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J. Sciare, O. Favez, Roland Sarda-Estève, K. Oikonomou, H. Cachier, et al.. Long-term observations of carbonaceous aerosols in the Austral Ocean atmosphere: Evidence of a biogenic marine organic source. *Journal of Geophysical Research*, 2009, 114 (D15), 10.1029/2009JD011998 . hal-03199235

**HAL Id: hal-03199235**

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Submitted on 15 Apr 2021

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## Long-term observations of carbonaceous aerosols in the Austral Ocean atmosphere: Evidence of a biogenic marine organic source

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Received 3 March 2009; revised 4 April 2009; accepted 15 May 2009; published 8 August 2009.

[1] Long-term observations of carbonaceous aerosols in the Austral Ocean are reported here for the first time from almost 5 years of continuous filter sampling performed at Amsterdam Island (37°48'S, 77°34'E). Black carbon concentrations determined by optical method were among the lowest reported for marine atmosphere, with monthly mean levels ranging from 2–5 ng C/m<sup>3</sup> during summer to 7–13 ng C/m<sup>3</sup> during winter. A clear seasonal pattern was also observed for organic aerosols, but in opposite phase, with maximum values during the austral summer period (>250 ng C/m<sup>3</sup>) and minimum concentrations (100 ng C/m<sup>3</sup>) during winter. This seasonal variation of organic concentration was found to be almost entirely related to the water-insoluble organic carbon fraction, suggesting a primary origin for these organics, most probably through bubble bursting processes. Moreover, this summer maximum observed for organic aerosols was found to be correlated with satellite-derived chlorophyll a concentrations averaged over an oceanic region upwind of the sampling site and characterized by relatively high biogenic activity. This oceanic region being located at 1000–2000 km far away from the monitoring station, atmospheric ageing may have played a significant role on the levels and size-resolved properties of marine organics collected at Amsterdam Island. This biogenic marine organic source of primary origin in the Austral Ocean is fully consistent with similar observations previously reported for the Northern Atlantic Ocean and brings further evidences of the major role of marine organic emissions over remote oceanic regions.

**Citation:** Sciare, J., O. Favez, R. Sarda-Estève, K. Oikonomou, H. Cachier, and V. Kazan (2009), Long-term observations of carbonaceous aerosols in the Austral Ocean atmosphere: Evidence of a biogenic marine organic source, *J. Geophys. Res.*, 114, D15302, doi:10.1029/2009JD011998.

### 1. Introduction

[2] Marine aerosols play a major role on both the Earth's albedo and climate. However, most of the studies on marine aerosols have been focusing on sea salt particles and non-sea-salt (nss-) sulphate aerosols (originating from the oxidation of atmospheric dimethylsulfide) whereas size-resolved chemical characterization of organic aerosols, their hydrophilic/hydrophobic properties and their role as cloud condensation nuclei (CCN) remain poorly investigated [O'Dowd and de Leeuw, 2007]. The presence of marine biogenic organic aerosols in the form of microcolloidal aggregates were reported by Leck and Bigg [2005] at various remote oceanic sites at low and high latitudes. Using Transmission Electron Microscopy (TEM) techniques, these authors have shown that these particles, originating from the surface micro-layer, could account for a significant number fraction of CCN. A significant source of

marine organic aerosols of primary origin has been also reported recently at Mace Head station in N. Atlantic during the period of high biological activity [O'Dowd *et al.*, 2004; Yoon *et al.*, 2007; Ceburnis *et al.*, 2008]. Size-resolved eddy covariance measurements of primary marine aerosol emissions performed recently at this station of Mace Head further confirmed a bubble-bursting process for this primary biogenic organic source [Nilsson *et al.*, 2007] and predicted that the organic carbon fraction increase with decreasing diameter in consistency with simultaneous chemical data [Cavalli *et al.*, 2004; Facchini *et al.*, 2008]. These studies were performed at a North Atlantic site and represent probably the most exhaustive characterization of marine organic aerosols. On the other hand, they clearly point out the need for similar studies in other biogenically productive and remote oceanic regions in order to better assess the central role of marine organics at a global scale.

[3] Recent studies performed in the Austral Ocean (Cape Grim, Tasmania) during summertime have brought new insights on primary marine organics in submicron aerosols and their potential role as CCN [Fletcher *et al.*, 2007; Bigg, 2007]. Remote sensing measurements performed over another region of the Austral Ocean (Southern Atlantic Ocean)

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have revealed a close relationship between ocean productivity and CCN size and number concentrations [Meshkizze and Nenes, 2006]. Although all these results clearly enlighten the major climatic role of marine organic emissions, their global and regional distribution still need to be better documented, in particular in the very pristine and highly productive southern ocean.

[4] Amsterdam Island (southern Indian Ocean) is one of the three major atmospheric stations located in the Austral Ocean (with Cape Grim, Tasmania; and Cape Point, South Africa). It is the only one located far from continents and holds the longest times series on the biogeochemical sulphur cycle [Sciare et al., 2000; Baboukas et al., 2002, 2004] with more than 20 years of continuous record of atmospheric dimethylsulfide (DMS) and its oxidation products. In order to get a more complete picture of the chemical composition of marine aerosols in the Austral Ocean, these measurements have been completed by a continuous filter-based monitoring of carbonaceous aerosols (Equivalent Black Carbon, EBC; organic carbon, OC; and water-soluble organic carbon, WSOC) initiated since January 2003. Four and half years of bulk EBC and OC measurements, completed by almost 3 years of bulk WSOC measurements are presented here for the first time in the Austral Ocean atmosphere. The role of marine biogenic emissions is discussed here from concomitant seasonal variations of these carbonaceous species and chlorophyll a. Comparison is also performed with similar observations reported previously in the northern hemisphere, at the marine station of Mace Head.

## 2. Instrumentation and Analyses

### 2.1. Sampling Site Description and Meteorological Overview

[5] Amsterdam Island (37°48'S, 77°34'E), is located in the southern Indian Ocean sector of the Austral Ocean, at 3400 km and 5000 km from the nearest lands upwind, Madagascar and South Africa, respectively (Figure 1). Most of the year, it benefits of pristine marine conditions [Miller et al., 1993], especially during summer when high pressure conditions (low wind speeds) are prevailing. Atmospheric monitoring activities have been performed at this island for the last twenty years and are part of the World Meteorological Organization-Global Atmospheric Watch (WMO-GAW) network. These atmospheric measurements are performed at 30 m above sea level; 2 km upwind of the scientific base (20 persons). The pristine marine conditions prevailing at Amsterdam Island and the very low occurrence of local contamination originating from the scientific base have been reported for many atmospheric compounds such as ozone [Gros et al., 1998], carbon monoxide [Gros et al., 1999], nitric oxide (J. Sanak, personal communication, 2002), Black Carbon (H. Cachier, unpublished data, 2008) and total aerosol number concentration [Sciare et al., 2001]. The lack of continental margin around Amsterdam Isl. (1000 m off the coast is typically at 1000 m depth) and the very small tidal amplitude minimize the influence of coastal shelves which may play an important role on the levels of condensation nuclei and cloud condensation nuclei.

### 2.2. Filter Sampling

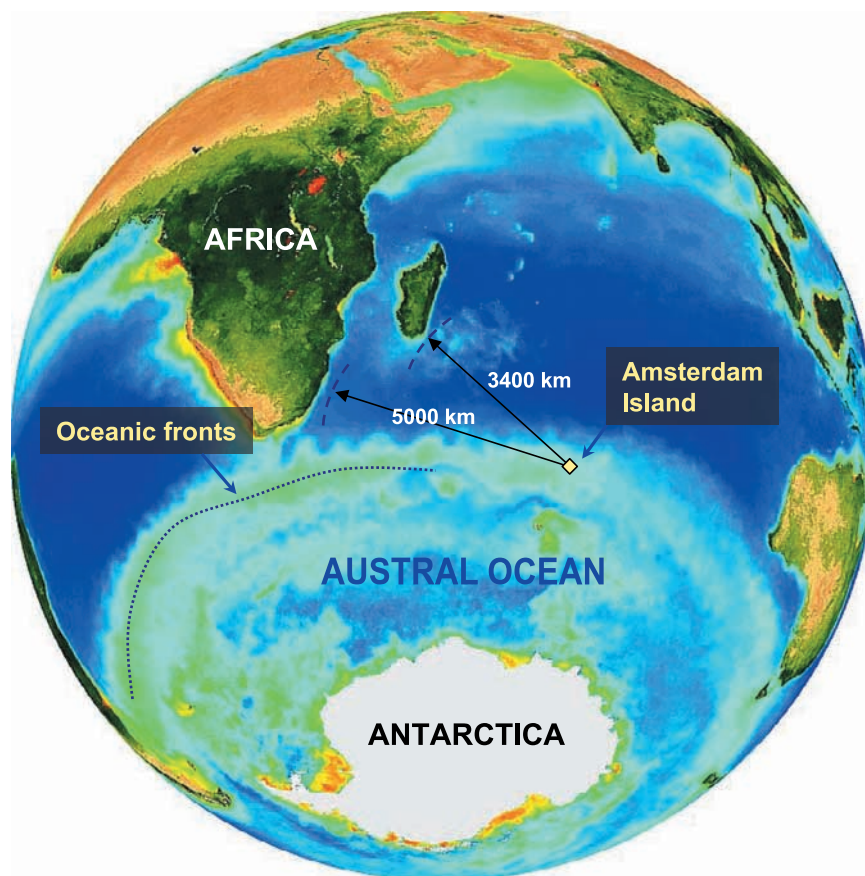
[6] Bulk aerosols were continuously collected on a 10-day basis from May 2003 to December 2004 (using pre-fired 25-mm diameter Whatman QMA quartz filters) and on a 8-day basis from January 2005 to November 2007 (using pre-fired 47-mm diameter Whatman QMA quartz filters). No cut-off was applied on this open face filter sampling. However, a 1-year comparison with size-segregated measurements performed with a cascade impactor running in parallel has shown that total carbon (TC) concentrations obtained from bulk sampling were similar to those obtained from the cascade impactor for the aerosol size fraction below 10  $\mu\text{m}$  (Sciare et al., manuscript in preparation). It is also important to note that these two sets of TC measurements have been obtained from different sampling system (filtration and impaction, respectively) and, for that reason, have been affected in different ways by artefacts inherent to the filter sampling of organic aerosols (adsorption and/or volatilization of organic vapors). Although biases because of these artefacts may certainly exist, the good agreement found between the two TC data sets suggests that they do not affect in a significant way the TC concentrations reported from bulk filter sampling.

[7] A total number of 192 filter samples was collected, covering a period of 4 years and half (May 2003–November 2007). Air flowrate was typically of 1.7 and 2.5  $\text{m}^3/\text{h}$  for these two periods (January 2005–December 2004) and (January 2005–November 2007), respectively. Filter samples were taken in the field every month for the determination of blank values for ions and carbon analyses. Once sampled, all the filters were stored at  $-18^\circ\text{C}$  till their analyses at LSCE (France).

### 2.3. Ion Species

[8] Ion chromatography analysis of the QMA filters was performed at LSCE in order to determine selected anions (acetate, propionate, formate, methanesulfonate ( $\text{MS}^-$ ), glutarate, succinate, oxalate, chloride, sulfate, nitrate, and phosphate) and cations (sodium, ammonium, potassium, magnesium, and calcium) using the protocol reported by Sciare et al. [2007]. Briefly, the analysis of anions is conducted using a 4-mm diameter AS11-HC model pre-column and column, a 300  $\mu\text{l}$  injection loop, and Ion Chromatograph (IC, Model DX-600, DIONEX) equipped with a reagent free system (automated eluent generation and self-regenerating suppression). A gradient program, ranging from 1 to 40 mM of eluent (KOH), is used in order to properly separate light organic anions for typical chromatograph duration of 40 min. The analysis of cations is conducted using a 4-mm CS12 model pre-column and column, a 75  $\mu\text{l}$  injection loop, and Ion Chromatograph (IC, Model DX-600, DIONEX) equipped with a reagent free system. Separation of the five cations is achieved in isocratic mode at 20 mM of eluent (methanesulfonic acid, MSA) for typical chromatograph duration of 16 min.

[9] Quality control of ion chromatography analyses performed at LSCE is performed every 6 months within the intercomparison laboratory exercises organized by WMO-GAW; errors are found to range from 2 to 4% for the major anions and cations. The overall error in the determination of ionic species is estimated to be of the order of 5% and takes



**Figure 1.** Location of Amsterdam Island in the Southern Indian Ocean. SEAWIFS chlorophyll map of the Austral Ocean obtained during austral summer.

into account the filter blank variability as well as filter extraction efficiency.

[10] The charge closure of ion species collected on the QMA filter samples was also checked and showed that ion balance was achieved ( $\Sigma^+$  (neq/m<sup>3</sup>) = 0.98  $\Sigma^-$  (neq/m<sup>3</sup>);  $r^2$  = 0.99; N = 192). Sensitivity, detection limit ( $3\sigma$  of signal-to-noise ratio), blank values, and atmospheric concentrations of MS<sup>-</sup> measurements are summarized in Table 1.

#### 2.4. Equivalent Black Carbon (EBC)

[11] A circle punch of 18 mm diameter was taken on each QMA filter to perform a non-destructive optical measurement of the light absorption using a modified aethalometer

(model AE-9) manufactured by Magee Scientific [Hansen *et al.*, 1982; Lioussé *et al.*, 1993]. This aethalometer is working with an incandescent light with a broad spectral distribution. The spectral response of a similar instrument (AE-10) is given by Weingartner *et al.* [2003]. The aerosol absorption coefficient ( $b_{ATN}$ ) determined in this way may differ significantly from the true aerosol absorption coefficient ( $b_{abs}$ ) of airborne particles. Therefore, calibration factors C and R(ATN) are introduced, which can convert aethalometer attenuation measurements to “actual” absorption coefficients following the equation:

$$b_{abs} = \sigma_{abs} * b_{ATN} / (\sigma_{ATN} * R(ATN)) \quad (1)$$

**Table 1.** Results of the Chemical Determination of Filter Samples

Species	Type of Analysis	Unit	Sensitivity	Detection		N	Range	Average	Filter Blanks
				Limit	Uncertainty				Average
MS <sup>-</sup>	Ion Chromatography	ng C/m <sup>3</sup>	0.001	0.01	5%	192	0.013–29.54	4.20	<0.01
EBC	Absorption	ng C/m <sup>3</sup>	0.01	0.1	10%	192	0.1–62.02	35.2	<0.1
TC	Thermo-optical EC-OC on 25-mm QMA filter	ng C/m <sup>3</sup>	0.1	15	5%	60	47.6–289.9	139.2	10
TC	Thermo-optical EC-OC on 47-mm QMA filter	ng C/m <sup>3</sup>	0.1	15	5%	132	16.9–548.4	153.1	5
WSOC	TOC on 47-mm QMA filter	ng C/m <sup>3</sup>	0.1	9.0	12%	132	27.4–149.2	60.9	9.0 <sup>a</sup>

<sup>a</sup>Includes blank values of water used for extraction.

where  $\sigma_{\text{abs}}$  and  $\sigma_{\text{ATN}}$  ( $\equiv \sigma_{\text{abs}} * C$ ) are the mass specific absorption and attenuation cross-section (in units of  $\text{m}^2/\text{g}$ ), respectively. Following the recommendation of the constructor a  $\sigma_{\text{ATN}}$  value of  $19 \text{ m}^2/\text{g}$  was taken here. Our absorption coefficients were then calculated with R and C values of 1 and 1.9, respectively. Absorption measurements were converted into Equivalent Black Carbon (EBC) mass concentration (expressed in  $\mu\text{g C}/\text{m}^3$ ) using a mass absorption efficiency of  $19 \text{ m}^2/\text{g}$  given by the constructor.

[12] In this study, attenuation values determined for each QMA filters were the average of two optical measurements showing attenuation difference less than 1 unit, corresponding to an average error of the order of 3%. Attenuation values given by the blank filters collected in the field were stable showing variability of the order of 5%. The overall uncertainty of EBC measurements was then estimated to be typically of the order of 10%. Based on our filter sampling time integration, an EBC detection limit of about  $0.1 \text{ ng C}/\text{m}^3$  was calculated here. Sensitivity, detection limit, blank values, and atmospheric concentrations of EBC measurements are summarized in Table 1.

## 2.5. Elemental Carbon (EC) and Organic Carbon (OC)

[13] Two punches of  $1 \times 1.5 \text{ cm}$  were taken from each quartz filters for the determination of elemental carbon (EC) and organic carbon (OC). A thermo-optical transmission carbon analyzer system (Sunset Laboratory instrument, OR; *Birch and Cary* [1996]) was used for the mass determination of EC and OC. Carbonates from sea salt aerosols collected on the QMA filters may interfere in the determination of the carbon analysis by releasing  $\text{CO}_2$  at high temperatures in the range  $550\text{--}1020^\circ\text{C}$  [*Webb and Kruger*, 1970]. Based on a mass ratio ( $\text{HCO}_3^-/\text{Cl}$ ) of 0.0075 typical for sea salt aerosols, carbonate concentrations were calculated for each individual QMA sample from Chloride concentrations determined by IC. Carbonates levels showed values ranging from  $2.5$  to  $42.6 \text{ ng C}/\text{m}^3$  (average  $16.2 \text{ ng C}/\text{m}^3$ ), leading to an overestimation of TC ranging from 1.3 to 34.1% (average 12.7%). To avoid this non negligible interference by sea salt carbonates, all the filter samples were decarbonated by HCl fumes using the protocol designed by *Cachier et al.* [1989]. Three-to-four punches were analyzed simultaneously with the Sunset Lab analyzer in order to improve the detection limit of the instrument. However, because of very low concentrations, the determination of EC determination could be achieved on few samples only. For that reason, the thermo-optical analyses were only used to derive TC concentrations. Concentrations of OC were then calculated as the difference between TC (determined by thermo-optical method) and EBC (determined by optical method). Total Carbon levels were corrected from the blank filters taken every month in the field. Based on filter blank uncertainty of typically  $0.25 \mu\text{gC}/\text{cm}^2$ , a detection limit ( $3\sigma$  of blank uncertainty) of about  $15 \text{ ng C}/\text{m}^3$  was calculated for the sampling and analytical conditions applied here. Sensitivity, detection limit, blank values, and atmospheric concentrations of TC measurements are summarized in Table 1. The overall uncertainty of TC measurements includes blank uncertainty and analytical uncertainty given by the constructor ( $0.2 \mu\text{g C} \pm 5\%$ ).

## 2.6. Water-Soluble Organic Carbon (WSOC)

[14] Water-soluble organic carbon analyses were achieved on the same QMA quartz filters used for ion, EBC, and TC measurements and comprise a total of 132 samples covering a period of 3 years (December 2004–November 2007). Analyses were performed following the protocol reported by *Sciare et al.* [2008], using a total organic carbon analyzer (TOC, Model Sievers 900, Ionics Ltd, USA) in which ammonium persulphate and UV light (185 and 284 nm) are used for the oxidation of organic carbon. Methanesulfonate was detected by the TOC system and contributed to the WSOC concentrations determined by this instrument. Extraction of the soluble fraction was performed on filter portions of about  $8 \text{ cm}^2$  placed in boro-silicated Erlenmeyer flasks with 25 mL of ultra pure water (obtained by ELGA maxima HPLC). This extraction step was conducted overnight under soft shaking. Prior to analysis, the extract solution was filtered through Teflon (PTFE) filters ( $0.2 \mu\text{m}$  pore size diameter), in order to remove suspended particles.

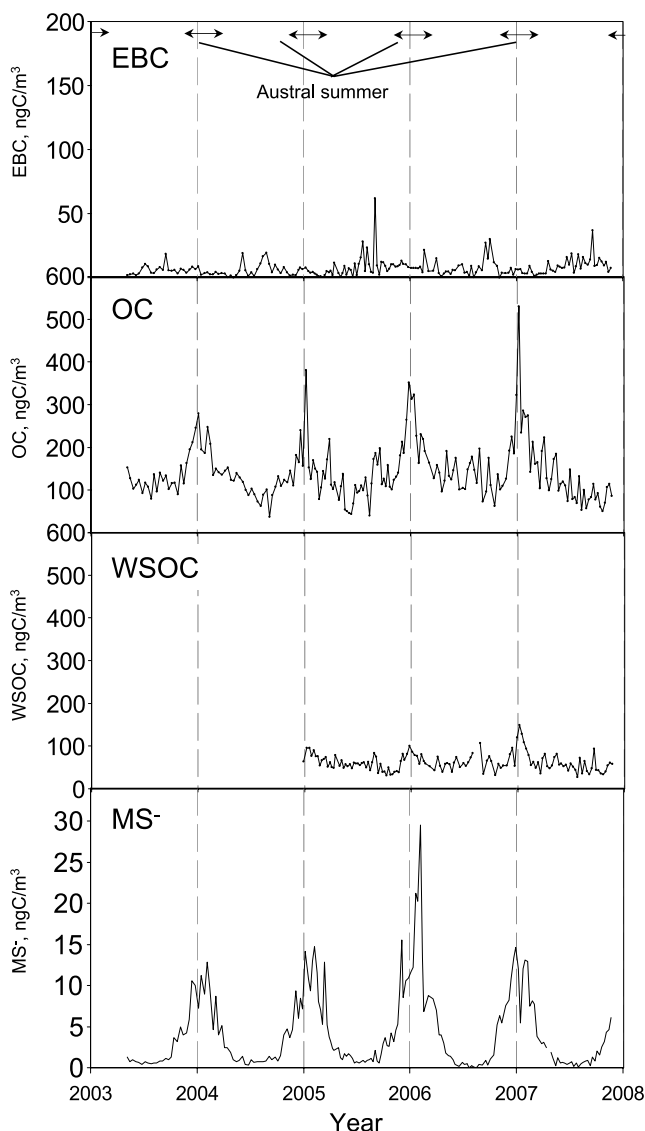
[15] The measurement uncertainty given by the manufacturer is of the order of 7% and does not include uncertainties associated with WSOC contained in the water used for extraction and WSOC contained in the QMA filters prior to sampling. WSOC concentration contained in the water used for extraction was found to be of the order of  $50.7 \pm 12 \text{ ppb}$  which corresponds to blank values of  $3 \pm 2 \text{ ng C}/\text{m}^3$  for our sampling conditions. Several filter blanks were taken in the field and showed an average WSOC concentration of  $6 \pm 2 \text{ ng C}/\text{m}^3$  for our sampling conditions. Analyses were systematically duplicated for each filter sample and a good reproducibility was obtained with a mean deviation of  $1.0 \pm 0.7\%$  between the two measurements. WSOC concentration of atmospheric samples was ranging from  $27.4$  to  $149.2 \text{ ng C}/\text{m}^3$  (average of  $60.9 \pm 21.0 \text{ ng C}/\text{m}^3$ ) and was systematically corrected from blank values (water used for extraction and blank filters). Blank values contribute on average to  $14.0 \pm 5.5\%$  of atmospheric sample concentrations. Sensitivity, detection limit ( $3\sigma$  of blank variability), blank values, and atmospheric concentrations of WSOC measurements are summarized in Table 1. The overall uncertainty of WSOC measurements includes blank uncertainty and analytical uncertainty given by the constructor. Water Insoluble Organic Carbon (WIOC) mass concentrations reported in the following were calculated as the difference between OC and WSOC mass concentrations.

## 2.7. Radon

[16] Radon 222 (Rn) was monitored on a 2-hour basis by measuring the decrease of the alpha radioactivity of atmospheric aerosols collected on filters. The measurement has precision of 2% and has been described in details by *Polian et al.* [1986].

## 2.8. Chlorophyll a

[17] Satellite-derived chlorophyll a (chl-a) concentrations were obtained from SeaWiFS data, available at the NASA's Goddard Space Flight Center (GSFC)/Distributed Active Archive Centers (DAAC) at the website "Giovanni Ocean Color Time-Series Online Visualization and Analysis" (<http://reason.gsfc.nasa.gov/OPS/Giovanni/ocean.aqua>).



**Figure 2.** Temporal variation of Equivalent Black Carbon (EBC), Organic Carbon (OC), Water soluble Organic Carbon (WSOC), and Methanesulfonate ( $\text{MS}^-$ ) concentrations in bulk aerosols at Amsterdam Island. (Austral summer = December–January–February)

shtml). The chl-a SeaWiFS images ( $9 \text{ km} \times 9 \text{ km}$  resolution) were generated based on the global OC4v4 algorithm.

### 3. Results and Discussion

#### 3.1. Impact of Local Contamination

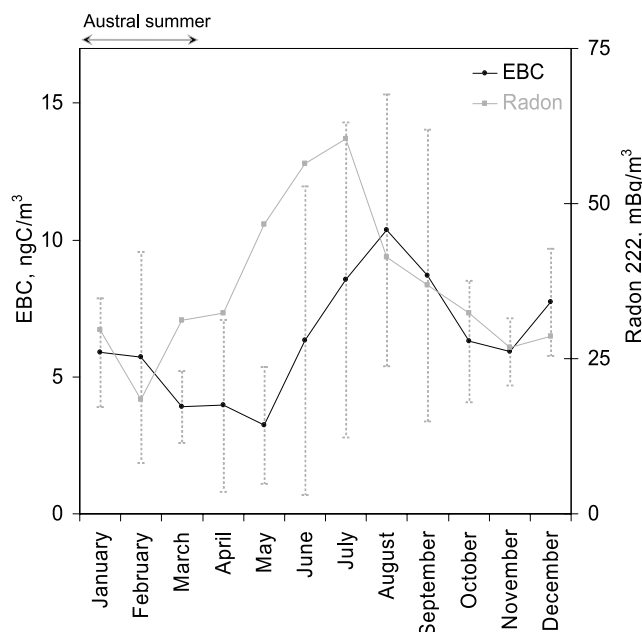
[18] Impact of local pollution from the scientific base (essentially from the power generator) could have punctually contaminated carbonaceous measurements since no wind direction criteria were applied on our filter sampling. However, this local contamination is expected to play a negligible role here, considering the very low levels of EBC ( $5.8 \pm 2.8 \text{ ng C/m}^3$  on a yearly average) and scarcity of wind blowing from the base (few hours per year). This insignificant contribution of local contamination is reinforced by the fact that most of EBC peaks ( $>15 \text{ ng C/m}^3$ ) are

concomitant with radon peaks (data not shown here), pointing out a long-range origin (from the African continent) rather than local pollution for these peaks of EBC. Similarly, impact of local contamination on the OC concentrations is expected to be particularly weak (maximum 10 to  $30 \text{ ng C/m}^3$ ) which is one order of magnitude lower than the summertime OC concentrations.

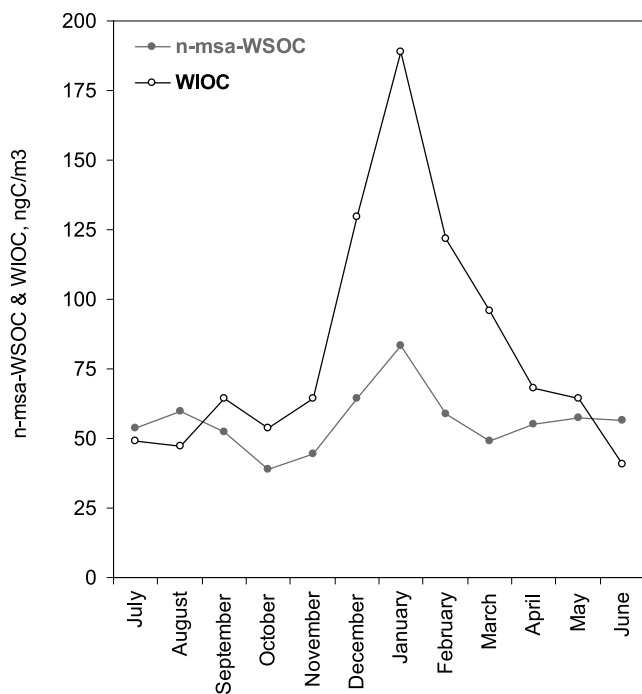
#### 3.2. Seasonal Variations of EBC

[19] Concentrations of the main carbonaceous components (EBC, OC, WSOC, and  $\text{MS}^-$ ) are presented in Figure 2 for the whole investigated period (May 2003–November 2007). By comparison with the other carbonaceous species, EBC concentrations are particularly low, ranging from below the detection limit ( $0.2 \text{ ng C/m}^3$ ) to  $62.3 \text{ ng C/m}^3$  ( $5.8 \pm 2.8 \text{ ng C/m}^3$  on a yearly average) and stand among the lowest concentrations of EBC reported in literature for remote marine atmospheres [Bodhaine, 1995; Wolff and Cachier, 1998]. Comparison with EBC measurements performed at the marine station of Mace Head (Ireland) can be made directly since EBC measurements are performed at this station using a similar aethalometer (model AE8, Magee Scientific) and a similar calibration factor (1.9). Yearly mean EBC concentrations at Mace Head for the clean air masses are on average of  $14.8 \pm 2.1 \text{ ng C/m}^3$  for the period 1989–1995 [Cooke et al., 1997]. This data set is restricted to wind direction corresponding to the open sea sector and EBC levels below  $75 \text{ ng C/m}^3$ . This yearly EBC concentration is almost a factor of three higher compared to our annual mean of  $5.8 \text{ ng C/m}^3$ , obtained without wind direction and/or EBC criteria. This result denotes the very pristine marine conditions prevailing of the Austral Ocean.

[20] Seasonal variations of EBC and Radon are reported in Figure 3 and are calculated for the 4.5-year period when the two measurements were available. Although most of the



**Figure 3.** Seasonal variation of Equivalent Black Carbon (EBC) and Radon at Amsterdam Island.



**Figure 4.** Seasonal variation of the bulk concentrations of non-methanesulfonate water soluble organic carbon (n-ms-WSOC) and water insoluble organic carbon (WIOC).

peaks ( $>15 \text{ ng C/m}^3$ ) of EBC are concomitant with Radon peaks, denoting a long-range transport origin of air masses from Africa and Madagascar, the seasonal maximum of EBC and Radon do not coincide in time; the Radon maxima being observed for June–July whereas the peak of EBC maximum is centered on August. Fossil fuel emitted mainly from South Africa and biomass burning originating from the whole Southern Africa and Madagascar are the major combustion sources that can contribute to the levels of EBC recorded at Amsterdam Island. Insights on the relative contribution of biomass burning on EBC levels recorded at Amsterdam Isl. can be investigated here from hotspots/fire map products obtained using data from the MODIS (Moderate Resolution Imaging Spectroradiometer) instrument and downloaded from the web fire mapper built by the NASA funded Fire Information for Resource Management System (FIRMS, <http://maps.geog.umd.edu/firms/>). A strong seasonal variation was found for these fires with a maximum in August coinciding with the maximum of EBC and thus denoting a major influence of biomass burning aerosols at Amsterdam Island during austral wintertime. This assumption is supported by the concomitant seasonal maxima of EBC, non-sea-salt potassium and oxalate (determined in our QMA filter samples), the latter two compounds being commonly used as tracers for biomass burning. This is also consistent with the contribution of biomass burning to the levels of carbon monoxide at Amsterdam Island as reported by Gros *et al.* [1999]. Note that among the 18 filter samples showing EBC values above  $15 \text{ ng C/m}^3$ , 16 are comprised in the biomass burning season (July–September).

### 3.3. Seasonal Variations of Organic Aerosols

[21] Concentrations of OC reported in Figure 2 exhibit a quite important variability of more than one order of magnitude, with values ranging from 37 to  $530 \text{ ng C/m}^3$ . The major feature of this data set is the high OC levels ( $>200 \text{ ng C/m}^3$ ) systematically observed every austral summer (December, January) when EBC levels are at their lowest. These high OC values do coincide with the period of the year when marine productivity is at its maximum. In that sense, they are consistent with the hypothesis of a biogenic marine source of organics as proposed by O’Dowd *et al.* [2004].

[22] Both OC and methanesulfonate ( $\text{MS}^-$ ) reported in Figure 2 show an increase during summer that can be linked to a similar increase of marine productivity. On the other hand, the high summertime OC values are much more variable than  $\text{MS}^-$  concentrations which exhibit constant high values all along this season. The summer maxima of OC are also much more limited in time and comprise generally no more than 4–5 samples (4–6 weeks) per year. By comparison,  $\text{MS}^-$  maxima are observed for the whole summer season (10–12 consecutive weeks). Winter-to-summer amplitudes are also much more contrasted with values ranging from 2 to 4 for OC against amplitudes of almost a factor of 10 for  $\text{MS}^-$ . As a result, factors controlling the atmospheric concentrations of OC and  $\text{MS}^-$  are likely to differ significantly.

[23] Interestingly, the seasonal pattern found for OC is poorly related in WSOC (Figure 2) which shows rather stable levels for over the 3-year period available in this data set. Consequently, OC maxima observed during summertime should be mainly driven by WIOC. This organic fraction is often referred as poorly oxidized and is usually associated with primary emissions. Primary emissions of biogenic organics are discussed in the following from monthly mean concentrations of WIOC.

### 3.4. Seasonal Variations of WIOC and Non-Methanesulfonate WSOC

[24] The contribution of methanesulfonate ( $\text{MS}^-$ ) as water-soluble organic material should be considered here uppermost. During the summer period, the levels of  $\text{MS}^-$  (expressed in  $\text{ng/m}^3$ ) are particularly high and reach a mean value of the order of  $100 \text{ ng/m}^3$  for the months of January–February. Contribution to water-soluble organic matter (WSOM) ranges from 4 to 70%, when a carbon-to-mass conversion factor of 2.1 is used to convert WSOC into WSOM concentrations [Turpin and Lim, 2001]. In order to properly determine the levels of organic aerosols that are not originated from the oxidation of DMS,  $\text{MS}^-$  concentrations were subtracted from OC and WSOC as non-methanesulfonate organic carbon (nms-OC) and non-methanesulfonate water-soluble organic carbon (nms-WSOC) using the following equations expressed in  $\text{ng C/m}^3$ :

$$[\text{nms-OC}] = [\text{OC}] - [\text{MS}^-] \quad (2)$$

$$[\text{nms-WSOC}] = [\text{WSOC}] - [\text{MS}^-] \quad (3)$$

Note that the calculation of WIOC concentrations is not influenced by  $\text{MS}^-$ .

[25] Monthly mean concentrations of nms-WSOC and WIOC are reported in Table 2 together with EBC and  $MS^-$ . Their seasonal variations are displayed in Figure 4 for the 3-year period when OC and WSOC measurements were available (December 2004–November 2007). Levels of these two fractions are stable and comparable (in the range 40 to 60 ng C/m<sup>3</sup>) for 8 consecutive months (April to November) covering almost three seasons (autumn, winter, spring). During the course of the summer period (December to March) WIOC levels are strongly increasing and show a clear maximum in January with a mean value of the order of 200 ng C/m<sup>3</sup> which is a factor of 4 higher compared to the rest of the year.

[26] These results are consistent with those reported for the North Atlantic by *O'Dowd et al.* [2004], *Cavalli et al.* [2004], and *Yoon et al.* [2007] who have also reported maximum WIOC concentrations during the period of high biogenic marine productivity. Chemical characterization of this WIOC fraction has shown a marine fingerprint [*Decesari et al.*, 2007; *Facchini et al.*, 2008], mechanically produced through bubble bursting processes from hydrophobic organic matter which accumulates in the surface micro-layer of the ocean [*Blanchard*, 1964; *Oppo et al.*, 1999]. Although similar analyses could not be performed on the samples collected at Amsterdam Island, it is reasonable to assume that our WIOC fraction follows a quite similar bubble bursting production mechanism.

[27] By comparison with WIOC, the seasonal pattern of nms-WSOC is much less pronounced but still shows a slight increase during summer. There is no clear sample-to-sample correspondence between the summer peaks of WIOC and nms-WSOC, which suggests different sources for these two different organic fractions. On the other hand the summer peaks of nms-WSOC are concomitant with peaks of  $MS^-$ , which would suggest similar (secondary) production mechanism. Without any other information on this nms-WSOC, it remains difficult to explain this slight increase during summertime. This could comprise the formation of secondary organic aerosols which are commonly found as water-soluble organics [*Arnold et al.*, 2009]. Secondary formation of amines, as recently proposed by *Facchini et al.* [2009], is another possibility that could explain this slight summer maximum. The ageing of primary (water-insoluble) organics and the subsequent formation of more oxidized (more water-soluble) organics cannot be excluded and is consistent with the high photochemical chemistry that occurs in the 35–45° latitudes during summer.

### 3.5. Source Region of WIOC and Links to Chlorophyll a

[28] The oceanic region surrounding Amsterdam Island is poorly productive when compared to the rest of the Austral Ocean. The seasonal variation of chl-a in this area is not very pronounced and shows a weak maximum in November which fails to explain the OC maximum observed in January. Alternatively, these organic aerosols may be transported from upwind oceanic regions characterized by higher levels of chlorophyll a. As reported by *Sciare et al.* [2000] from a 10-year climatology of winds reaching Amsterdam Island, these oceanic regions are mainly located in a southwest upwind sector which corresponds to an oceanic region lying between 40° and 45° South latitude, and 60 to 80° East longitude (Figure 5). This region encompasses a

**Table 2.** Monthly Mean Concentrations of Equivalent Black Carbon (EBC), Water Insoluble Organic Carbon (WIOC), Non-Methanesulfonate Water Soluble Organic Carbon (nms-WSOC), and Methanesulfonate ( $MS^-$ ) in Bulk Aerosols<sup>a</sup>

Month	EBC ng C/m <sup>3</sup>	WIOC ng C/m <sup>3</sup>	nms-WSOC ng C/m <sup>3</sup>	$MS^-$ ng C/m <sup>3</sup>
January	4.8 (±2.4)	189 (±62)	83 (±28)	12.0 (±3.0)
February	5.0 (±4.3)	122 (±53)	59 (±6)	12.0 (±3.3)
March	1.9 (±1.6)	96 (±6)	49 (±9)	6.4 (±1.8)
April	4.7 (±2.1)	68 (±15)	55 (±3)	2.9 (±1.0)
May	2.4 (±0.9)	64 (±32)	58 (±7)	1.1 (±0.3)
June	5.1 (±2.4)	41 (±28)	56 (±2)	0.6 (±0.4)
July	7.1 (±4.2)	49 (±10)	54 (±8)	0.6 (±0.1)
August	8.0 (±4.7)	47 (±17)	60 (±7)	0.6 (±0.3)
September	12.7 (±5.2)	64 (±43)	53 (±2)	1.0 (±0.4)
October	6.6 (±3.3)	54 (±30)	39 (±5)	2.4 (±0.5)
November	4.6 (±3.1)	64 (±27)	44 (±6)	5.1 (±1.0)
December	6.5 (±3.3)	130 (±39)	64 (±7)	9.7 (±1.6)

<sup>a</sup>Values in bracket stand for ±1 standard deviation.

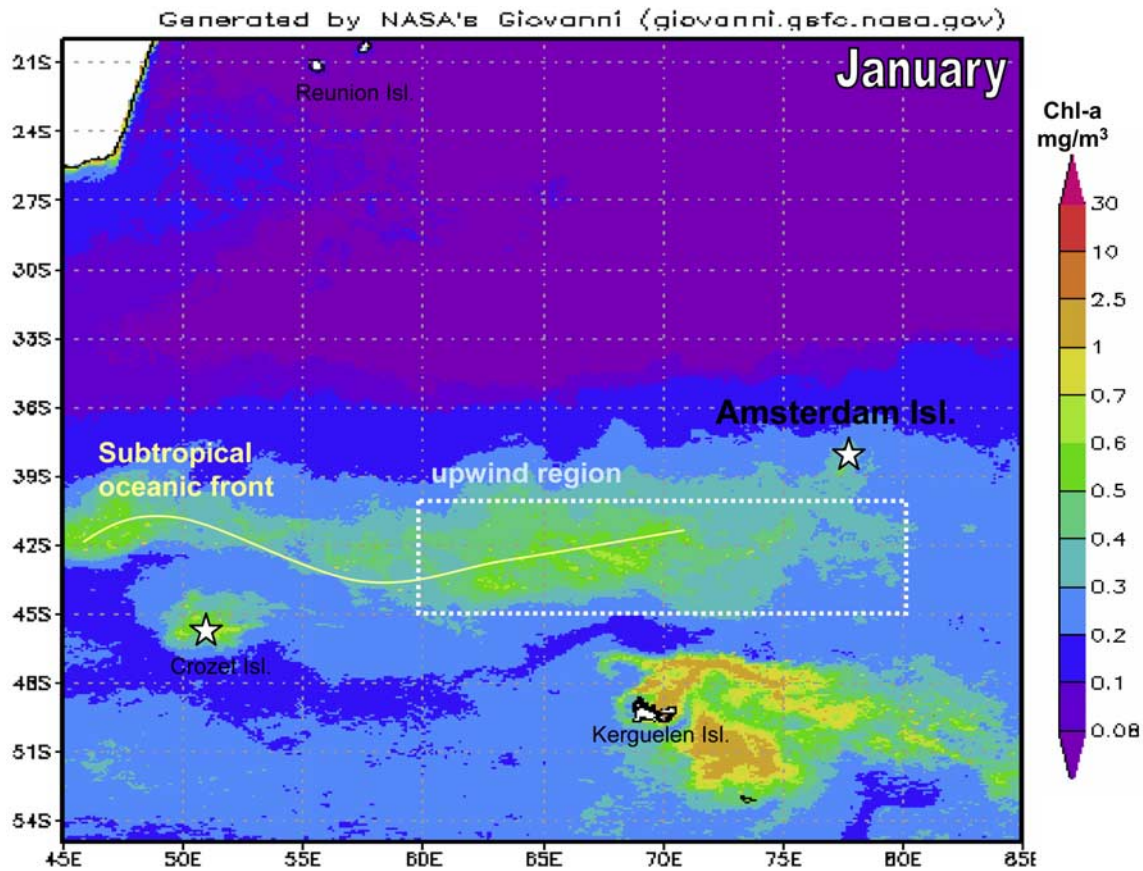
highly productive area covering the subtropical oceanic fronts. Monthly mean chl-a concentrations averaged over this region are compared with monthly mean OC data in Figure 6 for the period May 2003–November 2007 (N = 55) and show quite similar seasonal variations in phase, with a maximum around December–January and sometimes a second maximum (much smaller) in the late summer (March–April) observed in 2003, 2004, 2006, and 2007. A correlation coefficient (*r*) of 0.60 is calculated from these two time series, pointing out a direct link between marine productivity (characterized here by chl-a) and marine organic aerosols.

[29] Consequently, most of the marine organic aerosols sampled at Amsterdam Island are likely to originate from productive regions located at more than 1,000 km upwind the island, corresponding to an atmospheric transit time of the order of 2–3 days. The atmospheric dilution induced by this long-range transport of marine organics sampled at Amsterdam Island may partly explain the different levels observed between this station and Mace Head which exhibits organic levels an order of magnitude higher [*Yoon et al.*, 2007]. Note that high rates of atmospheric DMS may be co-emitted simultaneously with marine organic aerosols since these productive oceanic regions are particularly rich in oceanic DMS precursors [*Sciare et al.*, 1999]. Photochemical ageing that will occur during the transport of these air masses to Amsterdam Island may significantly increase  $MS^-$  and nss-SO<sub>4</sub> concentrations in submicron particles, which in turn may substantially modify the aerosol mixing state. Ageing may also promote other processes such as coagulation and cloud processing that should alter the aerosol mixing state as well as the size distribution. Although such processes may certainly modify the microphysical properties of marine organics, no physical measurements were available here to further support the influence of ageing on marine organics and their contribution to CCN.

## 4. Conclusions

[30] Long-term measurements of carbonaceous aerosols are reported here for the first time at a remote location of the



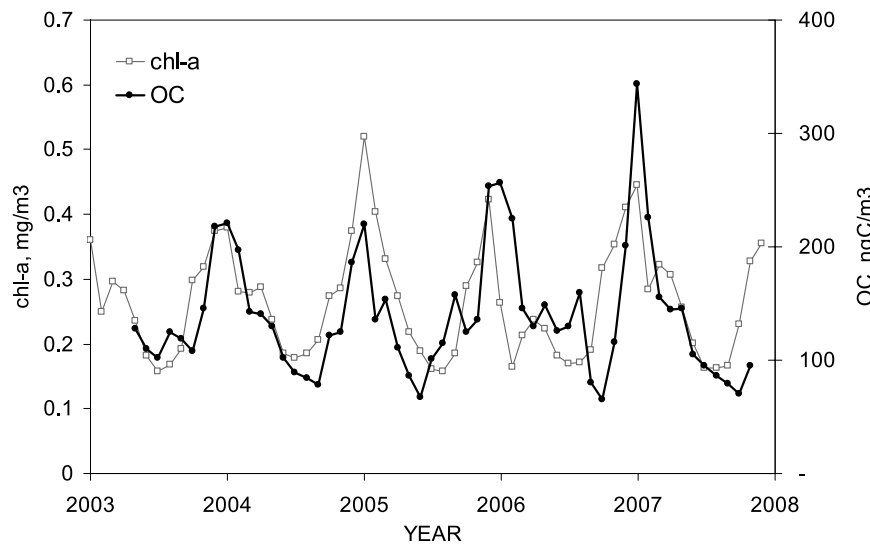


**Figure 5.** SEAWIFS chlorophyll a map (for the month of January) for the Indian Sector of the Austral Ocean. Dashed white rectangle stands for the oceanic region upwind of Amsterdam Island where chl-a have been averaged.

Austral Ocean (Amsterdam Island, southern Indian Ocean). Atmospheric concentrations of equivalent black carbon (EBC) have shown to be among the lowest reported in literature for the marine troposphere ( $5.8 \pm 2.8 \text{ ng C/m}^3$  on a yearly average). Maximum of EBC observed in winter

and originated from long-range transport (3000–5000 km) of biomass burning aerosols from Southern Africa and Madagascar.

[31] These pristine conditions, associated with negligible local contamination, have offered us a unique opportunity



**Figure 6.** Monthly mean concentrations of bulk OC concentrations and chl-a for the period May 2003–November 2007.

to investigate marine organic seasonal variations from long-term and continuous observations. A clear seasonal cycle was observed in OC with high levels observed during the period of high marine productivity (December/January). Most of the high summer values are related with the water-insoluble fraction of organic aerosols, denoting a major primary origin for these marine organic aerosols (most probably from bubble bursting). These results in the Austral Ocean are in line with the observations of marine organic aerosol reported for the Northern Atlantic Ocean. They further support the potential impact of organic aerosol as CCN in the global marine environment.

[32] Comparison between OC and chl-*a* concentrations have shown that the marine organic aerosol source is affecting Amsterdam Island via long-range transport of organic aerosol from a very productive oceanic area located around 40°S, in a region of well-marked oceanic fronts. Atmospheric dilution induced by this long-range transport of marine organics may partly explain the one-order-of-magnitude difference between the concentrations of marine organics at Amsterdam Island and at Mace Head (North Atlantic). Intense photochemical ageing during the atmospheric transport may have altered the size spectra and chemical properties of organics, and subsequently the contribution of organics to CCN.

[33] More detailed size-resolved information on marine organic aerosols in the remote atmosphere of the southern Ocean remains needed to further conclude on the contribution of organics to CCN. Atmospheric fate of these marine organic aerosols needs also to be also better evaluated as it may significantly modify their ability to produce CCN.

[34] **Acknowledgments.** This work is a contribution to the AERO-TRACE observatory program (funded by the French Polar Institute, IPEV) and to the E.U. funded program OOMPH. All the VCAT who have contributed to the sampling at Amsterdam Island are gratefully thanked here.

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