Response to Reviewer #1 Christophe MIGON

We would like to thank Prof. Migon for the comments that have helped us to prepare this final version. All suggestions have been taken into account and all raised issues are answered one by one. Below is a point-by-point answer to the reviewer's comments (by Italics).

-1:Chemical analysis: Detection limits and blanks are not expressed in the same units.

Many thanks for the indication, the inconsistency was corrected

- 2: Partitioning between nss- and ss-ions:
a) if I am not wrong, those acronyms are introduced in the text ;
b) the authors do not explain how they discriminate nss- and ss-ions

This information is now inserted in the manuscript.
Non sea salt calcium and sulfate (nss-Ca^{2+} and nss-SO_4^{2-}) as well as sea salt sulfate (ss-SO_4^{2-}) are estimated based on the following equations:

nss-$Ca^{2+} = [Ca^{2+}] - 0.3184*[Mg^{2+}]$nss-$SO_4^{2-} = [SO_4^{2-}]_{total} - 2.0958*[Mg^{2+}]$
nss-$SO_4^{2-} = [SO_4^{2-}]_{total} - 2.0958*[Mg^{2+}]$
ss-$SO_4^{2-} = [SO_4^{2-}]_{total}$ - nss-SO_4^{2-}

- 3: I am a bit surprised by the use of BC concentrations to characterize continental influences. To my knowledge, this is not usual, and might not be appropriate, because BC emissions from ships are very significant (e.g., ships tracks can be easily detected over marine areas by BC concentration plumes).

We agree that BC is also a tracer for ship plumes, however in this remote part of the world (Austral Ocean) shipping is really limited and the main source of BC at Amsterdam Island is transport from continental sources (Africa). The covariation of BC with Radon (a continental tracer) justifies our assumption. At the revised version the origin of BC at Amsterdam Island will be clarified.

Anonymous Referee #2

General comments:

I believe this paper would benefit from major revisions, but because the topic and data are sound, I hope to support the publication of this paper in a later version assuming revisions are satisfactory. Currently, the study has a compelling introduction, easy to understand figures, and sound methods and data collection. Their data add helpful new information in key regions where WSON has not previously been measured. Additionally, the topic is important. Elucidating the marine sources of WSON will enable better interpretation of previously collected marine WSON data because it will provide a better understanding of the fraction of new atmospheric N inputs (as opposed to recycled inputs) into the ocean, which has implications on marine productivity.

However, the discussion and interpretation of the data require major revisions before I would want to fully endorse its acceptance into Biogeosciences. In particular, I have not seen the evidence to convince me from their data that productive marine waters are an important source WSON, which is one of the main points of the paper. One main concern is that the primary basis for the argument is correlation used to indicate causation, which is problematic, particularly because the potential for other WSON sources that affect interpretation of the proposed relationship was not discussed satisfactorily. Because they rely so heavily on correlations, it is additionally problematic that the authors base their arguments only on r^2 and p values, and neglect to show the actual data. This practice makes it difficult for the reader to put the r^2 value in context of possible outliers skewing the relationships. In order to better assess whether other aerosol sources could be producing a false association between WSON and marine productivity indices, I suggest including a more thorough discussion of other chemical tracers and potentially, better verification of sources from satellite data to the extent possible. Additionally, the discussion would benefit from a more thorough comparison with related findings from other studies.

We would like to thank the anonymous reviewer for his/her comments that have helped us to prepare a final version and we really appreciate the effort and time he/she spent on the manuscript. All suggestions have been taken into account and all raised issues are answered one by one.

We agree with the reviewer's concerns but presenting all regressions would make the manuscript too large and we don't think it will be informative. There is little doubt that the number of data points is not too high and there is a clear need to obtain more data to confirm our concluding remarks. We tried thus to decrease the "tone" of our conclusions and we intend to collect more data in the near future. Below is a point by point answers (by Italics) to the specific reviewer's comments.

Specific comments

The most important comments are regarding the marine WSON source hypothesis. At all 3 sites I find that the evidence provided for the marine WSON source hypothesis needs more support to be valid.

Tropical N. Atlantic: p. 11370, line 4: The two final statements in this section need more evidence: a) "Marine sources seem to control the fine mode WSON concentration levels, since significant correlation of WSON was found with ss-SO42- ($r^2 = 0.6$, $p < 0.001$, $n = 15$)" and b) "The highest concentration of WSON was observed on 3 August (Fig. 4), when the air mass back trajectory had marine origin (Fig. 3b)." For statement a), I remind the authors that correlation does not equal causation, so perhaps a better wording would be something like, "high ss-SO4 values were associated with high WSON values (r^2 =. . .)". But even if the wording is changed, I still don't think one can really say that marine sources control the fine mode WSON at this site based only on the WSON/ss-SO4 association. First, a correlation of 0.6 still typically incorporates a great deal of variability. Secondly, the sample size is relatively small (n=15). Thirdly, assessments based on correlation coefficients alone can sometimes lead to false associations due to outliers. For this third reason, the r^2 values by themselves are not particularly useful for the reader. Therefore, if the *authors want to discuss the association between WSON and ss-SO4, I suggest adding a new figure showing the actual data the correlation is based on.*

Finally, and most importantly, because correlation does not equal causation, it is important to show that other data sources were closely monitored to rule out other WSON sources on the days that had high WSON and high ss-SO4 in combination. Because WSON can be transported long distances, there needs to be more evidence to make a compelling case for a large marine WSON source, particularly their hypothesis seems to directly contradict others studies that found low total WSON on clean marine days, including in the same study region of the tropical North Atlantic (e.g., Lesworth et al., 2010; Zamora et al., 2011) (not to mention the author's own findings at Amsterdam Island, where WSON was low even though upwind Chl a concentrations were still relatively high).

-We agree with the reviewers statement that "correlation does not equal causation" and tried to be very cautious throughout the manuscript, however the WSON fraction is a complex mixture of compounds and almost unknown. During this study the only available tool to have some robust results regarding the sources is the correlation with known tracers. It is true that there are many things to be done in the future research, regarding the speciation of WSON fraction.

The sentence "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)was replacedwith the phrase:

"Marine sources seem to contribute to the fine mode WSON concentration levels, since high ss-SO$_4^{2-}$ values were associated with high WSON values (r^2=0.6, p<0.001, n=14). Insignificant correlations were found between fine mode WSON and continental tracers such as nss-Ca^{2+} and nss-SO$_4^{2-}$.".

For statement b), I would not call that trajectory "purely marine" because it goes right by the coast of Africa where dust storms routinely blow and where pollution from northern Africa and Europe frequently mix in. In fact, when I looked at the AOD, true color, and CALIPSO aerosol subtypes for that day, it seems that there was a great deal of dust in the atmosphere above the sample (see Figures 1-3 in the supplement attached), which may have impacted the results, as dust is known to carry WSON. To me, this casts strong doubt on whether this was truly an example of a "purely marine" day and so this argument should not be used to support the hypothesis of a marine WSON source. If this sample, which the authors said was the sample with the highest concentration of WSON, was removed from the WSON-ssSO$_4$ plot because of the likely interference from high dust concentrations, what would the resulting r^2 and p value be?

-Indeed in Figures 1-3 in the supplement attached by the reviewer it seems that there was dust in the atmosphere during the sample collection. Although, this dust event seems not to be recorded by the sample, since in Fig. 2 on 3th August the nss-Calcium concentration (in coarse mode) is lower comparing with the whole sampling period. Note that we were very cautious in our interpretation and we never used the word "purely marine" in this section. The sentence was replaced by this "The highest concentration of WSON was observed on 3 August (Fig. 4), when the air mass back trajectory indicate marine origin although influence from continental sources (dust) cannot be totally ruled out (Fig. 3b).

South Atlantic: p. 11371, l. 3: "When the ship crossed the episode- A area (Fig. 6), air masses had pure marine origin with extremely low BC levels....." First, there was no clear definition for how a sample was determined to be "pure marine," so it is important to define that in the methods section.

-We agree with reviewer's commend "there was no clear definition for how a sample was determined to be "pure marine,". In his work in Science, Andeae et al., (2007) suggested that "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". The text with the reference was inserted in the manuscript.

As far as I can tell though, in the South Atlantic a "pure marine" sample was defined from a combination of back trajectories, BC concentrations, and DMS levels, and at the other two sites, "pure marine" was defined only back trajectories. At minimum, that in consistency should be noted and discussed. However, for the following reasons, I don't think the authors really have the basis to define air masses "pure marine" based on their current criteria anyway, and I strongly suggest rewording the sections that contain this phrase.

-For Amsterdam Island the definition of "pure marine" is not based only on trajectories but also on the extremely low levels of anthropogenic tracers such as BC and CO measured there (See also in the manuscript; page 11366, line 8-12). "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)."
Finally as we understand that definition of "pure marine" is a subtle issue for this reason the phrase "pure marine" was replaced by the phrase "pristine oceanic"

First, back trajectories alone are problematic because air masses are constantly mixing and the older the back trajectory, the more error there is. For example, at least one of the other days in the tropical North Atlantic that was defined as having a "pure marine" source from a back trajectory actually likely had another significant dust WSON source (see my point in the comment above). The BC criteria, meanwhile, were unspecified and unsubstantiated. Please quantitatively define what is meant in the sentence above by "extremely low BC levels" and also please define the cutoffs that constituted "pure marine" air.

-"extremely low BC levels" come from the comparison of that concentration with the whole sampling period, however the phrase "extremely low BC levels" was replaced with the phrase "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)"

While using BC as a tracer is helpful, it must be used in combination with other components before calling an air mass "pure marine". For example, dust is known to occur in the Southern Hemisphere (e.g., Johnson et al., 2010, Gasso et al. 2010; Gaiero et al., 2013) and that cannot be accounted for from BC alone. If DMS concentrations were also used to determine "pure marine" samples, that method would also be flawed, because while high DMS concentrations do indicate that an air mass passed over productive marine DMS sources, they don't tell one what other sources of WSON might be in the air mass concurrently.

-This issue was addressed above and pure marine is now replaced by "pristine oceanic"

The three following points below are related to this issue:
South Atlantic: p. 11371, l. 1: "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)." As mentioned, while DMS can indicate biological activity, it cannot be used to assess whether biological activity is the main source of WSON.

-We agree with the reviewer and the sentence was corrected as following “The evaluation of biogenic activity as possible source of atmospheric organic nitrogenous compounds was based …………”.

South Atlantic: p. 11371, l. 3: “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 ± 3.3 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.” Because the authors have not convincingly shown that there are no other sources of WSON in the air, I don’t think they have the basis to claim that the WSON is from a marine source and not some other source.

-The sentence was reworded based on the previous discussion as following: “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 ….. ”

South Atlantic: p. 11371, l. 8 and Table 1: “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 ± 1.2 nmol N m-3) corresponding to 43 % of TDN.” I notice from Fig. 6 that in some parts of these remote regions where WSON is low, DMS concentrations were equally high (e.g., from Jan 23-25) as the DMS levels when WSON levels were high (in the 11.3 ± 3.3 nmol N m-3 range). This information casts doubt on the marine WSON source hypothesis.

-We already addressed the concerns of the reviewer in the questions above. Note that during this study as influence from remote marine area is considered the period from 26-29 Jan (n=4). The DMS was low during that period (Fig.6), so the phrase "which is considered as remote marine area" was replaced by the phrase "which is considered as remote marine area, with low biogenic activity".

Can the authors look at satellite data from this time period to see if there were other recognizable WSON sources during the episode A period? I am also unclear about which days were binned into “S. Atlantic Ocean, High Chl a marine area” and “middle S. Atlantic, Marine remote” in Table 1 and the samples discussed in the above text from the paper. Please a) clearly define what days were in each period, b) indicate on Figure 5 where remote vs. non-remote days were located, and c) explain the criteria for this binning. Based on Fig. 5, much of the cruise took place in high Chl a regions, and so I am unsure why the authors separated out “High Chl a” and “remote” periods, and I also think the term “High Chl a” in Table 1 might be a bit misleading. An alternative wording could be “Highest Chl a period”? Regarding the binning, how did the authors deal with days with low WSON but high DMS days- were these days included or excluded, and why? For Fig. 5, (this is only a suggestion), it would be interesting to plot SeaWiFS Chla along the track against WSON, DMS, and BC; that might make it easier for the reader to understand why the authors binned the days as they did.

The discrimination was based on the concentration levels of DMS and not on the levels of Chl-a. The changes have been done accordingly in Table 1.

Location		Sampling period	D_a(μm)	FineWSON (nmol N m^{-3})	% to TDN	D_a(μm)	Coarse WSON (nmol N m^{-3})	% to TDN
North 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
South Hemisphere								
S. Atlantic Ocean	marine area with highest Chl a period	30-31 Jan 2007(n=4)	$PM_{2.5}$	11.3±3.3	84		-	-
middle S. Atlantic	Marine remote	26-29 Jan 2007(n=4)	$PM_{2.5}$	0.8±1.1	43		-	-
Indian Ocean (Amsterdam Isl.)	Marine remote	2005 (n=42)	$PM_{2.5}$	0.8±1.4	32	$PM_{2.5-10}$	0.2±0.4	35

Amsterdam Island: p. 11372, l. 18: "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." Based on the detection limits (DL) listed in the methods, it seems that the DL for WSON should be greater than _0.64 nmol N/m3 (as _0.64 nmol N/m3appears to be the DL for TDN). That excludes all but 2 of the coarse sample values during the summer period as best I can tell based on Fig. 8. Therefore I think any correlations with MS for these samples are probably not valid. Plus, in Figure 8, I only see 6 samples of coarse WSON during the austral summer. Perhaps the symbols are hidden and there are more samples than I can discern (in which case the authors should change Fig. 8 so that they are more visible), but either way please check consistency here as N=10 was listed in the text.

We agree with the reviewer's comments and the discrimination between summer and winter was better clarified in the figure 8 to better indicate the number of samples.
On the other hand, there is no real detection limit for WSON as TDN and the inorganic species were always present in our samples in significant amounts. It is clear that the correlation is based on a number of points with low WSON but we don't see how this can invalidate the relation between MS and WSON.

Amsterdam Island: p. 11372, l. 15: "The fine mode WSON was found to correlate significantly with fine mode MS- (r2 = 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." Please plot the data.
Again, beware correlation and causation issues. Because of the small sample size, I would change "implying that probably part of WSON was produced secondary from biogenic marine precursors" to "implying that part of WSON might have been produced secondarily from biogenic marine precursors"

Following reviewer's suggestion the phrase was changed accordingly.

Amsterdam Island: Figure 10: what is the thin yellow line? Did all upwind air pass through the dotted box, or is that only typical? Why didn't the authors do back trajectories like with the other two sites in the Atlantic? Are the data shown in Fig. 10averaged for all of January (if so, please state that)? There still seems to be relatively high chlorophyll a upwind, so the low WSON seems to conflict with the suggestion that local marine sources are a large or dominant source of WSON in the S. Atlantic.

Details on Amsterdam Island climatology can be found in Miller et al., 1993, now referenced in the manuscript) and from this work it is clear that the southwest sector (100°-250°) dominates much of the year.

Relation between chlorophyll amounts and WSON levels at both Amsterdam Island and the S. Atlantic is not easy to make on the basis only of chlorophyll levels. For instance, information on the dominant phytoplankton species at both areas as well as on the relation between Chlorophyll and WSON are clearly needed. All this information is out of the scope of this manuscript.

Other suggestions/comments (in no particular order) are listed as follows:

p. 11370, l. 11: "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." First, I am unclear about why the authors differentiated between episodes in the first place. The first episode was said to occur from Jan. 30-31, and the next bloom started on Feb. 1 (the very next day), and went to the end of the cruise. So what is the scientific reason to differentiate between episodes a and b?

The second bloom was under the influence of continental air mass at the day of sampling.

On the map the bloom looks essentially contiguous, with the low point in chlorophyll a values present only because the ship went temporarily outside of the bloom. Also, wouldn't February be a better month to average Chla over for Fig. 5since that is when the blooms were, primarily? As an aside, when I tried to re create Figure 5 from Giovanni (which is where the authors listed that they got the data), I got a slightly different looking picture with better data coverage (see Figure 4 in supplement attached). I wonder why this difference occurred? It could be possible that Giovanni altered something between when the authors downloaded the data and when I did? Either way, since now a version is available with better data coverage, perhaps the authors should use the more comprehensive data to overlay the cruise track instead?

Or even better yet, they could obtain the values of satellite-derived chlorophyll a that coincide with the cruise track and plot those below Fig. 5. That would be a lot easier on the reader to interpret the location and strength of the blooms. Just a suggestion.

Following reviewer's suggestion the picture was changed accordingly.

p. 11369, l. 14: "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[compounds]." What evidence is there for dust being a primary rather than secondary source of WSON? 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., Zamora et al., 2011; Wang et al., 2013). Because the authors also mention that nss-SO4 was present, it seems possible that the WSON might have been from pollution mixed in with the dust rather than having dust itself be the primary source. There were multiple other places in addition to the ones listed above where correlations were used to infer causation. I'd like to see more care being taken throughout the paper to reword these instances and to frame the interpretation with greater ambiguity. I also suggest adding figures plotting the data for any important correlations discussed in the paper.

The sentences provided by the reviewer “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)” as well as the relevant references were added in the manuscript.

While it appears that the methods for each study are sound, they are different for each of the sites. There were different collection filters (Teflon vs. quartz), collection methods (denuder vs. cascade impactor), desorption techniques (ultrasound vs. soft shaking), and pore size of extract filter (0.2 μm vs. 0.45 μm vs. unlisted for S. Atlantic(please do list this in the next version)). In the next version, please briefly discuss these differences and their potential impact on site intercomparison discussed

We totally agree with the reviewer and a sentence on that direction was added in the manuscript where the results of table 1 are presented. “Note the different sample substrate and the different cut-offs used in the data presented at Table 1 which have an impact on the comparison between the various sites”.
Note however that:

1) Although the results reported in the literature for WSON are not collected or analyzed using uniform techniques (actually there are no recommendations for WSON sampling and analysis) a comparison is always performed in every publication.
2) The main difference between our results could only come from filter media (Teflon vs Quartz) as the differences in cut-offs or filter porosity is very small. In addition based on tests performed in our laboratory no difference has been observed between extraction using ultrasound vs. soft shaking. Quartz Filters were only used during the Meteor cruise.

in section 4.p. 11369 line 15: “No correlation was found with inorganic nitrogen, indicating different sources.” No correlation with what? A dust tracer? Inorganic N? Any of the other tracer compounds? Please be more specific.
-No correlation was found with either NO_3^- or NH_4^+

p. 11369: the information from the first paragraph would be clearer and easier for the reader to digest if organized in a Table.
- All the relevant information regarding WSON (the main focus of the work) exists in Table 1

p. 11371, second paragraph: This could also be better summarized in a table I think.
- All the relevant information regarding WSON (the main focus of the work) exists in Table 1

Technical corrections Section 2.1.2, l. 13.a low volume aerosol sampler placed on [the] prow of the research vessel
- It was corrected.

p. 11365, l. 23:” Samples were stored at the ship in the freezer (4°C) till the laboratory analysis.” Did the authors mean in the freezer -4 degrees, or in the refrigerator at4 degrees?

- The samples were stored in the refrigerator; It was corrected accordingly.

Figure 1. The figure seems to indicate that Finokalia is a sampling site, which is a bit misleading. Perhaps better would be to distinguish between sites sampled in this study, and those discussed in context later by using different symbols and adding explanation of the symbols in the caption.

-The legend of Fig.1 was changed as: Sampling sites around the world during this study. Finokalia station is used for comparison reasons.

p. 11367 l. 13, please define LSCE
-LSCE:Laboratoire des Sciences du Climat et de l'Environnement

p. 11369 L. 4 and Table 1 caption, please define in the paper "D" and "Da" (aerosol diameter I presume), and make them consistent with each other throughout the paper.
-D was replaced with Da

Table 1 and Figures 2 and 4 captions, and throughout the text: I suggest changing North Atlantic to tropical North Atlantic. Or, samples were really only taken in the eastern part of the tropical N. Atlantic, being even more specific about the location.

-"North Atlantic" was changed to "tropical North Atlantic"

Table 1: I find the titles of the columns to be confusing. Why are there 2 columns with the title "D(μm)"? I guess to show the cutoffs between "coarse" and "fine" mode fractions? But if that is the case, why is the "% to TDN" (which is also confusing wording to me but which I think means % contribution to TDN) less than 100% when coarse and fine are added together? Rewriting/ reorganizing these columns so that they are clearer would be helpful to the reader.

-Reorganization of table 1 was done following reviewer's suggestions.

Fig. 6: is the Jan 21 sample taken over more than 24 hours (since the cruise started on the 19th?)

Although cruise started on the 19th, first sample was collected 2 days later. The average sampling resolution was 12 hours.

p. 11369 lines 12 and 14: did the authors mean to say, "organic nitrogenous compounds"in this sentence?
We mean both organic and inorganic N species.

p. 11372.Methanesulfonateisdefined (twice) as MS, but then the authors use MS-later.
Please be consistent.
-MS was replaced with MS-

p. 11372, l. 10: "During austral summer increased concentrations of MS were observed that can be linked to a similar increase of marine productivity." Reference?
-The reference Sciare et al., (2009) was inserted.

p. 11372, last paragraph: I think the authors can get rid of this paragraph as it does not add much to the main point.
We kept this paragraph as reviewer 1 asked for clarifications of the origin of BC in this location and we believe it will also help the reader to better understand the Figs. 8 & 9.

References

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

Violaki Kalliopi[1], Sciare Jean[2], Williams Jonathan[3], BakerAlex R.[4], Martino Manuela[4]and Mihalopoulos Nikos[1,5]

[1]Environmental Chemistry Processes Laboratory, Department of Chemistry, University of Crete, P.O. Box 2208, 71003 Heraklion, Greece.

[2]LSCE, CEA-CNRS-UVSQ, UMR1572 Laboratoire des Sciences du Climat et de l'Environnement, Gif-sur-Yvette, France

[3]Max Planck Institute for Chemistry, Air Chemistry Department, D-55128 Mainz, Germany.

[4]Centre for Ocean and Atmospheric Sciences School of Environmental Sciences, University of East Anglia, Norwich, UK

[5]Institute for Environmental Research and Sustainable Development, National Observatory of Athens, 15236, P. Penteli, Athens, Greece

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±3.3 nmol N m^{-3}) accounting for about 84% of the total dissolved nitrogen(TDN). Such ~~levels are~~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~~Sahara dust was also identified as a significant source of WSONin 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 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 & Me~~a~~skhidze, 2013). Marine aerosols consist of salts, organic matter and living organismsoriginatingmainly 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), 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 (Meskhidze &Nenes, 2006).

The amount and type of organic material in seawater varies with location and time~~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 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., 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).

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The chemical composition of organic nitrogen in the atmosphere ~~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~~ had 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 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~~refrigerator~~ (~~4^{0}C~~-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.

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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_3solution, 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~~freezer~~(4^0C) 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.

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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 (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 ~~marine~~ 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 (Williamset 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 42samples were collected on teflon filters from 29January 2005to 22December 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~~ 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 by overnight 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$_2$O$_4^{2-}$). Cations (Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, Ca^{2+}) were analyzed by using a CS12-SCcolumn 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 (~~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).

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

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

~~$nss\text{-}SO_4^{2-} = [SO_4^{2-}]_{total} - 2.0958*[Mg^{2+}]$~~

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

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

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 100^0-110^0C. 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~~colored azo dye. The intensity of the produced color is measured by a spectrophotometer at 543nm (Standard Methods for the Examination Water and Wastewater, 998).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 6.2nmol 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~~, denoting the important role of dust as aprimary source of organic nitrogenous~~. 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 ~~with~~ 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=0.5, 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 (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$_4^{2-}$.~~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 indicate marine origin although based on nss-Ca^{2+} levels, influence from continental sources (dust) cannot be totally ruled out (Fig. 3b). ~~The highest concentration of WSON was observed on 3th August (Fig.4), when the air mass back trajectory had marine origin (Fig. 3b).~~

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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 ~~The evaluationof biogenic activity as primary source of atmospheric organic~~

~~nitrogenous compounds was based on~~ DMS, since the last 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 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)"~~extremely low BC levels~~ 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., 2008a). ~~These samples presented high average contribution of WSON to TDN (84%), whichindicatesan important role ofthe marine biologicalactivity in the biogeochemical cycleof organic nitrogen~~. 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~~as remote marine area~~, 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).

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The fine mode WSON was found to ~~significantly~~ correlate significantly with fine mode MS^- (r^2=0.7, p<0.01, N=9) during austral summer, implying that part of WSON might have been produced secondarily from biogenic marine precursors ~~implying that probably part of WSONwas produced secondary from biogenic marine precursors~~, ~~following similarproduction 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~~ 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 ~~when~~ during which a relatively polluted marine atmosphere was affected by strong dust outbreaks from the Sahara desert~~affected the area~~.~~This enables the evaluationof the contribution of dustto the levels ofatmospheric 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. 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. ~~A significant source of c~~Coarse mode WSON in the northern hemisphere (NH)~~isthe~~was strongly associated withSaharan~~desert~~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).

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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~~; 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 the more than ten times higher concentration of WSON comparing with the remote marine areas of southern hemisphere (middle southern Atlantic & 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~~ 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 a ~~highlighting the~~significant role of marine productivity as a source of WSON in remote marine regions with significant biogenic activity.

Acknowledgments: The research project was financed by the EU projects OOMPH (FP6) and Perseus (FP7). The authors wish to thank Prof. C. Migon and an anonymous reviewer for their comments which allow us to improve the submitted version.

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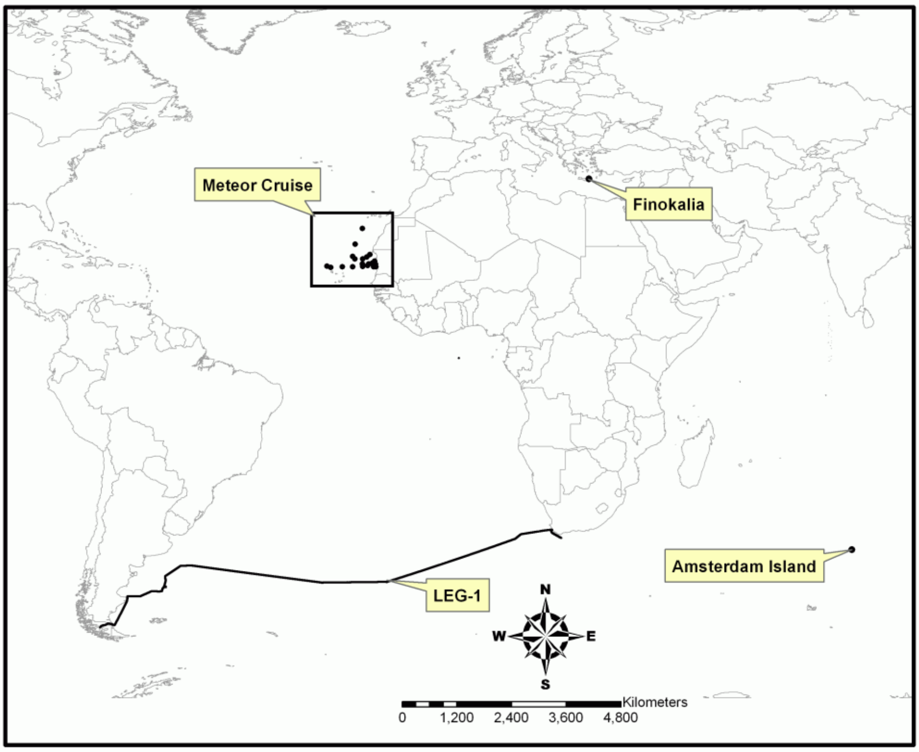

Fig. 1: Sampling sites around the world during this study. Finokalia station is used for comparison purposes.

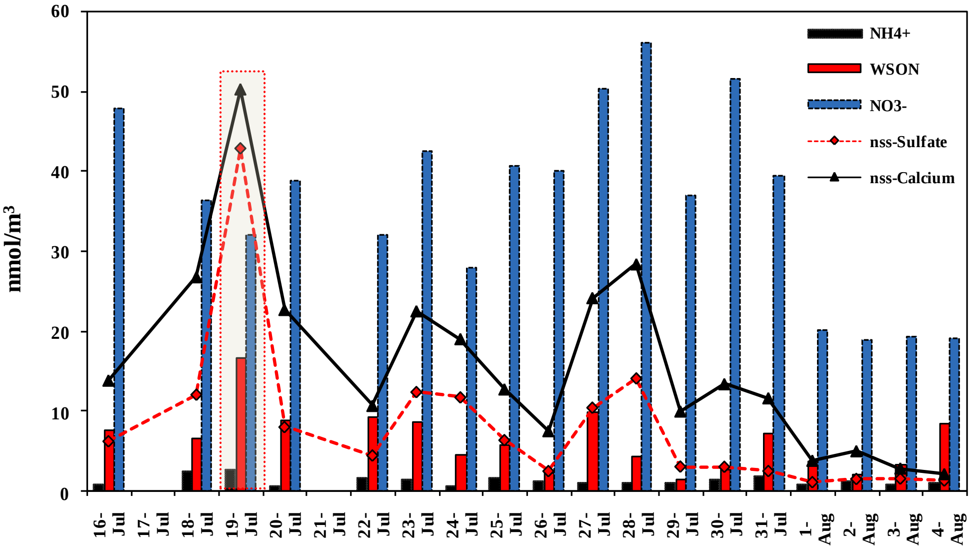

Fig. 2: Temporal variation of nitrogen species,nss-SO$_4^{2-}$ and nss-Ca^{2+}concentration in coarse particles (Da>2 µm)over the tropical North Atlantic atmosphere. The frame defines the air mass back trajectory with dust mixed with anthropogenic emission (19th July 2006).

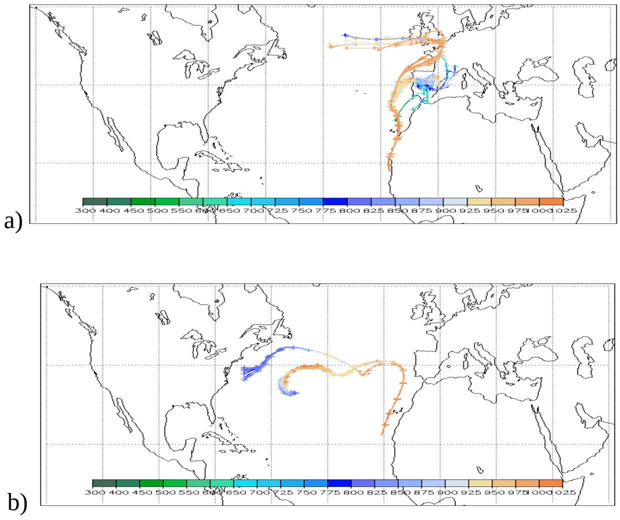

Fig. 3: Five day air mass back trajectories 19th July 2006 (a) and 3th August 2006 (b). The color indicates the pressure level (hPa).

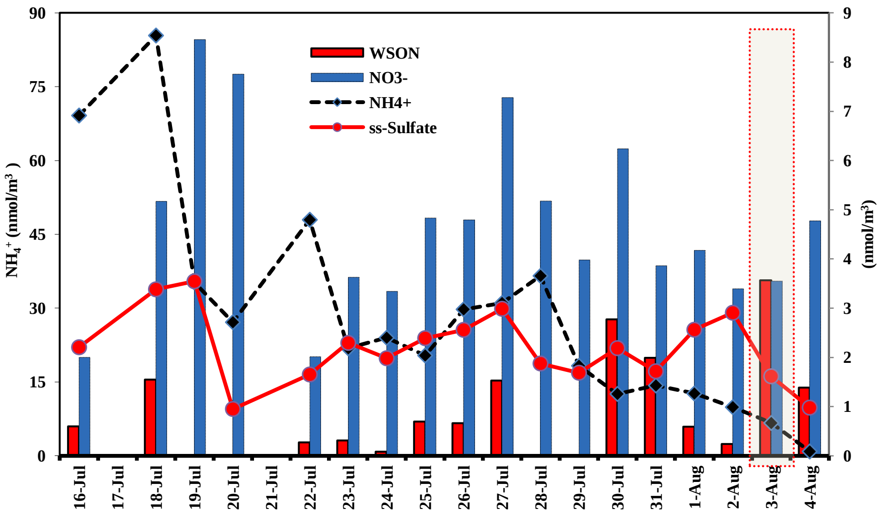

Fig. 4: Temporal variation of nitrogen species &ss-SO$_4^{2-}$, concentration in fine particles (Da<2 µm) over the tropical North Atlantic atmosphere. The frame defines the air mass back trajectory with pristine marine origin (3th August 2006).

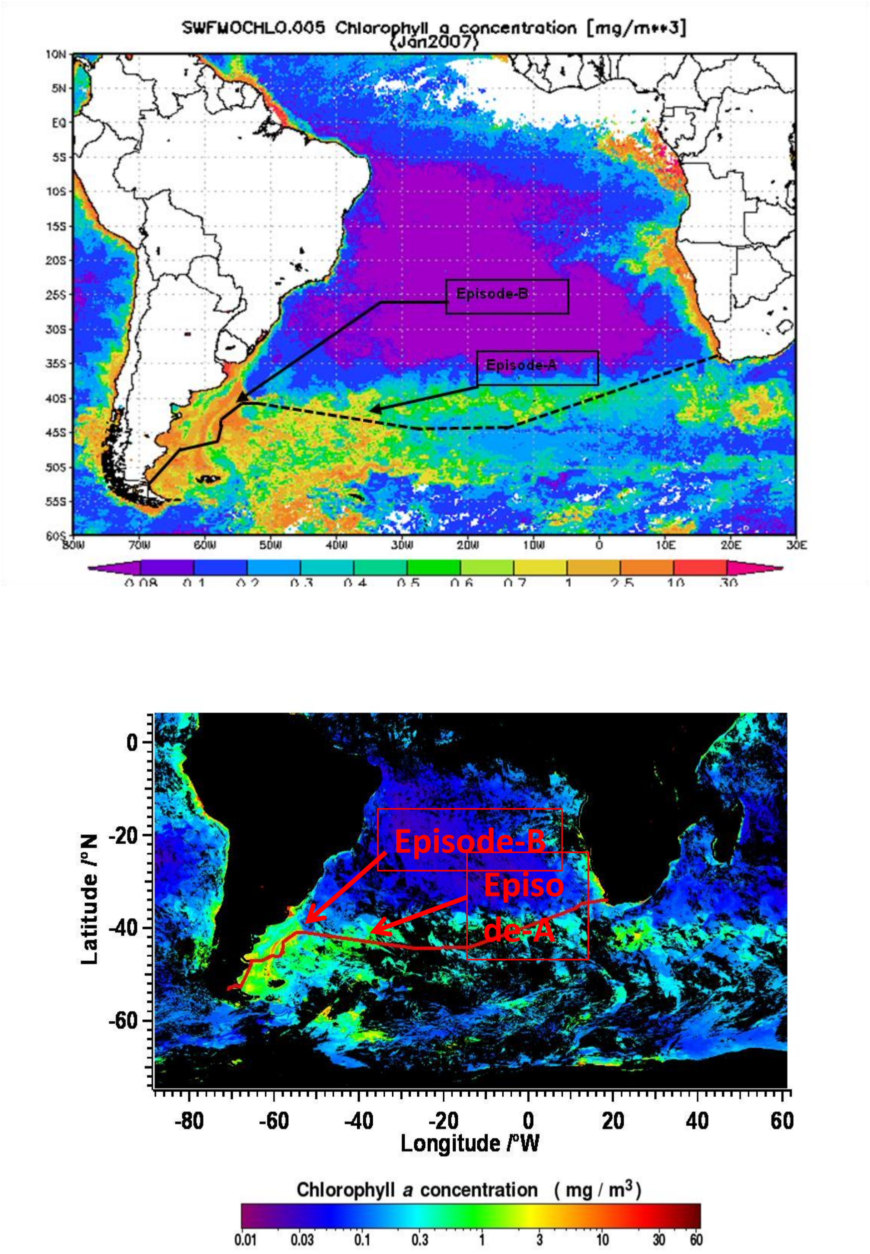

Fig. 5: Two distinct phytoplankton bloom episodes are presented in SeaWiFS chlorophyll-a map at South Atlantic Ocean during January 2007along with cruise track (http://disc.sci.gsfc.nasa.gov/giovanni).

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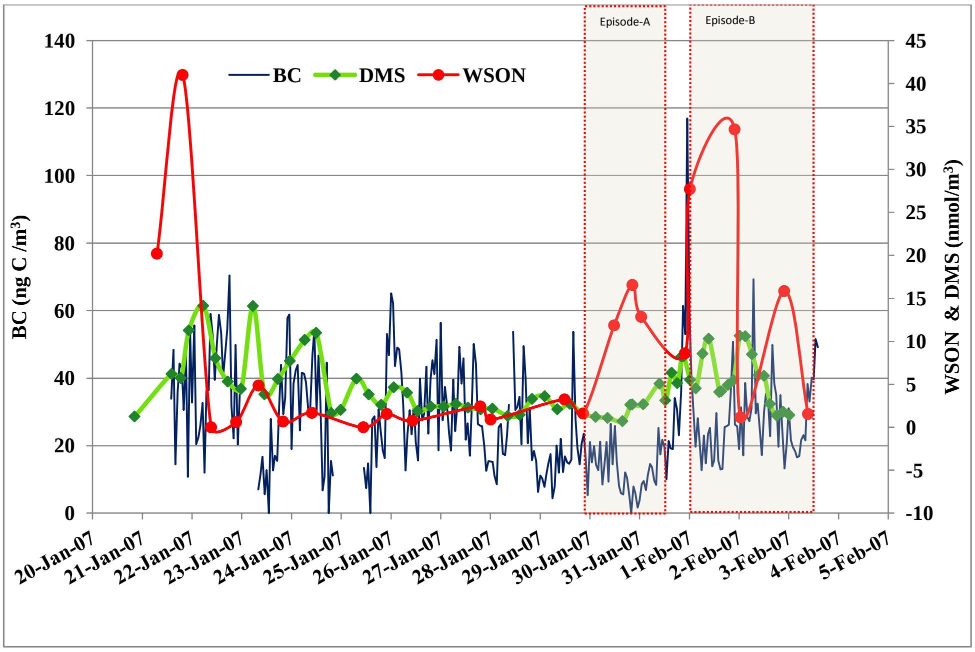
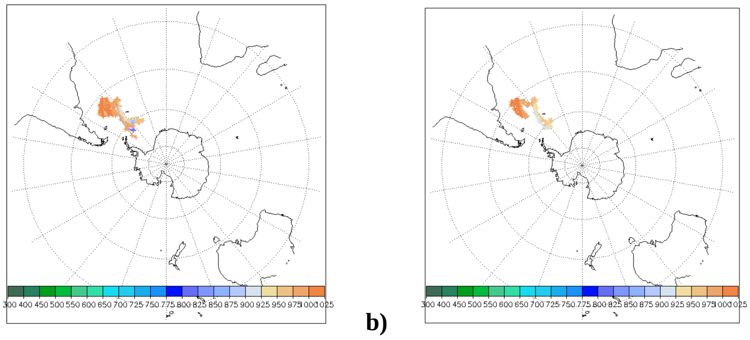


Fig. 6: Temporal variation of WSON and DMS concentration in fine particles ($PM_{2.5}$) together with BC concentration during the cruise in South Atlantic atmosphere. The frames define the marine areas with intense biogenic activity (Episode-A and -B).



a) b)

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

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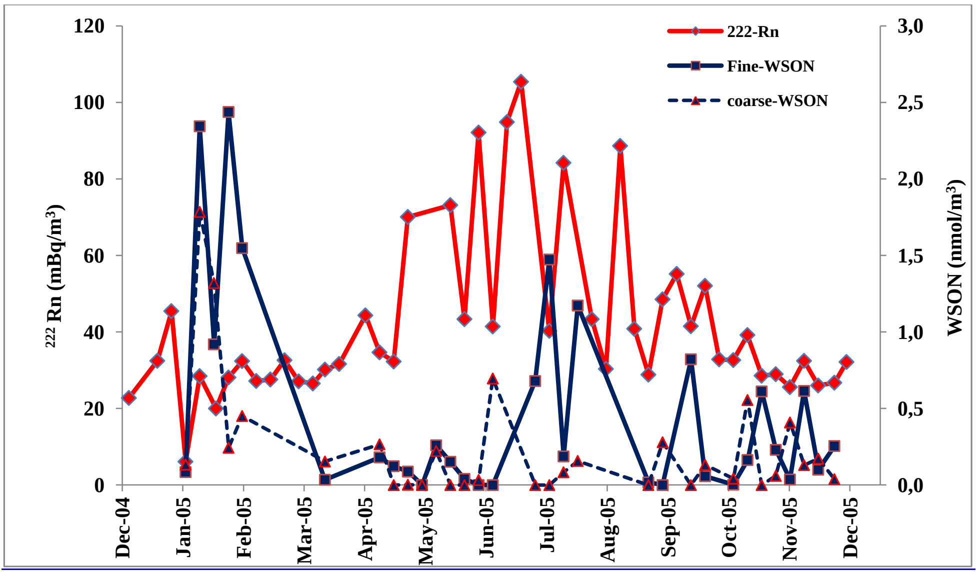

Fig.8: Seasonal variation of fine & coarse mode WSON with Radon at Amsterdam Island. Austral Summer is defined from December to April & winter from May to November.

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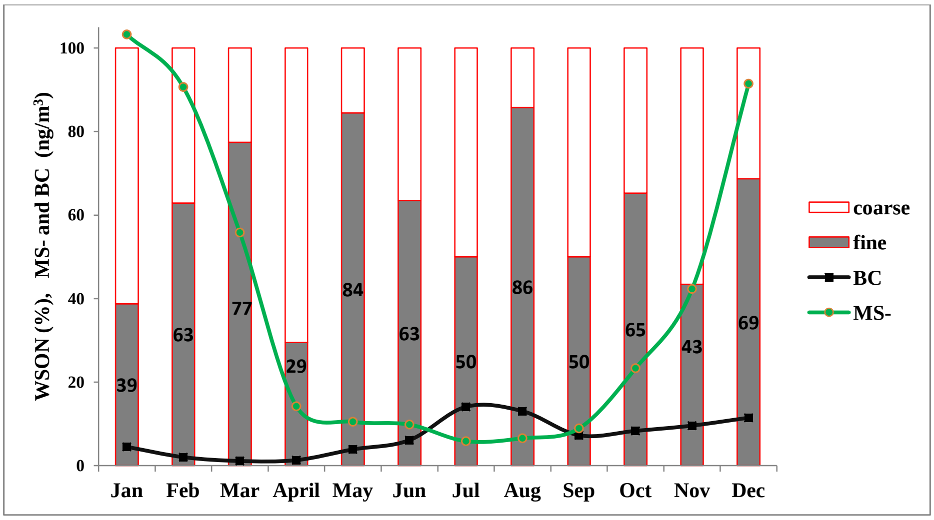
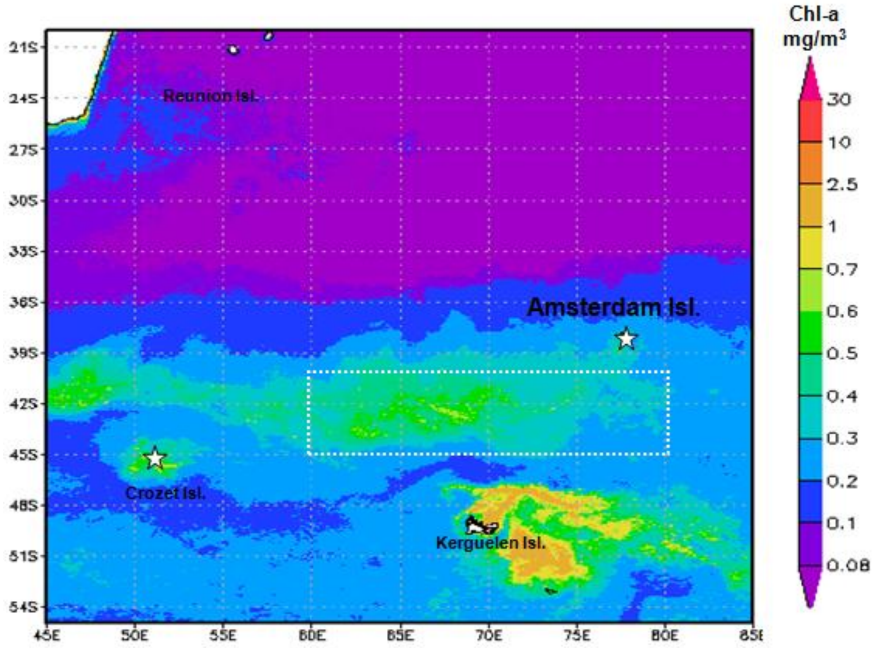


Fig.9: Average monthly concentration of bulk MS$^-$ and BC together with the percentage contribution of WSON in fine and coarse mode at Amsterdam Island (Indian Ocean) during 2005~~.~~



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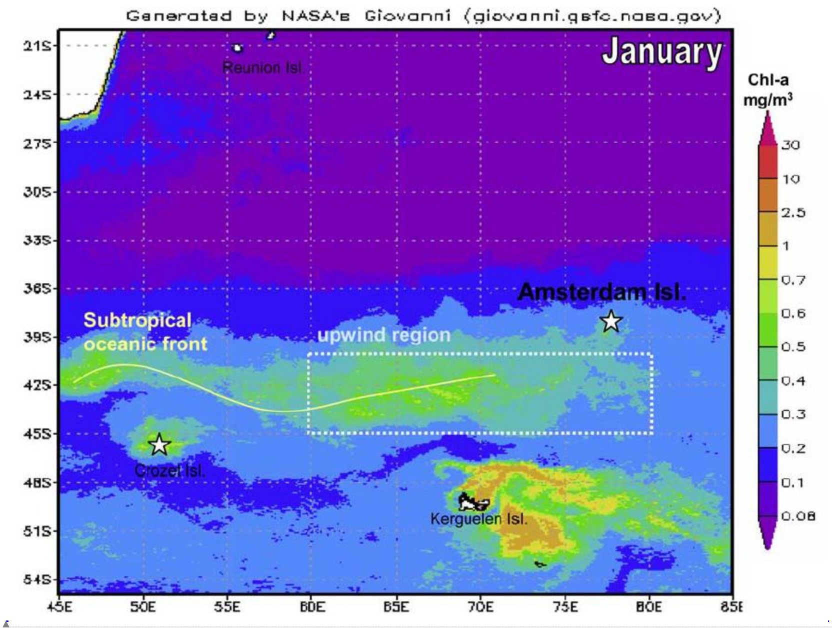

Fig.10: Chlorophyll map obtained for January (SEAWIFS data) for the Indian sector of the Austral Ocean. The white frame corresponded to the source region which contributes to the levels of marine organics at Amsterdam Island. ~~This high productive region stands for the oceanic fronts (subtropical &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

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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})	% to TDN	D_a(μm)	Coarse WSON (nmol N m^{-3})	% to TDN
				North 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
				South Hemisphere				
S. Atlantic Ocean	marine area with the highest Chl-a content	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

~~WSON (nmol N m^{-3})~~	~~Location~~	~~D(μm)~~	~~Fine~~	~~% to TDN~~	~~D(μm)~~	~~Coarse~~	~~% to TDN~~
			~~North Hemisphere~~				
~~E. Mediterranean~~*	~~Marine with anthropogenic influence~~	~~$PM_{1.3}$~~	~~11.6±14.0~~	~~13~~	~~$PM_{1.3-10}$~~	~~5.5±3.9~~	~~13~~
~~Tropic Atlantic Ocean~~	~~Marine with Sahara dust influence~~	~~D<2μm~~	~~0.9±1~~	~~5~~	~~D>2 μm~~	~~6.3±3.8~~	~~14~~
			~~South Hemisphere~~				
~~S. Atlantic Ocean~~	~~High Chl-a marine area~~	~~$PM_{2.5}$~~	~~11.3±3.3~~	84		-	-
~~middle S. Atlantic~~	~~Marine remote~~	~~$PM_{2.5}$~~	~~1.1±1.2~~	43		-	-
~~Indian Ocean (Amsterdam Isl.)~~	~~Marine remote~~	~~$PM_{2.5}$~~	~~0.8±1.4~~	32	~~$PM_{2.5-10}$~~	~~0.2±0.4~~	35

*Violaki andMihalopoulos (2010b)

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