



## Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background

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[1] Atmospheric levoglucosan has been determined as a proxy for “biomass smoke” in samples from six background stations on a west–east transect extending from the Atlantic (Azores) to the mid-European background site KPZ (K-Pusztá, Hungary). Concentration levels of levoglucosan (biannual averages) in the west–east transect range from 0.005  $\mu\text{g}/\text{m}^3$  at the oceanic background site AZO (Azores) to 0.52  $\mu\text{g}/\text{m}^3$  at AVE (Aveiro, Portugal). The atmospheric concentration of “biomass smoke” (biannual averages) was derived from the levoglucosan data with wood-type-specific conversion factors. Annual averages of wood smoke levels ranged from 0.05  $\mu\text{g}/\text{m}^3$  at AZO to 4.3  $\mu\text{g}/\text{m}^3$  at AVE. Winter (DJF) averages at the low-level sites AVE and KPZ were 10.8 and 6.7  $\mu\text{g}/\text{m}^3$ , respectively. Relative contributions of biomass smoke to organic matter (OM) range from around 9–11% at the elevated sites SIL, PDD and SBO, as well as for AZO, to 36% at the low-level site AVE and 28% at KPZ. Surprisingly high relative concentrations of biomass smoke in OM (68 and 47%) were observed for wintry conditions at the continental low-level CARBOSOL sites AVE and KPZ. Thus biomass smoke is a very important constituent of the organic material in the mid and west European background with summer contributions to organic matter of around 1–6% and winter levels of around 20% at the elevated mountain sites and 47–68% at rural flat terrain sites, not including secondary organic aerosol from biomass combustion sources.

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### 1. Introduction

[2] The major organic components of smoke particles from biomass burning are monosaccharide derivatives from the pyrolysis of cellulose, generally accompanied by smaller amounts of straight-chain aliphatic and oxygenated compounds and terpenoids from vegetation waxes, resins/gums, and other biopolymers. Levoglucosan and related degradation products from cellulose can be utilized as specific and general indicator compounds for the presence of emissions from biomass burning in samples of atmo-

spheric fine particulate matter [Simoneit *et al.*, 1999]. Levoglucosan is emitted in large amounts, is sufficiently stable and is specific to burning cellulose-containing substances [Locker, 1988; Simoneit *et al.*, 1999, 2004]. Thus it meets all important criteria to serve as an ideal molecular marker of biomass burning. A series of papers has appeared investigating the relationship of levoglucosan and PM in the exhaust of fire places and wood stoves, based on fire wood used in the United States [Fine *et al.*, 2001, 2002, 2004a, 2004b]. On the basis of these data, data from a study conducted in Austria [Schmidl, 2005] and data from field measurements in areas with high biomass smoke impact, a conversion factor for estimating the contribution of wood combustion from levoglucosan data was derived. In Europe, wood fire emissions are considered to form around 60% of the primary pyrogenic OC [Bond *et al.*, 2004]. Major sources are fuel wood combustion in the winter season, agricultural and garden waste burning, and in summer forest fires, in particular in Mediterranean countries. The factor for the conversion of levoglucosan mass concentration to biomass smoke differs between fuels and combustion types, which will be discussed in detail in section 3.3. In the following text, we use the term “biomass smoke” to include the different source types producing the levoglucosan tracer.

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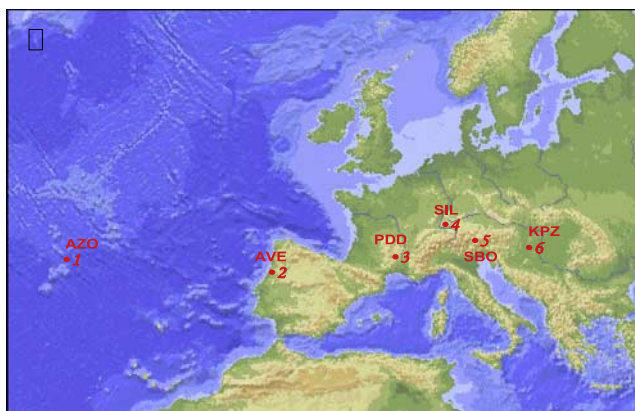
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**Figure 1.** CARBOSOL sampling sites. AZO, Azores (38°38'N, 27°02'W); AVE, Aveiro (40°34'N, 8°38'W); PDD, Puy de Dôme (45°46'N, 2°57'E); SIL, Schauinsland (47°55'N, 07°54'E); SBO, Sonnblick (47°03'N, 12°57'E); KPZ, K-Puszt (46°58'N, 19°35'E).

[3] Levoglucosan is accompanied by other stereoisomeric monosaccharides anhydrides (mannosan and galactosan) which were also detected in our samples. These compounds result from the pyrolysis of hemicelluloses, although the emitted amounts are substantially lower than those of levoglucosan [Shafizadeh, 1984]. Mannosan and galactosan are, however, not subject of this paper.

[4] Considerable research on the contribution of biomass smoke to ambient aerosol levels has been performed for rain forest areas [e.g., Andreae et al., 2002; Mayol-Bracero et al., 2002; Zdráhal et al., 2002; Formenti et al., 2003] and the aerosol outflow from the Indian subcontinent [e.g., Novakov et al., 2000; Guazzotti et al., 2003]. However, also at rural U.S. sites wood combustion constitutes a major source to atmospheric PM<sub>10</sub> or PM<sub>2.5</sub> levels [e.g., Zheng et al., 2002; Liu et al., 2005]. Other main sources of biomass smoke in North America are wild fires [Sapkota et al., 2005; Ward and Smith, 2005] and agricultural burns [Jimenez et al., 2006]. In Europe, a range of papers about smoke emissions from fire places appeared from Scandinavian groups [e.g., Johansson et al., 2003; Kjallstrand and Olsson, 2004], as well as reports about long-range transport of biomass smoke [e.g., Damoah et al., 2004]. Limited data on the contribution of wood combustion to the OC using levoglucosan as a tracer are available for Ghent, Belgium [Zdráhal et al., 2002; Pashynska et al., 2002] and Oslo, Norway [Yttri et al., 2005] during winter periods. In Ghent, this contribution was estimated to be about 35%, while in Oslo the data indicate that about 24% of the OC comes from wood burning. Using <sup>14</sup>C measurements, Szidat et al. [2006] estimated that wood combustion accounts for up to 41% of the OC during winter in Zürich, Switzerland. However, so far there was no general awareness of a wide spread wood smoke impact on fine particle levels in Europe.

[5] Here, we investigate the spatial and temporal evolution of atmospheric levoglucosan and the fraction of soluble potassium not related to sea-salt and soil particles across a west–east transect extending from the Azores to central Europe over a time span of two years. Samples from Azores, Aveiro (Portugal), Puy de Dôme (France), Schauinsland

(Germany), Sonnblick (Austria) and K-Puszt (Hungary) were obtained from the CARBOSOL sampling network. The climatologies of the two qualitative tracers of biomass combustion are compared and the observed differences discussed. The work then focuses on the spatial-temporal evolution of levoglucosan at the CARBOSOL sites in view to assess the impact of biomass combustion in the European background aerosol.

## 2. Experimental Section

### 2.1. Sampling

[6] Aerosol samples were collected at six different sampling sites across Europe. For the situation of the sites, see Figure 1; for details, see Pio et al. [2007]. The sites can be classified into low- and high-level sampling sites. Low-level sampling sites include the Azores (Terceira Islands, Portugal, 50 m asl, maritime background site; AZO), Aveiro (Portugal, 40 m asl, rural coastal site with maritime influence; AVE), and K-Puszt (Hungary, 136 m asl, rural continental site; KPZ). High-level sampling sites are at Schauinsland (Germany, 1205 m asl, rural mountain site; SIL), Puy de Dôme (France, 1405 m asl, continental background mountain site; PDD) and Sonnblick (Austria, 3106 m asl continental background/free troposphere site; SBO). The aerosol sampling period was for two years (mid-2002 to mid-2004). At AVE and AZO, sampling was performed from July 2002 until July 2004. At KPZ, sampling began in July 2002 and ended in May 2004. At PDD, SIL and SBO, the aerosol collection was performed from October 2002 to October 2004. Weekly aerosol samples were collected with a High Volume Sampler (Hi-Vol) on quartz fiber filters. At AZO, AVE, and KPZ, home-built Hi Vol samplers were deployed [see Pio et al., 2007], while at PDD, SIL and SBO, manually operated DIGITEL's DH77 samplers with PM<sub>2.5</sub> or dual size (PM<sub>2.5</sub>, PM<sub>10-2.5</sub>) inlets were used. All data reported are for the PM<sub>2.5</sub> size fraction. The typically sampled volumes in a week ranged from 3020 to 10700 Nm<sup>3</sup> for the different sampling sites.

### 2.2. Analysis

#### 2.2.1. Determination of Levoglucosan

[7] Methods for the determination of levoglucosan have been reviewed by Schkolnik and Rudich [2006]. In the present work, we apply a HPLC method with a column for separation of carbohydrates. Filter parts of around 5–12 cm<sup>2</sup> (1–5% of the filter area) were used. The filter parts were extracted with 2–4 mL Milli-Q water in an ultrasonic bath (45 min). Samples were introduced into the chromatographic system with a SPARK sample changer. The vials used were 1.5 mL Eppendorf PP, and about 1 mL of the centrifuged extract was used for analysis. The injected volume was 10 μL.

[8] The determination of levoglucosan was performed with an electrochemical detector (ED40, Dionex). The detection mode was pulsed amperometry with a gold working electrode. The detector potential waveform applied was +0.10 V from seconds 0.00–0.40; –2.00 V for seconds 0.41–0.42; +0.60 V for seconds 0.43; and –0.10 V for seconds 0.44–0.50. Integration took place during the time step 0.20–0.40 s. The separation was performed on a high

**Table 1.** Biannual Average, Minimum, and Maximum Concentrations of Levoglucosan in Monthly Pooled Samples at the CARBOSOL Sampling Sites, as Well as in Summer and Winter Periods (Meteorological Summers and Winters, in Parentheses Summer and Winter Half Years) and Winter/Summer Ratios<sup>a</sup>

Levoglucosan, ng/m <sup>3</sup>	AZO, 50 m	AVE, 40 m	PDD, 1405 m	SIL, 1205 m	SBO, 3106 m	KPZ, 136 m
Average	5.2	517	17.0	24.4	7.8	309
Minimum	0.3	19.6	1.6	7.2	<0.7	13.0
Maximum	19.2	1651	46.5	55.5	55.6	922
Summer	2.0 (2.3)	31.5 (76.3)	7.1 (11.4)	12.3 (16.9)	10.2 (5.5)	21.1 (66.3)
Winter	6.6 (8.5)	1290 (957)	18.3 (21.6)	33.7 (32.0)	12.4 (9.9)	653 (576)
Winter/summer	3.3 (3.7)	41.0 (12.5)	2.6 (1.9)	2.7 (1.9)	1.2 (1.8)	31 (8.7)

<sup>a</sup>Summer: First number is the average of June, July and August; number in brackets is the 6 month average (April–September). Winter: First number is the average of December, January and February; number in brackets is the 6 month average (October–March).

pH anion exchange column for sugar analysis (DIONEX CarboPac PA1, 250 × 4 mm). The eluent was NaOH 0.5 mM from the start to the fifth min. Elution was achieved by mixing Milli-Q water as solvent A (90%) and NaOH 5 mM as solvent B (10%). This step was followed by elution with NaOH 20 mM (from the fifth to the 29th min), mixing solvent A (90%) with NaOH 200 mM (solvent C, 10%). Cleaning of the column with NaOH 200 mM (100% solvent C) occurred between the 29th and the 49th min, equilibration (0.5 mM NaOH, same composition as in the first step) followed for 14 min. Flow rate was 1 mL/min throughout the 63 min of the whole program, the eluent was delivered to the system by a Dionex GP50 gradient pump. Before analysis, the Milli-Q water used for the eluents was vacuum-degassed by placing it in a sonicator, drawing a vacuum on the filled reservoir for 10 min and then purging with helium at approximately 0.5 bar for another 10 min. Area evaluation of the chromatographic peaks was performed with a lab data system Dionex UCI-50 using PeakFit software.

### 2.2.2. Interferences

[9] A potential interference of the levoglucosan signal from arabitol, a constituent of fungal spores [Lewis and Smith, 1967] had been identified by one of the coauthors (M. Claeys). Our method was carefully optimized to achieve a separation between levoglucosan and arabitol. Thus our data reported here are free from an interference of arabitol.

### 2.2.3. Determination of OC and BC

[10] OC and BC were determined with a thermal method with optical charring correction in the laboratory of Casimiro Pio [Pio *et al.*, 2007].

### 2.2.4. Determination of Soluble Potassium and Its Non-Sea-Salt and Nondust Fraction

[11] A small part of the filter (1 to 3 cm<sup>2</sup> of a total surface of 150 or 400 cm<sup>2</sup>, depending on sites) was extracted with ultra pure Milli-Q water. The liquid extract was analyzed for cations by ion chromatography with conductivity detection, using a Dionex 500 chromatograph equipped with a CS12 separator column as detailed by Pio *et al.* [2007]. For sodium, magnesium, calcium, and potassium the detection limit was close to 1 ng m<sup>-3</sup>.

[12] On the basis of size-segregated aerosol sampling it was shown that a dominant fraction of soluble potassium is present in the submicron size fractions at continental CARBOSOL sites and that only a minor fraction related to sea salt and mineral dust is present in larger size fractions [Pio *et al.*, 2007]. The fine fraction of soluble potassium, thought to be related to biomass combustion [Cachier *et al.*, 1991], was estimated by subtracting, from the soluble potassium level observed on bulk aerosol filters, the sea-salt contribution,

thereby making use of the mass ratio of potassium to sodium in seawater (0.038) and marine sodium levels [see Pio *et al.*, 2007]. Since dust material contains leachable potassium we also have considered this fraction to evaluate soluble potassium related to biomass burning. On the basis of the relationship between K and Ca at continental CARBOSOL sites, as detailed by Pio *et al.* [2007], we also corrected potassium from the dust contribution at all sites by using non-sea-salt calcium levels and assuming a mean K/Ca ratio of 0.12.

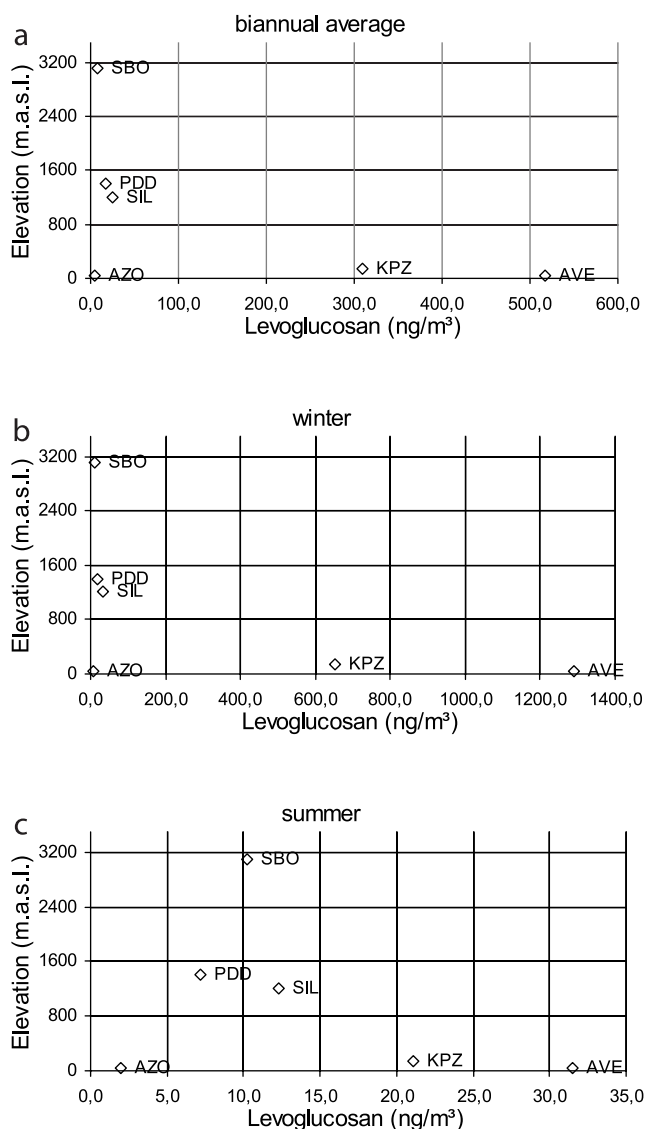
## 3. Results and Discussion

### 3.1. Detection Limit

[13] For deriving the detection limit of the complete analytical procedure and to check for potential contamination during the shipping, storage, sampling and assembling of the filter holder, field blanks were taken along with the samples at every sampling site. The detection limits were determined by taking three times the standard deviation of the field blanks and normalizing them to an average air volume collected for the weekly samples. This volume varies between the sampling sites. The average sampled volumes were 10081 Nm<sup>3</sup> for AZO, 10691 Nm<sup>3</sup> for AVE, 8025 Nm<sup>3</sup> for PDD, 7380 Nm<sup>3</sup> for SIL, 3019 Nm<sup>3</sup> for SBO and 4457 Nm<sup>3</sup> for KPZ. The practical detection limits achieved for levoglucosan determinations at the CARBOSOL sites, based on 3 sd of the variation of field blank samples was in the range of 0.7–0.2 ng/m<sup>3</sup> air equivalent (for weekly samples with 3000–10,000 m<sup>3</sup> sample volume) and aliquots of 0.7–1.3% of the filter area for the determination of levoglucosan.

### 3.2. Levoglucosan Annual Averages at the CARBOSOL Sites

[14] Table 1 summarizes the average, minimum and maximum values, as well as summer and winter averages for levoglucosan at all six sampling sites. These values vary considerably between the sampling sites and the seasons (Table 1). Three sites are situated at low level and three at high level. At low level are the Atlantic background site AZO, the coastal semiurban site AVE and the central European rural site KPZ. At the Atlantic background sampling site AZO, the lowest concentrations of levoglucosan were observed. The biannual average at AZO was around 5 ng/m<sup>3</sup> with a range of 0.3–19 ng/m<sup>3</sup>. At the two other low-level sites, AVE and KPZ, the concentration levels of levoglucosan were around a factor of 60–100 higher than at the Azores. At AVE, the biannual average



**Figure 2.** (a–c) Elevational distribution of the biannual, winter (DJF) and summer (JJA) average of levoglucosan at the CARBOSOL sites.

was  $517 \text{ ng/m}^3$ , with a range of  $20\text{--}1651 \text{ ng/m}^3$ , while at KPZ the biannual average was  $309 \text{ ng/m}^3$ , with a range of  $13\text{--}922 \text{ ng/m}^3$ .

[15] Three high-level mountain sites SIL, PDD and SBO, situated from around 1200 to 3100 m, were included in the CARBOSOL sampling network. The highest biannual average concentration of levoglucosan at the mountain sites was observed at SIL, a rural site at the lowest elevation of these sites (1205 m). Here, the biannual average was  $24 \text{ ng/m}^3$  with a range of  $7\text{--}56 \text{ ng/m}^3$ . At the next higher site PDD (1450 m), an average of  $17 \text{ ng/m}^3$  with a range of  $2\text{--}47 \text{ ng/m}^3$  was noted, while at the “free tropospheric” background site SBO (3106 m), an annual average of  $8 \text{ ng/m}^3$  with a range of  $<0.7\text{--}56 \text{ ng/m}^3$  was observed. The SBO sampling site is representative for the free troposphere, in particular during the cold season [Kasper and Puxbaum, 1998].

[16] The remote Atlantic site AZO and the free tropospheric site SBO exhibit some similarities with regard to the concentrations of levoglucosan. In particular, the average of

the biannual data set for SBO is relatively close to that of AZO. The winter averages are at SBO around a factor of 2 higher than at AZO, while summer averages are around a factor of 5 higher. SBO receives air masses from lower levels during the warm season [Tscherwenka *et al.*, 1998], which leads to higher background levels, than the lateral transport from the continents to the Azores.

[17] Winter/summer ratios were highly variable between the sites. At AVE and KPZ, a strong winter dominance was observed with a winter/summer ratio of 41 and 31, respectively. At AZO, winter ratios were around three times higher than summer ones, while at the elevated sites, winter ratios were 1.2–2.7 times higher than summer ones. The winter/summer ratio decreases with increasing elevation (Table 1).

[18] The winter/summer relationships between the CARBOSOL sites may be explained with different elevational gradients during the winter and summer seasons (Figures 2b and 2c). During winter the mixing height in the alpine valleys is low and therefore the atmosphere at mountain peaks is effectively decoupled from the lower sites. Although a considerable consumption of biomass fuels in valleys may be assumed, the impact at the mountain sites is decreasing with elevation (Figure 2b). In summer, elevated sites receive air masses from lower levels and the elevational gradient becomes less steep.

### 3.3. Seasonal Variation of the Atmospheric Levoglucosan Concentration

[19] The annual cycles of levoglucosan at the CARBOSOL sites are presented in Figures 3a–3f.

[20] More or less pronounced seasonalities with winter or early spring maxima were observed at all sites, except for SBO.

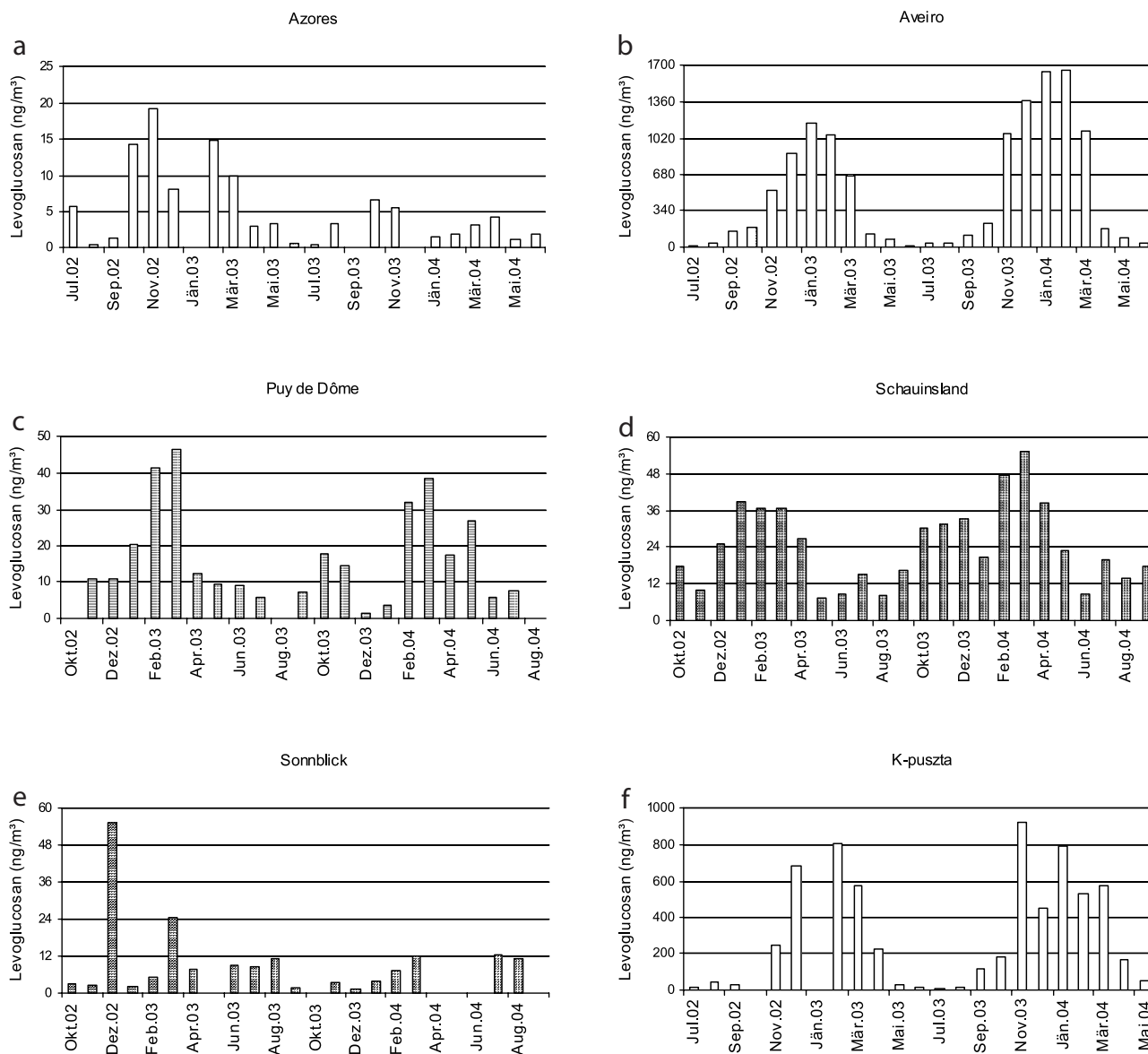
[21] AZO is a maritime background site with very small local emission sources; hence the observed levoglucosan concentrations were low. However, a seasonality with a winter maximum was observed in the first year of the biannual cycle, whereas in the second year hardly any seasonality was evident. The wintertime increase may originate from local effects or from long-range transport.

[22] At the AVE site, the most pronounced seasonal variation of all sites was observed for levoglucosan, with highest concentrations in winter and lowest ones in summer (Figure 3b). AVE is a coastal semiurban place, with moderate winter temperatures of around  $10^\circ\text{C}$ . The use of wood for domestic heating is common on the countryside in north Portugal. For KPZ the seasonal variation is also pronounced, with winter maxima and summer minima (Figure 3f). The winter/summer ratio as shown in the previous section is 31 compared to 41 in Aveiro.

[23] At the elevated sites PDD and SIL, the seasonal cycles of levoglucosan were also quite pronounced, with maxima in early spring (March). The annual cycle at SBO showed unexpected peaks in December 2002 and March 2003 (Figure 3e). Either a local influence from the valley below the Sonnblick Observatory, or transport events may have triggered the elevated levels.

### 3.4. Comparison of Levoglucosan, Potassium, and Other Tracers at CARBOSOL Sites

[24] The fraction of soluble potassium not related to sea-salt and soil particles (hereafter, denoted nss-ndust-K) was



**Figure 3.** (a–f) Annual cycles for levoglucosan at CARBOSOL sites.

formerly used widely as tracer element for the qualitative identification of biomass combustion [Cachier *et al.*, 1991]. However, the emission of this tracer element is highly variable for different combustion conditions and, accordingly to Sheffield *et al.* [1994], may be determined empirically for each situation. Muller-Hagedorn *et al.* [2003] showed that inorganic salts have strong influence on pyrolysis and as well on product distribution, e.g., the yield of levoglucosan. From this follows, that potassium from wood smoke is not necessarily correlated with levoglucosan.

[25] We note from Table 2 that the nss-ndust-K/levoglucosan ratio is quite variable between season and sites. In summer (JJA), the ratio is on average 5.7 for all sites with a range of 3.3–9, while in winter (DJF), the average ratio is 0.9 with a range of 0.2–2.1 (Table 2).

[26] The different behavior of nss-ndust-K and levoglucosan between the sites and seasons might originate from (1) different emission fluxes for different biomass combustion types (fuel types, oven types, agricultural fires, forest fires) or

(2) additional nss-ndust-K inputs from other sources, e.g., coal burning or bioparticles.

[27] We have derived potassium/levoglucosan ratios from data from different studies of biomass combustion (Table 3). It appears, that potassium/levoglucosan ratios are rather below 0.2 for wood combustion in fire places and ovens, while the ratio approaches 0.5 for open fires (Table 3). Thus a K/levoglucosan ratio <0.2 may indicate the prevalence of domestic heating with wood, while a K/levoglucosan ratio around 0.5 may indicate open fires or combustion of fuels such as slash, or straw. The winter values of the K/levoglucosan ratio of 0.2–2.1 at CARBOSOL sites are somewhat higher than those expected for wood stove and fire place emissions, except for Aveiro, where the K/levoglucosan ratio of 0.2 is relatively close to that expected for fire places and stoves. At KPZ, the K/levoglucosan ratio of 0.5 might be indicative for a notable contribution to the fine K from biomass fuels. For summer periods, the K/levoglucosan ratios of 3.3–9 at CARBOSOL sites are

**Table 2.** Biannual Arithmetic Average of Levoglucosan, Soluble Potassium, and Its nss-ndust Fraction for Summer (S) and Winter (W) at the CARBOSOL Sites<sup>a</sup>

Sites	Levoglucosan, ng/m <sup>3</sup>	Soluble K, ng/m <sup>3</sup>	nss-ndust-K, ng/m <sup>3</sup>	nss-ndust-K/Levoglucosan
AZO S	2 (2)	58 (62)	18 (14)	9.0 (7.0)
AZO W	7 (9)	119 (100)	15 (10)	2.1 (1.1)
AVE S	32 (76)	155 (158)	121 (125)	3.8 (1.6)
AVE W	1290 (957)	241 (225)	220 (201)	0.2 (0.2)
KPZ S	21 (66)	164 (174)	107 (110)	5.1 (1.7)
KPZ W	653 (576)	393 (326)	378 (302)	0.6 (0.5)
PDD S	7 (11)	66 (57)	43 (37)	6.1 (3.7)
PDD W	18 (22)	16 (28)	12 (21)	0.7 (1.0)
SIL S	12 (17)	128 (119)	85 (77)	7.1 (4.5)
SIL W	34 (32)	41 (61)	35 (44)	1.1 (1.4)
SBO S	10 (6)	33 (34)	<33 (<34) <sup>b</sup>	<3.3 (<5.7)
SBO W	12 (10)	7 (13)	<7 (<13) <sup>b</sup>	<0.6 (<1.3)
Average summer				5.7 (4.1)
Average winter				0.9 (1.0)

<sup>a</sup>Summer and winter are defined as June–July August and December–January–February, respectively. Numbers in parentheses relate to half-year summer (from April to September) and winter (from October to March) values.

<sup>b</sup>Estimation of the contribution of dust was not possible at SBO because of contamination of calcium levels by construction activities at that station [see *Pio et al.*, 2007].

around a factor of 10–20 higher than those expected for wild fires. In this case, other potassium sources possibly prevail in the atmosphere.

[28] Table 3 contains levoglucosan emission data from various studies (levoglucosan compound expressed in mg/g OC). The reciprocal factor (OC/levoglucosan) is used for deriving the amount of OC from wood or biomass combustion in ambient aerosol. The OC/levoglucosan relationship is quite variable for different burning conditions and wood types. For U.S. stoves and fire places, a factor of 7.35 [*Fine et al.*, 2002] is used. In Austria, test burns of wood common for alpine environments have been performed [*Schmidl*, 2005]. A mass-weighted average for beech and spruce yielded an OC/levoglucosan relationship of 7.1 which is quite close to the U.S. value. We think, that the value of 7.35 holds for conditions typical for the alpine region where generally a mixture of hard and softwood fuel is used for domestic heating. European Alpine conditions are considered for the sites in France (PDD), Germany (SIL) and Austria (SBO). In the work by *Gelencsér et al.* [2007], a factor of 7.35 is used with a range of 6.0–12.5. The lower factor is more typical for softwood fires in stoves and fire places, while the higher factor is typical for certain hardwood types (e.g., beech). The higher ratio was also observed for wild fires in Amazonia. It has to be proven yet, whether this holds also for wild fires in Europe. In Hungary, main tree species in forests are oaks (*Quercus petraea*, *Qu. pedunculata* and *Qu. cerris*, 30%), black locust (*Robinia pseudoacacia*, 19%), different species of poplar (*Populus*, 10%), and Scots Pine (*Pinus sylvestris*, 9%). Although except for some oak species no emission data are available for those wood types, we assume that the 7.35 ratio can be applied since the trees belong mainly to hardwood species, where generally ratios around 7 and up to 13 were reported (Table 3). In Portugal, main tree species are Mediterranean Pine (*Pinus pinaster*, 30%), Eucalyptus (mainly *Eucalyptus globulus*, 20%), and oaks (*Quercus robur* and *Quercus faginea*). While Eucalyptus is not well suited for firing stoves, it can be assumed that most fuel wood in small combustion units is pine, oak and other local species. For pine and oak OC/levoglucosan ratios from U.S. studies were

on the lower end of the range indicated above. Thus, for the Portuguese site a factor on the low end is applied (6.0). There is some uncertainty as levoglucosan emission data for western European tree species are currently only available for a few species indigenous in the eastern Alpine region [*Schmidl*, 2005]. The uncertainty of the OC/levoglucosan ratio for Austrian biomass combustion emissions stems from the unknown ratio of softwood and hardwood use in Austrian stoves and fire places. From the test burns of indigenous wood for Austria and information about use of wood types in Austria we derived an uncertainty of the OC/levoglucosan ratio of 15%, based on an assumed range of the softwood fraction in the combustion from 50 to 80%. As the other CARBOSOL countries outside the Alpine area, Hungary and Portugal, have distinctly other tree species in their woods, the uncertainty is assumed to be up to 30%, e.g., up to 30% lower in Portugal because of wood species emitting on the lower end of the range, and up to 30% higher in Hungary because of hardwood species emitting on the higher end of the 7.3 ± 30% range.

### 3.5. Contribution of Levoglucosan-C to OC

[29] The average contribution of levoglucosan-C to OC for the CARBOSOL sites is summarized in Table 4. The biannually averaged contribution of levoglucosan-C to OC for all sites varied between 0.7% (SBO) and 3.2% (AVE). The higher contributions of levoglucosan-C to OC were found at the more polluted low-level sites (AVE and KPZ). At AVE and KPZ, elevated contributions were expected because of the closeness to sources. At the more remote sites, the levoglucosan-C in OC fraction is in a narrow range between 0.7% (SBO) and 0.9% (PDD). The respective fraction at the AZO site is similar to the elevated SIL site. The relatively weak variation of levoglucosan-C to C ratios at the remote sites indicates that biomass smoke is a ubiquitous constituent in the European background aerosol. In particular during winter, the relative fraction of levoglucosan-C in OC is in a range of 1.3–6.1% at the CARBOSOL sites (Table 4). During summer the relative fraction is between 0.1 and 0.5%.

**Table 3.** EC, OC, Levoglucosan, and K in Fine Particulate Matter From Different Types of Biomass Combustion Compiled From Recent Studies

Source Type	Fuel Type	EC, mg/g PM	OC, mg/g PM	Levoglucosan, K, mg/g mg/g OC	Factor OC/Levoglucosan	K/Levoglucosan Ratio	Reference	
Fire place NE–US PM2.5	hardwood		866	129	10.6	7.8	<i>Fine et al.</i> [2001]	
Fire place NE–US PM2.5	softwood		911	76.4	10.8	13.1	<i>Fine et al.</i> [2001]	
Fire place S-US PM2.5	hardwood		787	136	8.7	7.4	<i>Fine et al.</i> [2002]	
Fire place S-US PM2.5	softwood		1000	42.6	5.4	23.5	<i>Fine et al.</i> [2002]	
Fire place MidW and W-US	hardwood	20	767	183	8.9	5.5	<i>Fine et al.</i> [2004a]	
Fire place MidW and W-US	softwood		890	123	3.5	8.1	<i>Fine et al.</i> [2004a]	
Wood stove US PM2.5	hardwood		553	164	17.4	8.1	<i>Fine et al.</i> [2004b]	
Wood stove US PM2.5	softwood		620	353	7.5	2.8	<i>Fine et al.</i> [2004b]	
Fire place S-US PM10	Quercus		560	235		4.3	<i>Schauer et al.</i> [2001]	
Fire place S-US PM10	eucalyptus		591	523		1.9	<i>Schauer et al.</i> [2001]	
Fire place S-US PM10	Pinus		437	259		3.9	<i>Schauer et al.</i> [2001]	
Wood stove Austria PM10	beech	191	513	79	2.1	12.6	<i>Schmidl</i> [2005]	
Wood stove Austria PM10	spruce	206	537	206	1.6	5.0	<i>Schmidl</i> [2005]	
Asian biomass fuel PM2.5	leaves, straw, dung	32.4	525	79	20	12.6	<i>Sheesley et al.</i> [2003]	
Forest fire SE-US PM2.5	pine dominated	39.2	603	95	5.7	10.5	<i>Lee et al.</i> [2005]	
Ambient Observations	Conditions	EC, $\mu\text{g}/\text{m}^3$	OC, $\mu\text{g}/\text{m}^3$	Levoglucosan, $\mu\text{g}/\text{m}^3$	K, $\mu\text{g}/\text{m}^3$	OC/ Levoglucosan	K/ Levoglucosan	Reference
Rondônia pasture site	haze, PM2.5	1.4	29.2	2.5	0.8	11.9	0.3	<i>Graham et al.</i> [2002]
Rondônia forest site	haze, PM2.5	0.7	14.5	1.2	0.4	12.3	0.3	<i>Graham et al.</i> [2002]
Southern US PM2.5	Fresno dual sites		32.7	7.6		4.3		<i>Schauer and Cass</i> [2000]
Southeast Asia PM2.5	Kuala Lumpur urban-haze “day”		115	40		2.9		<i>Bin Abas et al.</i> [2004]
Averages		EC, mg/g PM2.5	OC, mg/g PM2.5	Levoglucosan, K, mg/g mg/g OC	Factor OC/Levoglucosan	K/Levoglucosan Ratio	Reference	
Recommended average US					7.35		<i>Fine et al.</i> [2002]	
Recommended average Austria					7.1 <sup>a</sup>		<i>Schmidl</i> [2005]	
Recommended average Portugal					6		estimate	

<sup>a</sup>Average from beech and spruce/test burns in a tiled stove.

**Table 4.** Biannual Average, Minimum, Maximum, Summer, and Winter Values of the Relative Fraction of Levoglucosan-C in OC for the CARBOSOL Sampling Sites<sup>a</sup>

Levoglucosan-C/Total OC, %	AZO, 50 m	AVE, 40 m	PDD, 1405 m	SIL, 1205 m	SBO, 3106 m	KPZ, 136 m
Average	0.89	3.23	0.89	0.72	0.66	2.03
Minimum	0.04	0.36	0.07	0.08	0.00	0.14
Maximum	3.71	7.96	2.90	1.81	4.67	7.02
Summer	0.15 (0.28)	0.50 (1.11)	0.10 (0.29)	0.15 (0.27)	0.28 (0.16)	0.19 (0.61)
Winter	1.32 (1.56)	6.14 (5.34)	1.55 (1.38)	1.50 (1.16)	1.66 (1.12)	3.42 (3.59)
winter/summer	9.05 (5.58)	12.4 (4.81)	15.8 (4.76)	10.2 (4.37)	5.89 (7.07)	18.3 (5.89)

<sup>a</sup>Summer, winter data: first value corresponding to 3 month summer and winter quarters; values in parentheses correspond to summer and winter half years. The conversion factor for levoglucosan-C = levoglucosan \* 0.444.

**Table 5.** Concentrations of Biomass Smoke OC for the CARBOSOL Sites<sup>a</sup>

Biomass Smoke OC, ng/m <sup>3</sup>	AZO, 50 m	AVE, 40 m	PDD, 1405 m	SIL, 1205 m	SBO, 3106 m	KPZ, 136 m
Average	39	3099	125	180	57	2272
Minimum	3	117	12	53	0	96
Maximum	141	9903	342	408	409	6778
Summer	15 (17)	189 (458)	52 (83)	90 (124)	75 (41)	155 (487)
Winter	48 (62)	7739 (5740)	134 (159)	247 (235)	91 (73)	4800 (4234)
Winter/summer	3 (4)	41 (13)	3 (2)	3 (2)	1 (2)	31 (9)

<sup>a</sup>Summer, winter data: first value corresponding to 3 month summer and winter quarters; values in parentheses correspond to summer and winter half years.

### 3.6. Contribution of Biomass Smoke to OC and OM

[30] Concentrations of levoglucosan in fine particle (PM<sub>2.5</sub>) emissions from fireplace combustion of wood and for wood stoves in different regions of the United States were reported by *Fine et al.* [2001, 2002, 2004a, 2004b; *Schauer et al.*, 2001]. The results of these studies are summarized in Table 3.

[31] As explained in section 3.4 we use the conversion factor Biomass smoke OC = levoglucosan \* 7.35 for all sites, except Aveiro. For Aveiro we employ the factor 6 which is on the lower range of the assumed variability of the factor.

[32] The recommended conversion factor from the *Fine et al.* [2002] data is 7.35. This factor corresponds to a fraction of levoglucosan in OC of 13.6%. To calculate the concentration value of biomass smoke OC, the concentration of levoglucosan is multiplied by 7.35:

$$\text{Biomass smoke OC} = \text{levoglucosan} * 7.35$$

Table 5 shows the derived values of biomass smoke OC for the CARBOSOL sites.

[33] The site with the lowest biannual average of biomass smoke OC is AZO (39 ng/m<sup>3</sup>), followed by SBO with 57 ng/m<sup>3</sup>, PDD with 125 ng/m<sup>3</sup> and SIL with 180 ng/m<sup>3</sup>. Highest biannual averages of biomass smoke OC were obtained for KPZ (around 2300 ng/m<sup>3</sup>) and AVE (around 3100 ng/m<sup>3</sup>). The highest single weekly average of biomass smoke OC was around 7700 ng/m<sup>3</sup> during winter in Aveiro, while at KPZ the highest weekly average was around 4800 ng/m<sup>3</sup>.

[34] To derive the contribution of biomass smoke to organic matter (OM), biomass smoke OC, as well as aerosol OC has to be converted to allow for the contribution of H, O, and possibly heteroatoms. The conversion factors are not precisely known, neither for biomass smoke OC nor for aerosol OC. From the *Fine et al.* [2001, 2004] papers on fire place emissions an OC to OM conversion factor of 1.2–1.4 can be derived, while for more primitive fuels the factor is around 1.7–1.8 [*Sheesley et al.*, 2003]. As a first-order approximation we employ 1.4 as the conversion factor for biomass smoke from biomass OC and 1.7 conversion of aerosol OC to aerosol OM at background sites [*Puxbaum et al.*, 2004]; for OC and OM data, see the auxiliary material.<sup>1</sup>

[35] Table 6 presents the average contributions of biomass smoke to OM, maximum and minimum values, as well as the averages of summer and winter periods.

[36] The average contribution of biomass smoke to OM for all the sites ranges between 9 and 36%. The highest contributions were observed at the low-level sites AVE

(36%) and KPZ (28%). At the high-level sites, the contribution is between 9% (SBO) and 12% (PDD). At the Azores (AZO), the contribution (12%) is similar to those at the high-level sites. Thus the spatial differences of the contributions of the biomass smoke to OM are less pronounced than the absolute concentrations of levoglucosan.

[37] In winter, the contribution of biomass smoke to OM is generally higher than in summer. Normally in this season the temperatures are very low, the air mass exchange in the atmosphere is slower and higher emissions can be expected during the cold season. The contributions of biomass smoke to OM during winter range between considerable 18% and 68%. At the background (AZO) and mountain sites (SIL, PDD, SBO), winter levels of biomass smoke to OM are in a narrow range of 18–23%, indicating possibly similar regional emissions with respect to wood burning. At the sites that are anthropogenically affected, the contributions of biomass smoke to OM during winter are as high as 47% (KPZ) and 68% (AVE).

[38] The biomass smoke results can be compared to data from other sites. Most available data of biomass smoke contributions to the organic aerosol are currently from receptor model studies in the USA and Asia. For four sites in the Los Angeles area the annually averaged contribution of biomass smoke to organic fine material (PM<sub>2.5</sub>) was 5–22% [*Schauer et al.*, 1996]. At eight smaller urban and rural sites in the southeastern U.S. biomass combustion contributed 25–66% to fine particle organic carbon; with levels during winter at all sites >50% [*Zheng et al.*, 2002]. From these data it can be derived, that wood smoke impacts in small communities in the southeast United States is the overall dominant source for the wintry organic aerosol. As to available data from Ghent, Belgium, the contribution of biomass smoke to organic material (PM<sub>10</sub>) employing emission data of *Fine et al.* [2001] was estimated to be on average 35% during a 1998 winter period [*Zdráhal et al.*, 2002]. Relative levels of biomass combustion organic matter in the background aerosol as well as at directly wood smoke impacted sites in the eastern United States and Europe seem to be in a similar range (i.e., around 25–65%). The organic part of the aerosol has posed many open questions in European aerosol studies [e.g., *Jones and Harrison*, 2005; *Yin et al.*, 2005]. It is surprising that the identification of biomass smoke as a major contributor to organic material in fine particulate matter has received relatively little attention yet.

## 4. Balance of Organic Macroconstituents

[39] Major contributors of organic macroconstituents to the atmospheric aerosol are (1) plant debris (macrotracer cellu-

<sup>1</sup>Auxiliary material data sets are available at <ftp://ftp.agu.org/apend/jd/2006jd008114>. Other auxiliary material files are in the HTML.



**Table 6.** Relative Contribution of “Biomass Smoke” to OM for the CARBOSOL Sampling Sites, Biannual Averages, and Monthly Averaged Minimum and Maximum Values<sup>a</sup>

Biomass Smoke/Total OM, %	AZO, 50 m	AVE, 40 m	PDD, 1405 m	SIL, 1205 m	SBO, 3106 m	KPZ, 136 m
Average	12	36	12	10	9	28
Minimum	0.5	4.0	0.0	1.1	<1	1.9
Maximum	51	89	40	25	64	96
Summer	2.0 (3.8)	5.5 (12)	1.1 (3.6)	2.0 (3.6)	3.8 (2.2)	2.6 (8.3)
Winter	18 (21)	68 (59)	21 (19)	21 (16)	23 (15)	47 (49)
Winter/summer	9 (6)	12 (4.8)	20 (5.3)	10 (4.4)	6 (7)	18 (6)

<sup>a</sup>Summer, winter data: first value corresponding to 3 month summer and winter quarters; values in parentheses correspond to summer and winter half years. Factor biomass OC \* 1.4 = biomass OM. Factor aerosol OC \* 1.7 = aerosol OM.

lose), (2) HULIS (Humic-like substances), and (3) biomass smoke (macrotracer levoglucosan). Data for plant debris and for HULIS are available from companion papers [Sánchez-Ochoa *et al.*, 2007; Feczko *et al.*, 2007]. These results are combined with the biomass smoke data in Table 7, and each species is related to the OM.

[40] In the cold season, plant debris, HULIS and biomass smoke account for around 35–55% of the wintry organic material in the European background aerosol. At the sites affected by biomass smoke (KPZ and AVE), the respective contributions are 68 and 83%. During the warm season, this fraction is reduced to around 11–23% at all sites (Table 7).

[41] Plant debris is a primary biogenic aerosol constituent, while wood smoke originates from burning biogenic material. HULIS most likely corresponds to secondary organic material originating from various sources. A major formation pathway considered is secondary production from biomass smoke constituents [e.g., Gelencsér *et al.*, 2007]. Another source of HULIS is secondary formation from reactive biogenic emissions [e.g., Limbeck *et al.*, 2003; Iinuma *et al.*, 2004]. Other possible pathways of formation are discussed by Gelencsér [2004]. The three constituents considered in our OC mass balance represent the majority of the aerosol OC, which is accessible by chemical analysis. Not included in our analysis of biogenic aerosols are source contributions from cooking activities [Schauer *et al.*, 1996], viable particles such as bacteria and fungal spores [Bauer *et al.*, 2002], and secondary aerosol in addition to HULIS (“non-HULIS SOA”). The fraction of “nonfossil OC” in relation to TC in a summer and winter data set of CARBOSOL sites has been reported by Gelencsér *et al.* [2007]. The determination of the “nonfossil OC” was performed with sample pools that did not cover exactly the summer and winter periods in our study; however, we assume, that the relative fractions of fossil and nonfossil carbon in TC are

comparable. Gelencsér *et al.* [2007] find a relatively low contribution from nonfossil secondary organic aerosol (<20% of TC) in winter and a high contribution (>50% of TC) in summer.

## 5. Conclusions

[42] 1. Highest levels of levoglucosan in the biannual average were found at the low-level sites Aveiro and K-Puszt. Lowest concentrations were noted at the Atlantic background site Azores and the continental high-elevation site Sonnblick (3106 m). Average concentrations show a clear elevational gradient for the continental sites (KPZ, SIL, PDD, SBO), with a ratio of around 40 for KPZ versus SBO.

[43] 2. At the low-level sites AVE and KPZ, as well as at the elevated sites PDD and SIL, distinct seasonalities with winter maxima and summer minima were observed, while at the maritime background site, the winter/summer ratio was as low as 3, and summer and winter levels at the midtropospheric site SBO were relatively similar.

[44] 3. Relative contributions of levoglucosan-C to OC (2-year averages) in the west–east transect range from around 0.7% at the high mountain site SBO to 3.2% at AVE. Relative contributions of levoglucosan-C to OC do not show a pronounced elevational trend. At all sites, the values are higher in winter than in summer. Also at the oceanic AZO site, the relative fraction of levoglucosan-C to OC is enhanced in winter (winter/summer ratio = 9).

[45] 4. To derive a “biomass smoke” contribution to organic matter, conversion factors from Fine *et al.* [2002] and Schmidl [2005] and derived factors from field measurements are compared. For fires in small ovens the conversion factor CF for biomass smoke OC = CF \* levoglucosan is around 5, while for fire places it is around 7–10, and for open wild fires it is >10. We apply a factor of 7.35 which

**Table 7.** Relative Contribution of “Biomass Smoke” and “Plant Debris” to Organic Material (OM)<sup>a</sup>

Contribution to OM, %	AZO, 50 m	AVE, 40 m	PDD, 1405 m	SIL, 1205 m	SBO, 3106 m	KPZ, 136 m
Summer						
Biomass smoke	2.0	5.5	1.1	2.0	3.8	2.6
Plant debris	4.7	1.9	5.2	5.2	5.3	5.9
Hulis	12.6	15.8	10.9	3.8	10.6	12.3
Sum	19	23	17	11	20	21
Winter						
Biomass smoke	18.0	68.4	21.2	20.5	22.6	46.6
Plant debris	6.1	1.4	10.1	6.1	22.4	1.8
Hulis	10.6	13.6	21.5	20.6	10.2	19.3
Sum	35	83	53	47	55	68

<sup>a</sup>Averages in the summer and winter periods. Data for plant debris from Sánchez-Ochoa *et al.* [2007], while data for HULIS are from Feczko *et al.* [2007]. Summer: average of June, July and August; winter: average of December, January and February.

bears an estimated uncertainty of  $\pm 30\%$  for all sites, except for AVE, where a factor of 6 is applied. A seasonal variation of the conversion factor is likely. Namely, during the cold season biomass smoke emissions are rather from domestic heating (ovens), while in the warm season forest fires, burning of agricultural and garden waste, and cooking may contribute to the biomass smoke emissions. As the extent of these activities is not clear in western and central Europe, a single factor is applied.

[46] 5. The atmospheric concentration of “biomass smoke” (2-year averages) ranges from  $0.05 \mu\text{g}/\text{m}^3$  at AZO to  $4.3 \mu\text{g}/\text{m}^3$  at AVE. The highest monthly concentrations (up to  $14 \mu\text{g}/\text{m}^3$ ) were observed in winter at the continental AVE site, the second highest ( $9.5 \mu\text{g}/\text{m}^3$ ) at the KPZ site. As for levoglucosan, “biomass smoke” concentrations decrease with elevation.

[47] 6. Relative contributions of “biomass smoke” to organic matter (OM, 2-year averages) in the west–east transect range from around 9% at the high-elevation site SBO to 36% at the low-level site AVE. Relative contributions of “biomass smoke” to organic matter were similar at elevated sites and AZO (9–12%) and increased at KPZ and AVE (28 and 36%), sites affected by anthropogenic activities. Winter levels are higher than summer levels at all sites. At the oceanic AZO sites, the relative winter enrichment versus summer levels (factor of 9) of the fraction of “biomass smoke” in OM may originate from long-range transport or, additionally, from local emissions.

[48] 7. Surprisingly high relative concentrations of “biomass smoke” in organic matter were observed at all sites in winter, ranging from 18% at AZO to 21–23% at the elevated sites, and from 47 to 68% at KPZ and AVE. Thus “biomass smoke” is the major constituent of the organic material in the wintry European aerosol background. Also during summer, “biomass smoke” contributes to OM in relative fractions of 1–5.5%.

[49] 8. From the data we derive that typical mid and west European levels of the biomass smoke contribution to organic matter are around 10–30% on an annual basis and around 20–50% during the cold season. In emission regions (e.g., communities with a high share of biomass based domestic heating) the contributions will be possibly even higher. From this follows that biomass smoke is the predominant organic aerosol constituent in wintertime mid and western Europe.

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