# Atmospheric Water Soluble Organic Nitrogen (WSON) over marine environments: A global perspective

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## Abstract

To obtain a comprehensive picture on the spatial distribution of water soluble organic nitrogen (WSON) in marine aerosols, samples were collected during research cruises in the tropical and south Atlantic Ocean and also over the southern Indian Ocean (Amsterdam island) for one year period (2005). Samples have been analyzed for both organic and inorganic forms of nitrogen and the factors controlling their levels have been examined. Fine mode WSON was found to play a significant role in the remote marine atmosphere with enhanced biogenic activity, with concentrations of WSON (11.3±3.3 nmol N $m^{-3}$) accounting for about 84% of the total dissolved nitrogen (TDN). Such concentrations are similar to those observed in the polluted marine atmosphere of the eastern Mediterranean (11.6±14.0 nmol N $m^{-3}$). Anthropogenic activities were found to be an important source of atmospheric WSON as evidenced by the ten times higher levels in the northern hemisphere (NH) than in the remote southern hemisphere (SH). Furthermore, the higher contribution of WSON to TDN (40%) in the SH, compared to the NH (20%), underlines the important role of organic

nitrogen in remote marine areas. Finally, there was a strong association of WSON with dust in coarse mode aerosols in the NH.

## 1. Introduction

The ocean/atmosphere biogeochemical interactions are important in regulating atmospheric composition, marine ecosystem functioning and the Earth's climate. Oceans area major natural source of marine atmospheric particles (Bigg et al., 2003), with levels that depend on the meteorology, the seasonality and the marine biodiversity of aquatic ecosystems (Bigg et al., 2003; Gantt & Meskhidze, 2013). Marine aerosols consist of salts, organic matter and living organisms originating mainly from plankton, bacteria or other microorganisms (Monahan et al., 1983), while their organic fraction depends strongly on the biological activity of the ocean (O’ Dowd et al., 2004).

Primary emissions of marine aerosols from the oceans to the atmosphere occur by bubble-bursting and wave breaking production mechanisms and are estimated to be 5900 Tg $y^{-1}$ on a global scale (Bigg et al., 2003). It has been postulated that secondary aerosol formation from organic precursors emitted from the ocean such as isoprene and monoterpenes (Yassaa et al., 2008; Arnold et al., 2008), dimethylsulphide (Charlson et al., 1987) and aliphatic amines (Facchini et al., 2008) can significantly influence the cloud condensation nuclei (CCN) abundance and thereby the cloud albedo in the marine atmosphere (Meskhidze & Nenes, 2006).

The amount and type of organic material in seawater varies with location and time with a large fraction remains uncharacterized. However, an important fraction (1-3%) of dissolved organic matter (DOM) in the surface waters comprises N-containing organic compounds (Benner, 2002). These compounds could be a potential primary source of atmospheric organic nitrogen, since peptides and free amino acids have been detected in the marine atmosphere (Kuznetsova et al., 2005; Wedyan et al., 2008). N-containing compounds in reduced forms such as methylamines or in oxidized forms such as organonitrates, have been proposed to contribute to the organic matter of marine aerosols (Facchini et al., 2008; Galloway et al., 2009). During phytoplankton blooms, when biological activity is at its maximum, the organic fraction dominates in the marine aerosols mass, contributing up to 63% of the submicron aerosol mass (O'Dowd et al., 2004).

The chemical composition of organic nitrogen in the atmosphere is complex, reflecting a wide range of direct sources, both biogenic and anthropogenic, and biological/photochemical transformations during transport. It is difficult to quantify, whatever its form (gas, particle or solution), because of its chemical and biological complexities, and no studies have yet achieved a full description of its chemical composition (Cape et al., 2011 and references therein). However, Altieri et al., (2012) found in marine rainwater 2281 N-containing elemental formulas; with the compound class containing carbon, hydrogen, oxygen and nitrogen (CHON+) had the largest number of formulas in the marine rainwater, as it did also in continental rainwater samples.

The importance of WSON in marine biogeochemical cycles and its critical role in the atmosphere has been established. However, the origin and chemical composition of WSON in marine aerosols are largely uncertain (Kanakidou et al., 2012). The observations in marine regions are particularly scarce and limit the robust evaluation of marine organic nitrogen compared to that over continental areas. The present study provides new data for WSON, acquired during oceanographic cruises in the Atlantic Ocean as well as long-term sampling in the Indian Ocean, contributing to the global picture of WSON distribution. In the collected samples both organic and inorganic forms of nitrogen have been analyzed and the factors controlling their levels have been examined.

## 2. Sample collection and chemical analysis

### *2.1. Sampling sites and collection*

### *2.1.1 Tropical North Atlantic Ocean*

Within the framework of OOMPH project (Organics over the Ocean Modifying Particles in both Hemispheres; www.atmosphere.mpg.de/enid/oomph), samples have been collected during a cruise with the German research vessel *METEOR* which took place in the tropical North Atlantic ocean in summer 2006 (16 July - 4 August). The research cruise track, presented in Fig. 1, is characterized by frequent approaches to the African coast. During this cruise aerosol sampling was carried out with a 3-stage High-Volume Sierra type cascade impactor (Baker et al., 2007), which was operated at a flow rate of 1 $m^3$/min. The sampler had two impaction stages (P3 and P4 with cut-off diameters of 2.0 and 1.3 μm, respectively) and one back-up filter stage. During this study fine particles were defined as the sum of P4 and the backup filter while P3 stage was considered to collect the coarse one. A total of 21 daily high-volume aerosol samples were collected on Quartz Filters, pre-combusted at $450^0$C for 5h. Samples were stored at the ship in the freezer (-20°C) till the laboratory analysis. In the lab quartz filters were extracted with 20 mL Milli-Q water for 45 min in ultrasonic bath. Prior to analysis, the extracts were filtered through polyethersulfone membrane (PES) filters (0.45 μm pore size diameter) to remove suspended particles. $CHCl_3$ was added as biocide and then the extracts were preserved at $-18^0$C. All analyses have been performed within a month after collection.

### *2.1.2 South Atlantic ocean*

Ship-borne measurements of aerosols and trace gases were also made in the Southern Atlantic Ocean as part of the same project (OOMPH). The cruise took place with the French research vessel *Marion Dufresne* during the late Southern Hemisphere summer from Cape Town (South Africa) on 19th January to Punta Arenas (Chile) till 5th February 2007 (Fig. 1). Possible local/regional contaminations (ship/continents) were monitored by the black carbon (BC) concentrations measured by an aethalometer.

Aerosol samples were collected by a low volume aerosol sampler placed on the prow of the research vessel. The sampler consisted of two annular glass denuders in a row, connected by a Teflon filter holder. Both denuder tubes had an overall length of 24.2 cm, 2.2 cm inner cylinder diameter, and 0.1 cm annulus thickness. Details on the collection efficiency of the denuder are given by Lawrence and Koutrakis (1994).The first denuder was coated with $Na_2CO_3$solution, absorbing acidic trace gases such as $HNO_3$ and $SO_2$ and the second one with citric acid solution, absorbing $NH_3$.

Before use, denuders were filled with 10 ml of the coating solution, then dried using purified air and capped with Teflon fittings.

During this cruise only fine particles were collected ($PM_{2.5}$) on Teflon filters (n=23) on a 12h-basis from 21th January to 5th February 2007. Samples were stored at the ship in the refrigerator ($4^0$C) till the laboratory analysis. At the lab the aerosol samples were extracted with 15 ml of Milli-Q water for 45 min in ultrasonic bath and processed as the samples collected at the tropical Atlantic Ocean.

### *2.1.3 Amsterdam Island (Indian Ocean)*

Amsterdam is a small island in the southern Indian Ocean (37◦48 S, 77◦34 E) located at 3400 km SE of Madagascar and 5000 km from the coast of South Africa. Most of the year, the island experiences pristine marine conditions, especially during summer when meteorological high pressure conditions accompanied by low wind speeds prevail. For the last twenty years atmospheric monitoring activities have been performed at this island as part of the World Meteorological Organization-Global Atmospheric Watch (WMO-GAW) network (Miller et al., 1993, Sciare et al., 2009).

Aerosol concentrations approaching pristine conditions are mostly found over the oceans, especially in the Southern Hemisphere, where large expanses of open ocean and a low density of population and industry contribute to keeping the human impact at minimum. The natural aerosol over these remote ocean regions consists mainly of a mixture of sea salt particles, organics, and sulfates from the oxidation of biogenic dimethylsulfide; some mineral dust and smoke from wildfires may also be present (Andrae et al., 2007).

The pristine oceanic conditions prevailing at Amsterdam Island and the very low level of local contamination from the scientific base have been documented for many atmospheric compounds such as CO, hydrocarbons, radon, black carbon and total aerosol number concentration (Williams et al., 2001, Sciare et al., 2009).

Most atmospheric measurements were performed at 30 m above the sea level and 2 km upwind of the scientific base. The aerosol samples were collected by a three stage cascade impactor

(Dekati $PM_{10}$) with cut off diameters at 10, 2.5 and 1 µm and operating at a flow rate of 30 L $min^{-1}$. The sampler was located on the north side of the island at about 150m above sea level. A total of 42 samples were collected on teflon filters from 29 January 2005 to 22 December 2005, with one week average sampling time. In parallel, bulk aerosols samples were collected on pre-fired 47-mm diameter Whatman QMA quartz filters for BC analysis according to the analytical protocol described in Sciare et al., (2009).

The samples were stored in the freezer and transported frozen from Amsterdam Island to the laboratory for analysis. Filter samples were extracted overnight by soft shaking of the filter portion placed in borosilicate Erlenmeyer flasks with 15ml of ultra pure water. Prior to analysis, the extract solution was filtered through Teflon (PTFE) filters (0.2µm pore size diameter) to remove suspended particles.

To assess possible continental influence, 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).

### *2.2. Chemical analysis*

*Anions/Cations and Inorganic Nitrogen (IN):* A Dionex AS4A-SC column with ASRS-I suppressor in auto-suppression mode of operation was used for the analysis of anions ($Cl^-$, $Br^-$, $NO_3^-$, $SO_4^{2-}$, $C_2O_4^{2-}$). Cations ($Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$) were analyzed by using a CS12-SC column with a CSRS-I suppressor. The reproducibility of the measurements was better than 2% and the detection limit was 1 ppbv for the main anions and cations (1 ppbv corresponds to 0.37 ng $m^{-3}$ for a mean air volume of 40 $m^3$). Mean blank values were 5–10 ppbv for $Na^+$, $Ca^{2+}$ and lower than 3 ppbv for the rest of ionic species. Details on the chromatographic conditions are reported in Bardouki et al. (2003). Analysis of the aerosol filters, collected at Amsterdam Islands was performed at LSCE (Laboratoire des Sciences du Climat et de l'Environnement) by ion chromatography to determine selected anions (methanesulfonate, oxalate, chloride, sulfate, nitrate, and phosphate) and cations (sodium, ammonium, potassium, magnesium, and calcium). The method is detailed in Sciare et al. (2009).

Non sea salts Calcium and Sulfate (nss-$Ca^{2+}$and nss-$SO_4^{2-}$) for tropical North Atlantic data are estimated based on the following equations:

nss-$Ca^{2+}$= $[Ca^{2+}]$ - 0.3184*$[Mg^{2+}]$

nss-$SO_4^{2-}$= $[SO_4^{2-}]_{total}$ - ss-$SO_4^{2-}$

ss-$SO_4^{2-}$= 2.0958*$[Mg^{2+}]$

*Total Dissolved Nitrogen (TDN):* Determination of TDN is performed using the Persulfate Oxidation Method (PO). As such, all nitrogenous compounds are oxidized to $NO_3^-$ under alkaline conditions at $100^0$-$110^0$C. The produced $NO_3^-$ ions are then reduced by a Cu-Cd column to nitrite ($NO_2^-$) and subsequently diazotized with sulphanilamide and N-(1-naphthyl)-ethylenediamine forming a high colored azo dye. The intensity of the produced color is measured by a spectrophotometer at 543nm (Standard Methods for the Examination Water and Wastewater, 1998). The detection limit of this method is 24ppb N, while during this study the blanks were always below detection limit (Violaki et al., 2010a).

*WSON:* Water-soluble Organic Nitrogen (WSON) was determined by subtracting Inorganic Nitrogen ($NO_3^-$and $NH_4^+$) from the Total Dissolved Nitrogen (TDN). The determination of WSON concentrations by difference leads in some cases to negative concentrations, as discussed by Mace and Duce (2002) and Cornell et al. (2003). Discarding these values would have biased the statistical analysis towards the samples with higher DON concentrations and for the average and median estimations we set them as zero in agreement with previous works (e.g. Mace et al., 2003a; Violaki et al., 2010b).

*DMS:* For the samples collected in the southern Atlantic ocean, Dimethyl sulfide (DMS) was used as tracer of biological activity. Stainless steel canisters filled with inert gas were first evacuated to less than 1 mbar pressure using a stand-alone turbo pump. Evacuated canisters were then closed and attached to a pump and sampling line that was previously flushed with gas for more than 5 min.

Canisters were then opened to the sample air, pressurized and emptied at least 5 times prior to final closure and storage. Four canisters were collected per day and analyzed for dimethyl sulfide (DMS) using GC/MS (Lee et al., 1980).

### *2.3 Air Mass Back trajectory Analysis*

10-day backward air mass trajectories were calculated with the LAGRangian ANalysis TOol (LAGRANTO) (Wernli and Davies, 1997; Stohl et al. 2005). Every 3 hours about 10 air mass back trajectories were started within a ± 30-minutes time-range at the exact ship position. For these calculations, three-dimensional wind fields from the European Centre for Medium-Range Weather Forecasts (ECMWF) were used. The 6 hourly operational global analyses (T799L91) were complemented by intermediate 3-h forecasts interpolated onto a horizontal grid with a resolution of 1° latitude/ longitude. The resolution of the LAGRANTO model was 25 Km in the horizontal, 91 levels in the vertical, the computational time step for trajectory calculations was 30 minutes.

## 3. Results and Discussion

### *3.1. Tropical Atlantic Atmosphere*

During the cruise in the tropical Atlantic Ocean the observed WSON average concentration in coarse atmospheric particles (Da>2 μm, n=18), was 6.3±3.8 nmol N $m^{-3}$ (median 6.2 nmol N $m^{-3}$ in agreement with the findings by Lesworth et al. (2010), who reported similar WSON concentrations (6.1 nmol N $m^{-3}$) for coarse mode WSON (Da>1 μm) in air masses originating from the Sahara desert. Predominance of $NO_3^-$ was observed in the coarse mode, with average concentration of 36.1±11.6 nmol N $m^{-3}$ (median 38.0 nmol N $m^{-3}$), while coarse mode average concentration of $NH_4^+$ was 1.3±0.6 nmol N $m^{-3}$ (median 1.1 nmol N $m^{-3}$). The temporal variation of N aerosols components concentration is presented in Fig. 2. The average percentage contribution of coarse mode nitrogen species to the TDN pool was 14%, 82% and 4% for WSON, $NO_3^-$ and $NH_4^+$, respectively.

Almost 86% of WSON was found in the coarse mode atmospheric particles. Mace et al., (2003) presented the hypothesis that dust WSON might actually come mostly from adsorbed pollution and this hypothesis has since been supported by subsequent studies (e.g., Violaki et al., 2010b, Zamora et al., 2011; Wang et al., 2013). No correlation was found between WSON and inorganic nitrogen ($NO_3^-$ and $NH_4^+$), indicating different sources. A significant correlation between WSON and nss-$Ca^{2+}$ ($r^2$=0.5, $p<0.005$, n=18) confirms the continental transport of organic nitrogen by dust. WSON correlates also with nss-$SO_4^{2-}$ ($r^2$=0.6, $p<0.0005$, n=16), indicating significant anthropogenic contribution to the WSON pool. The highest concentrations of nss-$Ca^{2+}$, nss-$SO_4^{2-}$ and WSON were observed on the same day (19th July, Fig. 2). During that day a strong dust event took place while the ship was near the coast, resulting in air masses in which dust and anthropogenic emissions from Western Europe were mixed (Fig. 3a).

The fine mode (Da<2 μm, n=18) average concentration of WSON was found to be 0.9±1.0 nmol N $m^{-3}$ (median 0.6 nmol N $m^{-3}$), while the average concentrations of $NH_4^+$ and $NO_3^-$ ions were 28.0±21.6 nmol N $m^{-3}$ (median 22.9 nmol N $m^{-3}$) and 4.7±1.8 nmol N $m^{-3}$ (median 4.5 nmol N $m^{-3}$), respectively. The temporal variation of nitrogen species is presented in Fig. 4. The average percentage contributions to the TDN pool were estimated to be 5%, 19% and 76% for WSON, $NO_3^-$ and $NH_4^+$, respectively. No statistical significant correlations were found between fine mode WSON and continental traces such as nss-$Ca^{2+}$ and nss-$SO_4^{2-}$. The highest concentration of WSON was observed on 3 August (Fig. 4), when the air mass back trajectory indicate marine origin although based on nss-$Ca^{2+}$ levels, influence from continental sources (dust) cannot be totally ruled out (Fig. 3b).

### 3.2. Southern Atlantic Atmosphere

The cruise was performed in the temperate waters of the Atlantic Ocean during the early austral summer, when biogenic marine activity was at maximum (Meskhidze and Nenes, 2006). Two main episodes of phytoplankton blooms were encountered during the sampling period. These are clearly seen in Fig. 5, which depicts the chlorophyll-a map derived from SeaWiFS satellite retrievals (http://disc.sci.gsfc.nasa.gov/giovanni) and referred to monthly average values (January 2007). The episode-A encountered by the ship over two days (30-31January) and the episode-B began on 1st February and was followed until the end of the cruise. The average concentration of WSON during the whole sampling period was estimated at 8.5±11.7 nmol N $m^{-3}$ with negligible contribution from of $NO_3^-$ (0.2±0.5 nmol N $m^{-3}$; n=23), while the $NH_4^+$ average concentration was estimated at 1.6±1.2 nmol N $m^{-3}$.

The highest WSON values were reported in the beginning and at the end of the cruise (Fig. 6), when the ship was near the African and the Argentinean coasts, respectively, but also when the ship crossed the second phytoplankton bloom area (episode-B). Air-mass back trajectories analysis indicates significant continental influence on samples collected in the beginning of episode-B, which is confirmed further by the high concentration of BC (116.9 ng C $m^{-3}$). Thus these samples are expected to result from mixing of continental and marine sources.

The phytoplanktonic activity as possible source of atmospheric organic nitrogenous compounds was based on DMS, since the last could be considered as an indicator of marine phytoplanktonic activity (Sciare et al., 1999). When the ship crossed the episode-A area (Fig. 6), air masses had marine origin with lower BC levels (11.1±15.7 ng/$m^3$) comparing with the average concentration observed during the sampling period (27.2±15.7 ng/$m^3$) and the measured WSON average concentration was 11.3±3.3 nmol N $m^{-3}$. These samples presented high average contribution of WSON to TDN (84 %), which could indicate an important role of the marine biological activity in the biogeochemical cycle of organic nitrogen (Facchini et al., 2008). For the samples collected over the middle southern Atlantic atmosphere (26-29 Jan, n=4), which is considered as remote marine area, with low biogenic activity, the average concentration of WSON was much lower (1.1±1.2 nmol N $m^{-3}$) corresponding to 43% of TDN. The important contribution of material issued from oceanic biological activity to the total ON aerosols in the marine environment has been also underlined by Miyazaki et al. (2011). During that study two times higher average bulk ON concentrations in aerosols were measured in an oceanic region with higher biological productivity than in regions with lower productivity over the western North Pacific.

### *3.3. Indian Ocean (Amsterdam Island)*

Amsterdam Island, located in the middle of the southern Indian Ocean, is considered as a typical southern hemisphere marine background site, being far from major anthropogenic sources (Sciare et al., 2009). The average concentrations of WSON in coarse ($PM_{2.5-10}$) and fine ($PM_{2.5}$) particles were found to be 0.2±0.4 nmol N $m^{-3}$ and 0.8±1.4 nmol N $m^{-3}$ with percentage contributions to TDN of 35% and 32% respectively. These values are in good agreement with the values reported for bulk aerosols at the remote marine site of Cape Grim (average value 0.9 nmol N $m^{-3}$, n=2; Mace et al., 2003b) and slightly higher compared to the values reported at Barbados (0.5±0.3 nmol N $m^{-3}$ , Zamora et al., 2011).

Concerning the inorganic nitrogen species, $NH_4^+$ was mainly found in fine mode with average concentration of 1.3±1.0 nmol N $m^{-3}$ and 0.3±0.1 nmol N $m^{-3}$ for fine and coarse mode, respectively with percentage contributions to TDN of 53% and 39%, respectively. The average concentration of $NO_3^-$ was found to be 0.3±0.2 nmol N $m^{-3}$ and 0.2±0.1 nmol N $m^{-3}$ for fine and coarse mode respectively, while the percentage contributions to TDN were 14% and 26%, respectively.

The levels of WSON, especially in fine particles (Fig. 8) have shown distinct seasonal variation with the maximum values in both modes observed during austral summer. During that season (January-March), as also confirmed by the $^{222}Rn$ levels, the air masses were not significantly affected by long range transportation. In Fig. 9 is depicted the percentage contribution of WSON in fine and coarse mode together with bulk methanesulfonate ($MS^-$) and BC average monthly concentrations. During austral summer increased concentrations of $MS^-$ were observed that can be linked to a similar increase of marine productivity (Sciare et al., 2009). The closest DMS source is most probably located at 1000-2000 Km south west of Amsterdam Island (Sciare et al., 2009) as indicated by the high Chl-a levels seen by satellite at this location (Fig. 10).

The fine mode WSON was found to correlate significantly with fine mode $MS^-$ ($r^2=0.7$, $p<0.05$, $n=7$) during austral summer, implying that part of WSON might have been produced secondarily from biogenic marine precursors. Significant correlation was also found between coarse mode $MS^-$ and coarse mode WSON ($r^2=0.9$, $p<0.0001$, $n=10$) during summer period, which could be explained by adsorption of $MS^-$ produced from DMS on marine salts.

As reported by Sciare et al. (2009) the meteorological regime at Amsterdam Island supports the long range transport of air masses from Southern Africa and Madagascar during winter, affecting the atmospheric composition of the area, especially with emissions from combustion processes (fossil fuel and mainly biomass burning). The simultaneous increase of average monthly concentrations of BC and Radon during austral winter (Fig. 9), starting from May and maximizing in July and August (Fig. 8) confirmed the continental influence from Africa. During that season the intense biomass burning episodes occurred in Africa releasing fine mode aerosols including WSON, which were subsequently transported to the marine atmosphere of Amsterdam Island (Sciare et al. 2009).

## 4. Comparison between different samplings sites and concluding remarks

This study investigates the concentrations of atmospheric WSON in the marine environment under different influences. A ship cruise was carried out in the tropical Atlantic during which a relatively polluted marine atmosphere was affected by strong dust outbreaks from the Sahara desert. The cruise in the southern hemisphere was planned to coincide with the large-scale summer phytoplankton bloom, in order to investigate the role of marine biological activity in the sources of WSON compounds. Size-segregated aerosol sampling at Amsterdam Island in the Indian Ocean enabled the quantification of the WSON levels in a pristine marine atmosphere.

Table 1 summarizes the average concentration of WSON and its percentage contribution to the TDN pool separating fine from coarse atmospheric particles in both hemispheres. Note the different sample substrate and the different cut-offs used in the data presented at Table 1, which could have an impact on the comparison between the various sites. Coarse mode WSON in the northern hemisphere (NH) was strongly associated with Saharan dust. This is confirmed by comparing the levels of coarse mode WSON observed in East Mediterranean and Tropic Atlantic Ocean, both strongly influenced by Sahara dust and notably with same percentage contribution of WSON to TDN. Dust is considered as an excellent adsorptive surface not only for nitrogenous compounds but also for living biological organisms (Mathias-Maser et al., 1999; Prospero et al., 2004).

The concentrations of fine mode WSON in the NH show large divergence with more than ten times higher levels in the eastern Mediterranean (Violaki and Mihalopoulos, 2010b) than in the tropical Atlantic Ocean. The atmospheric marine boundary layer of the eastern Mediterranean is influenced by air masses originating from eastern Europe, in particular Turkey, Ukraine and Russia (Mihalopoulos et al., 1997, Lelieveld et al., 2002), which could enrich the atmosphere with WSON from anthropogenic activities. The important contribution of anthropogenic sources to the levels of WSON in the NH is revealed by the more than ten times higher concentration of WSON comparing with the pristine marine areas of southern hemisphere (middle southern Atlantic & Amsterdam island). Nevertheless, the higher percentages of fine mode WSON to TDN in both marine areas could indicate the substantial role of WSON in biogeochemical cycle of nitrogen in such pristine marine environments.

Particularly interesting are the increased levels of fine mode WSON over the pristine marine atmosphere when intense biogenic activity occurs (bloom area of the southern Atlantic). Indeed under such conditions the observed levels of WSON (11.3±3.3 nmol N $m^{-3}$) along with high percentage contribution (84%) to TDN were almost identical to that measured over the eastern Mediterranean (11.6±14.0 nmol N $m^{-3}$) pinpointing towards an important role of marine productivity as a source of WSON in pristine marine regions with significant biogenic activity.

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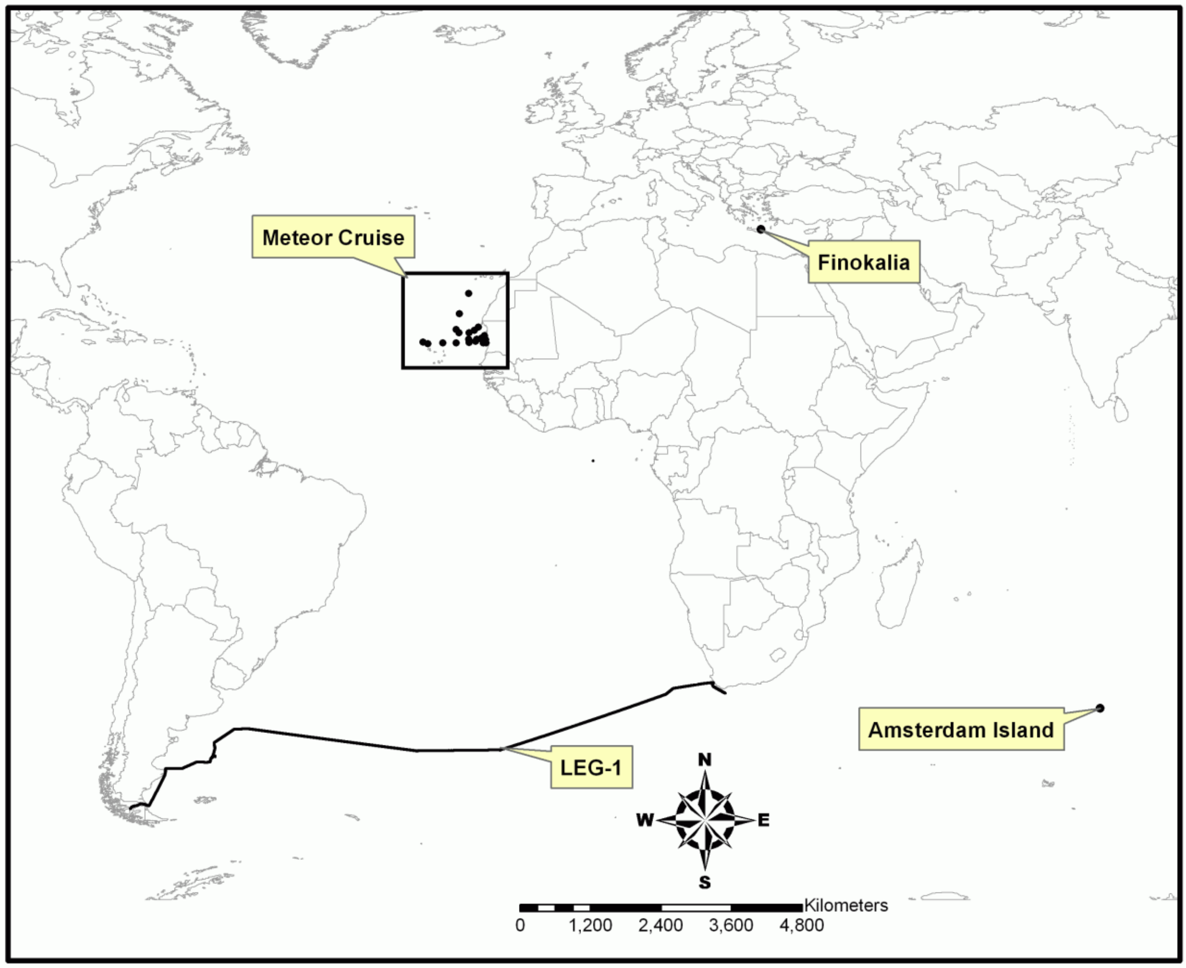

**Fig. 1:** Sampling sites around the world during this study. Finokalia station is used for comparison purposes.

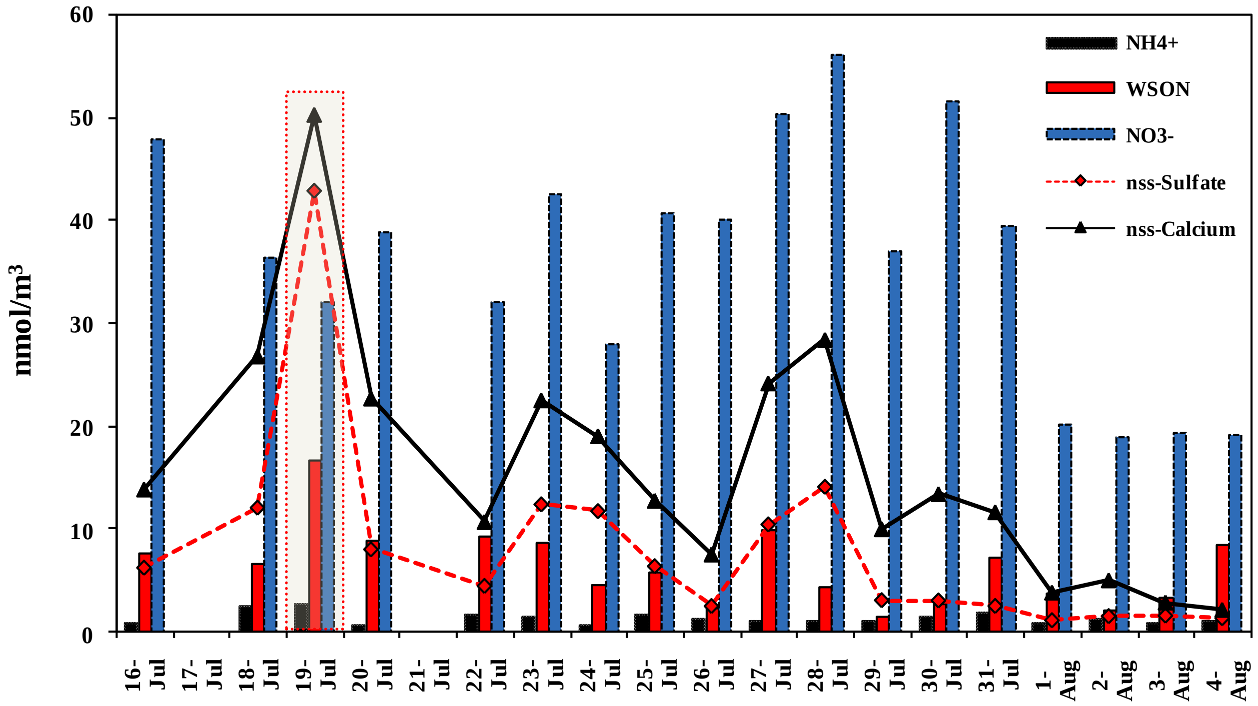

**Fig. 2:** Temporal variation of nitrogen species, nss-SO$_4^{2-}$ and nss-Ca$^{2+}$concentration in coarse particles (Da>2 µm)over the tropical North Atlantic atmosphere. The frame defines the air mass back trajectory with dust mixed with anthropogenic emission (19th July 2006).

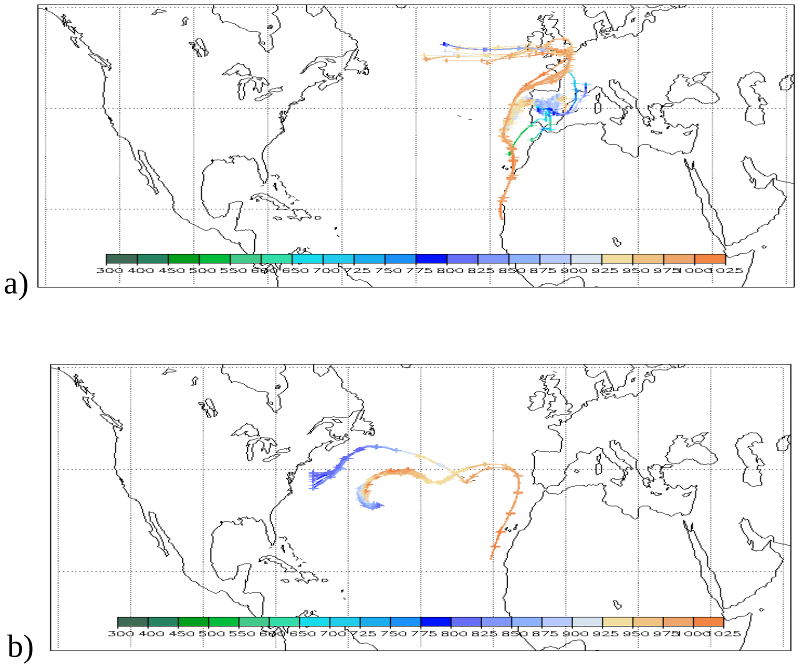

**Fig. 3:** Five day air mass back trajectories 19th July 2006 (a) and 3th August 2006 (b). The color indicates the pressure level (hPa).

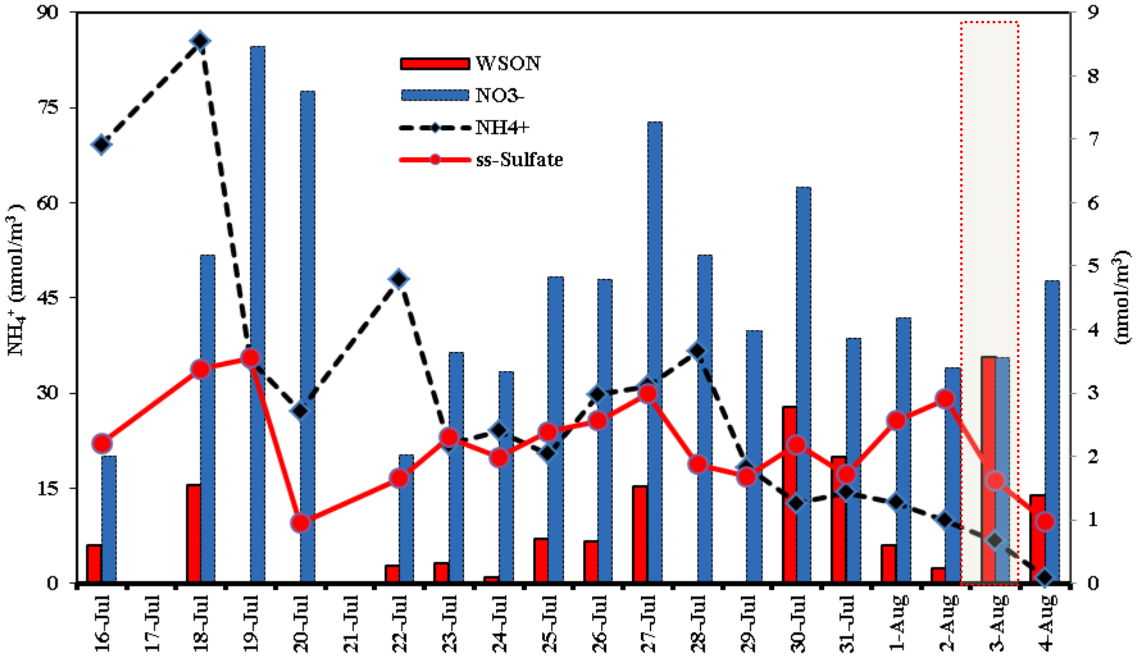

**Fig. 4:** Temporal variation of nitrogen species &ss-SO$_4^{2-}$, concentration in fine particles (Da<2 µm) over the tropical North Atlantic atmosphere. The frame defines the air mass back trajectory with pristine marine origin (3th August 2006).

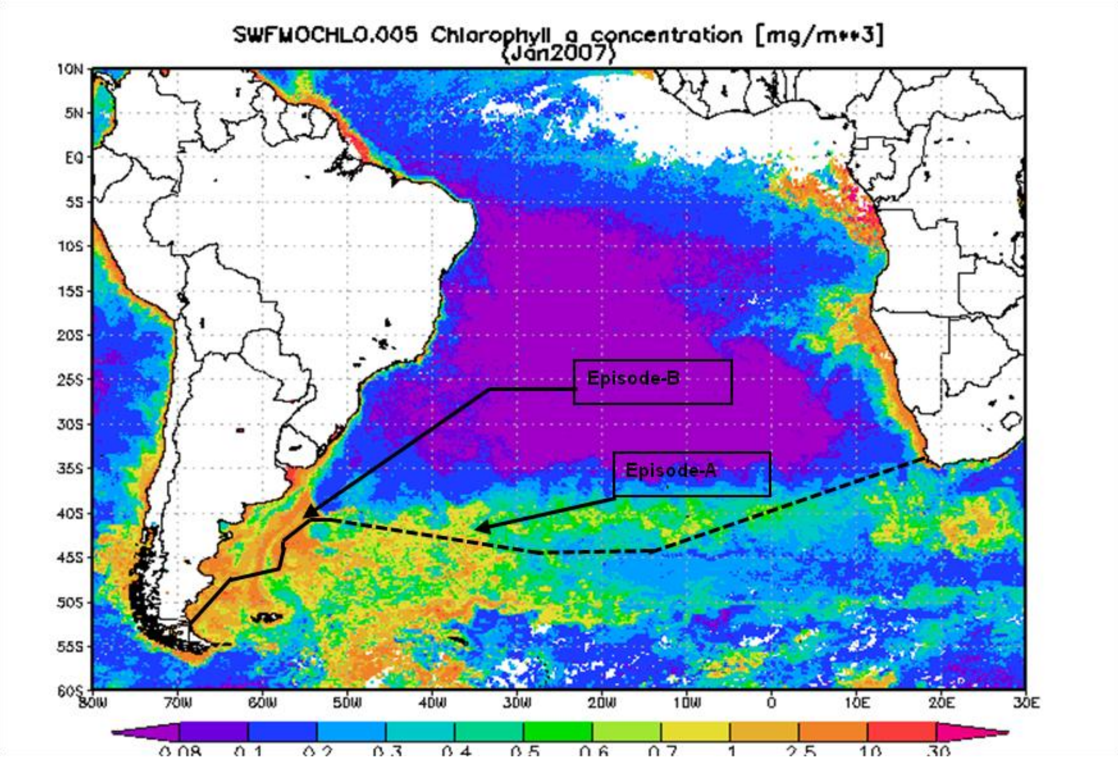

**Fig. 5:** Two distinct phytoplankton bloom episodes are presented in SeaWiFS chlorophyll-a map at South Atlantic Ocean during January 2007 along with cruise track (http://disc.sci.gsfc.nasa.gov/giovanni).

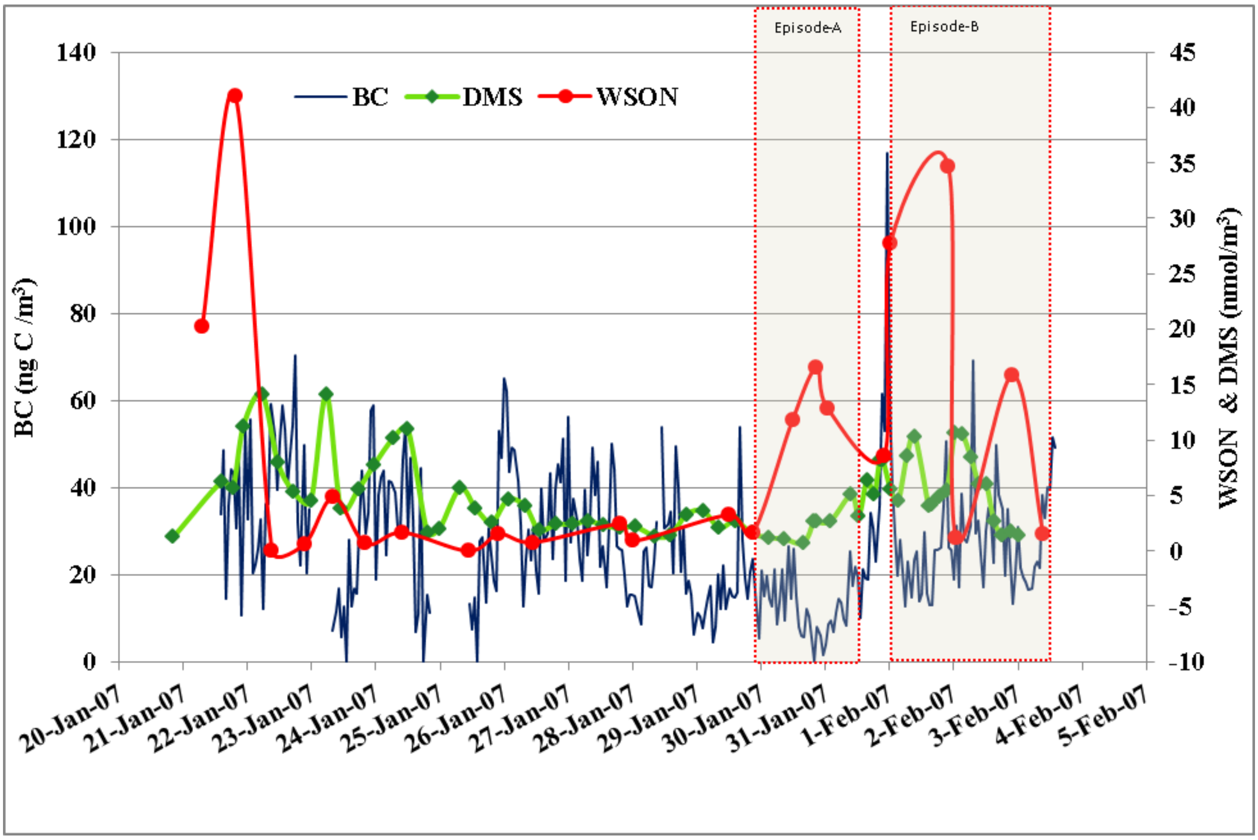

**Fig. 6:** Temporal variation of WSON and DMS concentration in fine particles ($PM_{2.5}$) together with BC concentration during the cruise in South Atlantic atmosphere. The frames define the marine areas with intense biogenic activity (Episode-A and -B).

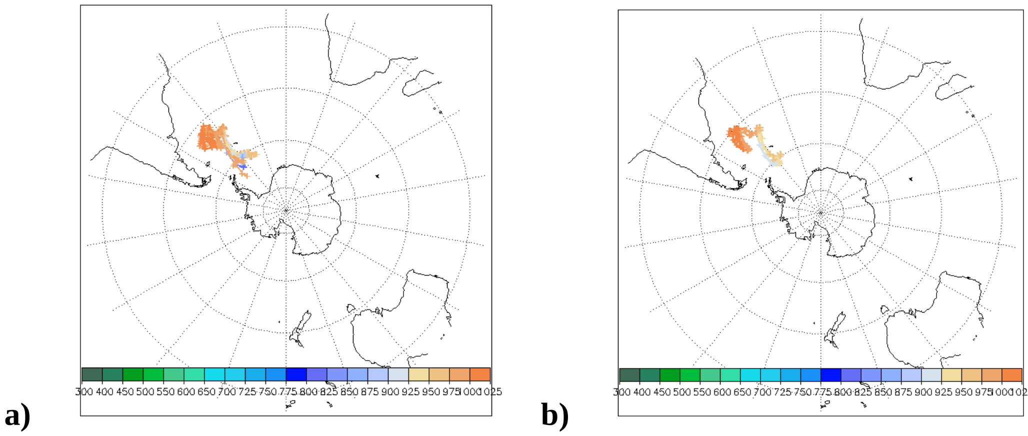

**Fig. 7:** Five day air mass back trajectories 30th January 2007 (a) and 31th January 2007 (b), during Episode-A. The colored code indicates the pressure level (hPa).

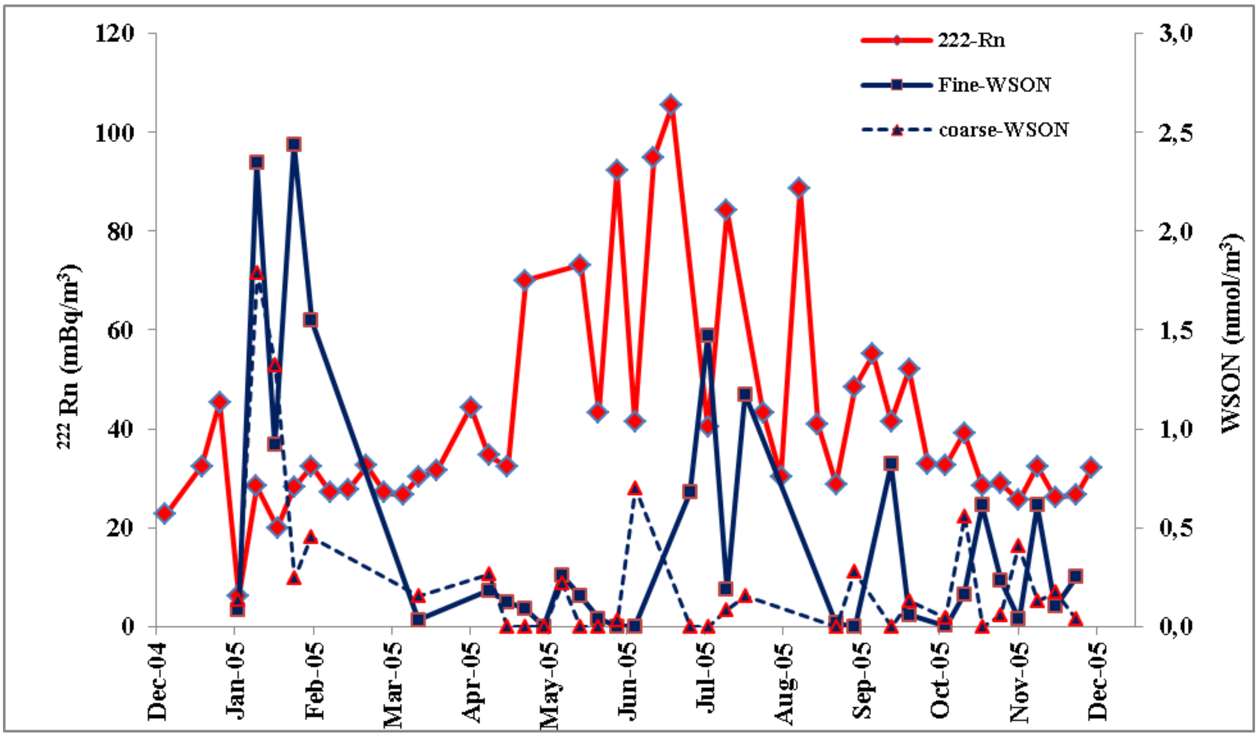

**Fig.8:**Seasonal variation of fine & coarse mode WSON with Radon at Amsterdam Island. Austral Summer is defined from December to April & winter from May to November.

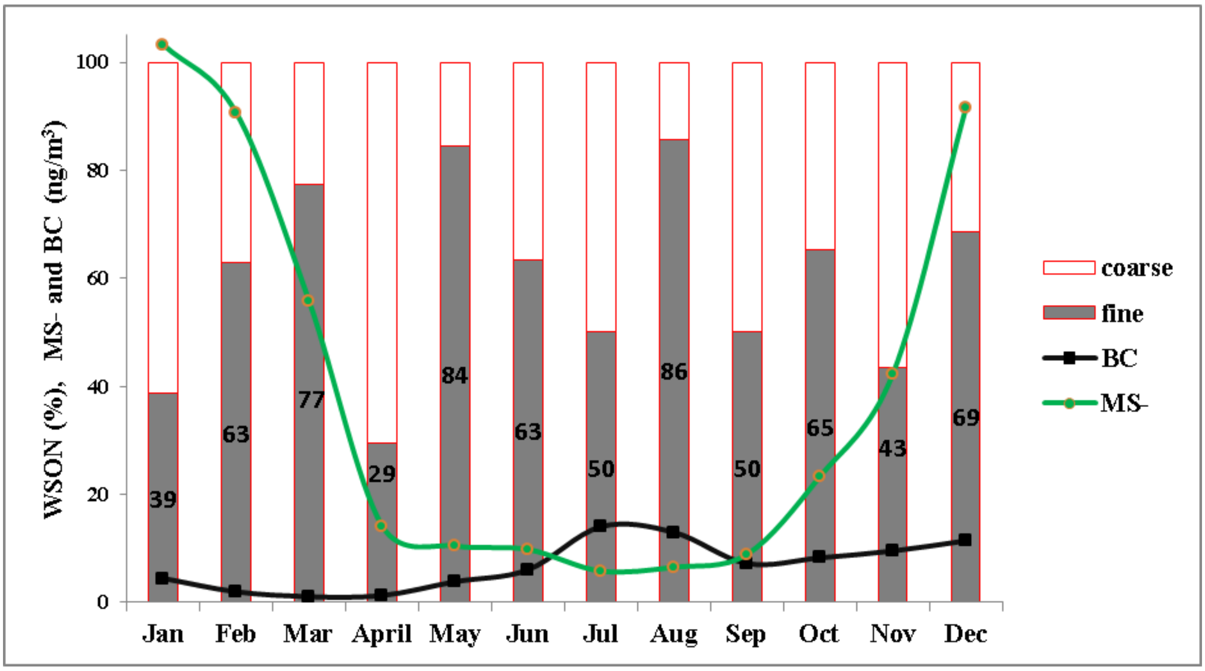

**Fig.9:** Average monthly concentration of bulk MS$^-$ and BC together with the percentage contribution of WSON in fine and coarse mode at Amsterdam Island (Indian Ocean) during 2005.

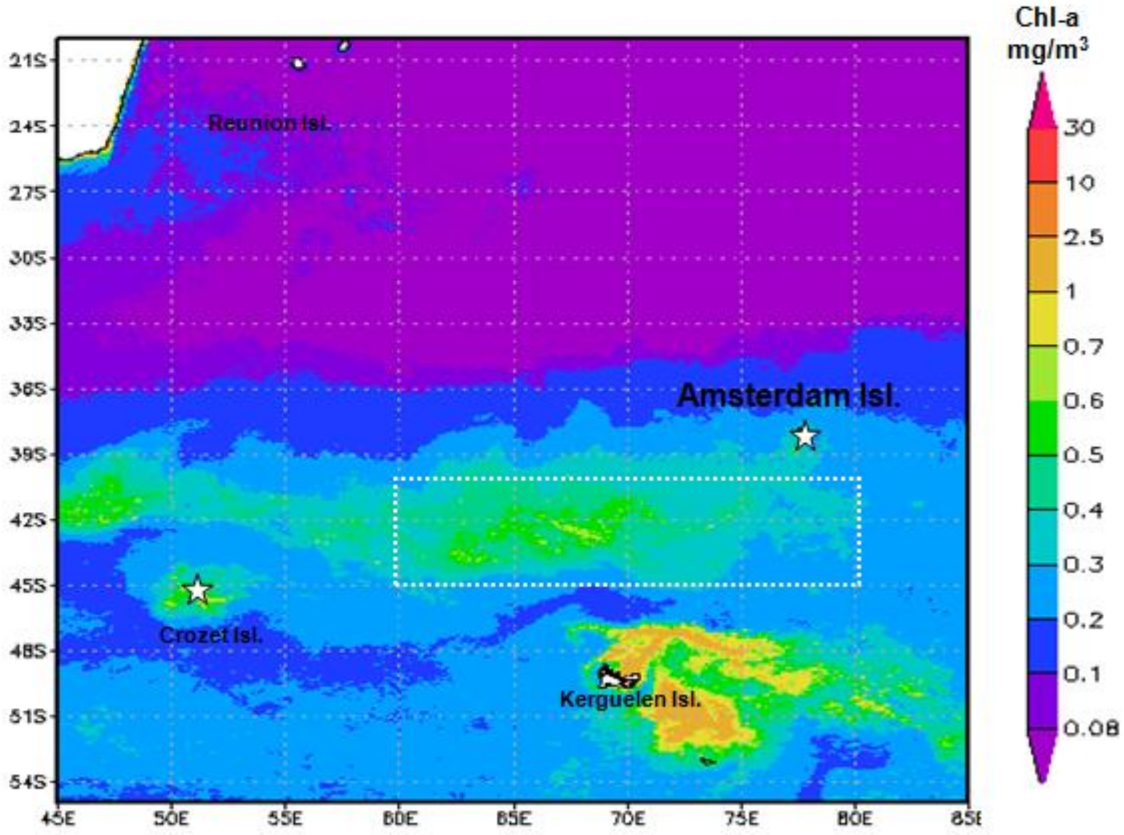

**Fig.10:**Chlorophyll map obtained for January (SeaWiFS data) for the Indian sector of the Austral Ocean. The white frame corresponded to the source region which could contribute to the levels of marine organics at Amsterdam Island.

***Table 1:***Average concentration of WSON and percentage contribution to TDN for fine and coarse particles in both Hemispheres.

| **Location** | | **Sampling period** | **$D_a$ (µm)** | **Fine WSON (nmol N $m^{-3}$)** | **% TDN** | **$D_a$(µm)** | **Coarse WSON (nmol N $m^{-3}$)** | **% TDN** |
|---|---|---|---|---|---|---|---|---|
| | | | **Northern Hemisphere** | | | | | |
| E. Mediterranean* | Marine with anthropogenic influence | 2005-2006 (n=65) | $PM_{1.3}$ | 11.6±14.0 | 13 | $PM_{1.3-10}$ | 5.5±3.9 | 13 |
| Tropic Atlantic Ocean | Marine with Sahara dust influence | 16 Jul–4 Aug 2006 (n=18) | <2 | 0.9±1 | 5 | >2 | 6.3±3.8 | 14 |
| | | | **Southern Hemisphere** | | | | | |
| S. Atlantic Ocean | marine with the highest Chl-a | 30-31 Jan 2007( n=4) | $PM_{2.5}$ | 11.3±3.3 | 84 | | - | - |
| middle S. Atlantic | Pristine marine | 26-29 Jan 2007 (n=4) | $PM_{2.5}$ | 0.8±1.1 | 43 | | - | - |
| Indian Ocean (Amsterdam Isl.) | Pristine marine | 2005 (n=42) | $PM_{2.5}$ | 0.8±1.4 | 32 | $PM_{2.5-10}$ | 0.2±0.4 | 35 |

*Violaki and Mihalopoulos (2010b)