Wet deposition of particulate carbon to the Central North Atlantic Ocean

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1 **Abstract**

2 Elemental carbon (EC) and water insoluble organic carbon (WIOC) concentrations were

3 measured in wet-only precipitation samples collected at Terceira Island (Azores,

4 Portugal), between December 2009 and October 2010, in order to investigate seasonal

5 variations, source regions and wet deposition fluxes. Global volume-weighted average

6 (vwa) concentrations were 134 ± 19 µgC L^{-1} for WIOC and 15.0 ± 1.6 µgC L^{-1} for EC,

7 which fall within the range of values that have been found in European background

8 atmospheres. WIOC concentration presented a seasonal variation with a minimum in

9 winter (vwa 88 ± 16 µgC L^{-1}) and a maximum in summer (vwa 477 ± 86 µgC L^{-1}). This

10 trend was due to a higher dilution effect of winter rains and possibly to an increase of

11 biogenic particulate carbon incorporation during the growing season. A different

12 seasonal variation was observed for EC concentration, with a minimum in summer (vwa

13 4.2 ± 3.3 µgC L^{-1}) and a maximum in spring (vwa 17.5 ± 2.2 µgC L^{-1}). The observed trend

14 was mainly related to changes in air mass circulation patterns over the Azores.

15 Backward trajectory analysis was applied to identify possible source regions of

16 particulate carbon. It was found that the highest WIOC and EC concentrations were

17 associated with air masses that remained more than four days over the Central North

18 Atlantic Ocean and to air masses arriving from Europe, respectively. Lower

19 concentrations were observed in samples collected under the influence of back-

20 trajectories coming from North America. Despite the lower abundance of particulate

21 carbon, wet deposition fluxes were higher for this group of samples, reflecting the larger

22 amount of precipitation that is normally associated with air masses arriving at the

23 Azores from the west and the northwest sectors.

24

25 Keywords: precipitation, organic carbon, elemental carbon, wet deposition, background

26 atmosphere

27

28 **1. Introduction**

29 Atmospheric aerosols contain a significant amount of carbonaceous matter, which is

30 commonly classified in two major fractions: elemental carbon (EC) and organic carbon

31 (OC). EC is a primary species that derives from incomplete combustion of fossil fuels

32 and biomass. OC originates from primary and secondary sources. Primary OC is

33 produced from combustion processes, in line with EC emissions, or mechanical

34   processes that release into the atmosphere organic materials such as pollen, spores, plant

35   debris, microorganisms, soil and sea spray. Secondary OC, in turn, is produced from

36   gas-to-particle conversion of the oxidation products of volatile organic compounds.

37   Wet deposition is known to play a dominant role in removing particulate carbon from

38   the atmosphere (Ducret and Cachier, 1992; Cerqueira et al., 2010). However, current

39   information on the spatial and temporal variability of particulate carbon in precipitation

40   is still scarce, which is an important limitation to: assess anthropogenic impacts on land

41   and ocean carbon biogeochemistry (Jurado et al., 2008); and validate global models that

42   simulate transport and concentration of carbonaceous aerosols, thus affecting

43   predictions of the anthropogenic forcing of aerosols on climate (Cooke et al., 2002;

44   Croft et al., 2005).

45   Previous measurements have shown that wet deposition of particulate carbon is more

46   significant in the vicinity of emission sources (Ducret and Cachier, 1992; Cerqueira et

47   al., 2010), which are known to be concentrated in inland areas. However, model

48   estimates also suggest that the global oceans are important receptors of EC and OC

49   incorporated in precipitation (Jurado et al., 2008), therefore indicating that new research

50   on particulate carbon wet deposition fluxes should be extended to oceanic areas.

51   This paper reports the first long-term measurements of water-insoluble organic carbon

52   (WIOC) and elemental carbon wet deposition fluxes to a remote marine site. The aims

53   of this study were to: (1) characterize the seasonal variation of WIOC and EC

54   concentrations in rain collected at Terceira Island (Azores, Portugal); (2) explore the

55   processes governing the seasonal pattern of WIOC and EC concentrations in rain at the

56   Azores; and (3) quantify wet deposition fluxes of particulate carbon to the Central North

57   Atlantic Ocean.

58

59   **2. Experimental**

60   **2.1 Site description**

61   The Azores archipelago is a set of nine volcanic islands located in the Mid-Atlantic

62   Ridge, about 1500 km from mainland Portugal and 1900 km from North America

63   (Figure 1). Climate of the islands is strongly influenced by the seasonal movement of

64   the Azores anticyclone. In late spring and summer the high-pressure cell is located over

65   the islands bringing relatively dry and sunny conditions. During autumn and winter the

66   anticyclone moves south of the Azores and low pressure systems track across the region

67   causing wet and stormy weather.

68 Sampling was performed at the Angra do Heroísmo Meteorological Observatory

69 (AHMO), located at the south coast of Terceira Island (38º39'32'' N; 27º13'23'' W; 74

70 m above sea level). The observatory is part of the Global Atmosphere Watch

71 programme (GAW ID: ANG) of the World Meteorological Organization. The monthly

72 average temperature at AHMO for the time period 1981 – 2010 ranged from 13.8 ºC

73 (February) to 22.2 ºC (August). During the same period, average monthly precipitation

74 amount ranged from 29 mm (July) to 155 mm (December) and the average annual

75 precipitation was 1099 mm (IPMA, 2014).

76

77 **2.2 Sampling and analysis**

78 Daily rain water samples were collected between 20 December 2009 and 28 October

79 2010 with an Eigenbrodt model UNS130/E automatic wet only collector. The sampler

80 consisted of a glass funnel with an open area of 500 cm^2, connected to a 5 L glass

81 storage bottle, a movable lid and a precipitation sensor to control start and stop of each

82 collection period. Prior to use, all the collector components that could come in contact

83 with samples were cleaned with water, followed by rinses of distilled and deionised

84 water.

85 For the analysis of EC, WIOC and WITC (water insoluble total carbon) a liquid aliquot

86 was filtered through a quartz fiber filter (Whatman QMA), previously ignited at 550 ºC

87 during 5 hours. The sample filtration was achieved by using a stainless steel filter unit

88 equipped with a mask in order to concentrate particles onto a circular spot of 10 mm

89 diameter. The filter was then dried at ambient temperature inside a desiccator for about

90 24 hours and stored frozen until the analysis was conducted at the University of Aveiro.

91 Possible sources of error, associated to sampling and filtration processes, and

92 precautions to minimize them are addressed in Cerqueira et al. (2010). The EC and OC

93 particulate fractions accumulated in filters were measured by the thermal-optical

94 method described in detail by Castro et al. (1999) and Pio et al. (2011). This method

95 was used before to quantify carbonaceous matter extracted from rain and snow samples

96 (Cerqueira et al., 2010).

97

98 **2.3 Air mass trajectories**

99 Four-day back-trajectories arriving at AHMO location at the altitudes of 500 m, 1000 m

100 and 1500 m above sea level (a.s.l.) were calculated for every rain event using the

101 HYSPLIT model (Draxler and Rolph, 2012). Model runs were performed with

102   meteorological data from the Global Data Assimilation System (GDAS) archives. The

103   mid-point of the rain sampling period was selected as the arrival time at AHMO.

104   To investigate the source regions of particulate carbon in rain each set of daily

105   trajectories was subjectively classified according to the prevailing air mass origin and

106   transport pathway into the following 5 groups:

107   - North America: air masses originating over Southern Canada, the United States of

108   America or Mexico

109   - Arctic: air masses originating over Northern Canada, Arctic Ocean, Greenland or the

110   area north of the British Islands

111   - Europe: air masses originating over continental Europe

112   - Azores: air masses originating over the North Atlantic, in the area located to the north

113   and west of the Azores, travelling strictly over the ocean, and arriving at AHMO

114   location after a clockwise turn

115   - North Atlantic: the remaining air masses originating over the North Atlantic and

116   passing strictly over the ocean before arriving at AHMO location

117

118   **3. Results and Discussion**

119   **3.1 Precipitation data**

120   103 daily precipitation samples were collected throughout the study period, most of

121   them (69) during the winter and spring seasons (Fig.1). The average volume of

122   precipitation events ranged from 3 mm day^{-1} in summer to 12 mm day^{-1} in winter and

123   spring. Total accumulated precipitation was 972 mm, which is somewhat lower than the

124   average annual precipitation at AHMO. Seasonal distribution of accumulated

125   precipitation was as follows: 508 mm in winter, 310 mm in spring, 53 mm in summer

126   and 100 mm in autumn. Fig. 2 presents four-day back-trajectory analysis of air masses

127   arriving at 1000 m a.s.l. during the precipitation events sampled at AHMO. The

128   seasonal variation of precipitation events and precipitation amount was linked to the

129   dynamics of the Azores anticyclone. From winter to early spring the anticyclone was

130   located, most of the time, southwest of the islands. Under these conditions precipitation

131   at the Azores was the result of the convergence of cold and dry air from the North

132   American continent and Polar region with warm and moist air coming from the tropics.

133   During summer, the anticyclone moved northwards, blocking the transport of cold air

134   and consequently the formation of convective precipitation. Occasional showers, which

135   are common at this time of the year, were triggered by the orographic uplift of moist air
136   over the islands.
137
138   **3.2 Concentrations in precipitation**
139   WIOC, EC and WITC concentrations in precipitation collected at AHMO are resumed
140   in Table 1. Global volume-weighted average concentrations found during this study
141   were 134 ± 19 μgC L^{-1} for WIOC and 15.0 ± 1.6 μgC L^{-1} for EC. These values were 1.2
142   and 4.8 times higher, respectively, than those measured in 2003 and 2004 at the Azores
143   during the CARBOSOL project (Cerqueira et al., 2010). The observed differences, that
144   are only significant for EC, should not be seen as surprising given that particulate
145   carbon concentrations reported before were based on a limited number of samples (a set
146   of 7) which may have biased the results. Even so data from the present study fall within
147   the range of values that have been found in European background atmospheres (Ducret
148   and Cachier, 1992; Cerqueira et al., 2010).
149   The average contribution of EC to WITC in rain was 13%. This share is about 2 to 4
150   times lower than that of continental background aerosols (Pio et al., 2007) and suggests
151   that wet deposition processes are more efficient in removing WIOC than EC from the
152   atmosphere. However, the relative contribution of both carbon fractions to WITC is the
153   result of a complex balance between emission, transformation and removal processes.
154   EC in the Central North Atlantic atmosphere is essentially the result of long-range
155   transport of air masses originating in continental areas, since EC emissions from the
156   ocean or from human activities at the surface of the ocean are thought to be negligible.
157   Although EC particles freshly emitted by combustion processes are mostly
158   hydrophobic, atmospheric ageing processes, such as mixing with secondary species or
159   chemical reactions, may convert these particles to hydrophilic aerosols (Tritscher et al.,
160   2011; Zhang et al., 2008; Zuberi et al., 2005). Due to this fact, EC emitted in continental
161   areas and transported to the Central North Atlantic Ocean is expected to be significantly
162   removed from the atmosphere by wet deposition processes (along with dry deposition
163   processes) before being transported to the Azores. On the other hand, a large fraction of
164   OC aerosols from continental areas is water soluble (Pio et al., 2007), which also
165   facilitates removal from the atmosphere by wet deposition during transport over the
166   Atlantic Ocean. Given that, most of the EC and WIOC particles emitted in continental
167   areas were most likely lost during transport of air masses to the Azores and that the
168   share of EC was lower than that of WIOC in rain sampled at AHMO, seems to be a

169 logical conclusion that the ocean appears to act as a source of organic carbon to the
170 local atmosphere. This possibility is further discussed in the next section.

171

172 **3.3 Seasonal variation of concentrations**

173 Results from this study showed a seasonal variation in the concentrations of particulate
174 carbon fractions (Table 1 and Fig. 3). Volume-weighted average WIOC concentrations
175 varied between a minimum of 88 ± 16 µgC L^{-1} in winter and a maximum of 477 ± 86 µgC
176 L^{-1} in summer. Interesting to note is that sampling events with high precipitation
177 volumes (typical of the winter and spring seasons) exhibited lower WIOC
178 concentrations than those with lower precipitation volumes (typical of the summer
179 season). This effect is evident from the regression analysis between logarithm of WIOC
180 concentration and logarithm of precipitation amount (Fig. 4(a)). The model obtained
181 from the analysis, with a standard error of 0.33 µgC L^{-1} and a correlation coefficient, r,
182 of -0.80, was,

183 $$\log_{10}(WIOC) = (2.77 \pm 0.05) - (0.77 \pm 0.06) \times \log_{10}(precipitation),$$

184 and shows that dilution is an important factor controlling the WIOC content of
185 precipitation. Additionally, these results indicate that organic particles are efficiently
186 scavenged from the atmosphere at the onset of rain events, and are then diluted by
187 subsequent rainfall.

188 Another possible factor that may play an important role in determining seasonal WIOC
189 differences is the input of biogenic organic carbon from the oceans. Organic carbon
190 contribution to submicrometer aerosol over the North Atlantic Ocean is known to vary
191 seasonally and is higher during the spring to autumn period when the biological activity
192 in the oceanic surface waters is more intense (O'Dowd et al., 2004). Most of this
193 organic carbon in the submicrometer marine aerosol is water-insoluble with a
194 significant contribution of phytoplankton exudates (Facchini et al., 2008). Breaking
195 waves were suggested to exert an overwhelming influence on the organic carbon
196 content of sea spray aerosol (Quinn et al., 2014). However, this influence was not
197 evident in the Azores samples, otherwise WIOC concentrations in rain should also
198 exhibit high values during the winter season, when wind conditions are more favourable
199 to sea spray formation. Biogenic emissions from Terceira island soils and plants were
200 reported to peak during the growing season (Alves et al., 2007) and are also possible
201 contributors to the WIOC content of precipitation.

202   A different seasonal trend was observed for EC, with a minimum volume-weighted
203   average concentration of 4.2±3.3 μgC L^{-1} in summer and a maximum of 17.5±2.2 μgC
204   L^{-1} in spring. The reported differences do not reflect any seasonal pattern of sources,
205   given that EC emissions above the North Atlantic waters (from islands or ship traffic)
206   are supposed to be of minor significance compared to emissions from continental areas
207   surrounding it. On the other hand, EC concentrations are not affected by the seasonal
208   change of daily precipitation amount. This is evident from the plot shown in Fig. 4(b),
209   where the logarithm of EC concentration does not present any correlation with the
210   logarithm of daily precipitation amount. These results show that EC particles are not as
211   efficiently scavenged from the atmosphere as WIOC particles, even considering that EC
212   particles can acquire hydrophilic properties by chemical ageing. As explained in more
213   detail in the following section, seasonal patterns in air mass transport are the main factor
214   controlling the EC concentrations in precipitation in the area of the Azores.
215
216   **3.4 Effects of air mass origin on concentrations**
217   Fig. 5(a) presents the volume-weighted average WIOC concentrations for samples
218   associated with the different classes of back-trajectories. The highest WIOC
219   concentrations (596±118 μgC L^{-1}) were obtained in rain samples collected exclusively
220   under the influence of air mass transport around the Azores, which mostly occurred
221   during summer. These values are linked to the above mentioned decrease of
222   precipitation volumes and increase of marine biogenic carbon incorporation during the
223   growing season. Relatively lower values were found in samples associated back-
224   trajectories from the North American continent (94±20 μgC L^{-1}) and were comparable
225   to values observed in rain samples that were collected under background maritime air
226   masses originating over the ocean, which mostly occurred during the non-growing
227   season (North Atlantic class; 91±12 μgC L^{-1}). These results suggest that most of the
228   WIOC emitted to the North American atmosphere and exported to the North Atlantic
229   with prevalent winds is already lost when air masses arrive at the Azores longitude.
230   Even though, the remaining WIOC is an important contributor to global wet deposition
231   fluxes as will be seen in the following section.
232   Fig. 5(b) shows a different pattern of variation for the volume-weighted average EC
233   concentrations. Concentration values associated with the Azores group of back-
234   trajectories were very low (1.5±0.6 μgC L^{-1}) and among the lowest measured so far in

235   rain samples (Ducret and Cachier, 1992; Cerqueira et al., 2010). These results confirm
236   that the Azores area is not a source of EC to the atmosphere and that air masses
237   spending a long time over the Central North Atlantic Ocean become nearly devoid of
238   EC. In contrast, air masses arriving at the Azores from the European continent show the
239   highest EC concentrations (41 ± 13 µgC L^{-1}). The transport of EC was particularly
240   intense with air masses originating in populated and industrialized regions of Northern
241   and Central Europe. A careful analysis of these back-trajectories indicates that air
242   masses take less than 2 days to be transported between coastal Europe and the Azores.
243   Rain events associated with trajectories arriving from North America, which is known
244   to be an important source region of EC to the global atmosphere, displayed a volume-
245   weighted average EC concentration that was about 3 times lower than that of the
246   European class of rain samples. The location of the Azores at a longer distance from the
247   east coast of North America than from the west coast of Europe, might explain the
248   observed difference. A longer distance means that more time is required for the air
249   masses to reach the Azores and greater is the probability of EC particles being removed
250   from the atmosphere. Even though, volume-weighted average EC concentration in the
251   North American group of samples (16 ± 2 µgC L^{-1}) was significantly higher than that of
252   the Azores samples. These results clearly demonstrate that air mass origin is a dominant
253   factor explaining the seasonal trend of EC concentrations at Terceira Island.
254
255   **3.5 Wet deposition fluxes**
256   Wet deposition fluxes were calculated on a daily basis by multiplying individual event
257   concentrations with the event precipitation amount. The time variation of WIOC and EC
258   wet deposition fluxes is shown in Fig. 6 and seasonal average values are shown in Table
259   2. WIOC wet deposition was higher in winter and early spring, decreased in summer
260   and raised again during autumn. This trend contrasts with the seasonal variation of
261   WIOC concentrations, with maxima in summer, and demonstrates that the magnitude of
262   wet deposition fluxes at the Azores is mostly controlled by the amount of precipitation.
263   Results of back-trajectory analysis presented in Fig. 2 have shown that winter air
264   masses arriving at the AHMO generally came from the west and northwest sectors. For
265   that reason, during the study period, North America was the main source region of
266   WIOC deposited by rain into the Azores. The time variation of EC daily fluxes
267   compares well with that of WIOC, but the spring to summer decrease was more
268   pronounced, since EC particles were almost absent from rain during summer (EC

269 concentration levels were close to the limit of detection of the analytical method used in
270 this study). According to the above seasonal distribution of backward trajectories, North
271 America was also the largest EC exporter region to the Azores.

272 As far as the authors know, to date there are no measurements of WIOC and EC wet
273 deposition fluxes into oceanic waters to compare with the results of this study. The
274 modelling study of Jurado et al. (2008) is the only one that presents estimates for these
275 fluxes based on satellite measurements of climatological data and aerosol concentrations
276 together with literature scavenging ratios. Average values of 0.53 mgC m^{-2} day^{-1} for
277 organic carbon (soluble and insoluble) and 0.10 mgC m^{-2} day^{-1} for black carbon were
278 estimated for a latitude band extending from 30º N to 60º N. The magnitude of these
279 values is comparable to that of measurements performed at the Azores, despite the
280 uncertainty associated with model predictions of wet deposition fluxes, which is mainly
281 a consequence of the scarcity of information about the distribution of particulate carbon
282 concentrations over the oceans and the use of the same value for the scavenging ratios
283 of organic and black carbon aerosols.

284

285 **4. Conclusions**

286 This paper reports the first long-term measurements of WIOC and EC concentrations in
287 precipitation collected at a remote marine site and contributes to a better understanding
288 of particulate carbon removal from the atmosphere. WIOC and EC concentrations in
289 precipitation from the Azores were within the range of values reported before for
290 European background atmospheres. A seasonal variation was observed for both
291 particulate carbon fractions: WIOC concentrations were lower in winter than in
292 summer, which was related with the dilution effect of winter rains and possibly with a
293 higher input of biogenic organic carbon during the growing season; EC concentrations
294 were higher in winter and spring than in summer, reflecting the seasonality of long-
295 range transport of air pollutants to the Azores. The summer maximum WIOC
296 concentrations were observed under the influence of air masses with a long residence
297 time over the Central North Atlantic Ocean, further supporting the possibility of organic
298 carbon incorporation from marine and island sources. The maximum EC concentrations
299 were associated with air masses arriving from populated and industrialized areas in
300 Europe, showing that EC residence time in the atmosphere is long enough to allow for
301 transport of EC particles to the Azores. Lower WIOC and EC concentrations in rain
302 were observed under air mass transport from North America. However, given that

303 precipitation amount was higher during these events than on the other days, the
304 corresponding WIOC and EC wet deposition fluxes were also higher and therefore
305 North America was found to be the main source region of particulate carbon deposited
306 by rain into the Azores region.

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Table 1 Volume-weighted average (vwa), volume-weighted standard deviation (σ), simple average and range of WIOC, EC and WITC
concentrations in precipitation at AHMO.

Season	n	WIOC (µgC L-1)			EC (µgC L-1)			WITC (µgC L-1)		
		vwa ± σ	average	range	vwa ± σ	average	range	vwa ± σ	average	range
Winter	43	88±16	108	23-503	15.2±1.8	19	3.1-57	103±17	126	31-543
Spring	26	89±13	215	26-636	17.5±2.2	48	5.4-236	107±14	263	31-871
Summer	20	477±86	1309	120-10426	4.2±3.3	5.1	0.0-46	482±87	1315	120-10473
Autumn*	14	324±151	618	66-1475	11.9±6.8	12	0.0-85	336±156	631	81-1481
Overall	103	134±19	438	23-10426	15.0±1.6	23	0.0-236	149±20	460	31-10473

* monitoring period was shorter than season length

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Table 2 Seasonal average WIOC, EC and WITC wet deposition fluxes at AHMO.

391

Season	WIOC ($\mu gC\ m^{-2}\ day^{-1}$)	EC ($\mu gC\ m^{-2}\ day^{-1}$)	WITC ($\mu gC\ m^{-2}\ day^{-1}$)
Winter	496	85	576
Spring	301	59	360
Summer	276	2	278
Autumn*	877	32	909
Overall	419	47	465

392 * monitoring period was shorter than season length

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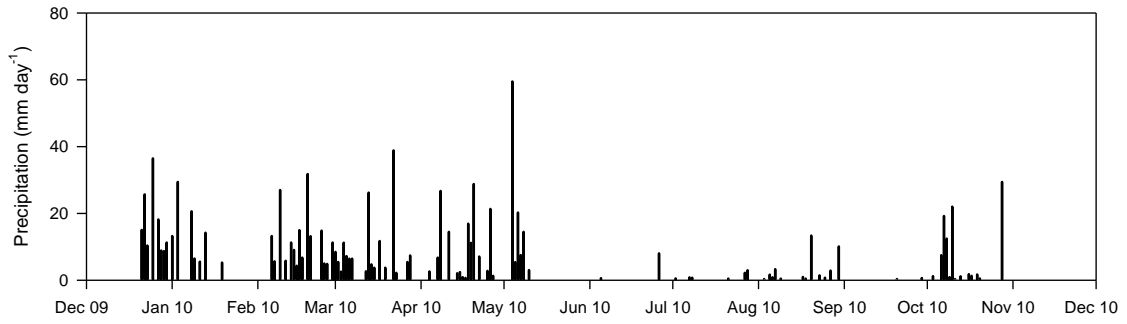
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418 **Figure 1** Time series of daily precipitation at AHMO during the study period.

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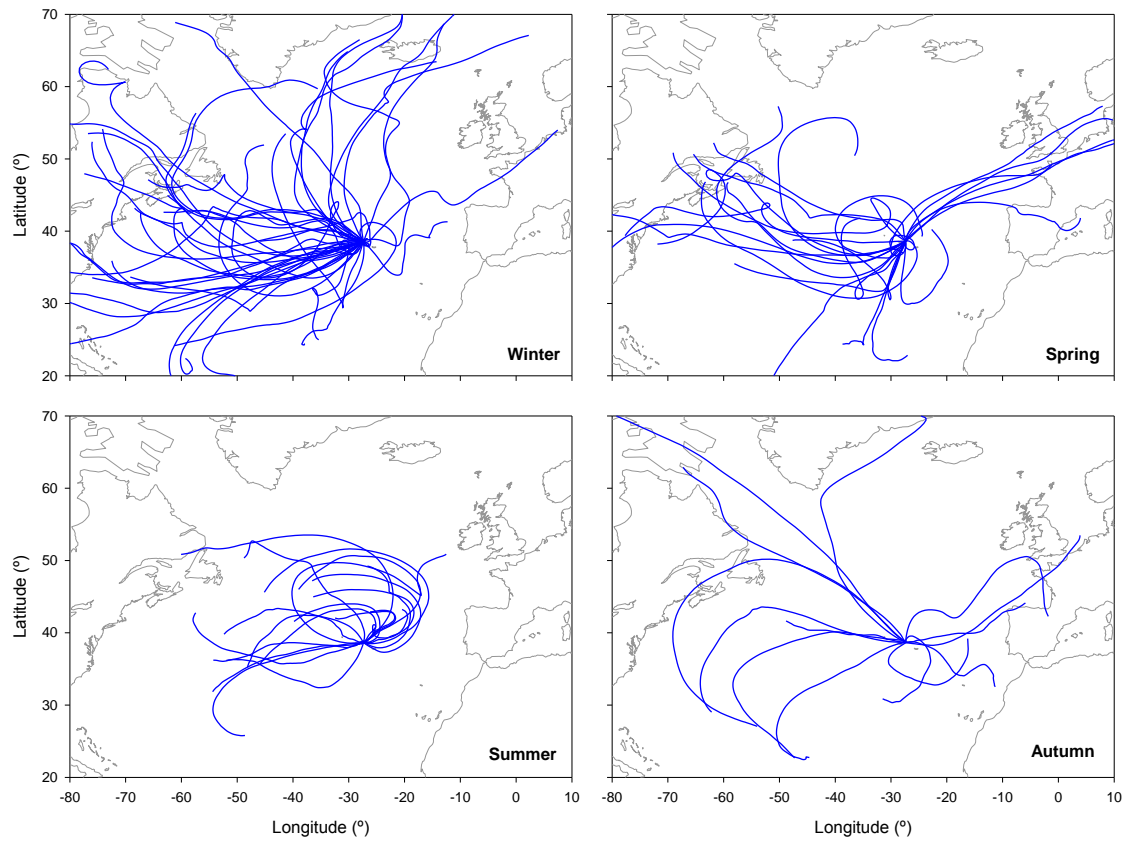
Figure 2 Four-day back-trajectories arriving at 1000 m a.s.l. during the precipitation
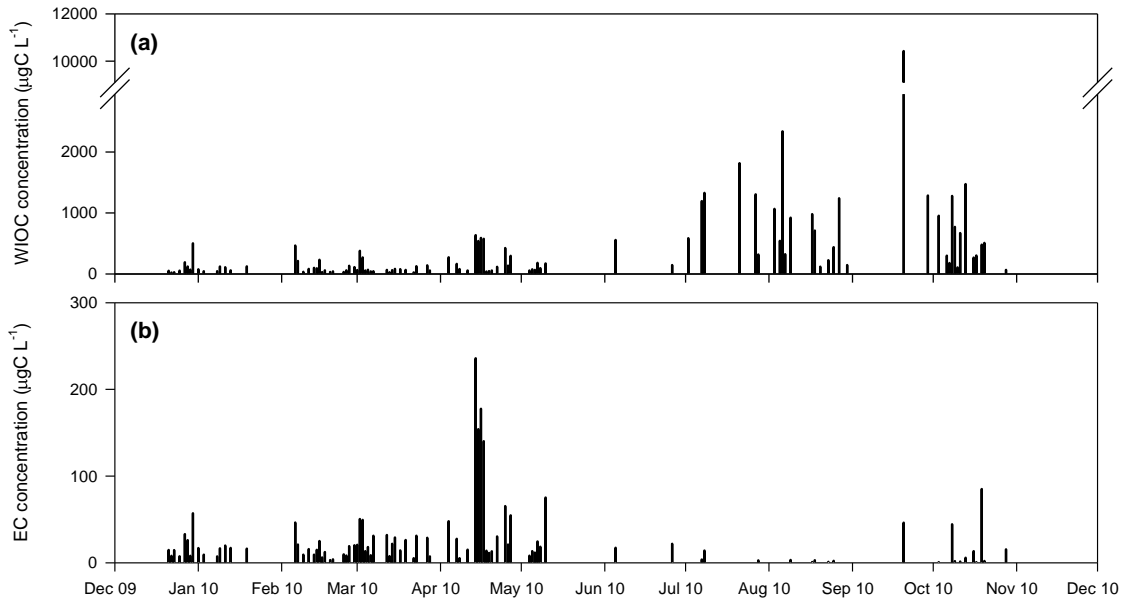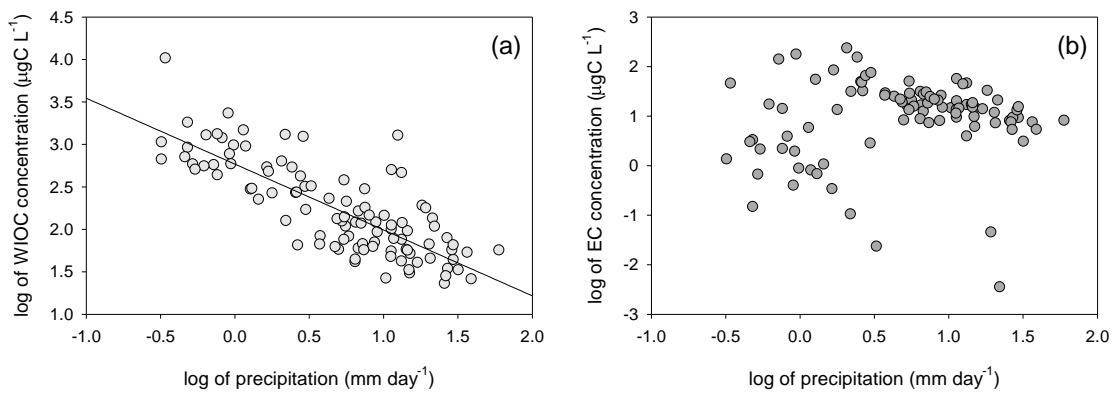
events sampled at AHMO.

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Figure 3 Time series of WIOC concentrations (a) and EC concentrations (b) in
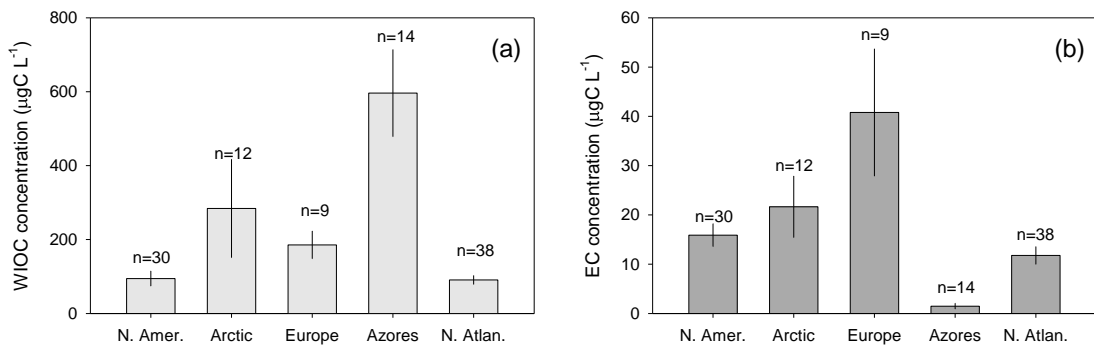precipitation at AHMO during the study period.

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Figure 4 Log-log plots of the relationship between the WIOC concentration and the
daily precipitation amount (a) and between the EC concentration and the daily
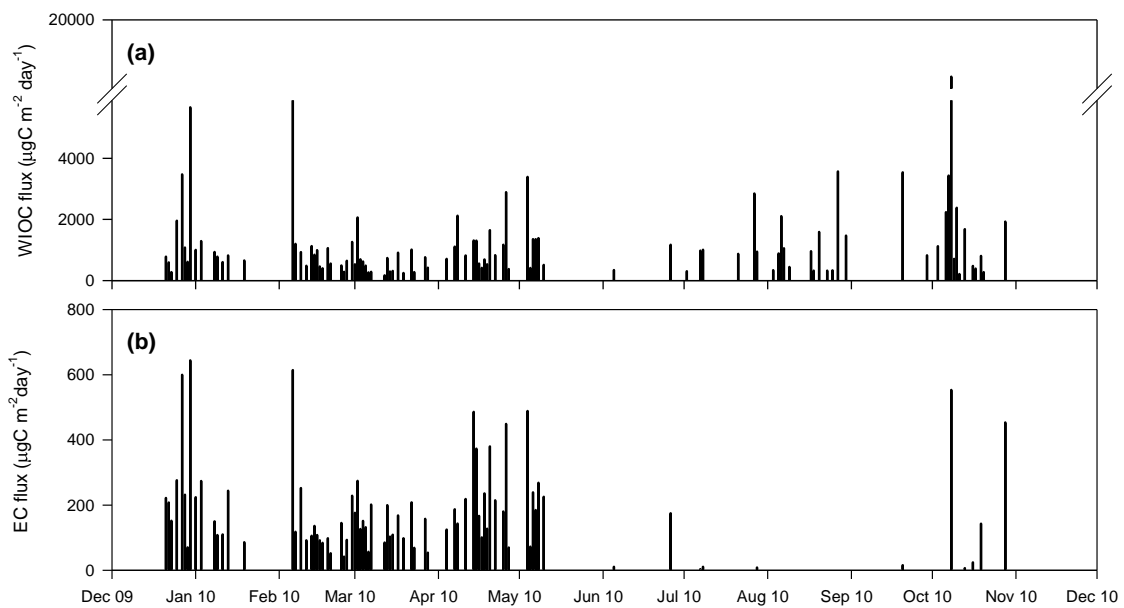precipitation amount (b).

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Figure 5 Volume-weighted average concentrations and volume-weighted average standard deviations for WIOC (a) and EC (b) as a function of air mass back-trajectory class. The *n* values above the bars indicate the number of sampled events associated to each class.

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Figure 6 Time series of WIOC daily wet deposition fluxes (a) and EC daily wet deposition fluxes (b) at AHMO during the study period.