JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 112, D23S08, doi:10.1029/2006JD008180, 2007

Concentration of atmospheric cellulose: A proxy for plant debris across a west-east transect over Europe

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Received 25 October 2006; revised 15 January 2007; accepted 26 March 2007; published 14 August 2007.

[1] Atmospheric "free cellulose" has been determined as a proxy for "plant debris" in samples from six background stations on a west-east transect extending from the Atlantic (Azores) to the mid-European background site KPZ (K-Puszta, Hungary). Concentration levels of cellulose (biannual averages) range from 16.3 ng/m^3 at the oceanic background site AZO (Azores) to 181 ng/m^3 at KPZ (Hungary). Concentrations decrease with elevation, winter levels at the midtropospheric Sonnblick site (SBO, 3106 m) are comparable to clean Atlantic conditions. The atmospheric concentration of plant debris (biannual averages) was derived from the cellulose data and ranges from 33.4 ng/m^3 at AZO to 363 ng/m^3 at KPZ. Relative contributions of plant debris to organic matter (OM) range from around 2% at the semirural coastal site Aveiro (AVE) to 10% at SBO. Surprisingly high relative concentrations of plant debris in OM were observed for wintry conditions at the elevated sites. The relative fraction of plant debris in OM ranged as averages from 6.1% at Schauinsland, Germany (1205 m) to 10.1% at Puy de Dome, France (1405 m) and 22.4% at Sonnblick, Austria (3106 m). Thus plant debris is a very important constituent of the organic material at elevated background sites with summer concentrations of around 5% and winter levels from around 6–22% depending on elevation. Since cellulose is considered rather long-lived with respect to atmospheric oxidation processes, it may become enriched on the way to background regions, which may explain the elevated relative levels at elevated sites.

Citation: Sánchez-Ochoa, A., A. Kasper-Giebl, H. Puxbaum, A. Gelencser, M. Legrand, and C. Pio (2007), Concentration of atmospheric cellulose: A proxy for plant debris across a west-east transect over Europe, *J. Geophys. Res.*, *112*, D23S08, doi:10.1029/2006JD008180.

1. Introduction

[2] In the last decade it was shown that biological constituents such as biopolymers are important contributors to the mass of organic compounds in rural and urban aerosol. *Matthias-Maser and Jaenicke* [1995] have demonstrated that up to 40% of the number of particles >0.2 μm aerodynamic diameter (AD) over a continental site were considered of "biogenic origin." Bioaerosols appear to contribute substantially to the global aerosol balance [*Jaenicke*, 2005].

[3] The most frequently occurring biopolymer in terrestrial environments is cellulose, as green plants contain in leaves around 50% of dry weight cellulose [*Butler and Bailey*, 1973]. Because of the seasonal cycles of the canopies of deciduous trees in temperate regions and the decay processes of the leaf litter, large fluxes of the decay products in the atmosphere have been invoked [*Brimblecombe*, 1986]. *Kunit and Puxbaum* [1996] described a method for the determination of atmospheric cellulose at the microgram level and showed that cellulose is an organic main species in the Vienna urban aerosol. Taking cellulose as a macrotracer for plant debris, around one to a few per cent of the organic aerosol has been attributed to plant debris [*Puxbaum and Tenze-Kunit*, 2003]. A similar result was obtained for sites in Los Angeles with a chemical-mass balance receptor model. Using fingerprints of higher alkanes a contribution of vegetative detritus to the organic aerosol of 1.1–2.1% was derived for PM2.5 aerosol samples [*Rogge et al.*, 1993, *Schauer et al.*, 1996]. Using a similar CMB approach for urban and rural sites in the south eastern US vegetative detritus was found to contribute up to 8.8% to organic carbon in PM2.5 during individual seasons [*Schauer and Cass*, 2000; *Schauer et al.*, 2002, *Zheng et al.*, 2002].

[4] Here we investigate the spatial and temporal evolution of atmospheric cellulose and the derived signal for plant debris across a west east transect extending from the Azores to central Europe over a time span of 2 years. Samples from Azores, Aveiro (Portugal), Puy de Dôme

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0148-0227/07/2006JD008180$09.00

(France), Schauinsland (Germany), Sonnblick (Austria) and K-Puszta (Hungary) were obtained from the CARBOSOL sampling network. The main focus of the work was the spatial-temporal evolution of the naturally occurring cellulose as a primary organic constituent of the organic aerosol in the European background.

2. Experimental Section

2.1. Sampling

[5] Aerosol samples were collected at six different sampling sites across Europe. The sites can be classified into low-level and high-level sampling sites. Low-level sampling sites are at Azores (Terceira Islands, Portugal, 50 m asl, maritime background site; AZO), at Aveiro (Portugal, 40 m asl, rural coastal site with maritime influence; AVE), and K-Puszta (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 2 years (mid-2002 to mid-2004). At AVE and AZO sampling was from July 2002 until July 2004. At KPZ sampling began in July 2002 and ended May 2004. At PDD, SIL and SBO the collection was from October 2002 to October 2004. At AZO, AVE, and KPZ home built HiVol samplers, at PDD, SIL and SBO manually operated Digitel's DH77 HiVol samplers were used. Inlet size cuts were 2.5 μm at AZO, AVE, SBO, 2 μm at KPZ; around 10 μm at PDD and SIL. The typically sampled volumes ranged from 3020 to 10700 Nm^3 for sampling intervals of one week. A map and details of the sites and sampling instrumentation are given by *Pio et al.* [2007].

2.2. Analysis

[6] Atmospheric cellulose was determined with the method of *Kunit and Puxbaum* [1996]. This method consists of three steps. In the first step, a "delignification treatment," to liberate cellulose associated with lignin and hemicellulose is applied. In the second step, the "saccharification," "free cellulose" is enzymatically hydrolyzed to D-glucose using two cellulolytic enzymes. The cellulase enzyme hydrolyzes the cellulose to low molecular weight break down products primarily glucose dimers (cellobiose) and glucose. The cellobiase enzyme hydrolyzes the cellobiose into two molecules of glucose. In the third step, "determination," D-glucose is determined using a test set from Boehringer Mannheim GmbH applying a UV-VIS spectrophotometer (Unicam 5625). The assay has no known cross sensitivities from other sugars or organic substances common in natural products (juices, food).

[7] A certain part of the cellulose of plant debris particles is encapsulated by lignin and thus not directly accessible to the enzymes. The relationship between "free cellulose" and "total cellulose" has been determined for filter samples from an urban site and found to be 0.72 (with a s.d. of 0.16) [*Puxbaum and Tenze-Kunit*, 2003]. Thus a significant amount of cellulose from plant debris can be obtained without delignification ("free cellulose"). For the large set of samples from CARBOSOL we therefore determined the "free cellulose." Thus all data in the following text are of "free cellulose."

[8] For deriving the contribution of "plant debris" to the organic matter we apply the conversion factor of 1/0.72 for the estimate of the "total cellulose" from "free cellulose." "Plant debris" is obtained from 2 * "total cellulose" [*Puxbaum and Tenze-Kunit*, 2003].

[9] With every analytical sequence were determined 5 "method blanks" for the complete laboratory procedure without the sample. The method blanks average was 0.005 mg per test with a s.d. of 0.0002 mg per test. The samples readings were corrected for the method blank.

2.3. Error Discussion

[10] The determination of the proxy "plant debris" is based on two conversion factors: The first conversion factor is used to derive "total cellulose" from the analyzed "free cellulose" signal. We have repeatedly investigated the relationship between "free" and "total" cellulose. In a larger series a factor of 0.72 (free/total cellulose) with a s.d. of 0.16 (or r.s.d. of 22%) was derived [*Puxbaum and Tenze-Kunit*, 2003]. For deriving the "plant debris" signal based on the total cellulose result, we rely on the average composition of green leaves, with an average content of around 50% cellulose [*Butler and Bailey*, 1973]. By this assumption we assume, that the majority of cellulose occurring in the atmosphere is derived from cellulose from debris of green plants. The decomposition of green plant leaves from deciduous trees is considered the major source of atmospheric cellulose, as annually high amounts of green leaves decompose aided by fungi, beetles and other decomposers [*Puxbaum and Tenze-Kunit*, 2003]. For plant debris originating from this process we assume a factor of 2 best to represent the amount of debris derived from the green leaves decomposition. However, we can additionally think of other cellulose sources, with a potentially different conversion factor from cellulose to plant debris. Many plants produce more or less pure cotton containing seeds fibers such as cotton, dandelion, willow, poplar, reed etc. For break down products of such plant compartments a conversion factor close to 1 would have to be assumed. We have, however up to no not observed considerable increases of the cellulose signal in seeding periods of the "cellulose fiber" plants. In contrast, we find a relatively low seasonal variation of the cellulose signal. Another process would tend to increase the conversion factor: When green plant debris becomes decomposed, cellulose is generally consumed faster than lignine constituents. Thus we think that the influence from cellulose containing seeds and from decomposed leaves will level out. The uncertainty of the conversion factor from free cellulose to plant debris can be estimated only at this time as no detailed information about the atmospheric mobilization processes of cellulose is available. Our best estimate is an uncertainty of 30% for the conversion factor of 2 for converting from total cellulose to plant debris. The estimated total uncertainty derived by error propagation assumptions is then 37%.

3. Results

3.1. Detection Limit

[11] For deriving the detection limit of the complete analytical procedure and to check for potential contamination during the shipping, storage, sampling and assembling

Table 1. Practical Detection Limit (DL) of Free Cellulose for Individual Sites[a]

Cellulose	AZO	AVE	PDD	SBO	SIL	KPZ
DL, ng/m^3	5.2	7.7	3.5	7.3	6.4	7.7
Number of FB	14	15	6	14	12	7

[a]FB, field blank.

of the filter holder, field blanks were sent with the samples to 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 with the sampling sites. The average sampled volumes were 10081 Nm^3 for AZO, 10691 Nm^3 for AVE, 8025 Nm^3 for PDD, 7380 Nm^3 for SIL, 3019 Nm^3 for SBO and 4457 Nm^3 for KPZ.

[12] The detection limits were calculated for all sites separately on the basis of 6–15 samples per site. The field blanks for SBO and KPZ showed high values (22.1–32.7 ng/m^3 respectively) for the first 3 blank samples, and lower blanks thereafter. It was concluded that a contamination source existed originally which was excluded later. The blanks for those sites are given excluding the high values. Also for SBO and KPZ spurious high blanks were observed which were excluded from the data set. Table 1 summarizes the detection limits for free cellulose achieved for the data sets excluding outliers.

3.2. Cellulose Annual Averages at the CARBOSOL Sites

[13] In all samples "free cellulose" was determined. "Total cellulose" was determined from "free cellulose" with the conversion factor of 1.4 (see section 2.2). The data we refer to as cellulose in the following text are "total cellulose" data.

[14] At the six "CARBOSOL" sampling sites cellulose was above detection limit in most of the samples, with the exception of the clean maritime AZO site, where a larger number of samples were below the detection limit (data available in auxiliary material[1]). The average concentration values of cellulose as well as the median, minimum and maximum values for the six sampling sites are summarized in Table 2. The biannual average of atmospheric cellulose ranged between 16.3 and 181 ng/m^3 for the six background sampling sites in Europe. At AZO, the oceanic background sampling site, the lowest biannual average concentrations of cellulose (16.3 ng/m^3, with a range of <5.0–51 ng/m^3) was observed. For the mountain sites the average concentration decrease with elevation: At SBO, a high alpine sampling site situated at 3106 m, with free troposphere conditions during the cold season an average of 47 ng/m^3 cellulose was found. At PDD (1405 m) the biannual average was 83 ng/m^3, while at SIL (1205 m), the biannual average concentration of cellulose was 122 ng/m^3. Consequently, the highest concentration (biannual average 181 ng/m^3) occurred at the low-level central European background site KPZ (136 m).

[15] At the coastal site AVE an intermediate behavior between clean maritime (AZO) and continental (KPZ) is observed, with concentrations slightly below 50% of the KPZ values. The site AVE is situated close to an urban area and is influenced during the year alternately from maritime and from continental air masses.

[16] Table 3 presents the averages of summer and winter periods and the ratio between both seasons. The period of December, January and February was averaged as winter, while the months of June, July, and August were summarized as summer period. The calculation of a summer/winter ratio represents the seasonal changes of the concentration values at the six sampling CARBOSOL sites. For all the sampling sites the averages of summer period were higher than winter concentration values, except for AVE. Here, the average of winter concentration values is a factor of 2 higher to summer period.

[17] Lower concentrations of cellulose during the cold season were expected for the mountain sites and the continental background site KPZ, as less plant debris production during the dormant season was assumed. The reasons for the higher winter concentrations at AVE are not clear yet, although winter conditions at the maritime AVE site differ considerably from other inland sites, as it is wet but not snow covered at AVE in winter.

3.3. Seasonal Variation of the Atmospheric Cellulose Concentration

[18] At SIL, PDD, SBO, as well as at KPZ the seasonal variation of cellulose showed higher concentration values during the growing season, in particular during spring and summer (see also Figure S1 in auxiliary material). In more detail SIL and KPZ showed relatively similar patterns, however with lower absolute values at the elevated site. Also, the patterns at PDD and SBO, both at higher elevation, were comparable. At the elevated site SIL, the pronounced spring maxima are observed from April–June. Lowest concentrations occur during winter. However, compared to other air contaminants the seasonal cycle is surprisingly weak, with higher winter levels than expected. At the low-level rural site KPZ in the Hungarian plain, elevated concentrations occur during all seasons, with an indication of a spring and an autumn maximum. PDD and SBO are two elevated mountain sites at 1405 and 3106 m elevation, which exhibit a similar general pattern of the cellulose concentration with lower values in winter, and a late spring maximum. The sampling site at SBO is receiving free tropospheric air masses during most of the winter season. For this reason, winter values for cellulose at SBO are not far from values observed at the remote maritime site

Table 2. Biannual Average, Median, Minimum and Maximum Monthly Mean Values of "Total Cellulose" at the Six Sampling Sites

Cellulose, ng/m^3	AZO 50 m	AVE 40 m	PDD 1405 m	SIL 1205 m	SBO 3106 m	KPZ 136 m
Average	16.3	71	83	122	47	181
Median	12.5	60	77	84	35	154
Min	<5.0	<7.0	<4.0	7.0	<6.0	28
Max	51	158	242	351	103	463

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[1] Auxiliary material data sets are available at ftp://ftp.agu.org/apend/jd/2006jd008180. Other auxiliary material files are in the HTML.

Table 3. Biannual Arithmetic Average of "Total Cellulose" for Summer and Winter Periods and Summer/Winter Ratio

Cellulose, ng/m^3	AZO 50 m	AVE 40 m	PDD 1405 m	SIL 1205 m	SBO 3106 m	KPZ 136 m
Summer	18.5	46.7	135	162	62.5	229
Winter	13.8	107	39.9	39.3	29.4	115
Summer/winter	1.3	0.4	3.4	4.1	2.1	2.0

AZO. At PDD the concentration values for cellulose are between concentrations at SBO and SIL, according to the elevation. Mountain sites are influenced by boundary layer air masses during summer, while in winter air masses are prevailing at the site are decoupled from the air below the mixing layer and can be representative for free troposphere conditions. This effect is considered to enhance the seasonal cycle which is assumed for cellulose to follow roughly the biogenic production of the leaves and of other plant parts, which in some cases are expelled in large quantities as semen during the growing season. The oceanic background site AZO receives rather low concentrations of cellulose throughout the year. The site is indeed influenced frequently by strong winds of oceanic air and the low concentrations of cellulose observed are appear to result predominantly from continental long-range transport, while local effects are

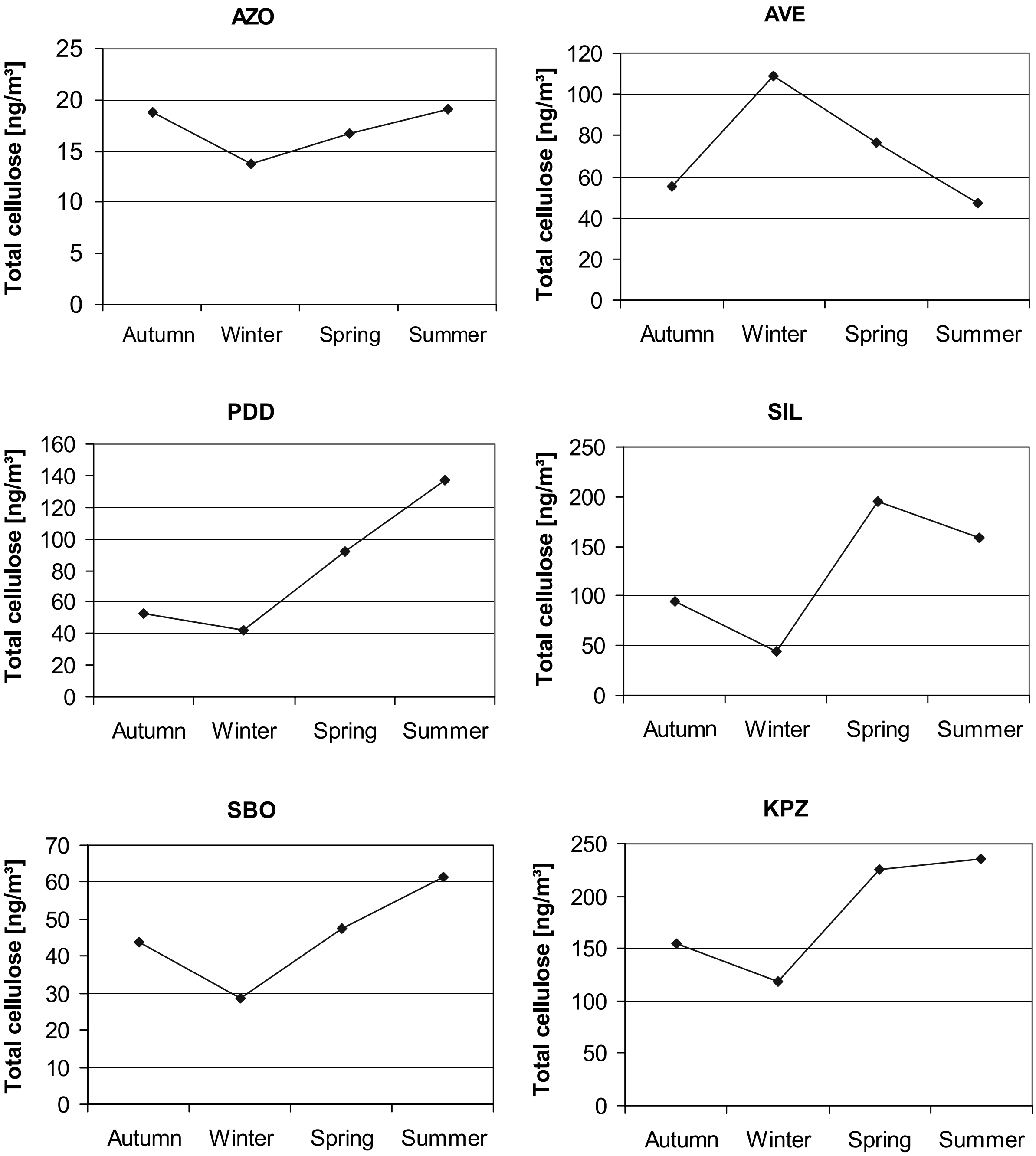

Figure 1. Seasonal variation (quarters) of total cellulose at the CARBOSOL sites (average from 2 years).

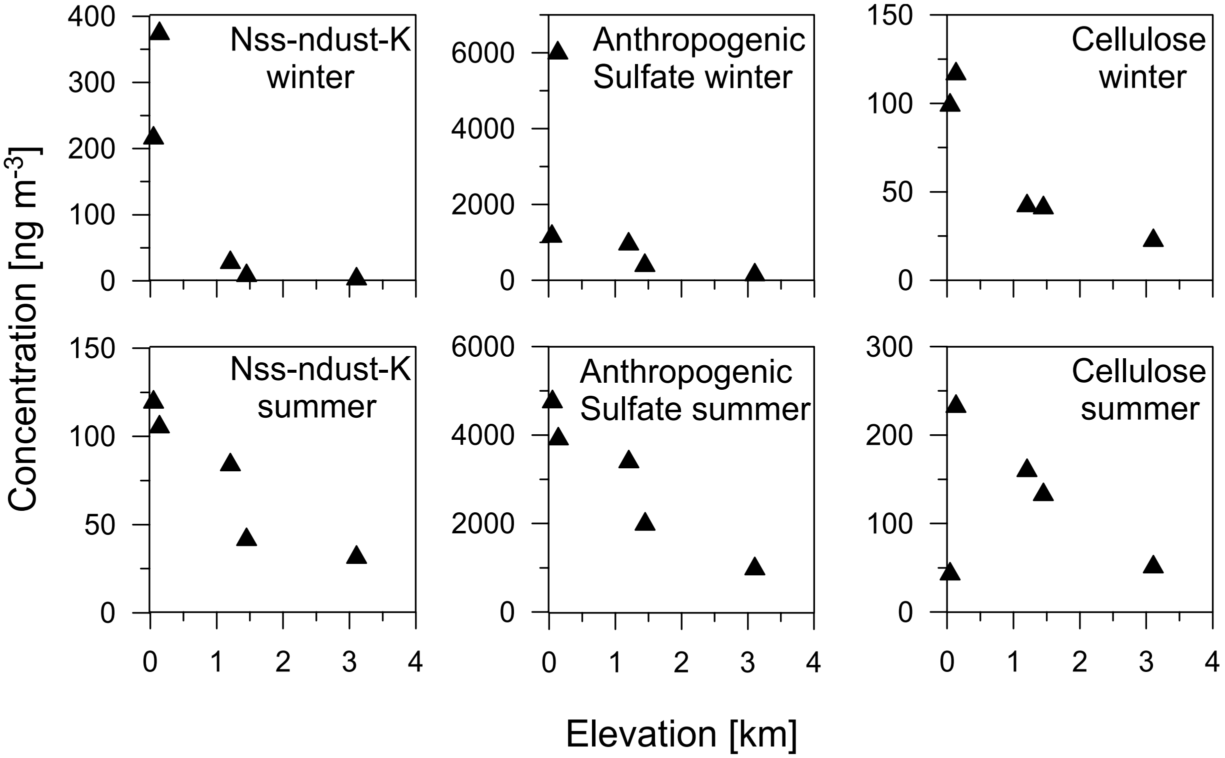

Figure 2. Elevational profiles of midwinter (December–February) and midsummer (June–August) averages of Nss-ndust-K, anthropogenic sulphate, and total cellulose at the CARBOSOL sites at the continent. Sulfate and potassium data are from *Pio et al.* [2007].

secondary. No seasonal variation was observed at the AZO site.

[19] For AVE the seasonal cycle observed was different as compared to the continental sites. Higher concentrations of cellulose were observed in the winter months. The seasonal variation was similar to another component in the CARBOSOL data set, levoglucosan [*Sánchez-Ochoa*, 2005]. Levoglucosan is a pyrolysis product of cellulose and serves as a tracer for wood combustion. One might derive a conclusion, that during biomass combustion, a certain fraction of cellulose aerosolizes unburned or in break down products, which undergo hydrolysis to glucose in our assay (e.g., cellubiose). Also at KPZ a certain wintry occurrence of cellulose was observed.

[20] However, in combustion experiments of different types of wood typically for mid-Europe in a tile stove cellulose was found, but in low concentrations in relation to the wood smoke emission (around 0.1% cellulose in wood smoke [*Schmidl*, 2005]). Thus wood combustion in stoves seems not to create marked emissions of cellulose. Still, no information is available about the situation from combustion in other oven types, fire places, or open field burning, which might exhibit higher cellulose emissions relative to wood smoke, than in a tile oven with quite low velocity of the exhaust gases.

[21] The seasonal variation (quarters) of cellulose at the different sampling sites are represented in Figure 1.

3.4. Elevational Profiles of Cellulose

[22] The elevational profiles of cellulose are compared with profiles of "anthropogenic sulphate" and "non-sea-salt-non-dust-potassium" (Nss-ndust-K) in Figure 2.

[23] During summer the decreasing tendency with elevation is comparable for the three investigated species, with the exception of the summer value at AVE, which is unexpectedly low. The origin of the deviation is not clear as no other information about regional differences of specific sources and their emission behavior of cellulose has been explored until now. During winter the decrease with elevation is considerably less pronounced for cellulose than for the sulphate and potassium under comparison. This behavior might be a result of a longer life time compared to highly water soluble sulphate and potassium salts. Plant debris is not water soluble and might be less efficiently scavenged than the other salts since it occurs in wide size distribution from 0.1 to 25 μm and a maximum of around 2 μm AD [*Puxbaum and Tenze-Kunit*, 2003]. Micrometer size particles will have practically no tendency to mix with accumulation mode particles. Furthermore, there might be also unknown emission processes for the submicrometer size cellulose particles. One might consider stormy weather which may produce plant debris from trees at elevated sites even in winter, since wind speed increases generally with elevation. Still, the relative enrichment of cellulose in winter at elevated sites is a puzzling result requiring either elevated winter sources (e.g., storm impact on trees) or higher lifetime of micrometer sized plant debris constituents com-

Table 4. Relative Contribution of "Cellulose"-C to OC[a]

Cellulose-C/OC, %	AZO	AVE	PDD	SIL	SBO	KPZ
Average	2.3	0.7	3.2	2.6	3.9	1.6
Minimum	0.5	0.1	0.3	0.1	0.4	0.1
Maximum	8.7	2.4	22	18	26	6.3
Summer	1.8	0.7	2.0	1.9	2.0	2.2
Winter	2.3	0.5	3.8	2.3	8.5	0.7
Winter/summer	1.3	0.7	2.0	1.2	4.2	0.3

[a] Biannual average, minimum and maximum, summer and winter values of the six sampling sites. Cellulose-C = "cellulose"/2.25.

Table 6. Relative Contribution of "Plant Debris" to OM for the Six Sampling Sites, Biannual Averages, and Monthly Averaged Minimum and Maximum Values

Plant Debris/OM, %	AZO	AVE	PDD	SIL	SBO	KPZ
Average	6.1	1.8	8.4	7.0	10.4	4.2
Minimum	1.3	0.2	0.8	0.4	1.1	0.2
Maximum	23	6.4	58	47	70	17

pared to accumulation mode particles. Further research will be required to explain the wintry elevational enrichment of cellulose.

3.5. Contribution of Cellulose-C to OC

[24] Table 4 summarizes the results of the contribution of cellulose-C to OC, average concentration values, as well as maximum and minimum values. The percentage of cellulose-carbon in organic aerosol carbon varied in the biannual averages between the sites from 0.7% to 3.9%. The highest contributions of cellulose-C to OC were observed at the mountain sampling sites (2.6% to 3.9%) and the lowest contribution at the low-level sampling sites (0.7% to 2.3%). The highest contribution was found at SBO (3.9%). The result at PDD (3.2%) was between SBO and SIL, while at SIL it was 2.6%. The higher relative concentrations at mountain sites can be explained by a generally lower OC concentration at elevated sites, but also with sources active in the mountainous regions, e.g., forests. At AZO cellulose as well as OC is very low, resulting in 2.3%, cellulose-C of OC). The lowest concentration values were obtained in KPZ and AVE, where the contribution of cellulose-C to OC is 1.6% and 0.7%, respectively. The low contribution at these sampling sites is likely a result of elevated OC from other sources; at AVE in particular from wood combustion [*Sánchez-Ochoa*, 2005; *Puxbaum et al.*, 2007].

[25] Table 4 also shows the average contribution of cellulose-C to OC for summer and winter periods as well as the ratio between winter and summer for all the sampling sites.

[26] For the clean maritime site AZO the relative fraction of cellulose-C in OC is similar during winter and summer. At the lower-level sites AVE and KPZ higher contributions occurred in summer. At mountain sites surprisingly cellulose-C to OC contributions were considerably higher in winter compared to summer. This is a result of very clean conditions with respect to wintry carbonaceous aerosol at the mountain sites. The increasing trend of cellulose-C to OC with elevation indicates that the OC decreases steeper with elevation than the cellulose-C. Again, there might be an input from the forests as source being active to some extent also during the cold season. Also, long-range transport of cellulose from warmer regions cannot be excluded.

Table 5. Biannual Average, Median, Minimum, and Maximum Values for Plant Debris

Plant Debris, ng/m^3	AZO 50 m	AVE 40 m	PDD 1405 m	SIL 1205 m	SBO 3106 m	KPZ 136 m
Average	33.4	142	168	245	93.3	363
Median	26.1	120	153	167	69.6	307
Minimum	13.6	10.1	14.3	10.0	12.7	56.1
Maximum	138	591	629	1024	461	1221

3.6. Contribution of Plant Debris to OM

[27] In leaves of terrestrial plants, the content of cellulose is around 50%, while lignin amounts to <20% and hemicelluloses 20–30% [*Butler and Bailey*, 1973]. As it is assumed that the major fraction of cellulose in continental aerosol originates from decomposition processes of leaves and other plant parts [*Puxbaum and Tenze-Kunit*, 2003], the portion of plant debris in aerosol was proposed to be estimated according to the mass fraction of cellulose in leaves by the relation: "Plant debris" = 2 * total cellulose. Table 5 shows the biannual average, median as well as minimum and maximum values for plant debris.

[28] A major goal of the present work was to assess the contribution of plant debris to organic matter (OM). To convert the mass of organic carbon to an estimate of organic compound mass, it must be multiplied by a scale factor (generally 1.2–1.4 for urban aerosol samples) to account for the oxygen, hydrogen, and other elemental content of the organics present [e.g., *Stelson and Seinfeld*, 1981]. *Hegg et al.* [1997] state that "for less urbanized environments, particularly those in which a substantial fraction of the aerosol derives from natural sources, the molecular-to-carbon mass ratio should be appreciably higher." They proposed a conversion factor of 1.7, based on the assumption that the factor has to lie between the factor for the urban environments and a factor for natural material. In the present study, a scale factor 1.7 was used to convert the mass of organic carbon to organic matter. Thus, to assess the relative concentration of plant debris in OM, the concentration value of "total cellulose" is multiplied by 2 (equation (1)). The relative contribution of plant debris to OM is obtained by dividing the concentration of plant debris OM by OM (OC * 1.7). The scheme of this calculation is as follows:

$$\text{Plant debris(OM)/OM}(\%) = \left(\text{“ total cellulose”}.^{*}2/\text{OC}^{*}1.7\right)^{*}100 \qquad (1)$$

[29] Table 6 shows the derived contribution of plant debris to organic matter (OM) for all sampling sites. The contribution of plant debris to OM ranged between 1.8% and 10.4%. The higher fractions of plant debris in OM were observed at the mountain sites, increasing from 7% to 10.4% from SIL to SBO. At the low-level sampling sites

Table 7. Relative Contribution of "Plant Debris" to OM[a]

Plant Debris/OM, %	AZO	AVE	PDD	SIL	SBO	KPZ
Autumn	8.0	1.5	9.3	6.3	10.3	3.4
Winter	6.1	1.4	10.1	6.1	22.4	1.8
Spring	7.5	2.6	9.5	10.8	6.3	5.5
Summer	4.7	1.9	5.2	5.2	5.3	5.9
Winter/summer	1.3	0.7	2.0	1.2	4.2	0.3

[a] Averages for the four periods and winter/summer ratio.

the contribution were lower; lowest at AVE with an average value of 1.8%, ranging from 0.2% and 6.4%, due to high OM levels from other emission sources. At AZO as an oceanic background site, although the concentration values of cellulose were very low and with many samples below the detection limit, the contribution of plant debris to OM was relatively high (6.1%, ranging from 1.3 to 23%). At KPZ the highest concentration values of cellulose were found, the contribution of plant debris to OM is between AVE and the mountain sites (4.2%, ranging from 0.2 to 17%).

[30] The seasons comparison of summer-winter shows that there are not marked differences between summer and winter at AZO, AVE, and SIL (Table 7). However, at SBO and PDD, major contributions of plant debris to OM are observed in winter with a ratio between winter-summer of 4.2 and 2.0 respectively. Elevated concentration values of cellulose during winter, in particular in winter 2004, were influential on the contribution of plant debris to OM. At KPZ as a rural low-level sampling site, the seasonal trend is opposite; the contributions of plant debris to OM are higher in summer than winter, resulting in a winter-summer ratio of 0.35.

[31] Comparable contributions of vegetative detritus to OC were also reported for semiurban sites by *Schauer et al.* [2002] and *Zheng et al.* [2002] (5.7% and 8.8%). In an African savanna, plant debris, determined from the cellulose content of the aerosol, accounted for 4% of the OM [*Puxbaum et al.*, 2000].

4. Conclusions

[32] 1. At the elevated sites and at KPZ concentrations of free cellulose were generally higher from spring to autumn, which coincides with the growing season of plants at midlatitudes. At the AVE site distinct winter maxima occurred, while at AZO concentrations are similar throughout the year. The reason for the winter maxima is unclear at present.

[33] 2. On the continent concentrations of free cellulose are higher in the growing season than in winter. Free cellulose decreases with elevation, winter levels at SBO (3106 m) are comparable to clean Atlantic conditions (AZO). Cellulose-C undergoes a relative winter enrichment compared to the OC levels at the elevated sites.

[34] 3. The atmospheric concentration of plant debris (2-year averages) ranges from 33.4 ng/m^3 at AZO to 363 ng/m^3 at KPZ. The highest monthly concentrations (up to 1221 ng/m^3) were observed during the growing season at the continental KPZ site. As for free cellulose, plant debris concentrations decrease with elevation.

[35] 4. Relative contributions of plant debris to OM (2-year averages) in the west-east transect range from around 2% at the coastal site AVE to 10% at SBO. Relative contributions of plant debris to OM increase with elevation. At elevated sites (SIL, PDD, SBO) winter levels are higher than summer levels and increase with elevation, while at low-level sites (AVE, KPZ) summer levels are more pronounced. At the oceanic AZO sites the relative fraction of plant debris in OM seems relatively independent of the season.

[36] 5. Surprisingly high relative concentrations of plant debris in OM were observed at the elevated sites. Thus plant debris is a very important constituent of the organic material at elevated background sites with summer concentrations of around 5% and winter levels from around 6–22% depending on elevation.

[37] 6. At typical mid-European level the plant debris fraction contributes on the average 4–5%, at the oceanic background site AZO (Azores) around 6% to OM, in both cases a main constituent.

[38] 7. Since cellulose and related material is considered rather long-lived with respect to atmospheric oxidation processes, it may become enriched on the way to background regions, which may explain the elevated relative levels at elevated sites.

[39] 8. Cellulose is a suitable macrotracer for "plant debris" (or in the US receptor model nomenclature "vegetative detritus"); its anticipated atmospheric robustness against oxidation may make it suitable as tracer for lifetime studies of less stable constituents.

[40] **Acknowledgments.** The authors acknowledge the contribution of many members of the CARBOSOL team for sampling, sample handling and transfer. Sampling at the Schauinsland site was performed by UBA on-site staff. The CARBOSOL project is funded by EU contract EVK2-CT-2001-00113.

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