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

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Received: 15 May 2014 – Accepted: 5 June 2014 – Published: 24 July 2014

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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 during a one year period (2005) over the southern Indian Ocean (Amsterdam island). 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 ($11.3 \pm 3.3 \text{ nmol N m}^{-3}$) accounting for about 84 % of the total dissolved nitrogen (TDN). Such levels are similar to those observed in the polluted marine atmosphere of the eastern Mediterranean ($11.6 \pm 14.0 \text{ nmol N m}^{-3}$). 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, Sahara dust was also identified as a significant source of WSON in the coarse mode aerosols of the NH.

1 Introduction

The ocean/atmosphere biogeochemical interactions are important in regulating atmospheric composition, marine ecosystem functioning and the Earth's climate. Oceans are a 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 and Maskhidze, 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).

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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 ocean such as isoprene and monoterpenes (Yassaa et al., 2008; Arnold et al., 2008), dimethyl sulphide (Charlson et al., 1987) and aliphatic amines (Facchini et al., 2008a) can significantly influence the cloud condensation nuclei (CCN) abundance and thereby the cloud albedo in the marine atmosphere (Meskizze and Nenes, 2006).

Seawater contains various amounts and types of organic material, depending on when and where it is collected, and 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 as methylamines or in oxidized forms as organonitrates, have been proposed to contribute to the organic matter of marine aerosols (Facchini et al., 2008a; Galloway et al., 2009). During phytoplankton blooms, when biological activity is at its maximum, the organic fraction dominates the marine aerosols mass contributing up to 63 % of the submicron aerosol mass (O'Dowd et al., 2004). Reactive trace gases emissions from such oceanic areas can significantly influence the local photochemistry (Yassaa et al., 2008; Williams et al., 2010).

The chemical composition of organic nitrogen fraction 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; the compound class containing carbon,

hydrogen, oxygen and nitrogen (CHON+) has the largest number of formulas in the marine rainwater, as it did 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 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 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 m³/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. A total of 21 daily high-volume aerosol samples were collected on Quartz Filters, pre-combusted at 450 °C for 5 h. Samples were stored at the ship in the freezer (4 °C) till the laboratory analysis.

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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°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 19 January to Punta Arenas (Chile) till 5 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 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 ($\text{PM}_{2.5}$) on Teflon filters ($n = 23$) on a 12 h-basis from 21 January to 5 February 2007. Samples were stored at the ship in the freezer (4°C) till the laboratory analysis. At the lab the aerosol samples were extracted with 15 mL Milli-Q water for 45 min in ultrasonic bath and processed as the samples collected at the tropical Atlantic Ocean.

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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 (Sciare et al., 2009). The pristine marine 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 PM₁₀) 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 150 m above sea level. A total of 42 samples were collected 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 WSOC, OC and BC analysis (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 by overnight soft shaking of the filter portion placed in borosilicate Erlenmeyer flasks with 15 mL of ultra pure water. Prior to analysis, the extract solution was filtered through Teflon (PTFE) filters (0.2 µm pore size diameter) to remove suspended particles.

To assess possible continental influence, radon (²²²Rn) was monitored on a 2 h basis by measuring the decrease of the alpha radioactivity of atmospheric aerosols collected

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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-} , $\text{C}_2\text{O}_4^{2-}$). 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 ppb for Na^+ , Ca^{2+} and lower than 3 ppb 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 by ion chromatography to determine selected anions (acetate, propionate, formate, methanesulfonate (MS^-), glutarate, succinate, oxalate, chloride, sulfate, nitrate, and phosphate) and cations (sodium, ammonium, potassium, magnesium, and calcium). The method is detailed in Sciare et al. (2009).

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 100–110 °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 coloured azo dye. The intensity of the produced color is measured by a spectrophotometer at 543 nm (Standard Methods for the Examination Water and Wastewater, 998). The detection limit of this method is 24 ppb 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 de-

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5 termination 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).

10 *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).

15 **2.3 Air mass back trajectory analysis**

20 10 day backward air mass trajectories were calculated with the LAGRangian ANalysis TOol (LAGRANTO) (Wernli and Davies, 1997; Stohl et al., 2005). Every 3 h about 10 air mass back trajectories were started within a ± 30 min 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 (T799 L91) 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 min.

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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 ($Da > 2 \mu\text{m}$, $n = 18$), was $6.3 \pm 3.8 \text{ nmol N m}^{-3}$ (median $6.2 \text{ nmol N m}^{-3}$) in agreement with the findings by Lesworth et al. (2010), who reported similar WSON concentrations ($6.1 \text{ nmol N m}^{-3}$) for coarse mode WSON ($Da > 1 \mu\text{m}$) in air masses originating from the Sahara desert. Predominance of NO_3^- was observed in the coarse mode, with average concentration of $36.1 \pm 11.6 \text{ nmol N m}^{-3}$ (median $38.0 \text{ nmol N m}^{-3}$), while coarse mode average concentration of NH_4^+ was $1.3 \pm 0.6 \text{ nmol N m}^{-3}$ (median $1.1 \text{ nmol N m}^{-3}$). 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, denoting the important role of dust as a primary source of organic nitrogenous. No correlation was found with inorganic nitrogen, 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-} ($r^2 = 0.5$, $p < 0.0005$, $n = 18$), 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 (19 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 ($Da < 2 \mu\text{m}$, $n = 18$) average concentration of WSON was found to be $0.9 \pm 1.0 \text{ nmol N m}^{-3}$ (median $0.6 \text{ nmol N m}^{-3}$), while the average concentrations of NH_4^+ and NO_3^- ions were $28.0 \pm 21.6 \text{ nmol N m}^{-3}$ (median $22.9 \text{ nmol N m}^{-3}$) and

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$4.7 \pm 1.8 \text{ nmol N m}^{-3}$ (median $4.5 \text{ nmol N m}^{-3}$), 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. Marine sources seem to control the fine mode WSON concentration levels, since significant correlation of WSON was found with ss-SO_4^{2-} ($r^2 = 0.6$, $p < 0.001$, $n = 15$). The highest concentration of WSON was observed on 3 August (Fig. 4), when the air mass back trajectory had marine origin (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 (Meskidze 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 (30–31 January) and the episode-B began on 1 February and was followed until the end of the cruise. The average concentration of WSON during the whole sampling period was estimated at $8.5 \pm 11.7 \text{ nmol N m}^{-3}$ with negligible contribution from NO_3^- ($0.2 \pm 0.5 \text{ nmol N m}^{-3}$; $N = 23$), while the NH_4^+ average concentration was estimated at $1.6 \pm 1.2 \text{ nmol N m}^{-3}$.

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 ($116.9 \text{ ng C m}^{-3}$). Thus these samples are expected to result from mixing of continental and marine sources.

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The evaluation of biogenic activity as primary source of atmospheric organic nitrogenous compounds was based on DMS, since it is considered as an indicator of marine biological activity (Sciare et al., 1999). When the ship crossed the episode-A area (Fig. 6), air masses had pure marine origin with extremely low BC levels and the measured WSON average concentration was $11.3 \pm 3.3 \text{ nmol N m}^{-3}$. These samples presented high average contribution of WSON to TDN (84 %), which indicates an important role of the marine biological activity in the biogeochemical cycle of organic nitrogen. For the samples collected over the middle southern Atlantic atmosphere, which is considered as remote marine area, the average concentration of WSON was much lower ($1.1 \pm 1.2 \text{ nmol N m}^{-3}$) 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 ($\text{PM}_{2.5-10}$) and fine ($\text{PM}_{2.5}$) particles were found to be $0.2 \pm 0.4 \text{ nmol N m}^{-3}$ and $0.8 \pm 1.4 \text{ nmol N m}^{-3}$ 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 $0.9 \text{ nmol N m}^{-3}$, $n = 2$; Mace et al., 2003b), and slightly higher compared to the values reported at Barbados ($0.5 \pm 0.3 \text{ nmol N m}^{-3}$, Zamora et al., 2011).

Concerning the inorganic nitrogen species, NH_4^+ was mainly found in fine mode with average concentration of $1.3 \pm 1.0 \text{ nmol N m}^{-3}$ and $0.3 \pm 0.1 \text{ nmol N m}^{-3}$ 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 $0.3 \pm 0.2 \text{ nmol N m}^{-3}$ and $0.2 \pm 0.1 \text{ nmol N m}^{-3}$ 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. 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^- ($r^2 = 0.7$, $p < 0.01$, $N = 9$) during austral summer, implying that probably part of WSON was produced secondary from biogenic marine precursors, following similar production mechanism with MSA. 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 release fine mode aerosols including WSON, which

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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 when strong dust outbreaks from Sahara desert affected the area. This enables the evaluation of the contribution of dust to the levels of atmospheric WSON concentration. 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. A significant source of coarse mode WSON in the Northern Hemisphere (NH) is the Sahara desert. 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 (Lelieveld et al., 2002; Krol et al., 2003), 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

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the more than ten times higher concentration of WSON comparing with the remote marine areas of Southern Hemisphere (middle southern Atlantic and Amsterdam island). Nevertheless, the higher percentages of fine mode WSON to TDN in both marine areas 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 remote marine atmosphere when intense biogenic activity occurs (bloom area of the southern Atlantic). Indeed under such conditions the observed levels of WSON ($11.3 \pm 3.3 \text{ nmol N m}^{-3}$) along with high percentage contribution (84 %) to TDN were almost identical to that measured over the eastern Mediterranean ($11.6 \pm 14.0 \text{ nmol N m}^{-3}$) highlighting the significant role of marine productivity as a source of WSON in remote marine regions with significant biogenic activity.

Acknowledgements. The research project was financed by the EU projects OOMPH (FP6) and Perseus (FP7).

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

WSON (nmol N m ⁻³)	Location	D(μm)	Fine	% to TDN	D(μm)	Coarse	% to TDN
E. Mediterranean* Tropic Atlantic Ocean	Marine with anthropogenic influence	PM _{1,3}	11.6 ± 14.0	13	PM _{1,3-10} D > 2 μm	5.5 ± 3.9 6.3 ± 3.8	13 14
	Marine with Sahara dust influence	D < 2 μm	0.9 ± 1	5			
	South Hemisphere						
S. Atlantic Ocean middle S. Atlantic Indian Ocean (Amsterdam Isl.)	High Chl <i>a</i> marine area	PM _{2,5}	11.3 ± 3.3	84	PM _{2,5-10}	– – 0.2 ± 0.4	– – 35
	Marine remote	PM _{2,5}	1.1 ± 1.2	43			
	Marine remote	PM _{2,5}	0.8 ± 1.4	32			

* Violaki and Mihalopoulos (2010b).

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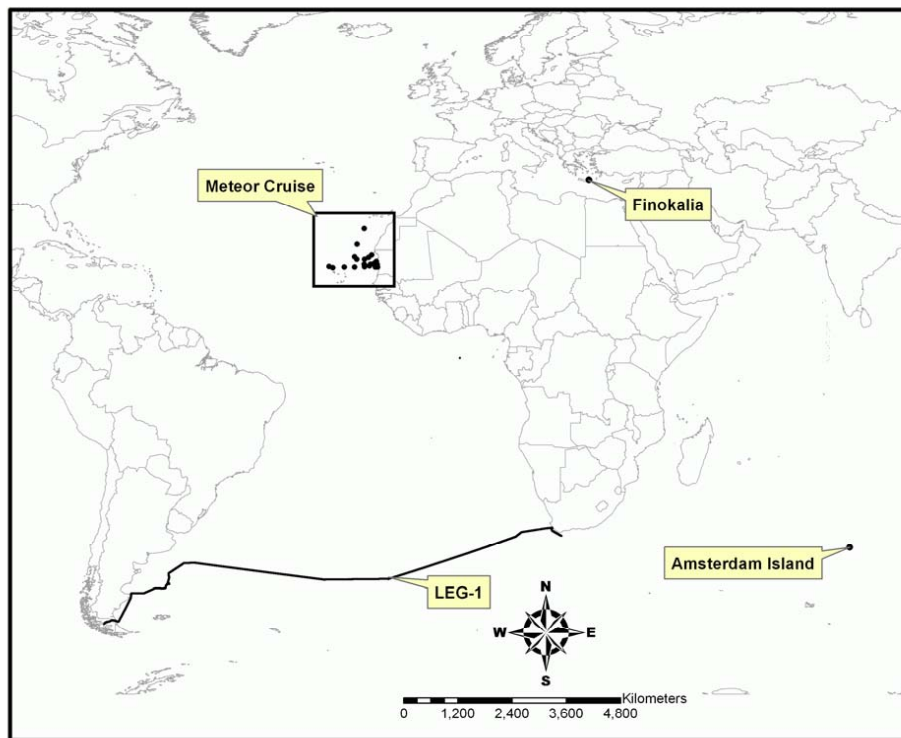


Figure 1. Sampling sites around the world during this study.

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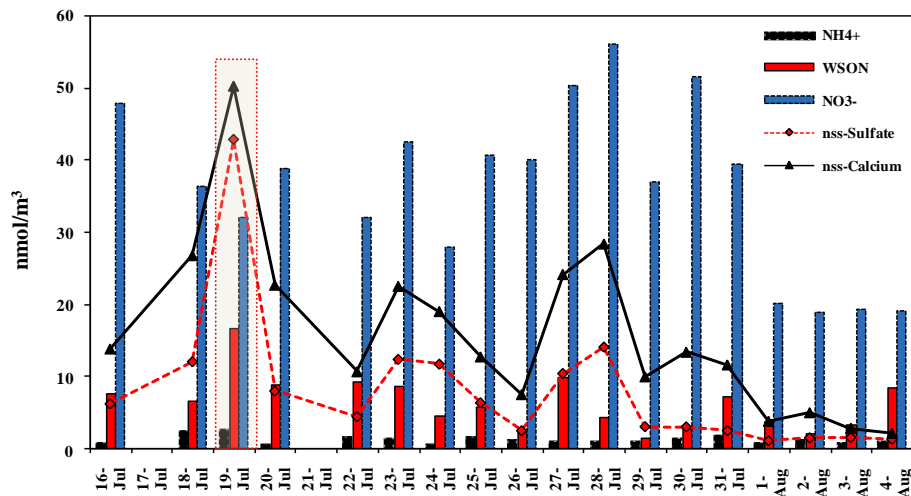


Figure 2. Temporal variation of nitrogen species, nss-SO_2^{-4} and nss-Ca^{2+} concentration in coarse particles ($\text{Da} > 2 \mu\text{m}$) over the tropical Atlantic atmosphere. The frame defines the air mass back trajectory with dust mixed with anthropogenic sources (19 July 2006).

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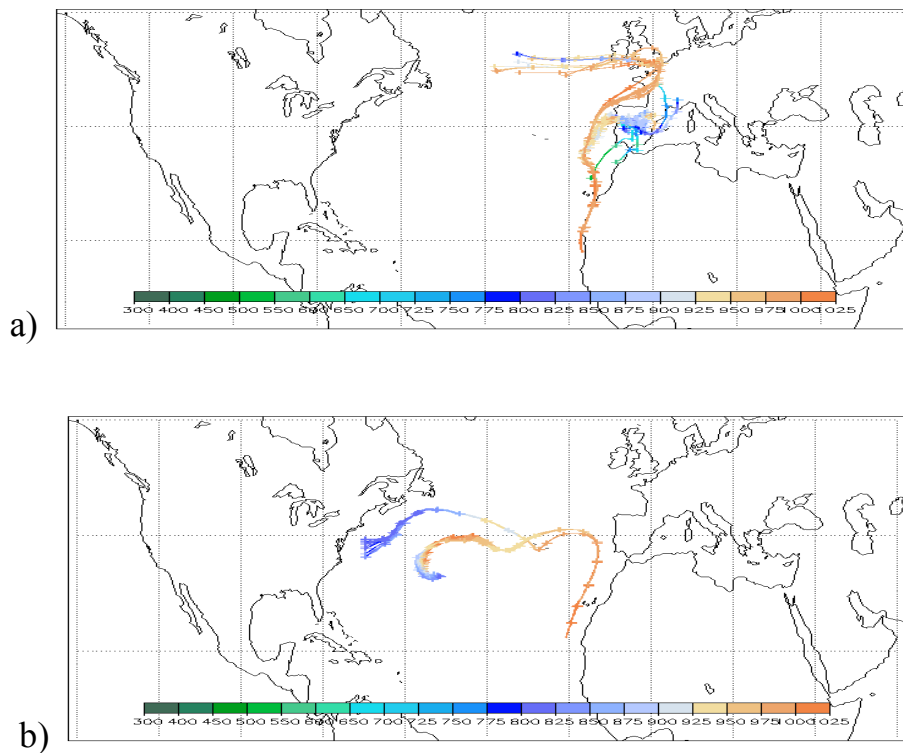


Figure 3. Five day air mass back trajectories 19 July 2006 (a) and 3 August 2006 (b). The color indicates the pressure level (hPa).

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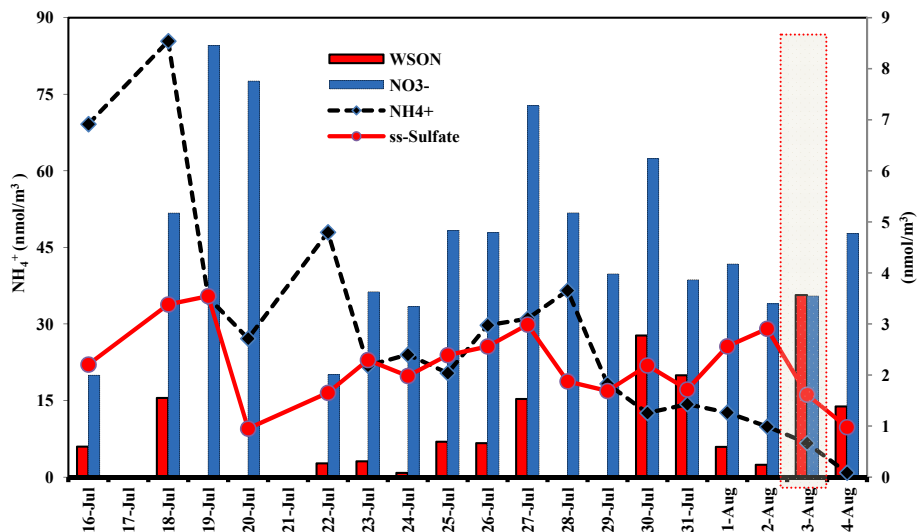


Figure 4. Temporal variation of nitrogen species and ss-SO_4^{2-} concentration in fine particles ($\text{Da} < 2 \mu\text{m}$) over the tropical Atlantic atmosphere. The frame defines the air mass back trajectory with marine origin (3 August 2006).

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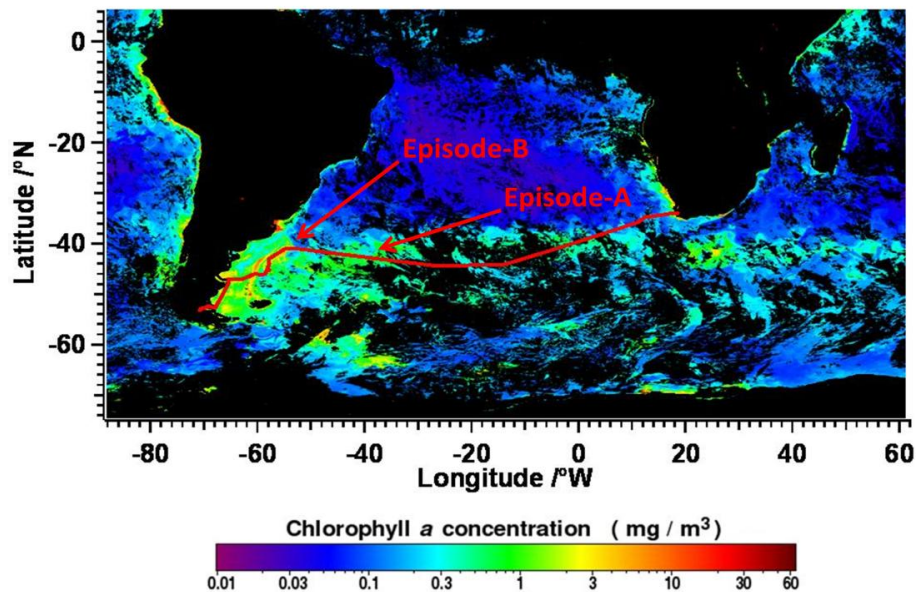


Figure 5. Two distinct phytoplankton bloom episodes are presented in SeaWiFS chlorophyll *a* map at South Atlantic Ocean during January 2007 along with cruise track (<http://disc.sci.gsfc.nasa.gov/giovanni>).

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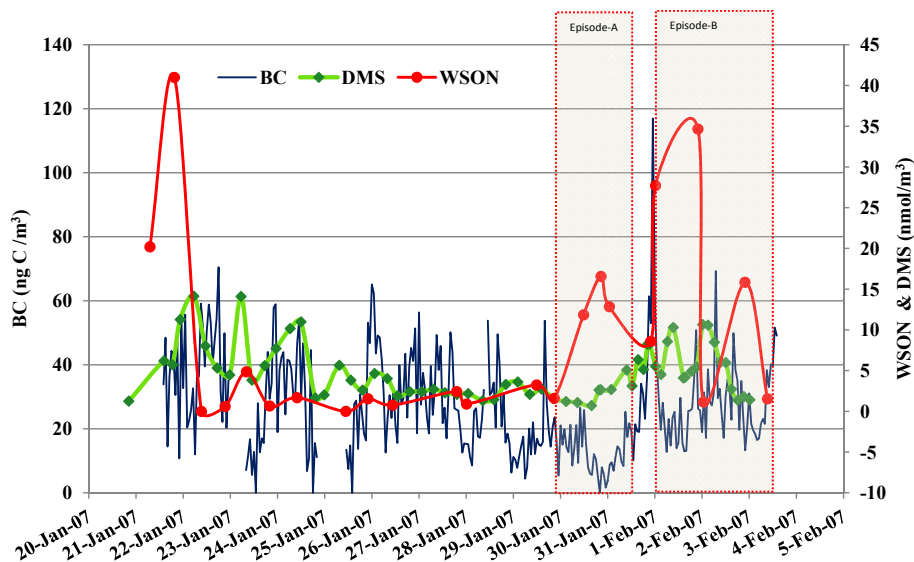


Figure 6. Temporal variation of WSON and DMS concentration in fine particles ($PM_{2.5}$) together with BC concentration during the cruise in South Atlantic atmosphere. The frames define the marine areas with intense biogenic activity (Episode-A and -B).

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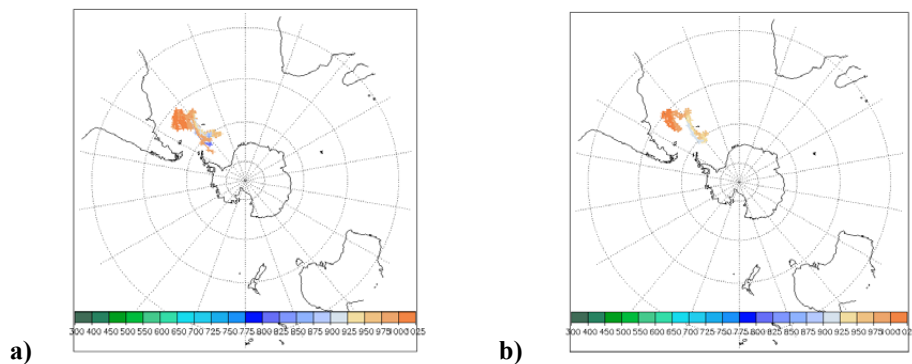


Figure 7. Five day air mass back trajectories 30 January 2007 (a) and 31 January 2007 (b), during Episode-A. The colored code indicates the pressure level (hPa).

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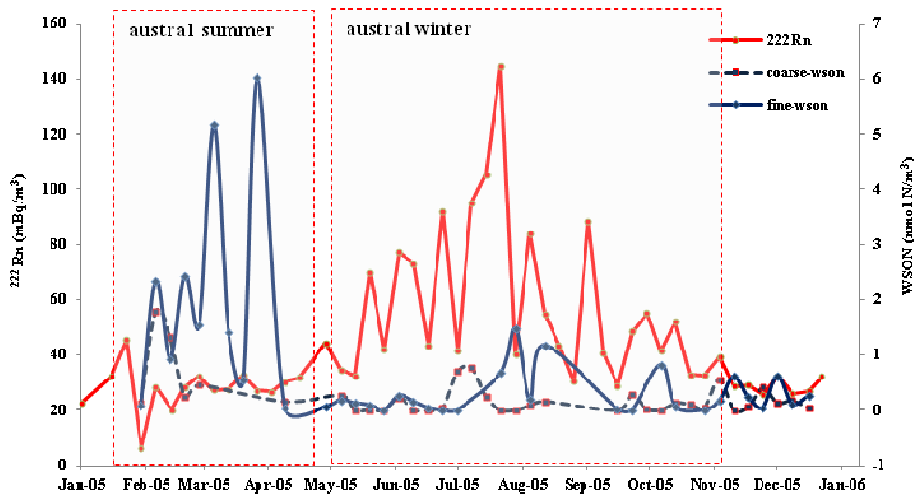


Figure 8. Seasonal variation of fine and coarse mode WSON with Radon at Amsterdam Island.

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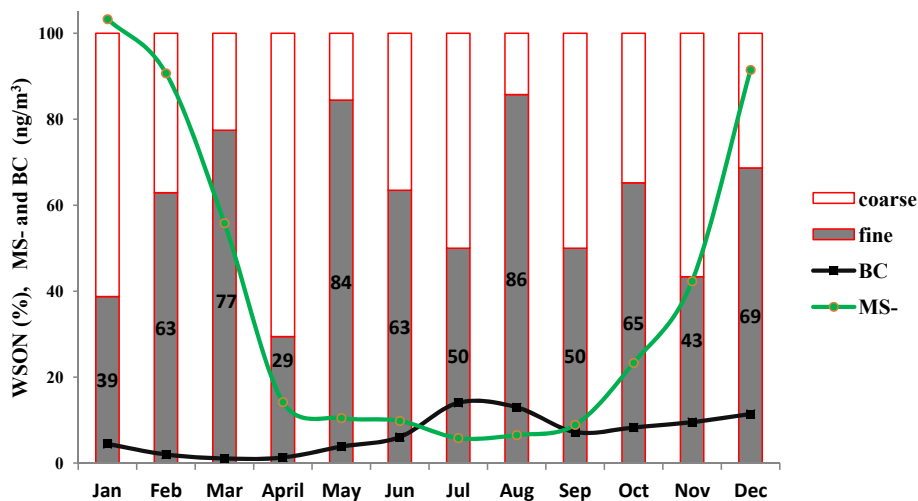


Figure 9. Average monthly concentration of bulk MS- and BC together with the percentage contribution of WSON in fine and coarse mode at Amsterdam Island (Indian Ocean) during 2005.

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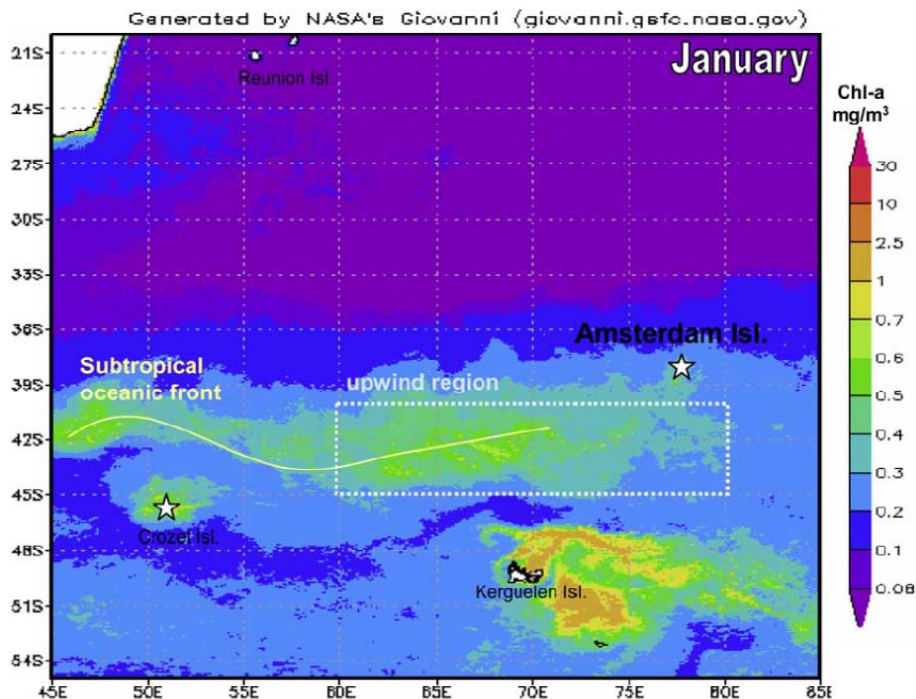


Figure 10. Chlorophyll map obtained for January (SEAWIFS data) for the Indian sector of the Austral Ocean. The white frame corresponded to the source region which contributes to the levels of marine organics at Amsterdam Island. This high productive region stands for the oceanic fronts (subtropical and subantarctic fronts).