OC <sub>ff</sub>	25	(17–33)	28	(19–37)	30	(21–39)	27	(17–36)
OC <sub>POA</sub>	7.8	(2–14)	9.7	(3–17)	10	(3–18)	9.2	(3–16)
OC <sub>ASOA</sub>	17	(5–30)	18	(5–32)	20	(6–34)	17	(4–31)
OC <sub>BSOA</sub>	11	(1–19)	11	(2–20)	12	(1–23)	8.6	(1–15)
OC <sub>PBAP</sub>	7.8	(4–12)	2.6	(1.7–3.6)	2.4	(1.6–3.3)	2.8	(1.8–4.0)
OC <sub>pbs</sub>	0.50	(0.3–0.6)	0.80	(0.5–1.0)	0.90	(0.6–1.0)	0.70	(0.5–0.9)
OC <sub>pbc</sub>	7.2	(4–11)	1.8	(0.9–2.8)	1.5	(0.8–2.4)	2.1	(1.1–3.3)

included, but that wood burning was the larger source. It might be that the rather high ambient temperature observed during the winter campaign (i.e. 2.2 °C compared to the long term mean of –1.5 °C at the urban background site) had an influence on the levoglucosan concentration, which was relatively low compared to previously reported studies (Yttri et al., 2005). In summer, the relative contribution of OC<sub>ff</sub> to TC<sub>p</sub> was higher than that of OC<sub>bb</sub> to TC<sub>p</sub> at both the urban (OC<sub>ff</sub> to TC<sub>p</sub> = 18–29%; OC<sub>bb</sub> to TC<sub>p</sub> = 8–18%) and the rural background site (OC<sub>ff</sub> to TC<sub>p</sub> = 7–11%; OC<sub>bb</sub> to TC<sub>p</sub> ~ 4%).

Combustion of fossil fuel was the major source of EC regardless of site, season, size fraction and time of the day, accounting for 9–17% of TC<sub>p</sub>. Further, there was an urban background increment for the EC<sub>ff</sub> and EC<sub>bb</sub> concentration compared to the rural background site, ranging from 1.7–3.5. As expected, the concentrations of EC<sub>bb</sub> grew larger in winter due to increased emissions from residential wood burning, accounting for about 35–60% of EC compared to 10–30% in

summer. A similar seasonal variation was reported by Szidat et al. (2006) for an urban background site in Zürich, using a combination of <sup>14</sup>C and organic tracer analysis, however the EC<sub>bb</sub> contribution to EC was slightly less in Zurich than is Oslo, i.e. 6 ± 2% in summer and 25 ± 5% in winter.

EC<sub>bb</sub> and OC<sub>bb</sub> concentrations typically increased somewhat during night, which in the present study was defined from 9 p.m.–9 a.m. Thus, the night only partly reflects the time period when people usually use their wood stoves for heating, i.e. between 5 a.m. and 11 a.m. and to some extent between 6 p.m. and 9 p.m. (Haakonsen and Kvingedal, 2001). This may explain why the diurnal variation was not more pronounced. Somewhat surprising the diurnal variation was most evident during summertime sampling. It is not obvious what caused this, but reasons might include larger day/night changes in dispersion conditions, or shifts in the timing of residential or barbecue-related wood-burning emissions.

**Table 8.** Calculated percentage contributions to total carbon from LHS analysis, PM<sub>1</sub>, summer sampling (19 June–15 July 2006). C.E. is central estimate (50th percentile), range is 10th–90th percentiles of LHS results.

	Hurdal-24 h		Oslo-24 h		Oslo-Day		Oslo-Night	
	C.E.	Range	C.E.	Range	C.E.	Range	C.E.	Range
EC <sub>bb</sub>	1.9	(1.3–2.3)	5.8	(4–7)	4.3	(3–5)	7.5	(5–9)
EC <sub>ff</sub>	10	(6–14)	13	(6–18)	9.9	(4–13)	15	(7–21)
OC <sub>bb</sub>	4.5	(3–5)	14	(10–16)	10	(7–12)	18	(13–21)
OC <sub>ff</sub>	11	(6–15)	26	(20–33)	29	(23–34)	24	(16–32)
OC <sub>POA</sub>	5.4	(2–8)	8.3	(3–15)	6.6	(2–12)	8.8	(3–15)
OC <sub>ASOA</sub>	5.6	(0–11)	18	(7–29)	22	(13–31)	15	(3–27)
OC <sub>BSOA</sub>	71	(66–74)	40	(34–45)	45	(40–49)	35	(28–41)
OC <sub>PBAP</sub>	1.7	(1.2–2.1)	0.90	(0.6–1.1)	1.2	(0.8–1.5)	0.60	(0.4–0.8)
OC <sub>pbs</sub>	1.1	(0.8–1.4)	0.50	(0.3–0.6)	0.60	(0.4–0.8)	0.40	(0.2–0.4)
OC <sub>pbc</sub>	0.60	(0.3–0.9)	0.40	(0.2–0.6)	0.60	(0.3–0.9)	0.30	(0.1–0.4)

**Table 9.** Calculated percentage contributions to total carbon from LHS analysis, PM<sub>1</sub>, winter sampling (1st–8th March 2007). C.E. is central estimate (50th percentile), range is 10th–90th percentiles of LHS results.

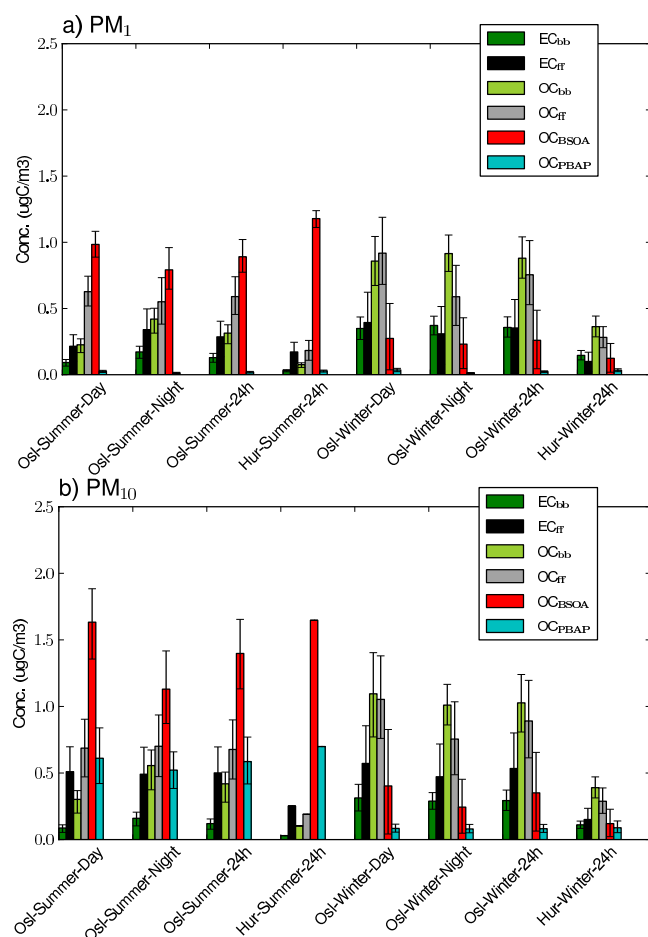
	Hurdal-24 h		Oslo-24 h		Oslo-Day		Oslo-Night	
	C.E.	Range	C.E.	Range	C.E.	Range	C.E.	Range
EC <sub>bb</sub>	14	(10–17)	14	(10–16)	12	(9–15)	15	(12–18)
EC <sub>ff</sub>	9.6	(2–16)	13	(3–21)	14	(4–22)	13	(3–21)
OC <sub>bb</sub>	35	(27–42)	34	(27–39)	30	(23–36)	38	(32–43)
OC <sub>ff</sub>	27	(19–34)	29	(20–38)	33	(24–42)	24	(15–34)
OC <sub>POA</sub>	6.2	(1–12)	8.2	(2–16)	9.0	(2–17)	7.3	(1–14)
OC <sub>ASOA</sub>	21	(8–32)	21	(6–35)	24	(8–38)	17	(4–31)
OC <sub>BSOA</sub>	12	(1–22)	9.9	(1–18)	9.7	(1–19)	9.5	(1–17)
OC <sub>PBAP</sub>	3.2	(2.2–4.3)	0.90	(0.6–1.1)	1.3	(0.8–1.7)	0.6	(0.4–0.6)
OC <sub>pbs</sub>	1.3	(0.9–1.6)	0.40	(0.3–0.5)	0.50	(0.3–0.6)	0.40	(0.3–0.5)
OC <sub>pbc</sub>	1.9	(1.0–3.0)	0.50	(0.2–0.7)	0.80	(0.4–1.2)	0.10	(0.0–0.2)

## 5.2 Biogenic secondary organic aerosol, OC<sub>BSOA</sub>

OC<sub>BSOA</sub> was a major contributor to the carbonaceous aerosol in summer, accounting for 56 % of TC<sub>p</sub> in the PM<sub>10</sub> fraction at the rural background site and 36 % at the urban background site. For PM<sub>1</sub>, OC<sub>BSOA</sub> was even more pronounced, constituting 68 % of TC<sub>p</sub> at the rural background site and 38 % at the urban background site. Summer time OC<sub>BSOA</sub> concentrations ranging from 1.1–1.7 μgCm<sup>-3</sup> were observed for PM<sub>10</sub>, whereas the range was 0.8–1.2 μgCm<sup>-3</sup> for PM<sub>1</sub>. A profound diurnal and seasonal variation was observed, with summertime OC<sub>BSOA</sub> concentrations being 1.2–1.4 times higher during daytime sampling compared to nighttime sampling, and concentrations being 1.2–1.3 times higher at the rural background site compared to the urban background site. In winter, no more than 12 % of TC<sub>p</sub> could be attributed to OC<sub>BSOA</sub>, and the concentrations were substantially lower (3–15 times) than those observed during summer. The diurnal variation was also evi-

dent in winter, while OC<sub>BSOA</sub> concentrations were found to be somewhat higher at the urban background site than at the rural background site in winter. The latter effect is presumably due to the increased condensational fraction of BSOA compounds that can arise in areas of high total OA concentrations (e.g. Donahue et al., 2009).

The reason for mean BSOA levels being higher at Hurdal than at Oslo may well be geographical. Hurdal is surrounded in all directions by forested areas, whereas Oslo lies on the edge of a fjord. Air masses arriving from southern wind directions may have passed over extensive oceanic areas. The increased daytime BSOA compared to nighttime BSOA at both sites is at first site puzzling. One simple possibility would be that the aerosol is being generated by fairly local sources, and since BVOC emissions are higher in daytime the BSOA contribution should also be higher. Modelling or observation-derived studies (e.g. Simpson et al., 2007; Tunved et al., 2006) suggest that BSOA formation should be a long-range process however, except for extreme situations



**Fig. 1.** Best estimate concentrations ( $\mu\text{g C m}^{-3}$ ) of different carbonaceous particle fractions for the SORGA samples. Uncertainty bars represent 10 and 90 percentiles from LHS calculations.

such as Mexico city (Jimenez et al., 2009). Another possibility is related to loss processes. Many OA species are expected to be lost to deposition (Bessagnet et al., 2010; Halquist et al., 2009), and near-surface loss rates will be greater at night, below any nocturnal boundary layer.

As discussed in Sect. 3.3, some of the modern carbon assigned to BSOA might instead represent SOA from biomass burning, since both sources of modern carbon are hard to distinguish. The use of  $(\text{TC/LG})_{\text{bb}}$  from ambient data helps to minimise this problem, but as with  $\text{TC}_{\text{bb}}$  we need to regard BSOA as an operational definition.

### 5.3 Primary biological aerosol particles $\text{OC}_{\text{PBAP}}$

Fungal spores and plant debris are likely the major sources of  $\text{OC}_{\text{PBAP}}$ . In the present study, OC associated with fungal spores ( $\text{OC}_{\text{pbs}}$ ) and plant debris ( $\text{OC}_{\text{pbc}}$ ) was calculated based on the aerosol filter samples content of mannitol and cellulose, respectively. The results show that  $\text{OC}_{\text{PBAP}}$  (here:  $\text{OC}_{\text{PBAP}} = \text{OC}_{\text{pbs}} + \text{OC}_{\text{pbc}}$ ) comprised on average

16 % of  $\text{TC}_{\text{p}}$  in  $\text{PM}_{10}$  at the urban background site and 24 % of  $\text{TC}_{\text{p}}$  in  $\text{PM}_{10}$  at the rural background site in summer.  $\text{OC}_{\text{pbs}}$  and  $\text{OC}_{\text{pbc}}$  contributed approximately equally to  $\text{TC}_{\text{p}}$  at the urban background site, whereas the fungal spore contribution was about three times higher than that of plant debris at the rural background site. In winter, the  $\text{OC}_{\text{PBAP}}$  contribution to  $\text{TC}_{\text{p}}$  was substantially lower than in summer. A higher relative contribution of  $\text{OC}_{\text{PBAP}}$  to  $\text{TC}_{\text{p}}$  at the rural site (7.8 %) compared to the urban site (2.6 %) was consistent with the pattern observed in summer. One major difference observed during winter compared to summer was that plant debris totally dominated  $\text{OC}_{\text{PBAP}}$  at the rural background site. For  $\text{PM}_{10}$ , the relative contribution of  $\text{OC}_{\text{PBAP}}$  to  $\text{TC}_{\text{p}}$  was only 1–3 % across all seasons and sites. From the results presented in Table 4 we find that  $\text{OC}_{\text{PBAP}}$  constituted about 60 % of  $\text{TC}_{\text{p,PM}_{10-1}}$  ( $1.3 \mu\text{g C m}^{-3}$ ) at the rural background site in summer, which we consider to be a very high share.  $\text{OC}_{\text{PBAP}}$  comprised a considerable contribution (ca. 40 %) to  $\text{TC}_{\text{p,PM}_{10-1}}$  ( $1.5 \mu\text{g C m}^{-3}$ ) at the urban background site as well. The abundance of  $\text{OC}_{\text{PBAP}}$  in the Scandinavian rural background environment, its pronounced seasonal variation, as well as its presence in the coarse fraction of  $\text{PM}_{10}$  have previously been addressed and reported by Yttri et al. (2007a,b) and Bauer et al. (2008b). However, this is the first time a quantitative measurement-based estimate of the  $\text{OC}_{\text{PBAP}}$  fraction has been made for this region. Our results confirm that  $\text{OC}_{\text{PBAP}}$  is an important source of the carbonaceous aerosol both in the rural and the urban background environment.

As  $\text{OC}_{\text{PBAP}}$  typically reside in the coarse fraction of  $\text{PM}_{10}$ , local sources can have a relatively large impact on concentrations. The apparent similarity of PBAP seen for Oslo and Hurdal is misleading: there are great differences in the relative composition of  $\text{OC}_{\text{PBAP}}$  with respect to  $\text{OC}_{\text{pbs}}$  and  $\text{OC}_{\text{pbc}}$  at the two sites (see above), implying that different source types contribute to  $\text{OC}_{\text{PBAP}}$  at the two sites. This is further supported by the diurnal and seasonal variation of the individual sugars and sugar-alcohols (Table S1). For example, arabitol, mannitol and trehalose in  $\text{PM}_{10}$  all peak during the night at the rural background site in summer, which likely reflects nocturnal discharge of fungal spores (Graham et al., 2003; Ion et al., 2005), while this is not observed at the urban background site. We also find that the individual concentrations of all sugars and sugar-alcohols are higher at the urban background site than for the rural background site in winter.

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

Carbonaceous aerosols arising (either as primary or secondary components) from fossil-fuel sources and biomass combustion ( $\text{EC}_{\text{bb}}$ ,  $\text{EC}_{\text{ff}}$ ,  $\text{OC}_{\text{bb}}$  and  $\text{OC}_{\text{ff}}$ ) are here defined as anthropogenic. Wild fire emissions can obviously be categorized as natural in cases when ignited by lightning,

but most incidences are due to human activity (Achard et al., 2008; Winiwarter et al., 1999). However, as noted in Sect. 3.3 no nearby fire-activity was detected by MODIS for this summertime measurement period.  $OC_{BSOA}$  and  $OC_{PBAP}$  are defined as natural sources, although anthropogenic emissions facilitate the transformation of biogenic VOCs to  $OC_{BSOA}$  (Tsigaridis and Kanakidou, 2003; Carlton et al., 2010; Donahue et al., 2009) and increased concentrations of  $OC_{PBAP}$  has been found in association with sewage plants and are associated with other anthropogenic activities as well, e.g. house demolition and agricultural activities (Matthias-Maser, 1998, and references therein).

As expected, natural sources were found to be particularly abundant in summer, and with a more pronounced influence at the rural compared to the urban background site. At the rural background site, 80 % of  $TC_P$  in  $PM_{10}$  and 70 % of  $TC_P$  in  $PM_1$  could be attributed to natural sources. The slightly lower percentage seen for  $PM_1$  is due to  $OC_{PBAP}$  primarily residing in the coarse fraction of  $PM_{10}$ . Natural sources accounted for about 50 % of  $TC_P$  in  $PM_{10}$  at the urban background site as well. As for the rural background site, the relative contribution of natural sources to  $TC_P$  in  $PM_1$  (ca. 40 %) at the urban background site was slightly less than for  $PM_{10}$ , but still quite substantial taken into account that it is an urban site. The natural source contribution was always dominated by  $OC_{BSOA}$ , regardless of season, site and size fraction. During winter the picture was reversed, as anthropogenic sources totally dominated the carbonaceous aerosol (ca. 80–90 %), whereas no more than ca. 10–20 % could be explained by natural sources. Combustion of biomass contributed slightly more than combustion of fossil fuel in winter, whereas emissions from fossil fuel combustion were more abundant in summer.

### 5.5 Alternative calculation

As discussed in Sect. 3.4, assumptions concerning the appropriate  $(OC/TC)_{bb}$  factor vary widely between different studies. We have preferred to use factors derived from Norwegian studies, as they are most likely to represent the biomass-burning combustion emissions for the SORGA sites, but Gilardoni et al. (2011) for example use a much wider range. For this reason we have run a version of our LHS system with  $(OC/TC)_{bb}$  factors of 0.66, 0.82 and 0.95, instead of the factors given in Table 3. Figure S1 of the Supplement illustrates the results obtained when we use these new factors.

Comparing these results with Fig. 1, the use of the wider uncertainty range is not seen to affect the main results in any important way. The biggest differences are for the  $EC_{bb}$  contributions, which are somewhat smaller with the alternative calculation. This is a direct result of allowing  $(OC/TC)_{bb}$  values as high as 0.95 (i.e. EC can be only 5 % of TC) instead of our default values of 0.82 for  $PM_{10}$  and 0.76 for fine-particles. This component is a small fraction of TC, however, and other components are not very sensitive to this uncer-

tainty. This calculation, along with a wide-range of other (unpublished) tests conducted within other projects utilizing the same basic LHS methodology (Gelencsér et al., 2007; Szidat et al., 2009; Yttri et al., 2011), confirms that the LHS methodology is quite robust with regard to the main conclusions. This conclusion should not be so surprising however, since the methodology is constrained to a large extent by the experimental data.

### 5.6 Consistency of results

The challenges associated with splitting  $OC_{PBAP}$ ,  $OC_{bb}$  and  $OC_{BSOA}$  have already been mentioned (See Sect. 3.3). As we have calculated the two major contributors to PBAP, i.e. OC associated with plant debris and fungal spores, the dominating uncertainty factors for  $OC_{BSOA}$  have been accounted for. On the other hand, the vast number of sources contributing to this highly heterogeneous group still makes the split between  $OC_{BSOA}$  and  $OC_{PBAP}$  somewhat uncertain. For example, Ceburnis et al. (2011) recently demonstrated 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. Tire debris is also a source of coarse mode contemporary carbon not accounted for in our source apportionment. Although, natural rubber only constitutes 0.5–3.5 % of the tire's tread (Edeskär, 2004) a certain contribution of contemporary carbon should be expected.

Emissions from cooking could make a significant contribution to contemporary carbon at the urban background site, while we find this less likely at the rural background site. Analysis of cholesterol from the filters could have provided valuable information on this matter, but such measurements have not been undertaken.

Nevertheless, the seasonality, the diurnal variation, and the regional character observed for  $OC_{BSOA}$  strongly support that BSOA has been quite successfully separated from other sources of contemporary carbon.

### 5.7 Carbonaceous mass contributions to PM

The preceding chapters have so far discussed estimates of the different fractions of OC and EC, and their contributions to TC. As shown in Table 4, measurements also included total  $PM_{10}$  and  $PM_1$  concentrations. We cannot make a full mass closure of these PM data as the major ions ( $SO_4^{2-}$ , etc.), and components that could quantify sea-salt or dust contributions, were not measured. However, the information arising from the source-apportionment can be used to estimate the mass contribution which the various TC components make to total PM concentrations.

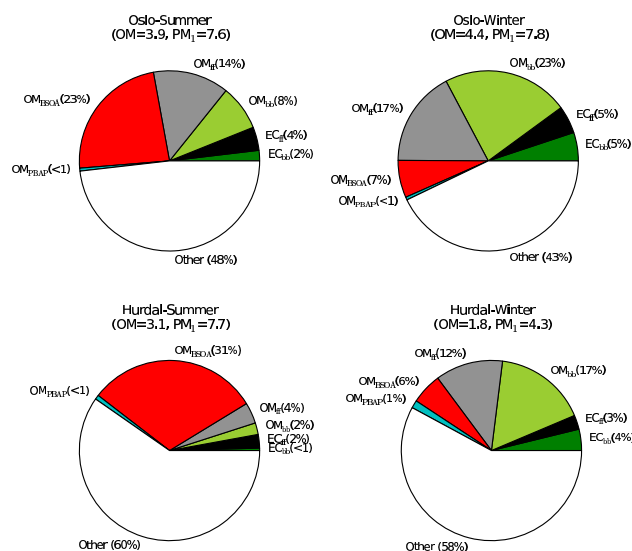
Converting the ambient aerosol OC fraction to organic matter (OM) with a high level of accuracy requires detailed speciation of OC at a level which currently is not available.

Further, using one fixed conversion factor will inevitably introduce an unknown level of uncertainty, as the source contribution varies between sites and seasons. By segregating OC into sub-fractions, and by using conversion factors for each of these, more accurate estimates of the aerosol OM fraction may be obtained. However, experimentally derived conversion factors are still scarce and would be needed for a wider range of environments to reduce the uncertainty further.

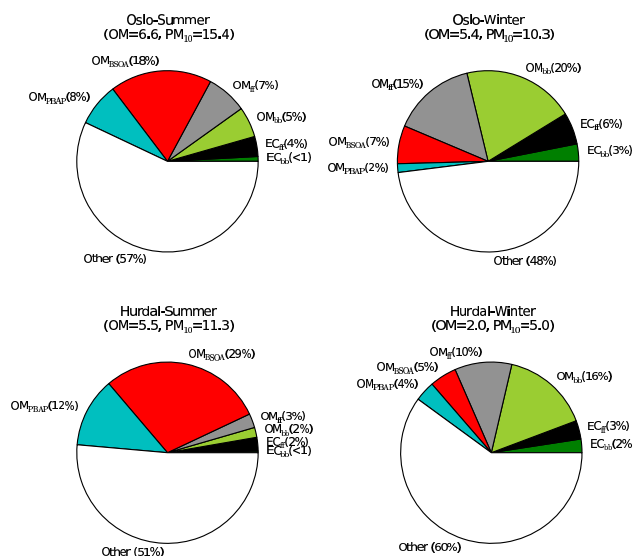
Reviewing theoretical and historic experimental conversion factors, Turpin and Lim (2001) concluded that a range of 1.9–2.3 would cover the aged aerosol, whereas 2.2–2.6 would be representative for the aerosol originating from biomass burning. A factor of 1.2–1.5 was suggested for water insoluble carbonaceous material. Their estimate for the aged aerosol has been supported by the experimentally derived conversion factor for the rural background site Kpuszta in Hungary, ranging from 1.9–2.0 (Kiss et al., 2002), whereas a conversion factor of 1.1 was derived for EC. Recently, OC:OM ratios derived from aerosol mass spectrometer (AMS) measurements have become available, which have confirmed conversion factors around 2 for the aged aerosol and the biomass burning aerosol (e.g. Lanz et al., 2008), although lower values have also been found in many cases (Aiken et al., 2008). AMS measurements have also reported OC:OM ratios of 1.2 for the hydrogenated organic aerosol (HOA) fraction likely to originate from traffic (Lanz et al., 2008). In the present study we have used a conversion factor of 2.0 for OC from wood burning ( $OC_{bb}$ ) and for SOA. Although tentative, as discussed in Sect. 3.9, the split of  $OC_{ff}$  between ASOA and POA is also used, with an OM:OC factor 2 for the ASOA fraction, and a factor 1.2 for the primary fraction of  $OC_{ff}$ . A conversion factor of 1.75 was used for  $OC_{pbs}$  and  $OC_{pbs}$ , and 1.1 for  $EC_{bb}$  and  $EC_{ff}$ .

Figures 2 and 3 illustrate the results of this mass closure estimates. These show that that particulate carbonaceous matter, i.e. OM + EC, made significant contributions to the mass concentration of the ambient PM regardless of size fraction, season, and site category. In general, there were no pronounced differences in the relative contribution of carbonaceous matter to PM with respect to season or between the two sites, although the “other” category is larger for the rural  $PM_1$  results. A somewhat larger fraction of  $PM_1$  (ca. 40–60 %) was accounted for by carbonaceous matter compared to  $PM_{10}$  (ca. 40–50 %). The likely explanation for this similarity is simply that Oslo is a relatively small city (ca. 0.6 million inhabitants). Both sites are strongly influenced by long-range transport, providing a common background, and local activities such as wood-burning for heating take place inside Oslo as well as in the countryside affecting Hurdal.

The substantial contribution of carbonaceous aerosol from natural sources to the PM loading in summer should be emphasized. We found that about about 25 % of the urban background  $PM_1$  and  $PM_{10}$  could be attributed to natural sources, whereas for the rural background site the contribution was



**Fig. 2.** Estimated contribution of carbonaceous matter components to  $PM_1$ . Estimates use central values from LHS analysis. OM,  $PM_1$  numbers in parenthesis give total aerosol concentrations and OM in  $\mu\text{g m}^{-3}$ . See Sect. 5.7 for assumed OM:OC ratios.



**Fig. 3.** Estimated contribution of carbonaceous matter components to  $PM_{10}$ . Estimates use central values from LHS analysis. OM,  $PM_1$  numbers in parenthesis give total aerosol concentrations and OM in  $\mu\text{g m}^{-3}$ . See Sect. 5.7 for assumed OM:OC ratios.

ca. 30–40 %. In winter no more than 9 % of the PM loading could be attributed to natural sources. Due to the rather low PM experienced during this wintertime sampling at the urban background site (mean  $PM_{10}$  mass concentration of  $10.3 \mu\text{g m}^{-3}$ , compared to  $19.1 \pm 4.0 \mu\text{g m}^{-3}$  for all Norwegian urban background sites for 2009–2010), we assume that the contribution of natural sources to PM is in the upper range of what can be expected in winter.



It is interesting to note that the lack of strong seasonality found here contrasts with results found in central Europe (Lanz et al., 2010), who found much higher OM loadings in summer compared to winter. Both regions are affected by similar sources, namely wood-burning in winter and BSOA in summer, so this difference likely reflects relatively higher emissions of BSOA precursors in warmer central Europe than in Norway.

## 6 Conclusions

Source apportionment of the ambient summer- and winter time carbonaceous aerosol ( $PM_{10}$  and  $PM_1$ ) has been conducted for one urban and one rural background environment site in Norway. Statistical treatment of data from thermal optical,  $^{14}C$  and organic tracer analysis using Latin Hypercube Sampling has allowed for quantitative estimates of seven different sources contributing to the ambient carbonaceous aerosol. These are: elemental carbon from combustion of biomass ( $EC_{bb}$ ) and fossil fuel ( $EC_{ff}$ ), primary and secondary organic carbon arising from combustion of biomass ( $OC_{bb}$ ) and fossil fuel ( $OC_{ff}$ ), primary biological aerosol particles ( $OC_{PBAP}$ ) from plant debris ( $OC_{pbc}$ ) and fungal spores ( $OC_{pbs}$ ), and secondary organic aerosol from biogenic precursors ( $OC_{BSOA}$ ). Hence, this approach makes it possible to separate between natural and anthropogenic sources, which is highly important in order to sort out abatement strategies for reducing man-made emissions.

The results show that particulate carbonaceous matter (PCM) made significant contributions to the mass concentration of the ambient PM regardless of season (summer/winter) and size fraction ( $PM_{10}/PM_1$ ).

Natural sources (here: BSOA and PBAP) contributed substantially to the rural (70–80 %) and the urban background (40–50 %) of total carbon ( $TC_p$ ) loading during summer for both size fractions. The natural contribution was dominated by BSOA both for the rural (56–71 % of  $TC_p$ ) and the urban background environment (38–40 % of  $TC_p$ ), but also primary biological aerosol particles (PBAP) were found to make a noticeable contribution, (e.g. PBAP accounted for 24 % of  $TC_p$  in  $PM_{10}$  at the rural background site).

Anthropogenic sources ( $EC_{ff}$ ,  $EC_{bb}$ ,  $OC_{ff}$ ,  $OC_{bb}$ ), which includes both primary and secondary components, contributed the most (>80 %) to  $TC_p$  during winter, regardless of size fraction and environment. Fossil-fuel derived sources were the major anthropogenic contribution to  $TC_p$  in summer, whereas there was a shift to wood burning in winter.

The results reported in the present study are highly complementary to those of Gelencsér et al. (2007) and Szidat et al. (2009), applying the same software/methodology, but updated for Norwegian conditions. Together they generate a picture of BSOA being the major contributor to the rural background carbonaceous aerosol during summer, not only for continental Europe, but also for its Northern parts.

In winter, BSOA levels are low, and as in parts of central Europe wood-burning makes the largest contribution. The suggested abundance of BSOA in Scandinavian winter time aerosol needs further investigation, in particular with respect to the potential confounding factors associated with compounds from wood burning, and to what extent long range transport and/or increased condensation of BSOA can contribute to the observed sources of modern carbon.

Finally, we would emphasize that use of source specific organic tracers,  $^{14}C$  and elemental analysis, combined with source apportionment and/or mass-balance approaches provide a much firmer basis for model evaluation than is possible using EC and/or OC measurements alone. The extra information enables evaluation of each component of the model system (emissions, separation of wood-burning from fossil-fuel sources, SOA formation, etc.). Such data and model evaluation are urgently needed before we can claim to understand the carbonaceous aerosol in the atmosphere. These aerosol phase measurements should be supported by simultaneous measurements of the likely biogenic and anthropogenic gas-phase precursors of the secondary carbonaceous aerosol, including their formation and degradation products.

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

<http://www.atmos-chem-phys.net/11/9375/2011/acp-11-9375-2011-supplement.pdf>.

*Acknowledgements.* This work was supported by the Norwegian SORGA Project. The work of D. S. was further supported by the EU 6th Framework Programme EUCAARI project (contract 34684), and the Swedish Clean Air Research Program ([www.scarp.se](http://www.scarp.se)), as well as by Cooperative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (EMEP) under UNECE. Christian Dye and Arve Bjerke (NILU), and Heidi Bauer and Karin Kassin (TUV), are thanked for laboratory analysis.

Edited by: A. S. H. Prévôt

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