



## Seasonal trends and possible sources of brown carbon based on 2-year aerosol measurements at six sites in Europe

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[1] Brown carbon is a ubiquitous and unidentified component of organic aerosol which has recently come into the forefront of atmospheric research. This component is strongly linked to the class of humic-like substances (HULIS) in aerosol whose ultimate origin is still being debated. Using a simplified spectroscopic method the concentrations of brown carbon have been determined in aqueous extracts of fine aerosol collected during the CARBOSOL project. On the basis of the results of 2-year measurements of several aerosol constituents at six European sites, possible sources of brown carbon are inferred. Biomass burning (possibly domestic wood burning) is shown to be a major source of brown carbon in winter. At elevated sites in spring, smoke from agricultural fires may be an additional source. Direct comparison of measured brown carbon concentrations with HULIS determined by an independent method reveals that the two quantities correlate well at low-elevation sites throughout the year. At high-elevation sites the correlation is still high for winter but becomes markedly lower in summer, implying different sources and/or atmospheric sinks of brown carbon and HULIS. The results shed some light on the relationships between atmospheric brown carbon and HULIS, two ill-defined and overlapping components of organic aerosol.

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### 1. Introduction

[2] The relevance of atmospheric aerosol in inadvertent climate modification has been recognized in the last decade [Fuzzi *et al.*, 2006]. Evaluation of its atmospheric effects is, however, associated with very high uncertainties, partly because of the fact that a considerable part of organic aerosol mass remained unidentified [Huebert and Charlson, 2000]. A better understanding of the sources of carbonaceous aerosol is critically needed in order to be able to predict its contribution to climate forcing. There are two

important yet ill-defined subsets of organic aerosol which likely strongly overlap: “brown carbon” defined as light-absorbing organic matter (other than soot) in atmospheric aerosol of various origins [Andreae and Gelencsér, 2006], and humic-like substances (HULIS) that are omnipresent in rural, urban and biomass burning aerosol [Graber and Rudich, 2006]. The existence of water-soluble brown carbon was firmly established by observations of spectral properties of the aqueous extracts of continental aerosol [Havers *et al.*, 1998; Zappoli *et al.*, 1999; Kirchstetter *et al.*, 2004] as well as by spectrally resolved aerosol light absorption measurements near specific combustion sources [Bond *et al.*, 1998; Bond, 2001; Day *et al.*, 2006]. A recent study has directly established the very high degree of overlap between water-soluble brown carbon and HULIS in biomass burning aerosol [Hoffer *et al.*, 2006], though earlier studies already implied that biomass burning is a probable primary source of HULIS and thus implicitly also of brown carbon [Zappoli *et al.*, 1999; Mayol-Bracero *et al.*, 2002]. Laboratory studies evaluating the possibility of atmospheric formation of HULIS have indirectly proven that brown carbon may be formed by heterogeneous reactions of isoprene in the presence of sulfuric acid as catalyst [Limbeck *et al.*, 2003], or in multiphase atmospheric reactions from semivolatile lignin pyrolysis products in clouds or hydrated aerosol [Gelencsér *et al.*, 2003; Hoffer *et al.*, 2004]. The possibility that light-absorbing organic aerosol

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may also originate from biogenic materials and their low-temperature oxidation and polymerization products was in fact first raised by *Andreae and Crutzen* [1997].

[3] The primary objective of our study is to reveal the variations of concentrations of water-soluble brown carbon in fine aerosol samples collected at six sampling sites in Europe over a period of 2 years, and establish its relationship with HULIS for which no standard analytical method is available. These measurements were conducted as part of the EU CARBOSOL project. An overview of the CARBOSOL project as well as the climatology of major carbonaceous aerosol components in the European region is presented in this volume [*Legrand and Puxbaum*, 2007; *Pio et al.*, 2007]. For the determination of brown carbon we used a direct spectroscopic method but expressed its mass concentrations in HULIS-equivalent as the calibration was performed with solutions of HULIS isolated from aqueous extracts of aerosol samples using a preparative-scale separation method [*Varga et al.*, 2001]. In order to establish a relationship with HULIS and to provide tentative source apportionment for both, comparison with HULIS concentrations determined from the same samples using a fundamentally different methodology [*Feczkó et al.*, 2007] is given. The spatial and temporal variation of mass concentrations are evaluated in the light of other aerosol constituents (e.g.,  $^{210}\text{Pb}$ , levoglucosan) to shed some light on the relative importance of potential sources and the relationship between brown carbon and HULIS in continental fine aerosol.

## 2. Experimental Section

### 2.1. Sampling

[4] Within the framework of the CARBOSOL project weekly aerosol samples were collected between September 2002 and September 2004 at two rural, three mountain and one oceanic site along an east-west transect across Europe. These nonurban sites, namely from west to east are: Azores (AZO), Aveiro (AVE), Puy de Dôme (PDD), Schauinsland (SIL), Sonnblick (SBO) and K-puszta (KPZ). Azores is a background oceanic site located on Terceira Islands, in Portugal (38°38'N, 27°02'W, 50 m a.s.l.) where marine atmosphere is frequently influenced by transport from the continents of North America, Europe and Africa. The two medium-elevation mountain sites are Puy de Dôme (central France, 45°46'N, 2°57'E, 1450 m a.s.l.) and Schauinsland (southwestern Germany, 47°55'N, 07°54'E, 1205 m a.s.l.). The high-elevation mountain site is on Sonnblick (Austrian Alps, 47°03'N, 12°57'E, 3106 m a.s.l.). All of the mountain sites (but especially Sonnblick) are frequently above the continental boundary layer, especially in winter. During summer, thermal convections may transport air masses containing pollutants from ground-level sources to the sites, which are mostly influenced by emissions (mostly fossil fuel combustion), related to agricultural and forestry works and transport in the region. The low-level sampling sites were Aveiro, located in Portugal (40°34'N, 8°38'W, 40 m a.s.l.), nearest to urban sources, representing mixed semiurban, rural and coastal conditions and K-puszta, the Hungarian background air pollution monitoring station (46°58'N, 19°35'E, 136 m a.s.l.) K-puszta is situated in a forest clearing of the Great Hungarian Plain, approximately

in the middle of the country. This station is located in a region with a low density of inhabitants with respect to the average for central Europe and is thus represents central-eastern European regional air.

[5] CARBOSOL aerosol samples were collected on quartz filters with Hi-Vol samplers at a flow rate of 60 m<sup>3</sup> per hour. The impactors were equipped with a sampling inlet of 2.5 μm cutoff. In the sampling setup no artifact correction method was applied. (For details of the sampling sites and procedure, see *Pio et al.* [2007]).

### 2.2. Analytical Methods

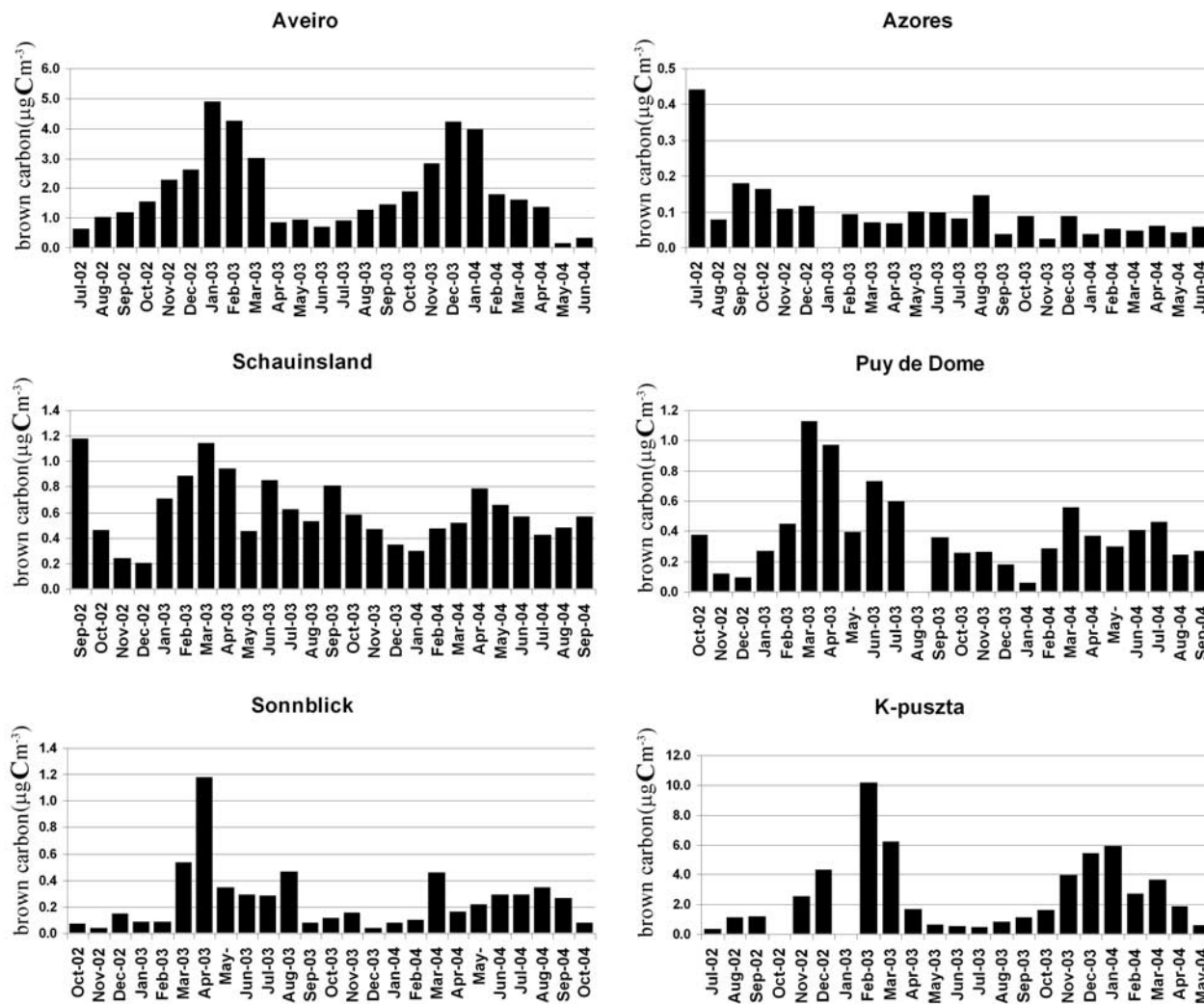
[6] Brown carbon mass concentrations were determined by spectroscopic measurements of the aerosol extracts and calibration was realized against HULIS isolated from a subset of CARBOSOL aerosol samples collected at Aveiro and K-puszta, between 8 July and 9 September 2002 and 5 August and 21 October 2002, respectively. Determination of HULIS from those samples was achieved using a preparative-scale separation method (see below and in detail in the work by *Varga et al.* [2001]).

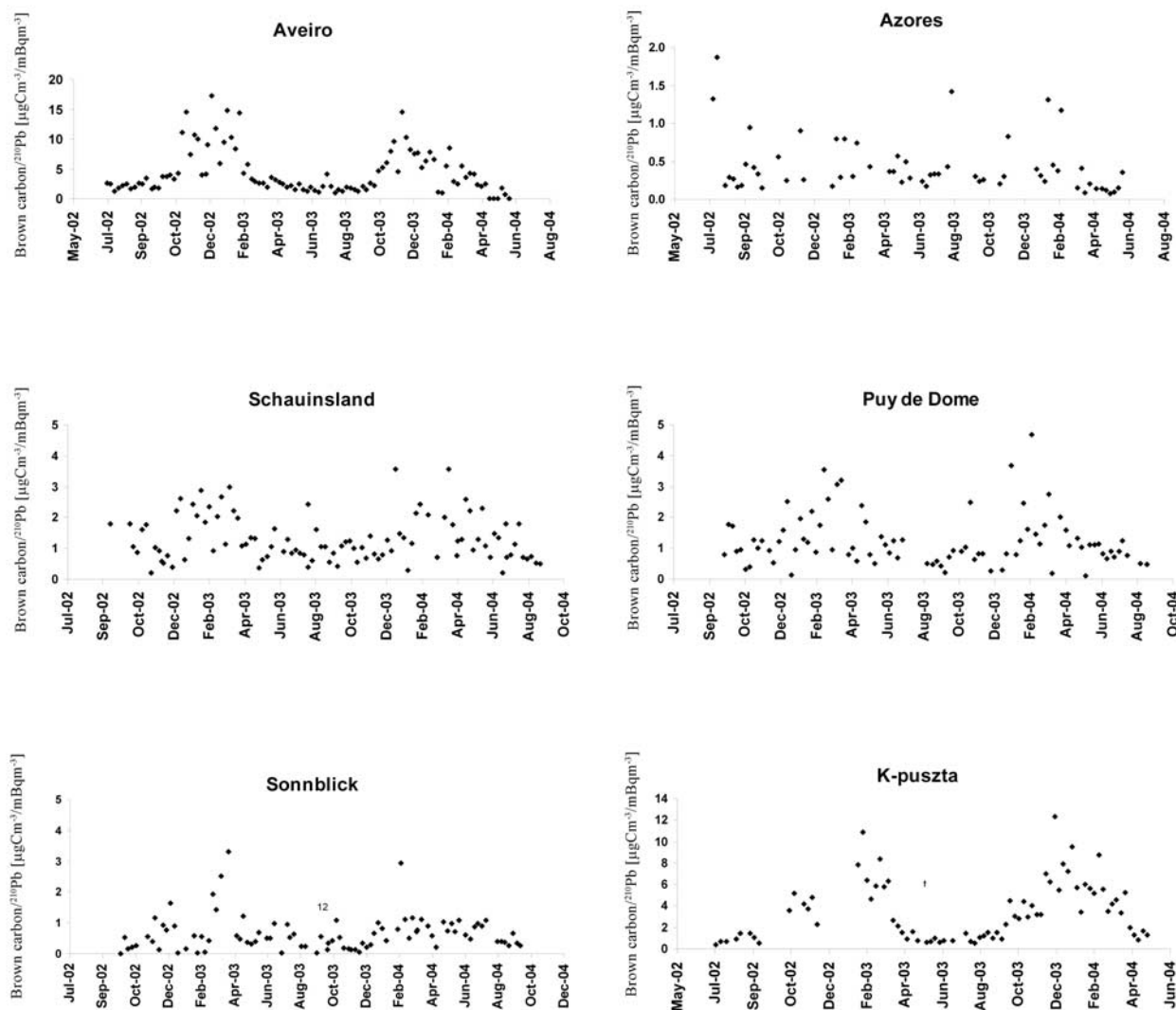
[7] Results are expressed in HULIS-equivalent carbon mass concentrations (μgCm<sup>-3</sup>) using a conversion factor of 0.504 to make comparison with HULIS concentrations measured by a principally different method possible [*Feczkó et al.*, 2007]. Within the frame of the CARBOSOL project, levoglucosan mass concentrations and  $^{210}\text{Pb}$  activities were codetermined from the same samples. Levoglucosan was determined by gradient-HPLC method with electrochemical detection (ED40, Dionex) using a CarboPac PA10 column (Dionex) for carbohydrate analysis,  $^{210}\text{Pb}$  activities were determined by nondestructive γ-spectrometry using solid state Ge-detectors. The methods are described in detail by *Puxbaum et al.* [2007] and *Hammer et al.* [2007].

[8] Hi-Vol aerosol filters were soaked in 2 × 45 mL MilliQ water over 2 × 12 hours, kept away from direct irradiation. The extracts were filtered on a Millex<sup>®</sup>-HV hydrofil Durapore<sup>®</sup> filter (PVDF material, 0.45 μm Ø, 25 mm internal and 30 mm external diameter). Brown carbon concentrations were determined by measuring absorbance of the extracts with a UV-VIS spectrophotometer at the wavelength of 350 nm. The extracts were diluted or preconcentrated by freeze-drying as necessary to yield absorbance values within the range of calibration. For calibration, absorbance values were compared with the results obtained by gravimetric measurements following isolation of HULIS from a subset of CARBOSOL samples. For isolation, the pH of the aqueous aerosol extracts was adjusted to 2 by cc. HCl and the acidified extracts were applied to Waters Oasis HLB SPE cartridges. The columns were preactivated with 3 mL methanol and 3 mL 0.01 M HCl (pH = 2) and rinsed with 2 × 2.5 mL MilliQ water after the elution. Finally the columns were dried in nitrogen, and humic-like substances, which are expected to be retained by the column, were eluted with 6 mL methanol. Gravimetric measurements were performed from effluent after drying in nitrogen and kept in a desiccator for 24 hours. The carbon content of analytes was measured by using an Astro Model 2100 TOC solid-analyzer. The concentrations were measured as CO<sub>2</sub> by a catalytic combustion method in oxygen at 680°C. Data acquisition and evaluation were performed by

**Table 1.** Biannual Average Mass Concentrations of Water-Soluble Brown Carbon and Their Share in TC and WSOC at Each CARBOSOL Sampling Site<sup>a</sup>

	Aveiro (AVE)	Azores (AZO)	Schauinsland (SIL)	Sonnblick (SBO)	Puy de Dôme (PDD)	K-pusztá (KPZ)
Brown carbon, $\mu\text{gC m}^{-3}$ , STP						
Average	1.92	0.10	0.61	0.26	0.42	2.79
Median	1.50	0.07	0.60	0.17	0.34	2.13
SD	1.56	0.09	0.41	0.30	0.37	2.62
RSD%	81%	89%	68%	114%	88%	93%
Brown carbon, % of TC						
Average	29%	29%	26%	35%	30%	39%
Median	30%	22%	25%	27%	24%	33%
SD	10%	26%	14%	40%	21%	50%
RSD%	33%	88%	51%	115%	70%	130%
Brown carbon <sub>(C)</sub> , % of WSOC						
Average	68%	64%	47%	72%	55%	61%
Median	61%	50%	37%	47%	41%	56%
SD	33%	56%	48%	82%	59%	38%
RSD%	49%	87%	101%	114%	107%	63%

<sup>a</sup>Unit is  $\mu\text{gC m}^{-3}$ .**Figure 1.** Variations of monthly means of absolute mass concentrations of brown carbon ( $\mu\text{gCm}^{-3}$ ) over the entire sampling period at the CARBOSOL sampling sites.



**Figure 2.** Time series of the ratio of mass concentrations of brown carbon ( $\mu\text{gCm}^{-3}$ ) to codetermined  $^{210}\text{Pb}$  activities ( $\text{mBqm}^{-3}$ ). (Data points are from weekly samples).

Maxima 820 software. (More details of the analytical technique are given by *Varga et al.* [2001].)

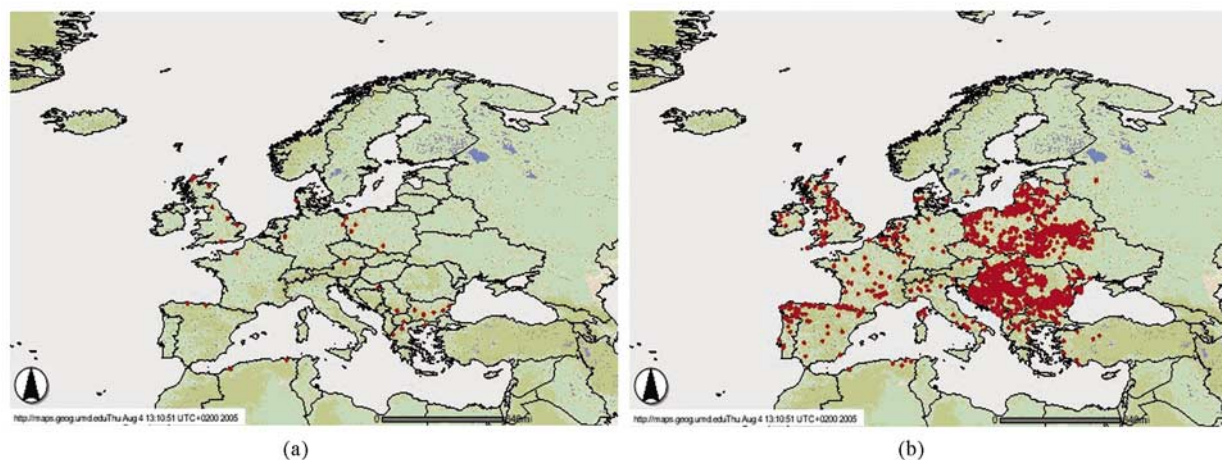
### 3. Results and Discussion

#### 3.1. Climatology of Brown Carbon

[9] As shown in Table 1, biannual average mass concentrations of brown carbon range from  $0.10$  and  $2.79 \mu\text{gCm}^{-3}$  (AZO, KPZ, respectively) in carbon-mass concentrations, which corresponds to  $0.19 \mu\text{gm}^{-3}$  (AZO) and  $5.53 \mu\text{gm}^{-3}$  (KPZ), based on the results of parallel carbon measurements. Absolute concentrations are significantly higher at Aveiro and K-pusztá than at the other sites, because of their vicinity to anthropogenic sources, but concentrations relative to TC and WSOC fall into a rather narrow range for all sites, 26–39% and 47–72%, respectively.

[10] Both seasonal variations (Figure 1) and average concentrations vary between sampling sites and the 2 years.

Overall, higher concentrations were observed in the year of 2002 and in 2003 winter than in the second part of the sampling period. The lowest concentrations were measured at Azores, where the sampled air mass was only occasionally influenced by continental effects, as shown by a few higher concentration values. Biannual average brown carbon concentrations were higher by a factor of 3 at Sonnblick than at Azores, the highest-altitude site among the CARBOSOL sites which is frequently lying above the continental boundary layer in winter, thus less affected by surface emissions in Europe. The regular seasonal variation of absolute brown carbon concentrations at SBO can be interpreted as the result of the yearly evolution of the boundary layer height [see also *Hammer et al.*, 2007]. At Puy de Dôme (PDD) and Schauinsland (SIL) brown carbon concentrations were found to be relatively higher in spring and early summer, and concentrations start to increase already in late winter (February and March). The flatter seasonal cycle seen at



**Figure 3.** (a) Open fires in Europe in the week between 27 February and 3 March 2003 as detected by MODIS fire monitoring satellites in a period with very low brown carbon/ $^{210}\text{Pb}$  ratio at SBO and PDD. (b) Open fires in Europe in the week between 20 and 27 March 2003 as detected by MODIS fire monitoring satellites in a period with very high brown carbon/ $^{210}\text{Pb}$  ratio at SBO and PDD.

these stations compared to Sonnblick is probably due to their more moderate elevation: they are more likely to be influenced by surface sources early in the year than SBO which lies at over 3 km. The relevance of atmospheric transport in the late winter period at these sites is also reflected in the covariation of brown carbon concentrations at the two sites.

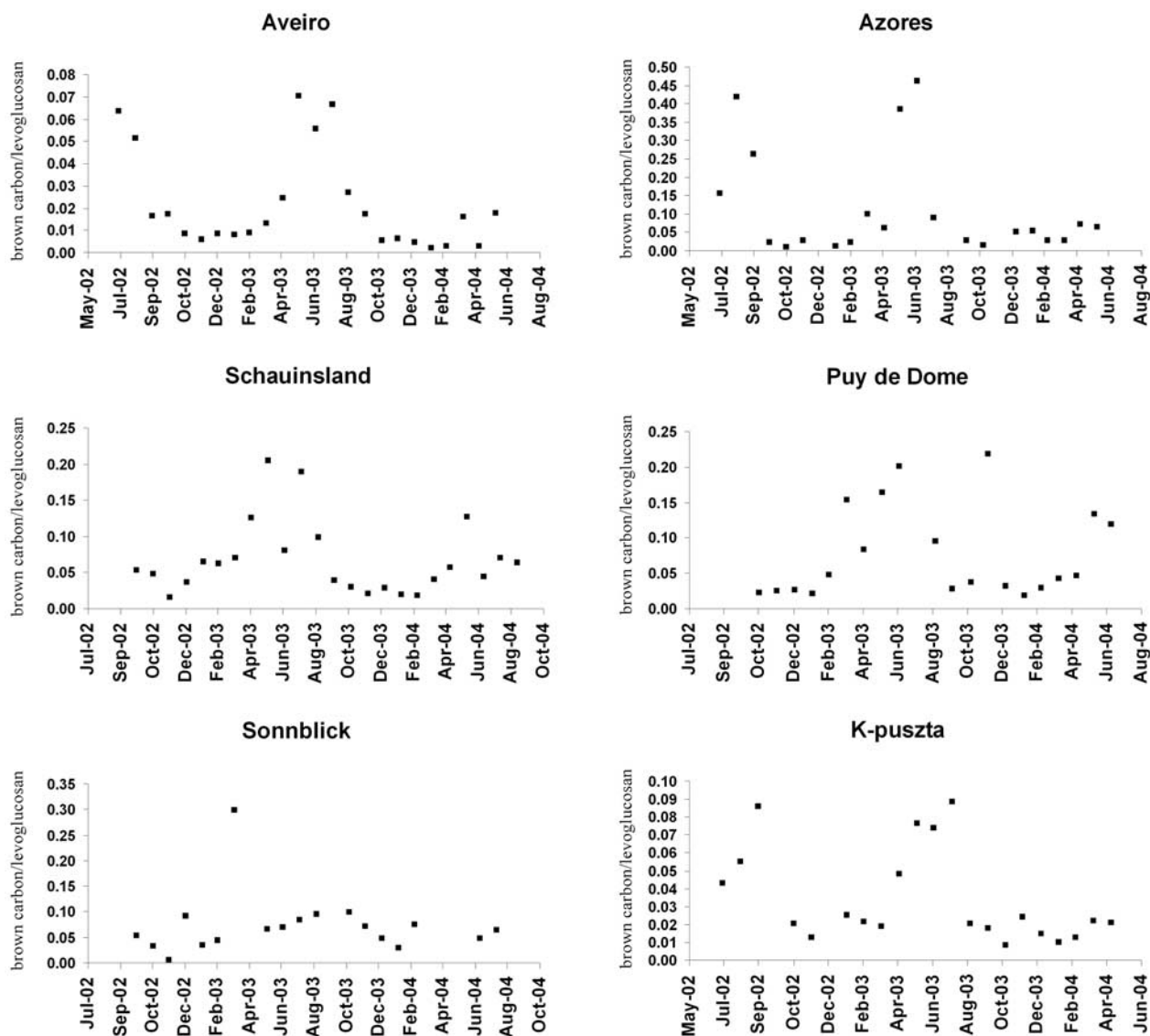
[11] However, at the low-level sites KPZ and AVE brown carbon concentrations were found to be a factor of 19 and 28 greater (respectively) than those found at AZO in winter and early spring. This is also the period when the contribution of anthropogenic heating emissions, and in particular residential biomass burning, is expected to be significant [see also *Gelencsér et al.*, 2007]. The effect of capped emissions from thermal inversions, frequent in winter, is also expected to increase aerosol mass concentrations (from primary emissions) during this period at these low-level sites.

### 3.2. Significance of Surface Sources and Atmospheric Transport

[12] Absolute mass concentrations of brown carbon were normalized by the codetermined  $^{210}\text{Pb}$  activities, which is a daughter element of  $^{222}\text{Rn}$  which has a uniform spatiotemporal emission rate, in order to evaluate the significance of surface sources and atmospheric transport [*Hammer et al.*, 2007]. Thus brown carbon/ $^{210}\text{Pb}$  ratios are obtained which are less influenced by the effects of atmospheric transport and boundary layer stability. Time series of the brown carbon/ $^{210}\text{Pb}$  ratio are shown in Figure 2 for all sites. At the maritime site Azores no temporal variation of the ratio can be seen. The two low-elevation sites AVE and KPZ show a clear seasonal pattern with a maximum during winter time and a broad minimum during summer. At both sites the winter maxima exceed the summer minima roughly by a factor of five. This feature clearly implies ground sources in winter, and given the results of the source

apportionment analysis of *Gelencsér et al.* [2007], or the levoglucosan measurements of *Puxbaum et al.* [2007], the most likely source is domestic wood burning for residential heating. The lack of a secondary summer maximum in this ratio also indicates that brown carbon sources (including biogenic sources) in the summer season are much less intense than those in the heating season. An interesting feature is that the  $^{210}\text{Pb}$ -normalized concentrations at PDD and SIL do not follow the absolute concentrations shown in Figure 1. The brown carbon/ $^{210}\text{Pb}$  ratios show a stronger seasonality than the absolute concentrations, which suggests that transport alone does not account for the seasonal changes. Instead, the relatively large brown carbon/ $^{210}\text{Pb}$  in springtime values must be explained by some combination of sources and/or chemical production. Since there is little sign of chemical production in the summertime, one possibility is that the peak is due to the combination of late winter emissions and increased vertical transport. After normalization (and removal of the transport effects), the trends at PDD and SIL show qualitatively the same seasonal cycle with maxima in winter–early spring observed for the low-level stations, also consistent with the idea that brown carbon advected to PDD and SIL were impacted by similar continental sources found in low-level stations.

[13] On the other hand, at the high-alpine site SBO there is very little seasonality in the brown carbon/ $^{210}\text{Pb}$  ratio, with the exception of a few weeks around midspring when atmospheric transport associated with high surface emissions impact the site. This lack of seasonality may partly reflect the very large “footprint” of such an elevated site, which includes sources from a very large area. For example, model calculations made for another elevated site from the CARBOSOL project, Col du Dôme (French Alps, 4250 m), suggested that in wintertime more than 50% of the sulfate originated from outside Europe, essentially from North America [*Fagerli et al.*, 2007]. In summertime this fraction was still 25%. Further, even the European countries which

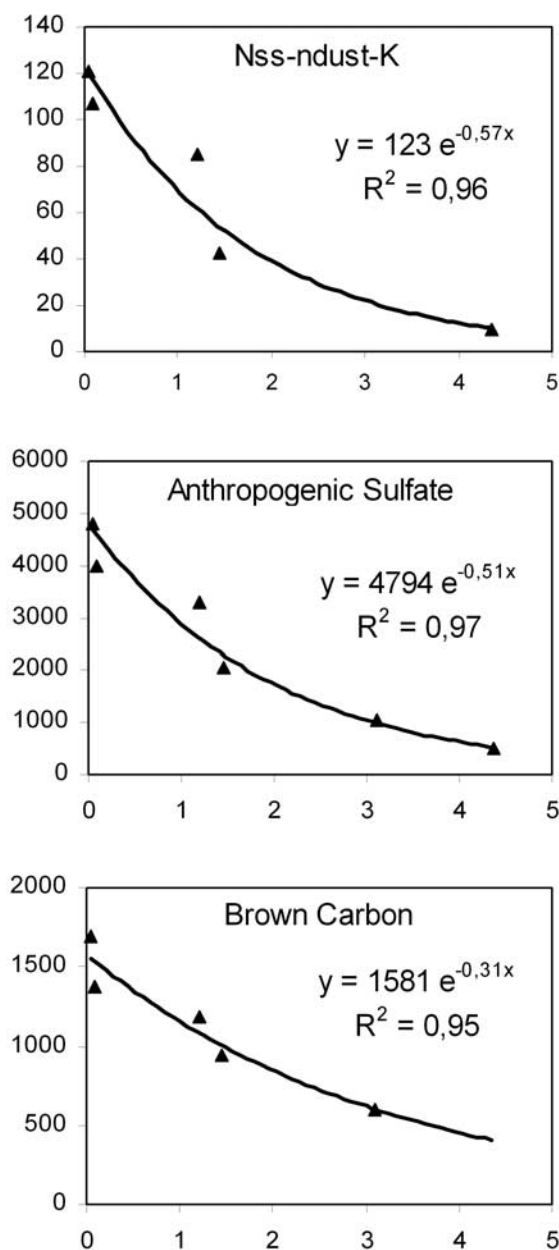


**Figure 4.** Ratio of monthly mean mass concentrations of brown carbon ( $\mu\text{gCm}^{-3}$ ) and levoglucosan ( $\text{ngCm}^{-3}$ ).

did contribute had very different climates, ranging from Spain to Great Britain. Seasonal cycles of emissions vary greatly across such vast areas, which would presumably minimize seasonal cycles seen in brown carbon at SBO. Apart from this, SBO is in the free troposphere over most of the periods characterized by high emissions in the Northern Hemisphere, thus water-soluble brown carbon was scavenged and the aerosol was internally mixed so that the brown carbon/ $^{210}\text{Pb}$  ratio was relatively constant.

[14] A comparison of images of MODIS fire-monitoring satellite (<http://firemaps.geog.umd.edu>) showing the distribution of open fires over Europe corresponding to specific weeks of very low and very high brown carbon/ $^{210}\text{Pb}$  ratios just a few weeks apart might provide some explanation. Figure 3 shows the distribution of open fires in Europe for weeks of very low and very high brown carbon/ $^{210}\text{Pb}$  ratios at high-elevation sites, respectively. It is clear that in the

former period (Figure 3a) open fires occurred only sporadically over Europe. On the other hand, the week when very high brown carbon/ $^{210}\text{Pb}$  ratios were detected at Sonnblick and Puy de Dôme (Figure 3b) was characterized by an extreme abundance of open fires throughout Europe, primarily in eastern-southern Europe, but also in northern Spain and France. These findings are in line with the conclusions drawn by *Niemi et al.* [2004] who suggested that large-scale field burning in eastern Europe may substantially affect PM<sub>2.5</sub> concentration in southern Finland under unfavorable meteorological conditions, even at distances of over 1000 km from the burning areas. It is known that in springtime agricultural field burning is a traditional cultivation technique, especially in eastern Europe. Hundreds of burning areas can be seen every spring in these regions by fire monitoring satellites.



**Figure 5.** Exponential decreases of the level ( $\text{ngm}^{-3}$ ) of non-sea-salt-non-dust potassium, anthropogenic sulfate, and brown carbon versus elevation (km) under midsummer conditions (June–August) at the CARBOSOL sites. The calculation of non-sea-salt-non-dust potassium and of anthropogenic sulfate is detailed by *Pio et al.* [2007].

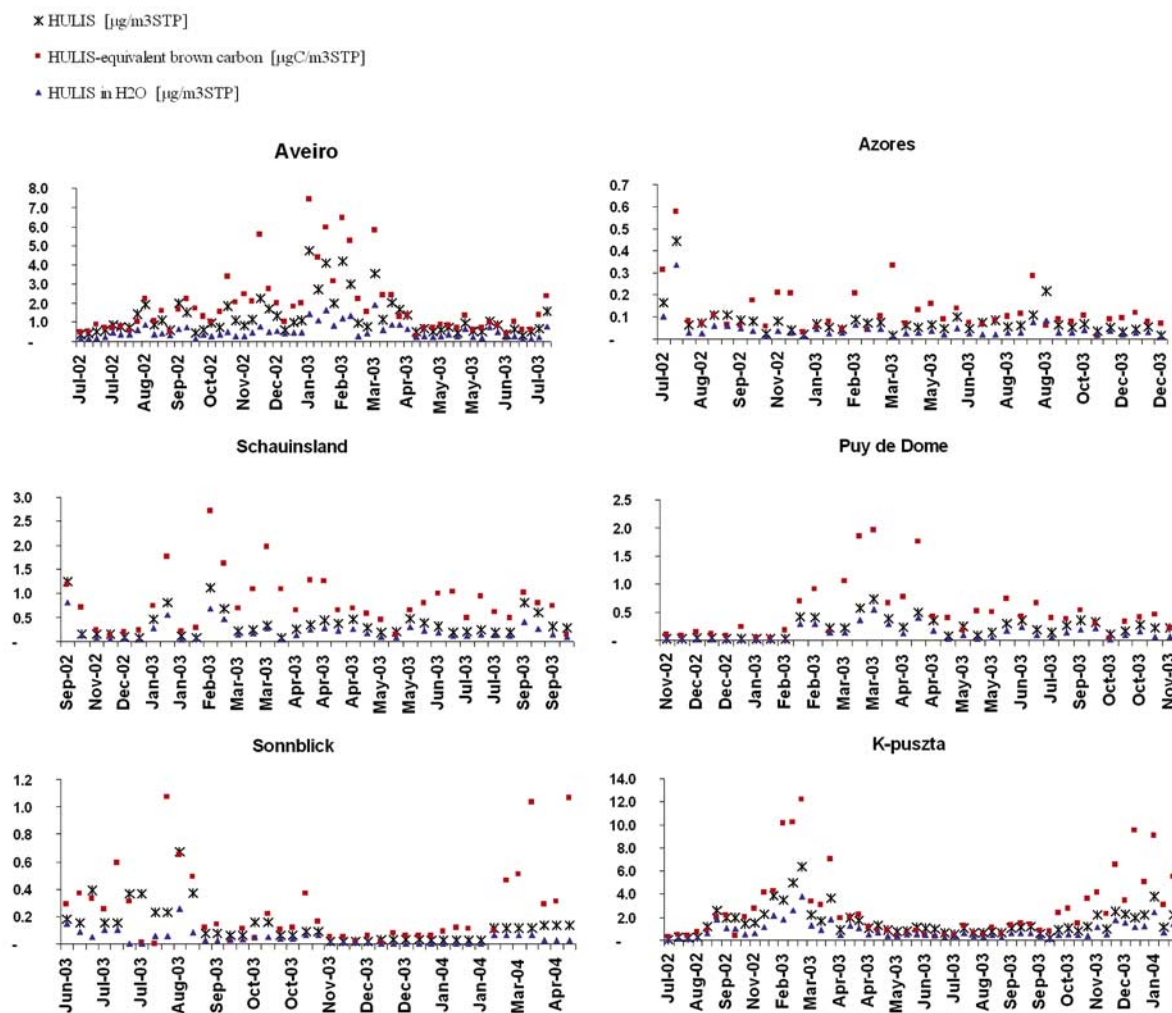
[15] Since levoglucosan is emitted in high quantities by the pyrolysis of cellulose in smoldering combustion [*Simoneit et al.*, 1999], levoglucosan was invoked as a tracer of biomass burning to assess the relative importance of wood burning as a primary source of brown carbon. The concentrations of levoglucosan were determined from monthly pooled samples and reported by *Puxbaum et al.* [2007]. The abrupt change in emission sources affecting elevated sites by long-range transport is also manifested in the monthly average brown carbon/levoglucosan ratio as shown in

Figure 4. This ratio is remarkably constant for all sites in the period from October to February in both years (average 0.04, RSD 66%), consistent with similar sources of both species and similar rate of scavenging, too. Starting from February, however, one can see a sudden increase in the brown carbon to levoglucosan mass concentration ratio, in particular in the year 2003. This clearly indicates contribution of other sources which yield levoglucosan and brown carbon at markedly different ratios than those typical of domestic wood burning in Europe. Although brown carbon-to-levoglucosan primary emission ratios are not available in the literature, reported levoglucosan-to-OC ratios may provide a hint: for forest and grassland burning in Amazonia a relative emission factor of  $80 \text{ mg g}^{-1} \text{ OC}$  is reported for levoglucosan [*Graham et al.*, 2003], whereas wood burning in stoves typically emits levoglucosan in relative amounts of  $150\text{--}350 \text{ mg g}^{-1} \text{ OC}$  [*Fine et al.*, 2004]. It is also possible that levoglucosan degrades more rapidly in summer as indicated in a recent study [*Holmes and Petrucci*, 2006]. Additionally, some brown carbon is presumably formed via secondary formation pathways, with no corresponding levoglucosan signal. However, it is not possible to further elaborate on secondary mechanism of brown carbon formation on the basis of the limited data set of weekly aerosol samples collected at the five continental sites.

[16] As shown in Figure 5 the decrease of concentrations with height in midsummer is less pronounced for brown carbon than for species such as anthropogenic sulfate and non-sea-salt-non-dust potassium, a submicron species primarily emitted in the atmosphere. The decrease of concentrations from surface sites of KPZ and AVE to the high-elevation alpine Sonnblick site is a factor of 2.7 for brown carbon instead of 4.5 for anthropogenic sulfate and 6 for nss-non-dust-K. The weaker vertical decrease of brown carbon and sulfate than those of a primary species like nss-non-dust-K suggests secondary production of brown carbon similarly to sulfate, though differential scavenging effects cannot be ruled out. The weaker increase of brown carbon may be due to increased condensation at higher elevations, due to reduced temperatures. In addition, atmospheric formation of brown carbon in multiphase reactions from semivolatile and colorless lignin pyrolysis products was suggested on the basis of laboratory experiments [*Gelencsér et al.*, 2003; *Hoffer et al.*, 2004]. Besides, organic nitrate formation may also yield colored water-soluble species.

### 3.3. Comparison With HULIS Concentrations

[17] The mass concentration of HULIS were determined in the aqueous and alkaline extracts of same set of aerosol samples using an online dual separation system with organic carbon detection [*Feczkó et al.*, 2007]. Despite the conceptual differences between atmospheric brown carbon and HULIS, and the methodologies used for their determination, absolute concentrations of both species followed similar trend over most of the year for all sites, as shown in Figure 6. Correlation between the different HULIS and brown carbon measurements are represented in Table 2. The covariation of both quantities is better for the low-level sites AVE and KPZ, and for the elevated sites SIL and PDD in winter. At the latter sites, springtime brown carbon levels are much higher, possibly indicating contribution of com-



**Figure 6.** Variations of concentrations of total HULIS and water soluble HULIS (in  $\mu\text{g}\text{m}^{-3}$  as determined by Feczko *et al.* [2007]) and that of brown carbon ( $\mu\text{gCm}^{-3}$ ).

pounds having different optical properties or polarity than HULIS, but covariation is largely preserved. On the contrary, in summer at PDD, SIL and SBO the trends become decoupled, implying that HULIS and brown carbon may not be linked to a single common source.

#### 4. Conclusions

[18] Our study clearly showed that water-soluble brown carbon concentrations exhibit pronounced seasonal pattern at all continental sites, with high absolute concentrations in winter and spring and low concentrations in summer. Normalization with codetermined  $^{210}\text{Pb}$  activities revealed that at low-level sites near anthropogenic sources these variations are clearly linked to source strengths. On the basis of the nearly constant ratio of brown carbon-to-levoglucosan, wood burning for residential heating was postulated to be the major source for brown carbon in the late fall-winter period, which is also consistent with findings using other methodologies from the CARBOSOL project [Gelencsér *et al.*, 2007; Puxbaum *et al.*, 2007]. During a transient period in spring additional sources may play a role as can be seen in the source-modulated time series of brown

carbon-to- $^{210}\text{Pb}$  ratios at elevated sites in Europe: likely sources are large-scale agricultural fires in eastern and central Europe, which also produce elevated levels of TC and OC in aerosol. In summer, on the basis of the weaker vertical decrease of brown carbon concentrations than those of a primary species such as nss-non-dust-K, we indirectly inferred some secondary production of brown carbon. However, this source is definitely much lower in intensity than primary emission by biomass burning. Comparison with codetermined HULIS concentrations revealed that the two quantities followed largely similar trend at all sites

**Table 2.** Correlation Coefficients ( $R^2$ ) Between Concentrations of Brown Carbon and Total and Water Soluble HULIS for All Sites, for the Entire Sampling Period

	HULIS (Total)	HULIS (Water Soluble)
AZO	0.46	0.57
AVE	0.88	0.72
PDD	0.68	0.72
SIL	0.45	0.54
SBO	0.15	0.19
KPZ	0.75	0.73



except for elevated sites in summer when they become decoupled.

[19] **Acknowledgments.** The authors acknowledge the contribution of many members of the CARBOSOL team for sampling, sample handling and transfer. We are grateful to József Bakos-Szalai, Szilvia Janitsek and Katalin Galló-Békefi for the spectroscopic analyses. The project was funded by EU contract EVK2 CT2001-00113. The helpful comments of the anonymous reviewers are gratefully acknowledged.

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