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# Particulate carbon in precipitation at European background sites

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The particulate carbon content of precipitation was investigated in samples collected at five background sites located over a west-east European transect, from the Azores, in the mid-Atlantic Ocean, to the Hungarian plain, in central Europe. Sampling was performed on an event basis and the particulate carbon (elemental carbon, EC, and water insoluble organic carbon, WIOC) content was concentrated on quartz filters for the subsequent analysis by a thermal optical method in order to separate the EC and WIOC fractions. The average EC concentrations range from low values at the Azores ( $2.8 \pm 4.3 \mu\text{g CL}^{-1}$ ) and at the high mountain site of Sonnblick ( $5.2 \pm 3.7 \mu\text{g CL}^{-1}$ ) to high values at the more inland sites of Schauinsland ( $28 \pm 38 \mu\text{g CL}^{-1}$ ) and K-Pusztá ( $24 \pm 24 \mu\text{g CL}^{-1}$ ). The average WIOC concentrations range from  $98 \pm 56 \mu\text{g CL}^{-1}$  at the coastal site of Aveiro and  $113 \pm 78 \mu\text{g CL}^{-1}$  at the Azores to  $358 \pm 194 \mu\text{g CL}^{-1}$  at the continental site of K-Pusztá. These results are discussed in terms of factors affecting the spatial distribution of particulate carbon, such as emissions from surrounding areas and prevalent meteorological conditions. EC is found to be a minor contributor to total particulate carbon present in rain and snow samples (from 2.5% to 15%). This is particularly true at the remote sites, where the EC contribution to total particulate carbon is  $< 6.5\%$ , consistent with a negligible impact of anthropogenic combustions locally. The EC and WIOC scavenging ratios were estimated and compared with those of sulfate, also evaluated at the same sampling sites. The results indicated that EC is removed from the atmosphere by wet deposition less efficiently than WIOC, and in turn this species is removed less efficiently than sulfate.

## 1. Introduction

Aerosol present in the atmosphere contains a significant fraction of carbonaceous matter, which is generally classified in two major components: elemental carbon (EC) and organic carbon (OC). EC is a primary species produced by the incomplete burning of fossil fuels and biomass. It is emitted directly into the atmosphere in the form of fine particles and has a chemical structure resembling that of graphite. Due to its high specific absorption of solar radiation, EC can have direct and indirect climatic effects, such as the reduction of the amount of solar radiation reaching the ground, enhancing the cloud absorption and the reduction of the albedo of snow and ice due to deposition of particles containing EC, whose balance can contribute to the warming of the atmosphere (Chuang et al., 2002; Hansen & Nazarenko, 2004; Jacobson, 2001).

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The OC component in the aerosols has both a primary and secondary origin. Primary OC may be produced from combustion processes and emitted mainly as submicron particles, or from mechanical processes that release into the atmosphere plant spores and pollen, vegetation debris, microorganisms, soil organic matter and marine aerosol, predominantly as coarse particles. Secondary OC is produced from gas to particle conversion of volatile organic compounds, either as a result of the condensation of low vapor pressure compounds, when concentrations exceed saturation levels, or from physical or chemical adsorption of gaseous species on aerosol particle surfaces (Seinfeld & Pankow, 2003). Studies on the aerosol chemical composition revealed that OC consists of a complex mixture of organic compounds, which is not yet completely resolved, and include, among others, aliphatic hydrocarbons, aromatic hydrocarbons, aldehydes, ketones, alcohols and carboxylic acids (e.g. Alves, Carvalho, & Pio, 2002). OC particles are very efficient at scattering light, and therefore exert a direct aerosol climate forcing and contribute to visibility reduction (Malm & Day, 2000; Molnár et al., 1999). Water soluble organic compounds often represent a significant contribution to the OC aerosol mass, making this fraction an important source of cloud condensation nuclei and thus possibly influencing indirect climate forcing (Corrigan & Novakov, 1999; Krivácsy et al., 2001).

Carbonaceous matter in atmospheric aerosols has been determined at many locations around the world, including sites in urban, rural, coastal, marine and polar areas (e.g. Castro, Pio, Harrison, & Smith, 1999; Hitztenberger et al., 1999; Krivácsy et al., 2001; Putaud et al., 2000; Sharma, Lavoué, Cachier, Barrie, & Gong, 2004, see Putaud et al., 2004 for a recent review focused on Europe). Most of the measurements were restricted to short-time campaigns, especially at background and remote regions, and there is a lack of information on seasonal variability in those conditions. This shortness of data motivated the European CARBOSOL project (A Study of the Present and Retrospective State of the Organic Versus Inorganic Aerosol over Europe) during which aerosol was studied over a time span of two years at a set of 6 rural/background sites arranged over a west-east transect from the Azores (Atlantic Ocean) to Hungary (Pio et al., 2007). This recent project provided a comprehensive aerosol data set for various conditions in Europe (marine versus continental, rural versus forested, boundary layer versus free troposphere, and winter versus summer) (Legrand & Puxbaum, 2007).

Current understanding on the atmospheric cycle of these particles is still largely incomplete since one of its key aspects, the wet deposition, which is considered to be an important process at removing particulate carbon from the atmosphere (Ducret & Cachier, 1992), is still poorly documented. To date, only a small number of studies were dedicated to the measurement of particulate carbon in precipitation. This paucity of our present knowledge on the spatial variability of wet deposition represents an important limitation to validate global models that simulate transport and concentration of atmospheric particulate carbon (Cooke, Ramaswamy, & Kasibhatla, 2002; Cooke & Wilson, 1996; Liouise et al., 1996) and consequently render difficult any accurate simulations of the anthropogenic forcing of aerosol on climate.

In this context, the present work aims to increase the current data set on the spatial variability of particulate EC and OC concentrations in precipitation to gain new insights on the atmospheric cycle of these carbonaceous species. In the frame of the CARBOSOL project, precipitations were collected at several sites (or at nearby locations) where atmospheric aerosol sampling was performed in parallel. Precipitation samples were analyzed for an extended array of organic and inorganic species, but this paper mainly focuses on particulate EC and OC. Simultaneous data on dissolved organic carbon (DOC), and inorganic ions (in particular sulfate) are used here as a supporting information to explore the processes that determine the scavenging of carbon particles from the atmosphere by wet deposition.

## 2. Experimental

Precipitation was collected at five background sites distributed along a west-east European transect, from the Azores islands (North Atlantic Ocean) to the Hungarian plains, in central Europe (Fig. 1). They include a marine background site at the Azores, two rural surface background sites (Aveiro in Portugal and K-Pusztá in Hungary), and two mountain sites (Schauinsland in Germany and Sonnblick in Austria). The main characteristics of these sampling sites are detailed in Pio et al. (2007).

Sampling at the Azores (100 m a.s.l.) was performed at the university campus, in the south of Terceira Island. Samples were collected on an event basis with a stainless steel funnel (an open area of 0.25 m<sup>2</sup>) connected to a pre-cleaned glass bottle. In order to minimize dry deposition of particles, the collector was deployed when rain started to fall and was removed immediately after filling or at the end of the event. Collection of samples at Aveiro (10 m a.s.l.) was conducted at the university campus, on the roof of the Department of Environment building, approximately 15 m above the ground level. Sampling equipment and protocol were similar to those at the Azores. At Schauinsland (1205 m a.s.l.) rain or snow samples were collected with a stainless steel bowl that was placed outside during every precipitation event. Sampling for some events lasted for more than one day, particularly during weekends, thus dry deposition was not completely avoided. At Sonnblick (3106 m a.s.l.) only snow sampling was performed. Fresh samples were taken from the surface of the snowpack after precipitation events that lasted for 24 h. At K-Pusztá (125 m a.s.l.) daily sampling was performed with an automatic wet-only collector, which was covered with a movable lid in the absence of precipitation.

Sampling was mainly focused on major precipitation events in order to collect large volumes over short time periods. In this way it would be possible to meet the requirements of analytical methods and simultaneously to avoid dry deposition effects and minimize sample degradation. Adequate protocols were developed for sample handling and processing in order to minimize contamination or loss. In particular, all the field and laboratory material dealing with samples was made of stainless steel or glass that was previously carefully cleaned.

For the analysis of EC (elemental carbon), WIOC (water insoluble organic carbon) and WITC (water insoluble total carbon) a liquid aliquot (from 100 to 1000 mL) was filtered through a quartz fiber filter (Whatman QMA), previously ignited at 550 °C

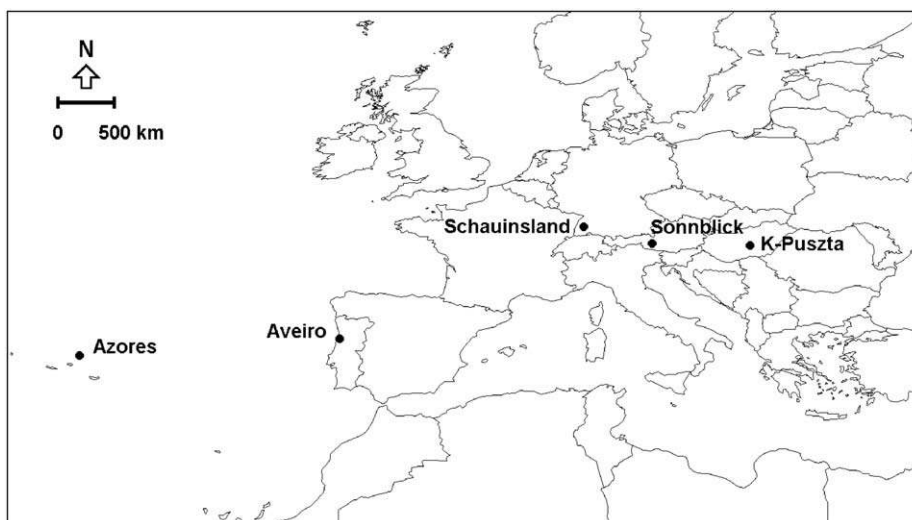


Fig. 1. Location of the five sampling sites in Europe.

during 4 h. The sample filtration was achieved by using a stainless steel filter unit equipped with a mask in order to concentrate particles onto a circular spot of 10 mm diameter. The filter was then dried at ambient temperature inside a desiccator for about 24 h and stored frozen until the analysis, conducted at the University of Aveiro. Precipitation samples that could not be filtered immediately after collection were kept frozen until filtration. The efficiency of the filtration procedure was previously tested and found to be highly efficient at removing carbon particles from precipitation samples (Cachier & Pertuisot, 1994). We tested our own procedure by using two filters mounted in series. It was shown that 10% or less of the OC amount detected on the first filter was present on the second filter, probably due to a contamination by dissolved organic matter adsorbed on the filter active sites during the water filtration procedure. Particle lost on the wall of the collecting devices was not evaluated in this study but the applied sampling protocol would have minimized it. In most cases, rain samples were indeed filtered immediately after collection and glass flasks used for collection were vigorously shaken by hand to minimize sticking of particles. The low volume unit used for the filtration would also have minimized the loss of particles during the filtration step. Ducret and Cachier (1992) have shown that losses of EC particles in the glass-bottles were, in the worst conditions (rainwater stored for more than one day), about 8% in mass. Wall losses on the collectors' components that were opened to the atmosphere (i.e. funnel or bowler) could not be minimized.

The EC and OC particulate fractions accumulated in filters were measured by the thermal-optical method previously described by Castro et al. (1999) to quantify carbonaceous matter in aerosols. The system comprises a quartz tube with two heating zones, a laser and a non-dispersive infrared (NDIR) CO<sub>2</sub> analyzer. A punch of the filter sample is placed vertically inside the quartz tube within the first heating zone, which is then heated to 600 °C in a helium atmosphere to vaporize the organic fraction of particles. EC is determined by sequential heating at 850 °C in a helium/air atmosphere. The second heating zone is filled with cupric oxide and maintained at 700 °C during the entire analysis process to guarantee the total oxidation of the volatilized carbon to CO<sub>2</sub>, which is quantified continuously by the NDIR analyzer. Correction for the pyrolysis contribution to EC from OC is achieved by monitoring the transmission of light through the filter with the laser beam. The OC/EC split is set when the transmittance reaches the same value as the one at the beginning of the analysis. Pyrolytic carbon (PC) is calculated from the mass of CO<sub>2</sub> emitted during the second heating phase, under the gas flow containing O<sub>2</sub>, until the recovery of filter light transmittance. For a filtration of 100 mL of liquid, the detection limits were 1 µg CL<sup>-1</sup> for EC (related to the noise of the analyzer) and 14 µg CL<sup>-1</sup> for OC (related to the variability of filter blanks). The methodology used in this study was tested with the NIST 8785 filter standard and in an inter-comparison experiment with real aerosol samples (Schmid et al., 2001), delivering EC/OC ratios between those obtained by the NIOSH and the IMPROVE protocols, close to the second one.

The analysis of DOC was done at the University of Heidelberg by UV oxidation and quantification of evolved CO<sub>2</sub> with a NDIR detector, as detailed in Schock et al. (2005). Inorganic ions including sulfate and sodium (used to calculate the non-sea-salt sulfate fraction) were analyzed at Grenoble, by ion chromatography (see Pio et al., 2007 and references therein).

### 3. Results and discussion

#### 3.1. Precipitation data

Table 1 summarizes the characteristics of precipitation events that were documented at the different sites. Mean daily precipitation rates were slightly higher at the mountain sites (Schauinsland and Sonnblick) than at low land sites (Azores and

**Table 1**

Precipitation statistics at the five CARBOSOL sites.

Site	Sampling period	Number of days with precipitation	Total amount of precipitation (mm)	Mean daily precipitation (mm/day)	Number of sampled events	Total amount of sampled events (mm)	Documented fraction of the total amount of precipitation (%)
Azores	February 03/June 04	281	1560	3.0	9	22	1
Aveiro	January 03/March 04	159	1332	3.0	36	145	11
Schauinsland	February 03/August 04	282	2486	4.3	42	842	34
Sonnblick	March 03 /July 04	316	2857	5.5	22	508	18
K-Puszt	September 02/June 04	211	851	1.4	19	386	45

**Table 2**Average, standard deviation and range of EC, WIOC, WITC, DOC and  $\text{SO}_4^{2-}$  concentrations in precipitation collected at the five sampling sites.

Site	Type	EC ( $\mu\text{g CL}^{-1}$ )			WIOC ( $\mu\text{g CL}^{-1}$ )			WITC ( $\mu\text{g CL}^{-1}$ )			DOC ( $\mu\text{g CL}^{-1}$ )			$\text{SO}_4^{2-}$ ( $\text{mg L}^{-1}$ )		
		N	Average	Range	N	Average	Range	N	Average	Range	N	Average	Range	N	Average	Range
Azores	Rain	7	$2.8 \pm 4.3$	0.4–12	7	$113 \pm 78$	25–224	7	$116 \pm 81$	26–228	6	$210 \pm 110$	60–385	6	$0.91 \pm 0.75$ ( $0.24 \pm 0.20$ )	0.34–2.41 (0.02–0.60)
Aveiro	Rain	33	$14 \pm 13$	0.0–65	33	$98 \pm 56$	12–237	33	$112 \pm 64$	14–264	20	$442 \pm 185$	200–800	29	$1.21 \pm 1.54$ ( $0.52 \pm 0.31$ )	0.27–8.51 (0.25–1.40)
Schauinsland	Rain/ snow	44	$28 \pm 38$	0.0–192	44	$205 \pm 266$	9.6–1400	44	$234 \pm 287$	3.6–1496	44	$1492 \pm 1291$	185–5070	38	$0.82 \pm 0.53$	0.04–2.17
Sonnblick	Snow	23	$5.2 \pm 3.7$	0.0–12	23	$145 \pm 174$	33–785	23	$151 \pm 173$	36–785	<sup>a</sup> <sup>a</sup>	<sup>a</sup>		23	$0.30 \pm 0.28$	0.02–1.35
K-Puszt	Rain	19	$24 \pm 24$	0.0–77	19	$358 \pm 194$	86–809	19	$381 \pm 204$	103–886	19	$1352 \pm 666$	570–2760	19	$2.13 \pm 1.65$	0.49–6.53

At the Azores and Aveiro the values under parenthesis refer to the estimated non sea-salt sulfate fraction.

<sup>a</sup>Data for Sonnblick were discarded due to contamination of samples.

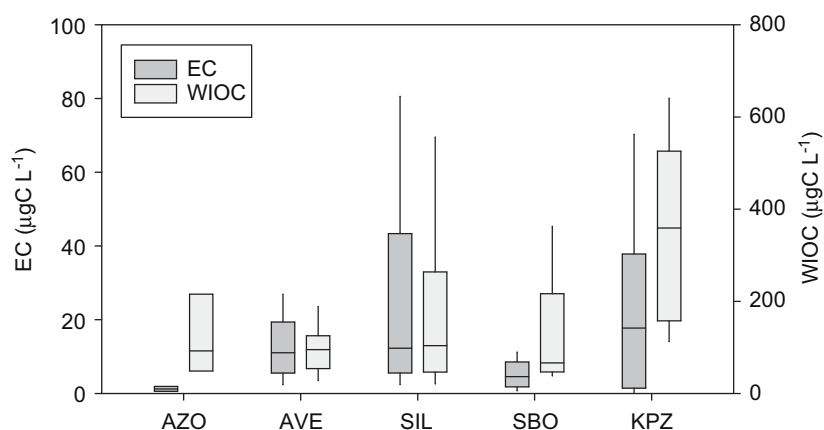
Aveiro). The number of documented events ranged from 9 at the Azores to 42 at Schauinsland. The representativeness of the documented precipitations with respect to all precipitations varies from 1% at the Azores to 45% at K-Puszt. In a large extent these differences reflect the variable number and intensity of precipitation events as well as variations in sampling periods, which lasted for a few hours at the Azores and Aveiro, for one day at Sonnblick, and up to two to three days at Schauinsland.

### 3.2. Concentrations in precipitation

Concentrations of EC, WIOC, WITC, DOC and  $\text{SO}_4^{2-}$  in precipitation samples collected at the five CARBOSOL sites are resumed in Table 2. Due to a large presence of sea-salt in precipitation at the marine sites (the Azores and Aveiro) we report in the same table the concentrations of non-sea-salt sulfate calculated by using the measured sodium concentrations and the mass ratio of sulfate to sodium in seawater (0.25). The highest  $\text{SO}_4^{2-}$  levels in precipitation are observed at K-Puszt, consistent with a large impact of anthropogenic  $\text{SO}_2$  emissions there, and the lowest at Sonnblick, a far more remote site. The intermediate sulfate values found at the Azores and Aveiro reflect the significant contribution of sea salt particles at these two sites. Indeed, the sea salt  $\text{SO}_4^{2-}$  content of these samples, estimated from the  $\text{Na}^+$  content and the mass ratio of  $\text{SO}_4^{2-}$  to  $\text{Na}^+$  in seawater, was higher than 35%. Considering only its non-sea-salt fraction the sulfate level at Aveiro ( $0.5 \pm 0.3 \mu\text{g L}^{-1}$ , Table 2) is consistently but not statistically significant larger than at the Azores ( $0.2 \pm 0.2 \mu\text{g L}^{-1}$ , Table 2) and lower than the one at K-Puszt.

It was sometimes possible to collect two consecutive samples during the same event at Schauinsland and Sonnblick (see the higher number of particulate carbon analysis than the number of documented events in Table 2). The small amount of collected precipitation had sometimes prevented analysis of DOC and sulfate. Two samples from the Azores and three samples from Aveiro were discarded from the data set due to analytical difficulties to separate the EC and OC fractions. These samples contain large amounts of dust as revealed by the distinct reddish-brown color of dust retained in the filters and after the thermal treatment of samples for EC/OC analysis. The backward trajectories calculated by the HYSPLIT model (Draxler & Rolph, 2003) indicate episodes of air mass transport from North Africa for these events, consistent with these high dust contents. Although the number of samples collected at the Azores is low and data should be interpreted with caution, they provide the first information on the particulate carbon content of rain at a very remote marine area.

Since data does not clearly reveal seasonal changes for the five sites they are presented only in terms of global averages (or medians). Box-Whisker plots (median values and percentiles) of EC and WIOC concentrations are plotted in Fig. 2. The lowest particulate carbon concentrations were observed at the Azores, Aveiro and Sonnblick ( $110\text{--}150 \mu\text{g CL}^{-1}$ ), and the highest ones at Schauinsland and K-Puszt ( $235\text{--}380 \mu\text{g CL}^{-1}$ ) (Table 2). For comparison we report in Table 3 the particulate carbon concentrations in precipitation samples collected at a few urban and rural areas of North America and Europe and at a coastal site in northern Europe. Note that, up to now, no information was available for marine remote areas or mountain sites located in the free troposphere. It has to be emphasized that comparisons between these previous studies and the present work have to consider that applied sampling and analytical methods were different.



**Fig. 2.** Box–Whisker plots of EC and WIOC concentrations in precipitation at the five sampling sites (AZO—Azores, AVE—Aveiro, SIL—Schauinsland, SBO—Sonnblick, and KPZ—K-Puszt). The box extents indicate the 25th and 75th percentiles. The lines inside the box refer to the value of the 50th percentile, whereas the bars indicate the 10th and 90th percentiles.

**Table 3**

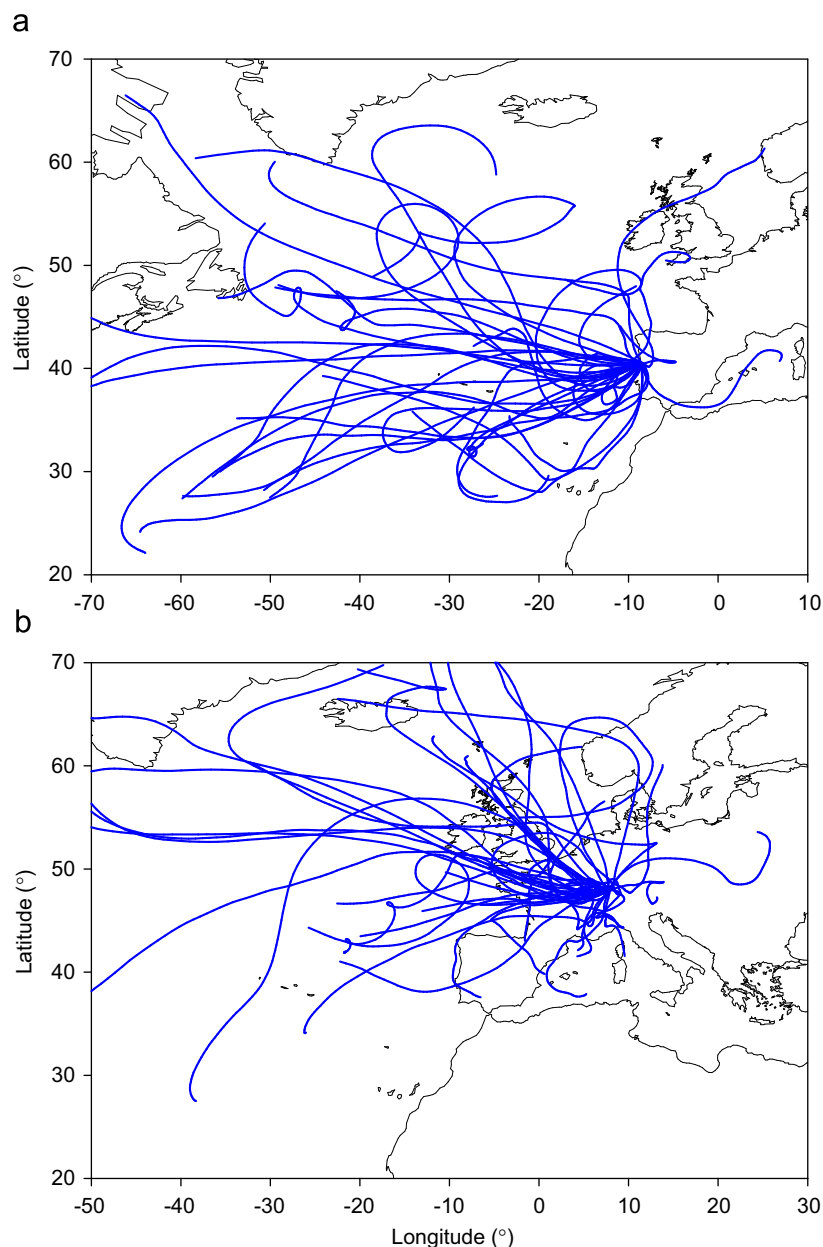
Average and range of EC, WIOC and WITC concentrations in precipitation samples from northern hemisphere sites.

Sampling site	Sampling time	Samples	Type	Concentration ( $\mu\text{gC L}^{-1}$ )			Reference
				EC	WIOC	WITC	
<i>Coastal</i>							
Mace Head, Ireland	October–November 1989	18	Rain	31 (9–94)	–	100 (47–323)	Ducret and Cachier (1992)
<i>Urban</i>							
Gif-sur-Yvette, Paris, France	1988–1990	58	Rain	333 (27–1348)	–	1184 (69–5868)	Ducret and Cachier (1992)
Halifax, Nova Scotia, Canada	January–May 1995	15	Rain	4.0 (0.0–11.1)	–	–	Chýlek et al. (1999)
	Winters 1995, 1996	11	Snow	11 (4.3–32)	–	–	
<i>Rural</i>							
Cheboygan, Michigan, USA	Winters 1983, 1985	25	Snow	72 (28–210)	750 (140–1300)	–	Cadle and Dasch (1988)
Bridgewater, Nova Scotia, Canada	January–September 1995	20	Rain	2.6 (0.0–8.2)	–	–	Chýlek et al. (1999)
	January–February 1996	3	Snow	1.7 (0.8–2.8)	–	–	

Data gained with this study (Table 2) show average concentrations of both EC and WIOC considerably lower than those in Paris (Table 3). High concentrations of carbonaceous particles are also present in snow samples collected at Cheboygan (Table 3), a rural place in Michigan, strongly influenced by long-range transport of polluted plumes. This difference is expected since the CARBOSOL sites are located away from large sources of pollution in contrast to urban atmospheres of large cities that contain a high load of combustion particles susceptible to being incorporated in precipitation. Note that the difference is always larger for EC than for WIOC, for instance a factor of 14 and 3 between Paris and K-Puszt, respectively.

WITC data from the Azores, Aveiro and Sonnblick compare fairly well with those from Mace Head, a remote site located on the west coast of Ireland experiencing westerly winds from the Atlantic. The average EC concentration in precipitation at Mace Head is, however, higher by a factor of 6 and 11 than those at the Alpine and mid-Atlantic sites, respectively. This discrepancy may be partly attributed to the difference in the applied analytical methods. Indeed the thermal method used by Ducret and Cachier (1992) to separate EC and WIOC fractions does not account totally for pyrolytic conversion of OC to EC, and thus may lead to overestimation of EC with respect to the method deployed in this study. EC concentrations in precipitation samples collected at urban and rural areas in Nova Scotia (Canada) fall in the range of those observed at the most remote places including those documented during the CARBOSOL project. According to Chýlek, Kou, Johnson, Boudala, and Lesins (1999) these low EC concentrations at the Nova Scotia sites result from extra tropical cyclones that often develop over the mid-latitudes to the east of Canada in relatively clean conditions of the marine boundary layer. Note, however, that this comparison has to be used with caution because the EC analytical method used by Chýlek et al. (1999) is based only on the filter optical characteristics.

It is also interesting to compare the Sonnblick precipitation data with the levels of particulate carbon found in ice cores extracted near the Mt. Blanc summit (Col du Dôme, French Alps, 4250 m a.s.l.) that are also relevant for elevated Alpine conditions. This ice record, which covers the 20th century, indicates rather constant summer concentrations of  $50 \mu\text{gC L}^{-1}$  of WIOC from 1960 to 1990 (Legrand et al., 2007). This WIOC value is very similar to the summer median value of Sonnblick precipitation ( $62 \mu\text{gC L}^{-1}$ ). For EC, the ice record indicates decreasing summer concentrations from  $16 \mu\text{gC L}^{-1}$  over 1962–1967 years to  $10 \mu\text{gC L}^{-1}$  for the



**Fig. 3.** Four-day backward trajectories arriving at (a) Aveiro and (b) Schauinsland at 1500m above sea level for every sampling event. The trajectories were calculated using the HYSPLIT model (Draxler & Rolph, 2003).

recent documented time period (1989–1991) (Legrand et al., 2007). As discussed by Fagerli et al. (2007), such a decrease of EC concentrations from the 1960s to the 1990s results from a decrease of the emission factor for EC vehicular emissions. A further decrease of EC vehicular emissions would partly explain the difference of EC values between precipitation collected at Sonnblick in 2003/2004 and the 1990 level in ice cores.

Table 2 clearly indicates a far larger geographical variability of EC with respect to the WIOC one, which we discuss below. In spite of remoteness from polluted regions of the European and North American continents, there is still a small amount of EC in precipitation at the Azores suggesting a remaining impact of combustion processes there. Contamination of the atmosphere by local emissions cannot be excluded but long-range transport of pollutants from continents likely contributes to this presence of EC in rain samples. Indeed, as concluded by Honrath et al. (2004) on the basis of CO measurements, air pollutants originating from far distant regions like Canada and Siberia can be detected at the Azores. A similar feature is expected for Aveiro, a coastal site where precipitation events are mainly associated with transport of air masses over the North Atlantic Ocean (Pio, Salgueiro,

**Table 4**

Average and standard deviation for the relative contribution of EC to WITC and of PC (pyrolytic carbon) to OC in precipitation and aerosol at the five sampling sites.

Site	EC/WITC (%)		PC/OC (%)	
	Precipitation	Aerosol	Precipitation	Aerosol
Azores	2.5 ± 1.9	25 ± 22	27 ± 12	16 ± 15
Aveiro	13 ± 8	34 ± 11	23 ± 12	52 ± 5
Schauinsland	15 ± 12	47 ± 32	22 ± 14	48 ± 8
Sonnblick	6.5 ± 5.1	57 ± 40	14 ± 10	27 ± 11
K-Puszt	7.6 ± 8.0	50 ± 24	11 ± 10	54 ± 6

& Nunes, 1991). However, despite the similarity of WITC concentrations at Aveiro and the Azores, the EC levels are five times higher at Aveiro than the Azores. These larger EC values at Aveiro are highlighted by examination of backward trajectories arriving at Aveiro during the sampled precipitation events (Fig. 3). Although the dominant transport pathway was oceanic, air masses crossed frequently continental areas of the western Iberian Peninsula during the last hours before arrival at Aveiro, and therefore may have incorporated regional anthropogenic emissions, particularly from densely populated areas in Portugal and northwestern Spain. An earlier study conducted in a coastal site southwest of Aveiro has also shown that contamination of marine background air masses is quite common and is probably related to regional atmospheric recirculation episodes (Pio et al., 1996). The fact that this additional anthropogenic input at Aveiro with respect to the Azores is detected on EC but not on WIOC suggests that a large fraction of WIOC was transformed into WSOC due to ageing processes, which are more efficient when acting on these particles than on changing the solubility of EC aerosol.

At the low level site of K-Puszt the WITC concentration was 2–3 times higher than those observed at the most pristine sites of the Azores and Sonnblick (Table 2). Note that the change between K-Puszt and remote sites is larger for EC than for WIOC. Intermediate WITC concentrations are found at Schauinsland. The values observed at the two mountain sites of Schauinsland and Sonnblick are more variable than those at surface sites. It is likely that such temporal variations are partly driven by changes of vertical stability of the atmosphere bringing upward (or not) polluted boundary layer air masses. According to Table 2, the highest average EC concentration was found at Schauinsland. However, this average is distorted by some extreme values and in fact the median EC value at this site is close to the one at Aveiro (Fig. 2). The greater variability of insoluble carbon concentrations at Schauinsland also seems to be related to the change of air mass trajectories arriving at the site (Fig. 3).

### 3.3. Contribution of EC to WITC and nature of WIOC

Examination of the contribution of EC to WITC can provide some insight into the sources and removal processes of atmospheric particulate carbon. The average relative content of EC in rain and snow samples collected during this study is reported in Table 4 and reveals that EC is a minor contributor to the total mass of particulate carbon in precipitation. The EC/WITC values range from 2.5% at the Azores to 15% at Schauinsland. At other sites, Ducret and Cachier (1992) have also found that EC represents a minor contributor to particulate carbonaceous matter in rain but the relative abundance of EC was found to be higher at Mace Head and Paris (29% for both sites) than those at the CARBOSOL sites. Such a difference can be partly explained by the diversity of emission sources of carbonaceous matter affecting the study areas. Indeed, the sites investigated by Ducret and Cachier were strongly impacted by emissions from urban areas. On the other hand, the above mentioned differences in analytical protocols used to separate the EC and OC fractions of particulate matter may also contribute to this departure.

The overall low contribution of EC to WITC likely reflects a lower incorporation of EC than WIOC (see Section 3.5) as well as a higher relative input of WIOC. Therefore, these results seem to support the notion that EC aerosol particles have a lower ability to act as CCN than WIOC. The remote sites in the marine boundary layer or within the free troposphere, have shown the lowest contribution of EC to WITC, suggesting a higher relative input of WIOC at these sites compared to surface sites.

The inspection of the carbon mass thermal evolution during analysis can highlight the nature of OC present in samples. Except in the case of the Azores, during the analysis of precipitation samples 77–89% of OC evolves at temperatures between 150 and 600 °C under N<sub>2</sub> and the contribution of pyrolytic carbon remained low (11–23%, Table 4). That contrasts with aerosol samples where pyrolytic carbon (PC) represents a large fraction (27–54% of OC, Table 4). Such a difference in the nature of OC of rain with respect to that of atmospheric aerosol, is simply due to the fact that during filtration of rain sample polar oxygenated species constituting the PC fraction has been removed due to their high water solubility.

### 3.4. WSOC as a source of DOC

Relating atmospheric aerosol OC concentrations to OC concentrations in rain is a challenge. Indeed, whereas the particulate WIOC fraction can be investigated by examining filterable OC of rain, the dominant fraction of atmospheric particulate OC which is water soluble (WSOC) cannot be directly determined in rain. Reversely, the DOC content of rain accounts for particulate WSOC as well as for various organic gases that are water soluble. We examine here the extent to which the atmospheric WSOC aerosol contributes to the amount of DOC in rain.



**Table 5**Average aerosol concentrations of EC, WIOC and  $\text{SO}_4^{2-}$  at the five CARBOSOL sites.

Site	N	EC ( $\mu\text{g C m}^{-3}$ )	WIOC ( $\mu\text{g C m}^{-3}$ )	$\text{SO}_4^{2-}$ ( $\mu\text{g m}^{-3}$ )
Azores	7	0.04	0.14	1.2 (0.23)
Aveiro	25	1.2	3.1	2.0 (1.8)
Schauinsland	32	0.29	0.67	2.4
Sonnblick	18	0.09	0.42	0.50
K-Pusztza	11	0.91	0.96	3.3

At the Azores and Aveiro the values under parenthesis refer to the estimated non sea-salt sulfate fraction.

The calculation of these values was based on the weekly measurements that encompassed periods of precipitation collection.

The ratio between the concentrations of WSOC and WIOC in aerosols can be used to estimate the contribution of organic particles to the global pool of dissolved organic carbon (DOC) in precipitation. However, the WSOC to WIOC ratio would be higher in precipitation than in aerosol since the incorporation of particles into hydrometeors is likely more efficient for WSOC than WIOC. Therefore, a lower estimate of the WSOC content of precipitation can be derived by multiplying the WIOC level of rain or snow by the WSOC to WIOC ratio observed in aerosol at the site. Based on the two years of measurements performed at the CARBOSOL sites, Pio et al. (2007) have shown that 50–80% of the OC aerosol mass was water soluble. For Aveiro, Schauinsland and K-Pusztza, the only three sites where enough information was available to do this evaluation, the average values for the ratio WSOC/WIOC in the aerosol were 1.0, 2.8 and 3.0, respectively. Therefore, using the average values from Table 2, the minimum contribution of WSOC to the DOC content of precipitation at Aveiro, Schauinsland and K-Pusztza is 22%, 38% and 79%, respectively. These findings show that WSOC is a very significant contributor to soluble organic carbon in precipitation. This source is clearly dominant for samples taken at K-Pusztza. For the other sites the origin of dissolved organic carbon is probably more influenced by the solubilization of atmospheric organic gases.

### 3.5. Scavenging ratios

Table 5 presents the aerosol concentrations of EC, WIOC and  $\text{SO}_4^{2-}$  (and nss- $\text{SO}_4^{2-}$  at the Azores and Aveiro) corresponding to the precipitation events that were documented at the five CARBOSOL sites. These values were calculated by averaging the weekly aerosol sampling done in the CARBOSOL project (Pio et al., 2007) that encompass the time of documented precipitation events. Although the aerosol sampling interval does not exactly coincide with the time of the precipitation, it is worth comparing the two sets of data, particularly if taking into account that carbonaceous aerosol particles increase their hygroscopicity—and therefore their probability to be incorporated in clouds or falling rain—by ageing processes that can take a few days.

Comparison of data reported in Tables 2 and 5 shows that the particulate carbon content of precipitation seems to reflect rather well the spatial distribution of carbonaceous aerosol. The most distinctive difference between the two data sets is that of carbon levels at Aveiro, which in the aerosols were among the highest records, comparable to those of K-Pusztza, whereas in precipitation were in the range of low concentrations. This discrepancy clearly demonstrates that carbonaceous particles emitted at a regional scale in the area surrounding Aveiro have a limited impact on the chemistry of local precipitation. Therefore, in cloud or below cloud incorporation of regionally emitted carbonaceous particles is irrelevant at Aveiro, reflecting the importance of North Atlantic as the source region of air masses that bring precipitation over Portugal, the local high aerosol concentrations having a limited effect on the precipitation chemistry.

It is worth to compare the abundance of EC found in precipitation samples with the one in aerosol. As seen in Table 4, the average EC/WITC ratio in aerosols, based on the weekly measurements that encompass periods of precipitation collection, was in the range of 25–57%. Whatever the sampling site, the contribution of EC to WITC tends to be higher in aerosols than in precipitation. It should be noted that precipitation data can be affected by contamination of filters during rainwater filtration with dissolved OC, but this effect cannot explain more than about 10% of the observed difference between aerosol and precipitation, in line with the results of filtration tests described in the experimental section. To a certain extent this difference may also reflect the non-coincidence of periods for sampling precipitation and aerosol. Another possible explanation may lie in the size distribution of aerosol particles sampled during the CARBOSOL project, which was below  $2.5 \mu\text{m}$  for most of the sites. Even though the aerosol fine fraction concentrates the largest part of the EC and OC mass of particles (Nunes & Pio, 1993; Offenberger & Baker, 2000), a still significant amount of OC, mainly derived from non-combustion sources and being water insoluble (plant debris, microbes, pollen), can be accumulated in the aerosol coarse fraction. Thus, since the range of particles incorporated by rain and snow also includes those that are larger than  $2.5 \mu\text{m}$ , a slightly lower EC to WITC ratio is expected in precipitation than in atmospheric aerosol. Finally, such a difference between air and precipitation may also suggest a more efficient removal of WIOC than EC particles, through cloud processes, a possibility that is supported by the calculation of scavenging ratios presented below.

The concept of scavenging ratio is commonly used in the literature to quantify the tendency of a species or component to be removed from the atmosphere by precipitation. The volume based scavenging ratio ( $\omega_v$ ) can be calculated by the equation (Kasper-Giebl, Kalina, & Puxbaum, 1999)

$$\omega_v = C_p \times \rho_w / C_a$$

**Table 6**Average scavenging ratios of EC, WIOC and  $\text{SO}_4^{2-}$  at the five sampling sites.

Site	$\omega_{\text{EC}} \times 10^{-6}$	$\omega_{\text{WIOC}} \times 10^{-6}$	$\omega_{\text{SO}_4} \times 10^{-6}$
Azores	0.20	0.81	0.82 (0.70)
Aveiro	0.02	0.06	0.94 (0.38)
Schauinsland	0.17	0.40	0.73
Sonnblick	0.18	0.63	1.16
K-Puszt	0.04	0.57	0.66

At the Azores and Aveiro the values under parenthesis refer to the scavenging ratios of the non sea-salt sulfate fraction.

where  $C_p$  is the concentration of the species in precipitation ( $\mu\text{g kg}^{-1}$ ),  $C_a$  is the concentration of the species in air ( $\mu\text{g m}^{-3}$ ) and  $\rho_w$  is the density of water ( $1000 \text{ kg m}^{-3}$ ).

Scavenging ratios for EC ( $\omega_{\text{EC}}$ ), WIOC ( $\omega_{\text{WIOC}}$ ) and  $\text{SO}_4^{2-}$  ( $\omega_{\text{SO}_4}$ ) were calculated using individual pairs of concentration in precipitation and in air. As explained before, the aerosol chemical composition was documented in the framework of the CARBOSOL project, on a weekly basis, for a long-term period that coincided with the collection of precipitation samples. The average scavenging ratios obtained during this study are given in Table 6. Results for the Azores should be considered with some caution, since the calculations were based on a limited number of precipitation and aerosol data.

EC shows the lowest average scavenging ratios (from  $0.02 \times 10^6$  to  $0.18 \times 10^6$ ) and  $\text{SO}_4^{2-}$  the highest ( $0.66 \times 10^6$  to  $1.16 \times 10^6$ ). Intermediate values (from  $0.06 \times 10^6$  to  $0.81 \times 10^6$ ) were found for WIOC. Current information on EC scavenging ratios available in the literature is still scarce. Cadle and Dasch (1988) calculated mean scavenging ratios of  $0.13 \times 10^6$  for EC at a rural location in northern Michigan (USA). The study of Ducret and Cachier (1992), based on data gained at various temperate and tropical locations, suggested an average EC scavenging ratio of  $0.20 \times 10^6$ . Therefore, data from the CARBOSOL sites (discarding the case of Aveiro, see discussions in Section 3.2) together with previous studies suggest that EC scavenging ratios have a higher spatial variability than was often previously assumed. This variability has important implications on model calculations of EC aerosol concentrations as recently pointed out by Tsyro et al. (2007). Interestingly, the authors have shown that modeled EC concentrations over Europe were, on average, 19% lower than field observations. Since their simulations were based on an average EC scavenging ratio of  $0.20 \times 10^6$ , which is in the upper range of values found at CARBOSOL sites, the adopted value could explain, at least partly, the model underestimates.

In the literature, available scavenging ratios are even scarcer for WIOC than for EC. Cadle and Dasch (1988) suggested an average value of  $0.46 \times 10^6$  for OC but this value was obtained by assuming that the entire OC mass accumulated in the filters during aerosol sampling was water insoluble, an assumption that is not supported by more recent knowledge on the aerosol composition (Pio et al., 2007).

In contrast with the scarcity of information for particulate carbon wet deposition,  $\text{SO}_4^{2-}$  scavenging ratios were previously determined at various sites. Again discarding the case of Aveiro, data from the present study compare well with those earlier results which for most of the sites have fallen in the range  $0.4 \times 10^6$ – $1.4 \times 10^6$  (Cadle & Dasch, 1988; Cadle, Vandekopple, Mulawa, & Dasch, 1990; Harrison & Allen, 1991; Hicks, 2005; Kasper-Giebl et al., 1999). It should be noted that results for  $\text{SO}_4^{2-}$  may be affected by the scavenging of  $\text{SO}_2$  and its subsequent aqueous-phase oxidation into  $\text{SO}_4^{2-}$ . Nevertheless, since this is not a very efficient process when compared to the removal of airborne particulate  $\text{SO}_4^{2-}$  (Hicks, 2005; Kasper-Giebl et al., 1999), its contribution to total precipitation  $\text{SO}_4^{2-}$  might be small or even negligible. Note also that the scavenging ratio of sulfate calculated for Sonnblick ( $1.4 \times 10^6$ ) is close to the grand average previously found by Kasper-Giebl et al. (1999) on the basis of two years of measurements performed at this mountain site ( $1.4 \times 10^6$ ).

The preceding results are in line with the affinity of substances to water. Although EC can acquire hydrophilic properties by chemical ageing, fresh EC is known to be hydrophobic, thus its scavenging ratio tends to be lower than those commonly found for more soluble air components such as  $\text{SO}_4^{2-}$ . OC aerosol particles comprise a significant fraction of water soluble compounds. This property facilitates the transfer of organic particles into hydrometeors and the incorporation of insoluble organic matter inside it, explaining why WIOC has an efficiency of scavenging that is intermediate between those of EC and  $\text{SO}_4^{2-}$ .

The comparison of scavenging ratios at the different sites (Table 6) shows that for all species or components scavenging ratios were lower at the low level sampling station of K-Puszt than at the high altitude station of Sonnblick (Aveiro was discarded). This may reflect the assumption that, for the calculation of scavenging ratios, aerosol concentrations are vertically uniform and similar to those observed at the ground level. In fact, this assumption is likely correct for sites that are located on the top of mountains but not for low land sites above which a significant vertical gradient of air concentrations is expected. Results from this study also point to a more efficient incorporation of EC particles at the maritime and mountain sites likely due to an ageing of aerosol during transport to areas that are far away from pollution sources. This is possible since the time scale needed for a significant evolution of externally mixed EC aerosol particles into other mixing states is of a few days (Jacobson, 2001).

### 3.6. Wet and dry deposition of EC and WIOC

Estimates of dry and wet deposition fluxes of EC and WIOC were performed for the five sampling sites. Calculations of the dry deposition fluxes were based on the average aerosol concentrations derived from the two years of measurements made at the CARBOSOL sites and on a dry deposition velocity of  $0.025 \text{ cm s}^{-1}$  for carbonaceous aerosols (Cooke et al., 2002). The wet

**Table 7**

Dry and wet deposition fluxes of EC and WIOC along with total precipitation for the period July 2003–June 2004 at the five sampling sites.

Site	Total precipitation (mm)	Dry deposition ( $\text{mg C m}^{-2} \text{ year}^{-1}$ )		Wet deposition ( $\text{mg C m}^{-2} \text{ year}^{-1}$ )	
		EC	WIOC	EC	WIOC
Azores	1132	0.3	1.3	5.0	114
Aveiro	729	7.9	20	7.5	61
Schauinsland	1574	2.2	4.6	38	378
Sonnblick	2082	1.1	3.1	10	234
K-Puszt	595	9.1	14	9.5	219

deposition fluxes were calculated for the period of July 2003 to June 2004 taking into account volume weighed concentrations and total accumulated precipitation at sites. The results are given in Table 7 and indicate that scavenging of carbonaceous particles is dominated by wet deposition processes. The relatively high dry deposition flux with respect to the wet deposition flux calculated for Aveiro compared to the other sites is caused by the fact that the dry flux is strengthened there by locally emitted particles that have not been incorporated into precipitation (see discussions in Section 3.2).

#### 4. Conclusions

The information gathered from this study increase our knowledge on particulate carbon content of precipitation. The lowest particulate TC levels in precipitation were found at the coastal site of Aveiro, at the remote site of the Azores islands, and at the elevated site of Sonnblick. On the other hand, the highest levels were found at the continental low land site of K-Puszt. EC was found to be a minor contributor to total particulate carbon in rain and snow samples. This was particularly true at the remotes sites due to a lower impact of anthropogenic emissions. Estimates of scavenging ratios confirm that EC is removed from the atmosphere by wet deposition less efficiently than WIOC, which in turn is removed less efficiently than  $\text{SO}_4^{2-}$ .

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