Response to Anonymous Referee #2.

We would like to thank the reviewer for his/her suggestions and the time he/she spent on the manuscript and hoping that he/she will be satisfied with our answers.

His/her comments are shown below in italics (black for first round of review, blue for the second round). Our responses below are in black non-italicized font for the first round and red for the second.

All the other issues raised by the reviewer and satisfactory addressed during the first round (as noted by the word *ok* of the reviewer) are not repeated below.

General comments, round 2:

Although the authors made some valid clarifications, and did take my advice on toning down their certainty about whether the WSON has a marine source based on the evidencethey had, many of my main concerns were incompletely addressed, and so I suggestfurther revision before acceptance into *Biogeosciences*. If the authors cannot fullyaddress my concerns, then I will at that point suggest rejection.As a quick side note for the authors: if they are not aware of it already, they might beinterested in the following recently published paper I recently became aware of, whichmight be of relevance to their work:

Altieri,K.E.,M.G.Hastings,A.J.Peters,S.Oleynik,andD.M.Sigman(2014),Isotopicevidenceforamarineammoniumsourceinrainwateratbermuda,GlobalBiogeochem.Cycles,28,10661080,doi:10.1002/2014GB004809.

The suggested reference was added in the revised version in the line 36.

Specific comments: *The most important comments are regarding the marine WSON source hypothesis. At all3 sites I find that the evidence provided for the marine WSON source hypothesis needsmore support to be valid.Tropical N. Atlantic: p. 11370, line 4: The two final statements in this section need moreevidence: a) "Marine sources seem to control the fine mode WSON concentration levels,since significant correlation of WSON was found with ss-SO42- (r2= 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), Iremind the authors that correlation does not equal causation, so perhaps a betterwording would be something like, "high ss-SO4 values were associated with high WSONvalues (r2=. . .)". But even if the wording is changed, I still don't think one can reallysay that marine sources control the fine mode WSON at this site based only on theWSON/ss-SO4 association. First, a correlation of 0.6 still typically incorporates a greatdeal of variability. Secondly, the sample size is relatively small (n=15). Thirdly,assessments based on correlation coefficients alone can sometimes lead to falseassociations due to outliers. For this third reason, the r2values by themselves are notparticularly useful for the reader. Therefore, if the authors want to discuss theassociation between WSON and ss-SO4, I suggest adding a new figure showing theactual data the correlation is based on.Finally, and most importantly, because correlation does not equal causation, it isimportant to show that other data sources were closely monitored to rule out otherWSON 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 tomake a compelling case for a large marine WSON source, particularly their hypothesisseems to directly contradict others studies that found low total WSON on clean marinedays, 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 AmsterdamIsland, where WSON was low even though upwind Chl a concentrations were stillrelatively high).*

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

I understand that this is all the data the authors may have, but if correlation is all the authors have to draw conclusions from, then the correct amount of caution must be applied when interpreting the data to avoid misleading readers. In the first review I suggested repeatedly that they plot the data, which gives people an idea of what degree of influence outliers may have, but that was not done.

Regarding the plots we are sorry to say that as the reviewer requested the correlations were plotted separately in supplement material which has been uploaded together with the revised version on the 25th of November 2014. Thus almost all the information requested was already available. Supplementary material has been updated and also included in this round of answers.

I also suggested that they 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, which would make using the correlations more valid. That was also not done satisfactorily, see point below.

This issue was addressed below.

The sentence “Marine sources seem to control the fine mode WSON concentration levels, since significant correlation of WSON was found with ss-SO$_4^{2-}$ (r2=0.6,p<0.001, n=15) was replaced with the phrase: “Marine sources seem to contribute tothe fine mode WSON concentration levels, since high ss-SO$_4^{2-}$ values were associated with high WSON values (r2=0.6, p<0.001, n=14). Insignificant correlations were found between fine mode WSON and continental traces such as nss-Ca2+and nss-SO42-."

This change is mostly satisfactory (pending that outliers did not drive the already somewhat poor correlation, again please show the data), but just saying that there were insignificant correlations between nssCa2+ and nssSO4 is not as helpful as saying what these concentrations actually were, and putting those concentrations in context of what one would expect in clean marine conditions.

As the reviewer can see in the revised version of the 25th of November the discussion on the regression between WSON and ss-SO$_4^{-2}$ was removed. We believe that this point caused confusion and therefore we decided to delete it. Unfortunately we forgot to underline this in the answers for the reviewer during the first round. We are really sorry about that confusion.

The plots of WSON with nss-SO$_4^{-2}$ and nss-Ca^{2+} are now added to the revised supplement material (Fig.S3 & S4).

Line 221: The following sentence was inserted following his/her suggestion: "The average concentration for coarse mode nss-Ca^{2+}and nss-SO$_4^{2-}$ were 15.9±11.9 nmol m^{-3} (median 13.0 nmol m^{-3}) and 8.1±9.7 nmol m^{-3} (median 5.4 nmol m^{-3}), respectively."

Line 223:

The sentence : "The highest concentrations of nss-Ca^{2+}, nss-SO$_4^{2-}$ and WSON were observed on the same day (19th July, Fig. 2)." was replaced by the sentence :" The highest concentrations of nss-Ca^{2+}(50.3 nmol m^{-3}), nss-SO$_4^{2-}$ (42.8 nmol m^{-3}) and WSON (16.6 nmol m^{-3}) were observed on the same day (19th July, Fig. 2)."

Line 235:The following sentence was inserted: "The average concentration for fine mode nss-Ca^{2+}and nss-SO$_4^{2-}$ were 5.9±4.3 nmol m^{-3} (median 4.8nmol m^{-3}) and 32.8±15.8 nmol m^{-3} (median 28.6nmol m^{-3}), respectively."

“Traces” should be changed to “tracers”.

Line 235: "traces" was corrected to "tracers".

For statement b), I would not call that trajectory “purely marine” because it goes rightby the coast of Africa where dust storms routinely blow and where pollution fromnorthern Africa and Europe frequently mix in. In fact, when I looked at the AOD, truecolor, and CALIPSO aerosol subtypes for that day, it seems that there was a great deal ofdust 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 castsstrong doubt on whether this was truly an example of a "purely marine" day and so thisargument should not be used to support the hypothesis of a marine WSON source. If thissample, which the authors said was the sample with the highest concentration of WSON,was removed from the WSON-ssSO42- plot because of the likely interference from highdust concentrations, what would the resulting r and p value be?

Indeed in Figures 1-3 in the supplement attached by the reviewer it seems that therewas dust in the atmosphere during the sample collection. Although, this dust eventseems 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 samplingperiod. Note that we were very cautious in our interpretation and we never used theword "purely marine" in this section. The sentence was replaced by this "The highestconcentration of WSON was observed on 3 August (Fig. 4), when the air mass backtrajectory indicate marine origin although influence from continental sources (dust)cannot be totally ruled out (Fig. 3b).

The authors have a good point that a coarse mode nss-Ca+ concentration of ~3nmol/m3 is relatively small compared to what one would expect if dust were asubstantial component. Out of curiosity, what was the filter color for that day? Ifreddish-tan dust was not visually apparent on the filter, that would be anotherway to strengthen the argument that dust was not present in high concentrations.

We cannot recall the color of the filter and unfortunately we have not taken any pictures of it after the sampling. All the filter was used for chemical analysis and therefore we cannot address the question, however the levels of nss-Ca^{2+} reported in the manuscript are very good indicators of dust amount.

One way or another, in the revised sentence above, I'd change "(dust)" to (e.g.,dust), because some influence of other aerosol sources cannot be ruled out either.

Line 239: Following reviewer's suggestion the word was changed accordingly.

The authors did not answer my question of how the WSON-ssSO4 plot would look if this anomalous data point were removed because of possible interference from dust concentrations. I wish this had been done, as it would have made it easier for me to evaluate the strength of their argument.

This point was addressed above.

South Atlantic: p. 11371, l. 3: "When the ship crossed the episode- A area (Fig. 6), airmasses had pure marine origin with extremely low BC levels....." First, there was noclear definition for how a sample was determined to be "pure marine," so it is importantto define that in the methods section.As far as I can tell though, in the South Atlantic a "pure marine" sample was definedfrom a combination of back trajectories, BC concentrations, and DMS levels, and at theother two sites, "pure marine" was defined only back trajectories. At minimum, thatinconsistency should be noted and discussed. However, for the following reasons, I don'tthink the authors really have the basis to define air masses "pure marine" based on theircurrent criteria anyway, and I strongly suggest rewording the sections that contain thisphrase.

We agree with reviewer's commend "there was no clear definition for how a samplewas determined to be "pure marine". In his work in Science, Andreae et al., (2007)suggested that, "Aerosol concentrations approaching pristine conditions are mostlyfound over the oceans, especially in the Southern Hemisphere, where large expansesof open ocean and a low density of population and industry contribute to keeping thehuman impact at minimum. The natural aerosol over these remote ocean regionsconsists mainly of a mixture of sea salt particles, organics, and sulfates from the oxidation of biogenic dimethylsulfide; some mineral dust and smoke from wildfiresmay also be present". The text with the reference was inserted in the manuscript.For Amsterdam Island the definition of “pure marine” is not based only ontrajectories but also on the extremely low levels of anthropogenic tracers such as BCand CO measured there (See also in the manuscript; page 11366, line 8-12). “Thepristine marine conditions prevailing at Amsterdam Island and the very low level oflocal contamination from the scientific base have been documented for manyatmospheric compounds such as CO, hydrocarbons, radon, black carbon and totalaerosol number concentration (Williams et al., 2001, Sciare et al., 2009).” Finally aswe understand that definition of “pure marine” is a subtle issue for this reason thephrase “pure marine” was replaced by the phrase “pristine oceanic”

Perhaps I should clarify. I was hoping the authors could clearly state the quantitative values of BC, CO, etc. used to call an air mass “pure marine” for each site, and since the data for this classification was not consistent between sites, it would have been good if authors had actually discussed what the differences were in the text and how that might influence the results.

That was great idea, however only for BC data have been simultaneously collected at all sites.

The average concentration of BC observed during the South Atlantic cruise was 27.2±15.7 ng/m^3. (See page 11, line: 262)

At Amsterdam Island we recorded BC average concentration of 8.8 ng/m^3 during the winter period and 4.1 ng/m^3 during the summer one. These values are extremely low when comparing with the observed values in the Mediterranean (about 268±175 ng/m^3, Koulouri et al., 2008) while the values observed at Amsterdam Island during summer are among the lowest reported in the literature. The above part was inserted in the manuscript (see page 12, lines 300-304).

During Meteor campaign fine mode (<2 μm) BC values were 174.4±154.4 ng/m^3, while for coarse mode values below d.l were obtained (W. Maenhaut personal communication)

The above quote from Andreae et al. (2007), which essentially says that clean conditions are often, but not always, found in the S. Hemisphere, does not clarify the methods, nor does changing the term “pure marine” to “pristine oceanic”. The original sentence (page 11366, line 8-12) that the authors point back to in their response is generally helpful for the one site it relates to (Amsterdam Island), but it still does not provide quantitative information for any of the sites.

This issue on quantitative information was addressed above by adding the BC values in the manuscript. We believe that the concentrations of BC observed during the three campaigns clearly show the transition from the continentally influenced atmosphere (Tropical Atlantic) to a “clean” atmosphere (S. Atlantic and Amsterdam Island).

In the manuscript there are references which provide further information for the readers, who may interested for more details.

Regarding the terms “pure” and “pristine”: both imply that there were no other aerosol sources other than marine. The authors should either prove they had a good way to ensure that these terms are accurate, or find a more suitable description for the air masses being described.

We believe that the discussion on the BC values is helpful, regarding the discrimination between continentally influenced atmosphere and clean/remote atmosphere. The distinction between “pure marine” and “pristine oceanic” continuous to be a subtle issue. For this reason the phrase “pure marine” and/or “pristine oceanic” was replaced by the phrase “marine" or “remote marine". This issue is beyond of the scope of this paper. As it is outlined through the lines 68-71 the scientific purpose of the present study is to provide new data for WSON acquired during oceanographic cruises in the Atlantic Ocean as well as via the yearly sampling in the Indian Ocean, contributing thus to the global picture of WSON distribution.

While using BC as a tracer is helpful, it must be used in combination with othercomponents before calling an air mass “pure marine”. For example, dust is known tooccur 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 concentrationswere 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 overproductive marine DMS sources, they don't tell one what other sources of WSON mightbe in the air mass concurrently.*

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

I don't see how this issue was addressed above- pure marine means the samething as pristine oceanic, and the reader is still left not knowing whether dust could have influenced the sample. One way they could address this concern is by looking at satellite or lidar observations, or qualitatively observing filter color, or providing nss-Ca concentrations if they are available, for example. Alternatively,if none of those options are available or acceptable to the authors, they canchange the wording from pristine oceanic to something less specific.

Lidar data are not available during the cruise. Satellite observations are useful but they give an idea of the total aerosol column amount and not of what is happening in the boundary layer and sometimes can give misleading info when dust is transported aloft (3-4 Km) and thus not influencing the BL. During this study we reported nss-Ca^{2+} data and in combination with BC the presence of anthropogenic (BC) and soil sources can be appointed. The average concentration of nss-Ca^{2+} for PM$_{2.5}$ particles during the high WSON levels period (30-31/1) during the South Atlantic cruise was 1.4 nmol m^{-3}, during the tropical Atlantic cruise 5.9 nmol m^{-3} (for particles with diameter less than 2 μm), while in Amsterdam Island only 0.3 nmol m^{-3} i.e a factor of 10 or more lower than that observed in Atlantic.

South Atlantic: p. 11371, l. 3: "When the ship crossed the episode- A area (Fig. 6), airmasses had pure marine origin with extremely low BC levels and the measured WSONaverage concentration was 11.3 ± 3.3 nmol N m-3. These samples presented highaverage contribution of WSON to TDN (84 %), which indicates an important role of the marine biological activity in the biogeochemical cycle of organic nitrogen." Because theauthors 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 notsome 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 couldindicate an important role of the marine biological activity in the biogeochemical cycle of organic nitrogen"

Ok, but why not discuss other possible sources? If BC is low, maybe you could check if dust is observable by satellite? If not, that might provide further substantiation for your hypothesis.

See discussion above on nss-Ca^{2+} and satellite data. The average concentration of nss-Ca^{2+} for PM$_{2.5}$ particles during that period was 1.4 nmol m^{-3}, while during Meteor cruise was 5.9 nmol m^{-3} (for particles with diameter less than 2 μm). On the other hand the concentration of WSON was 11.3 ± 3.3 and 0.9±1nmol N m-3 , respectively (See table 1). Thus neither dust nor combustion can account for the high levels of fine mode WSON observed during the S. Atlantic cruise.

South Atlantic: p. 11371, l. 8 and Table 1: "For the samples collected over the middlesouthern Atlantic atmosphere, which is considered as remote marine area, the averageconcentration 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 islow, DMS concentrations were equally high (e.g., from Jan 23-25) as the DMS levelswhen WSON levels were high (in the 11.3 ± 3.3 nmol N m-3 range). This informationcasts doubt on the marine WSON source hypothesis.

We already addressed the concerns of the reviewer in the questions above. Note thatduring this study as influence from remote marine area is considered the period from26-29 Jan (n=4). The DMS was low during that period (Fig.6), so the phrase "whichis considered as remote marine area" was replaced by the phrase "which is consideredas remote marine area, with low biogenic activity".

Ok, but the authors should clarify in the text that only these specific days were considered, and they should say why they only considered this subset.

All this information is now given in the Table 1. Moreover, additional details are given in lines 252-257 and 556-559 (Fig.5).

I am curious as to why days previous to January 26 were not considered.

Based on air mass trajectories, influence from the continent was observed during most of time before January 26.

It would also be nice if they could point out this "remote marine area, with low biogenicactivity" in Figure 5 as suggested in the my first review.

Following reviewer's suggestion the Fig.5 was changed accordingly.

Can the authors look at satellite data from this time period to see if there were otherrecognizable WSON sources during the episode A period?

The authors did not address this question and did not say why they did not.

See discussion on satellite data above. As said we are not sure if satellites can provide more information than the chemical analysis presented here.

I am also unclear about which days were binned into "S. Atlantic Ocean, High Chla 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 ineach period,

This was done, and is ok

b) indicate on Figure 5 where remote vs. non-remote days were located,

This suggestion was not addressed, and the authors gave no reason for not doingso.

Following reviewer's suggestion the Fig. 5 and its caption were changed accordingly.

and c) explain the criteria for this binning. Based on Fig. 5, much of the cruise took placein high Chl a regions, and so I am unsure why the authors separated out "High Chla"and "remote" periods, and I also think the term "High Chl a" in Table 1 might be a bitmisleading. An alternative wording could be "Highest Chl a period"?

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.

If the discrimination was based on the concentration levels of DMS and not on the levels of Chl-a, then why were the two periods described in the new Table 1 as"marine remote" and "marine area with highest Chl a period"?

There is a clarification in the text (Lines 258-260), while further explanation was added in Table 1.

Can the authors please actually specify that "discrimination was based on the concentration levels of DMS and not on the levels of Chl-a" in the text and specifically describe what DMS concentration cutoffs were used to discriminate between "marine remote"and "marine area with highest Chl a period" in Table 1? I find this wording confusing, and probably some other readers will be confused as well unless this is clarified.

This issue was addressed above.

Regarding the beginning, how did the authors deal with days with low WSON but high DMS- were these days included or excluded, and why?

This point was not satisfactorily addressed

The reviewer noticed 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).*"

As it was also indicated above during the period mentioned by the reviewer the ship was under continental influence. The observed WSON values were included only for the estimation of the average WSON concentration given in the manuscript for the whole sampling period and they were excluded from the discussion since in this study we focus on the role of remote marine atmosphere without continental influence.

Amsterdam Island: p. 11372, l. 18: "Significant correlation was also found between coarse modeMS and coarse mode WSON (r2 = 0.9, p < 0.0001, N = 10) during summer period." Based onthe detection limits (DL) listed in the methods, it seems that the DL for WSON should be greaterthan _0.64 nmol N/m3 (as _0.64 nmol N/m3appears to be the DL for TDN). That excludes all but2 of the coarse sample valuesduring the summer period as best I can tell based on Fig. 8.Therefore I think anycorrelations with MS for these samples are probably not valid. Plus, inFigure 8, I onlysee 6 samples of coarse WSON during the austral summer. Perhaps the symbolsarehidden and there are more samples than I can discern (in which case the authorsshouldchange Fig. 8 so that they are more visible), but either way please checkconsistency here asN=10 was listed in the text.text.

We agree with the reviewer's comments and the discrimination between summer andwinter was better clarified in the figure 8 to better indicate the number of samples.

The figure is much clearer now, although there are a few points that are difficultto tell whether they are summer or winter, because the authors use Dec. 5 an May5 as x axis markers, instead of Dec. 1 and May 1, which is where the delineationthey are using begins.

The x-axis represents the months of the year 2005 and not the dates of each month.

On the other hand, there is no real detection limit for WSON as TDN and theinorganic species were always present in our samples in significant amounts. It isclear that the correlation is based on a number of points with low WSON but we don'tsee how this can invalidate the relation between MS and WSON.

It is not true that "there is no real detection limit for WSON." Since WSON=TDN-inorganic N, their detection limit is at least the maximum of the detectionlimit of TDN (~0.64 nmol N/m3) or inorganic N, but common practice would be todetermine the detection limit of a derived property as the square root of the detection limits of it's components: $((DLTDN)^2+(DL\ inorganic\ N)^2)^{0.5}$*, which would make the DL of WSON larger than that of just that of TDN alone. In Fig. 8,WSON concentrations are very low (nearly always <1 nmol/m3, near the likely detection limits). Clearly, trying to get a correlation from values below their detection limits is invalid. And their point that most of the TDN is from inorganics makes it even more clear that one would expect there to be a large error in determining WSON correctly, as the majority of the TDN signal would benot from WSON but from inorganic N.*

Following reviewer's suggestion an indirect estimation of WSON detection limit was done based on the dl of TDN (24ppb) and Inorganic Nitrogen (0.7ppb and 0.5ppb in Nitrogen for NO_3^- & NH_4+, respectively). These calculations give 24 ppb, which for the given volume of air sampled results in 0.06 nmol N /m^3. Based on WSON dl, only one value in coarse WSON (0.05nmol/m^3) is below the dl. and was removed from the regressions.

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.

They did not plot the data, so I cannot evaluate the statement

Regarding plots we are sorry to say that as the reviewer requested the correlations were plotted separately in a supplement material which has been uploaded together with the revised version on the 25th of November 2014. Thus WSON- MSA plot was existing at the supplementary material.

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

Yes, but what about during your study in particular? A climatology, as in Milleret al., is not always representative of sampling conditions during the study.

Air masses origin during the studied period (2005) was in agreement with the climatology of the area. Thus 2005 was not an exceptional year.

There still seems to be relatively high chlorophyll a upwind, so the low WSON seems toconflict with the suggestion that local marine sources are a large or dominant source ofWSON in the S. Atlantic.

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

But if that is the case, what makes DMS so different? DMS is not a direct sourceof WSON, but you use that as an indicator in other sites?

We don't claim that DMS is a direct source of WSON and unfortunately DMS was not measured at all locations. However, the similar pattern observed between WSON and DMS in S. Atlantic as well as between WSON and MSA (oxidation product of DMS) at Amsterdam Isl. points for a possible common source (phytoplankton) between WSON and DMS. Nevertheless, more data are needed to validate this statement.

Other suggestions/comments (in no particular order) are listed as follows:p. 11370, l. 11: "Two main episodes of phytoplankton blooms were encountered duringthe 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 bythe ship over two days (30–31 January) and the episode-B began on 1 February and wasfollowed until the end of the cruise." First, I am unclear about why the authorsdifferentiated between episodes in the first place. The first episode was said to occur fromJan. 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.

Please state this in the text.

This is clearly stated through the lines 254-257.

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 NO3-or NH4+

Please clarify that in the text. Also, just because there is not correlation of WSON with NO3 or NH4 does not mean that they have different sources if their losseswere at different rates (e.g., adsorption to or chemical reaction with largerparticles).

Following reviewer suggestion in section page 9 line 215 the phrase "No correlation was found with inorganic nitrogen, indicating different sources." was replaced by "No correlation was found with inorganic nitrogen (NO_3^- or NH_4^+), indicating either different sources and/or their losses were at different rates (e.g., adsorption to or chemical reaction with larger particles)"

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

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Abstract

To obtain a comprehensive picture on the spatial distribution of water soluble organic nitrogen (WSON) in marine aerosols, samples were collected during research cruises in the tropical and south Atlantic Ocean and also over the southern Indian Ocean (Amsterdam island) for one year period (2005). Samples have been analyzed for both organic and inorganic forms of nitrogen and the factors controlling their levels have been examined. Fine mode WSON was found to play a significant role in the remote marine atmosphere with enhanced biogenic activity, with concentrations of WSON (11.3±3.3 nmol N m^{-3}) accounting for about 84% of the total dissolved nitrogen (TDN). Such concentrations are similar to those observed in the polluted marine atmosphere of the eastern Mediterranean (11.6±14.0 nmol N m^{-3}). Anthropogenic activities were found to be an important source of atmospheric WSON as evidenced by the ten times higher levels in the northern hemisphere (NH) than in the remote southern hemisphere (SH). Furthermore, the higher contribution of fine mode WSON to TDN (~~40~~51%) in the SH, compared to the NH (~~20~~13%), underlines the important

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

1. Introduction

The ocean/atmosphere biogeochemical interactions are important in regulating atmospheric composition, marine ecosystem functioning and the Earth's climate. Oceans 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 & Meskhidze, 2013). Marine aerosols consist of salts, organic matter and living organisms originating mainly from plankton, bacteria or other microorganisms (Monahan et al., 1983), while their organic/inorganic fraction depends strongly on the biological activity of the ocean (O’ Dowd et al., 2004; Altieri et al., 2015).

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

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

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

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

2. Sample collection and chemical analysis

2.1. Sampling sites and collection

2.1.1 Tropical North Atlantic Ocean

Within the framework of OOMPH project (Organics over the Ocean Modifying Particles in both Hemispheres), 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 450^0C for 5h. Samples were stored at the ship in the freezer (-20°C) till the laboratory analysis. In the lab quartz filters were extracted with 20 mL Milli-Q water for 45 min in ultrasonic bath. Prior to analysis, the extracts were filtered through polyethersulfone membrane (PES) filters (0.45 µm pore size diameter) to remove suspended particles. $CHCl_3$ was added as biocide and then the extracts were preserved at -18^0C. All analyses have been performed within a month after collection.

2.1.2 South Atlantic ocean

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

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

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

During this cruise only fine particles were collected ($PM_{2.5}$) on Teflon filters (n=23) on a 12h-basis from 21th January to 5th February 2007. Samples were stored at the ship in the refrigerator (4^0C) 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.

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

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

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

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

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

To assess possible continental influence, radon (^{222}Rn) was monitored on a 2-hour basis by measuring the decrease of the alpha radioactivity of atmospheric aerosols collected on filters. The measurement has precision of 2% and has been described in details by Polian et al. (1986).

2.2. Chemical analysis

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

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

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

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

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

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

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

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

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

2.3 Air Mass Back trajectory Analysis

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

3. Results and Discussion

3.1. Tropical Atlantic Atmosphere

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

Almost 86% of WSON was found in the coarse mode atmospheric particles. Mace et al., (2003) presented the hypothesis that dust WSON might actually come mostly from adsorbed pollution and this hypothesis has since been supported by subsequent studies (e.g., Violaki et al., 2010b, Zamora et al., 2011; Wang et al., 2013). No correlation was found with inorganic nitrogen (NO_3^- or NH_4^+), indicating either different sources and/or their losses were at different rates (e.g., adsorption to or chemical reaction with larger particles)" ~~No correlation was found between WSON and inorganic nitrogen (NO_3^- and NH_4^+), indicating different sources.~~ A significant correlation between WSON and nss-Ca^{2+} ($r^2=0.5$, $p<0.005$, $n=18$) confirms the continental transport of organic nitrogen by dust. WSON correlates also with nss-SO_4^{2-} ($r^2=0.6$, $p<0.0005$, $n=18$), indicating significant anthropogenic contribution to the WSON pool (see supplementary material Fig. S1 & S2). During the cruise the average concentration for coarse mode nss-Ca^{2+} and nss-SO_4^{2-} were 15.9±11.9 nmol m^{-3} (median 13.0 nmol m^{-3}) and 8.1±9.7 nmol m^{-3} (median 5.4 nmol m^{-3}), respectively. The highest concentrations of nss-Ca^{2+} (50.3 nmol m^{-3}), nss-SO_4^{2-} (42.8 nmol m^{-3}) and WSON (16.6 nmol m^{-3}) were observed on the same day (19th July, Fig. 2)."~~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 tracers such as nss-Ca^{2+} and nss-SO_4^{2-}~~.~~ (see supplementary material Fig. S3 & S4). The average concentration for fine mode nss-Ca^{2+} and nss-SO_4^{2-} were 5.9±4.3 nmol m^{-3} (median 4.8 nmol m^{-3}) and 32.8±15.8 nmol m^{-3}(median 28.6 nmol m^{-3}), respectively. The highest concentration

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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 (5,6 nmol m^{-3})~~,~~ influence from continental sources (e.g., dust) cannot be totally ruled out (Fig. 3b).

3.2. Southern Atlantic Atmosphere

The cruise was performed in the temperate waters of the Atlantic Ocean during the early austral summer, when biogenic marine activity was at maximum (Meskhidze and Nenes, 2006). Two main episodes of phytoplankton blooms were encountered during the sampling period. These are clearly seen in Fig. 5, which depicts the chlorophyll-a map derived from SeaWiFS satellite retrievals (http://disc.sci.gsfc.nasa.gov/giovanni) and referred to monthly average values (January 2007). The episode-A encountered by the ship over two days (30-31 January) 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} (n=23) 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} (n=23)~~.~~

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

The phytoplanktonic activity as possible source of atmospheric organic nitrogenous compounds was based on DMS, since the last could be considered as an indicator of marine phytoplanktonic activity (Sciare et al., 1999). When the ship crossed the episode-A area (Fig. 6), air masses had ~~marine origin with~~ lower BC levels (11.1±15.7 ng/m^3) compared to the average concentration observed during the sampling period (27.2±15.7 ng/m^3), low levels of nss-Ca^{2+} (1.4

nmol m^{-3}) considered as tracer of continental influence, ~~and~~ while the measured WSON average concentration was 11.3±3.3 nmol N m^{-3}. These samples presented high average contribution of WSON to TDN (84 %), which could indicate an important role of the marine biological activity in the biogeochemical cycle of organic nitrogen (Facchini et al., 2008). For the samples collected over the middle southern Atlantic atmosphere (26-29 Jan, n=5), which is considered as remote marine area, with low biogenic activity (Fig. 5), the average concentration of WSON was much lower (1.3~~1~~±0~~1~~.8~~2~~ nmol N m^{-3}, n=5~~)~~ corresponding to ~~43~~51% 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. As reported by Sciare et al. (2009) the meteorological regime at Amsterdam Island supports the long range transport of air masses from Southern Africa and Madagascar during winter, affecting the atmospheric composition of the area, especially with emissions from combustion processes (fossil fuel and mainly biomass burning). The simultaneous increase of average monthly concentrations of BC and Radon during austral winter (Fig. 9), starting from May and maximizing in July and August (Fig. 8) confirmed the continental influence from Africa. During that season the intense biomass burning episodes occurred in Africa releasing fine mode aerosols including WSON, which were subsequently transported to the marine atmosphere of Amsterdam Island (Sciare et al. 2009). At Amsterdam Island we recorded BC average concentration of 8.8 ng/m3 during the winter period and 4.1 ng/m3 during the summer one which are among the lowest reported in the literature. The very low levels of BC at Amsterdam Island (especially in summer) in conjunction with the very low nss-Ca^{2+} values (0.3 nmol m^{-3}) highlights the very limited contribution of continental sources (combustion and/or soil) on WSON levels during that season.

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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 correlate significantly with fine mode MS$^-$ (r^2=0.7, $p<0.05$, n=7, see supplementary material Fig. S5) during austral summer, implying that part of

WSON might have been produced secondarily from biogenic marine precursors. Significant correlation was also found between coarse mode MS$^-$ and coarse mode WSON ($r^2=0.9$, $p<0.0001$, n=~~10~~9, see supplementary material Fig. S6) during summer period, which could be explained by adsorption of MS$^-$ produced from DMS on marine salts.

4. Comparison between different samplings sites and concluding remarks

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

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

The concentrations of fine mode WSON in the NH show large divergence with more than ten times higher levels in the eastern Mediterranean (Violaki and Mihalopoulos, 2010b) than in the tropical Atlantic Ocean. The atmospheric marine boundary layer of the eastern Mediterranean is influenced by air masses originating from eastern Europe, in particular Turkey, Ukraine and Russia

(Mihalopoulos et al., 1997, Lelieveld et al., 2002), which could enrich the atmosphere with WSON from anthropogenic activities. The important contribution of anthropogenic sources to the levels of WSON in the NH is revealed by the more than ten times higher concentration of WSON comparing with the ~~pristine~~ 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 could indicate the substantial role of WSON in biogeochemical cycle of nitrogen in such ~~pristine~~ remote marine environments.

Particularly interesting are the increased levels of fine mode WSON over the ~~pristine~~ 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±3.3 nmol N m^{-3}) along with high percentage contribution (84%) to TDN were almost identical to that measured over the eastern Mediterranean (11.6±14.0 nmol N m^{-3}) pinpointing towards an important role of marine productivity as a source of WSON in ~~pristine~~ remote marine regions with significant biogenic activity.

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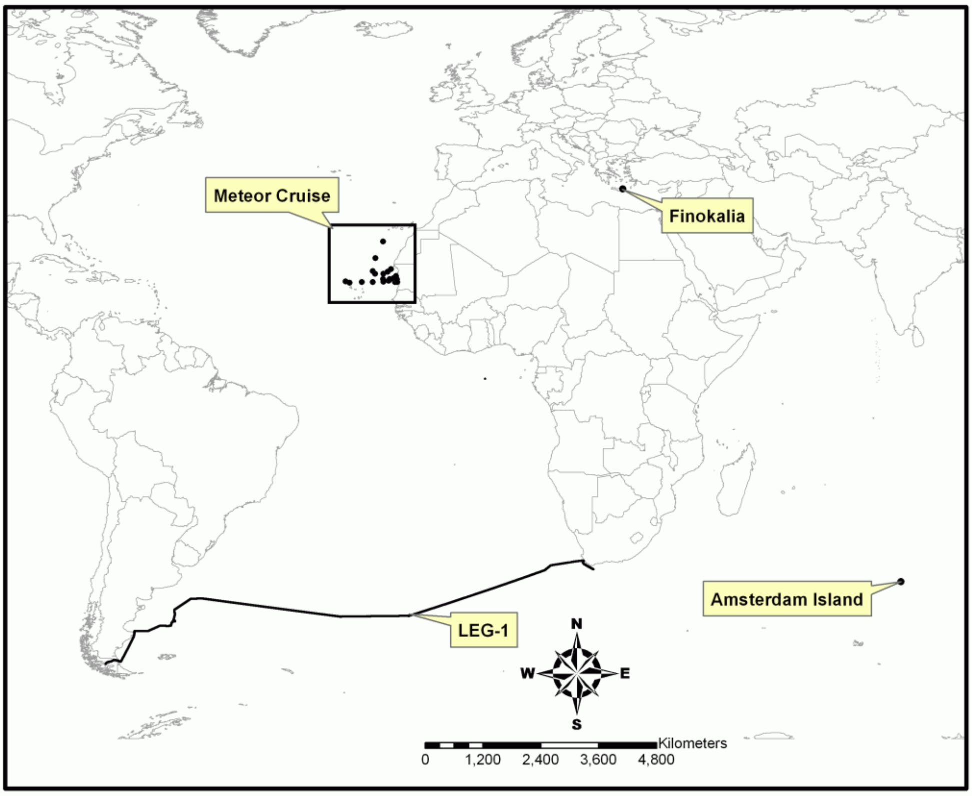


Fig. 1: Sampling sites around the world during this study. Finokalia station is used for comparison purposes.

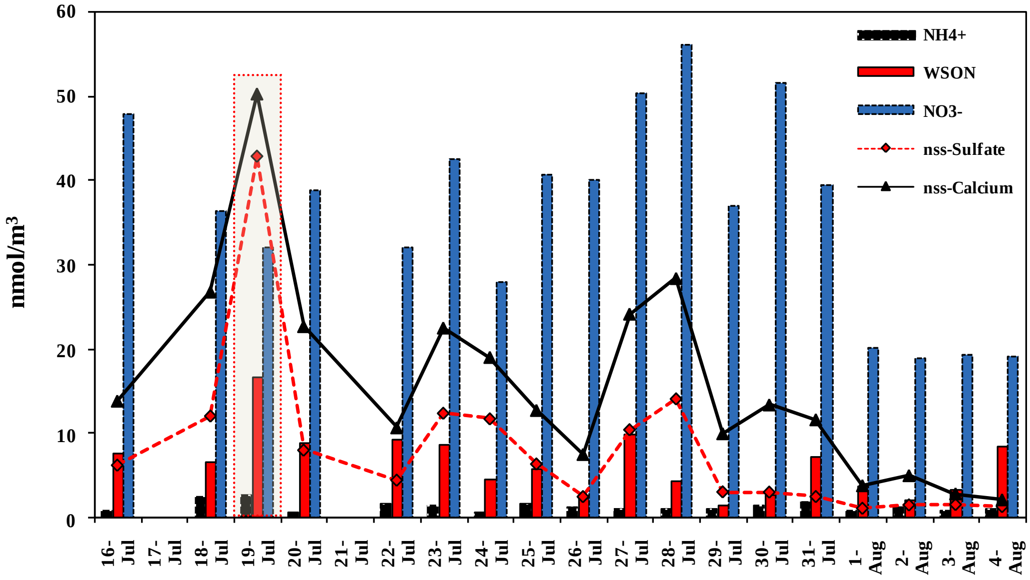


Fig. 2: Temporal variation of nitrogen species, nss-SO_4^{2-} and nss-Ca^{2+}concentration in coarse particles (Da>2 µm) over the tropical North Atlantic atmosphere. The frame defines the air mass back trajectory with dust mixed with anthropogenic sources (19th July 2006).

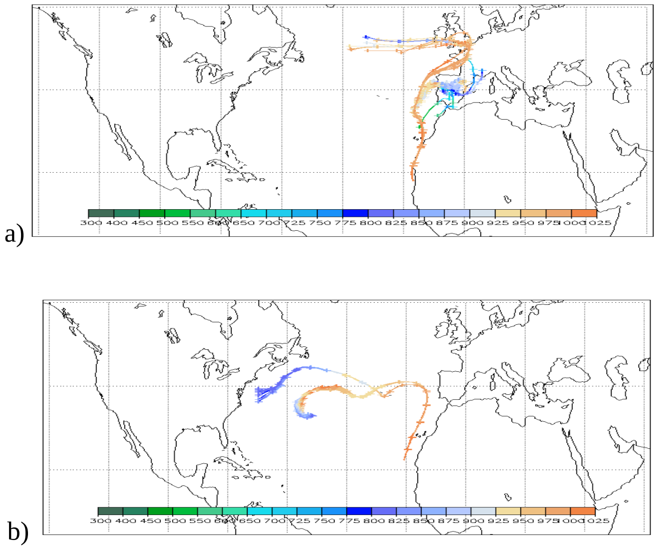
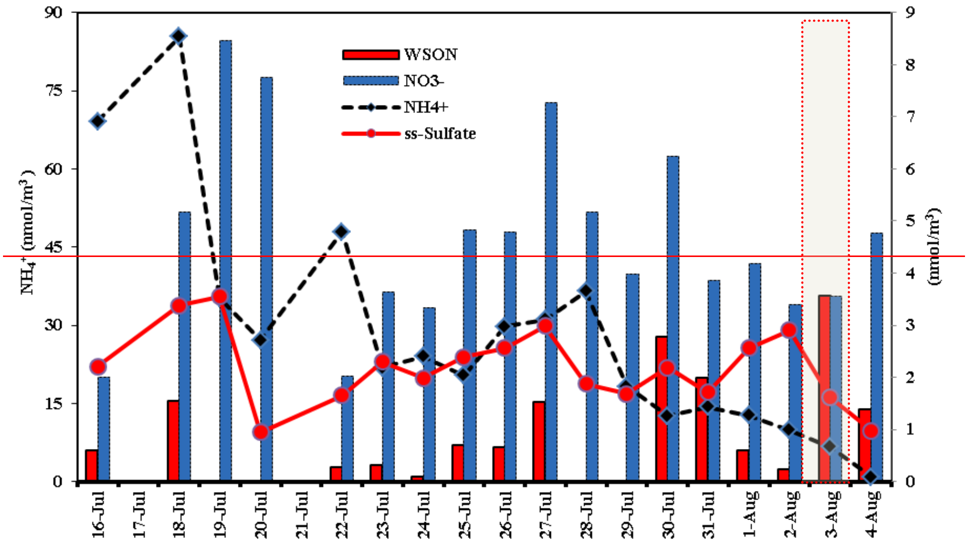


Fig. 3: Five day air mass back trajectories 19th July 2006 (a) and 3th August 2006 (b). The color indicates the pressure level (hPa).



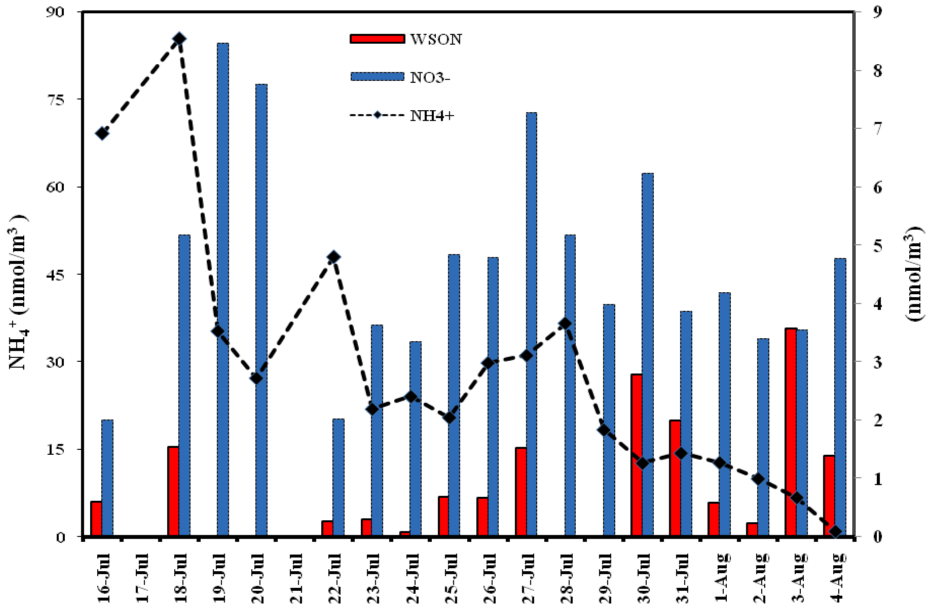


Fig. 4: Temporal variation of nitrogen species ~~&ss-SO$_4^{2-}$,~~ concentration in fine particles (Da<2 µm) over the tropical North Atlantic atmosphere. ~~The frame defines the air mass back trajectory with pristine marine origin (3th August 2006).~~

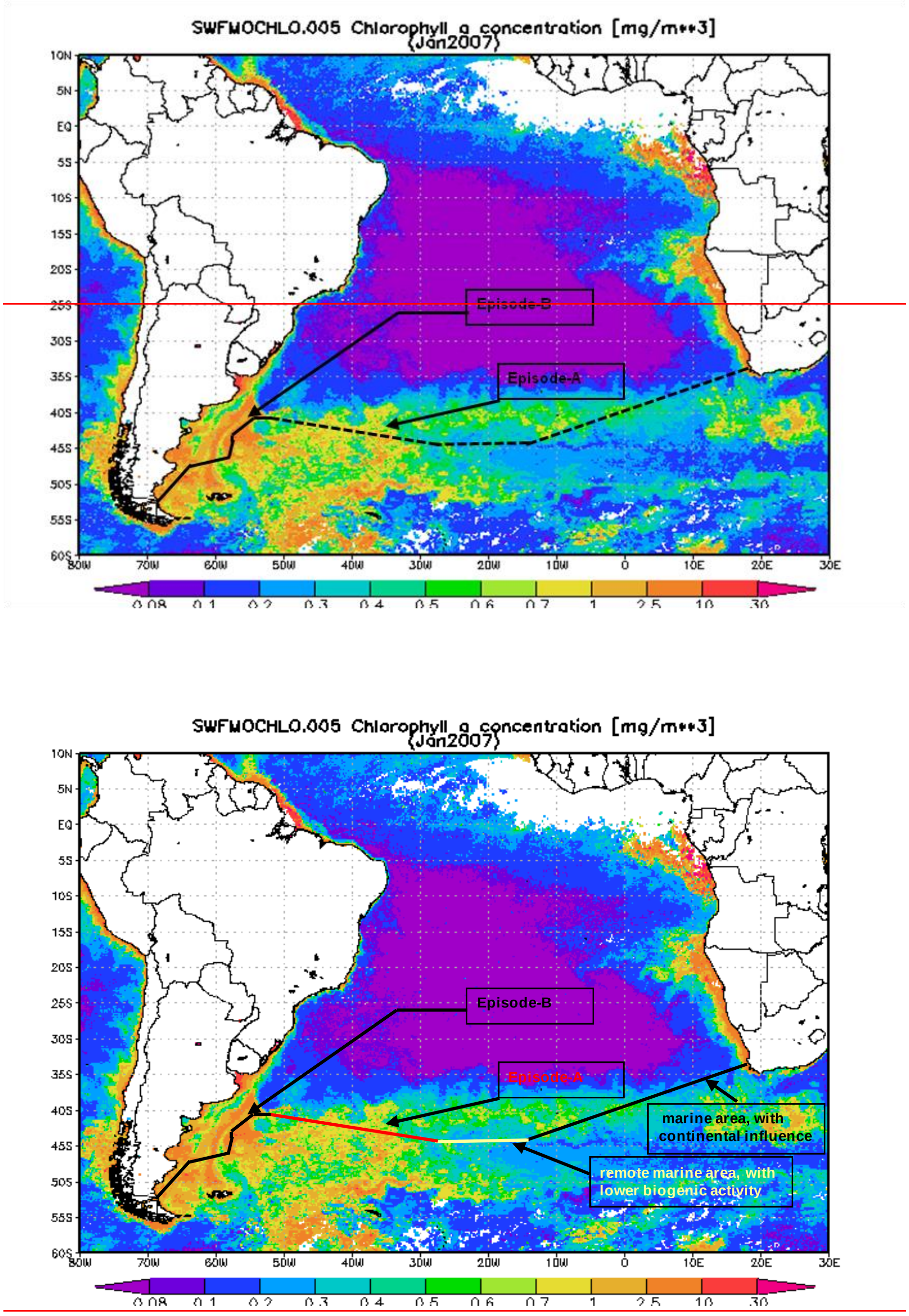


Fig. 5: Two distinct phytoplankton bloom episodes are presented in SeaWiFS chlorophyll-a map at South Atlantic Ocean during January 2007 along with cruise track

(http://disc.sci.gsfc.nasa.gov/giovanni). The episode-A encountered by the ship over two days (30-31 Jan. 2007, n=4) and the episode-B began on 1st February and was followed until the end of the cruise (n=5). Remote marine conditions with low biogenic activity last 4 days (26-29 Jan 2007, n=5), while marine conditions mixed with continental influence last 6 days (21-25 Jan. 2007, n=9).

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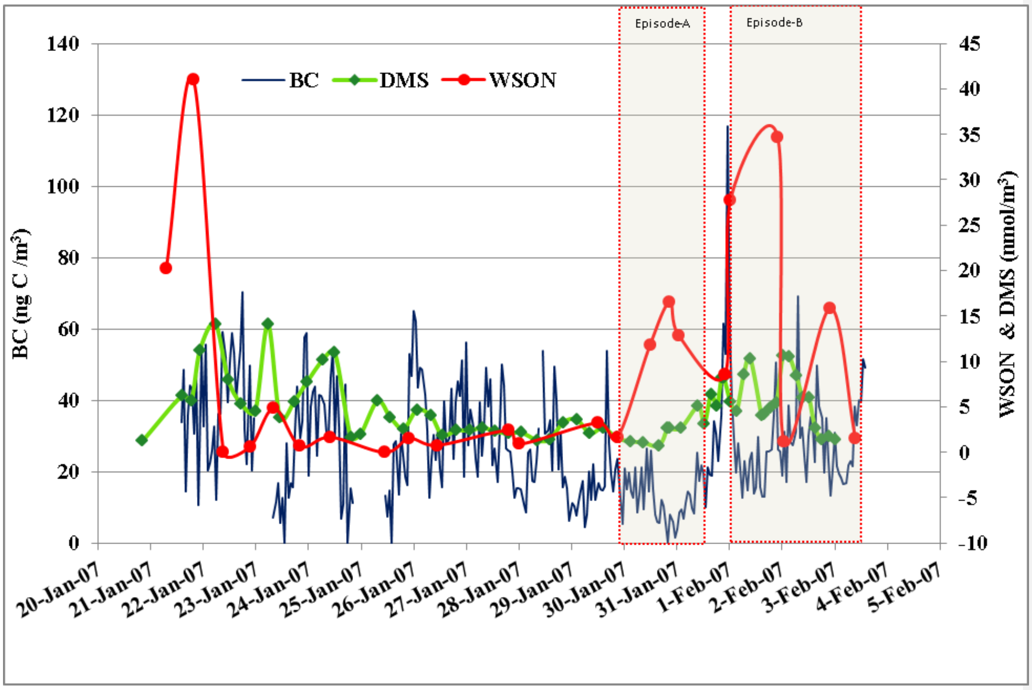

Fig. 6: Temporal variation of WSON and DMS concentration in fine particles (PM$_{2.5}$) together with BC concentration during the cruise in South Atlantic atmosphere. The frames define the marine areas with intense biogenic activity (Episode-A and -B).

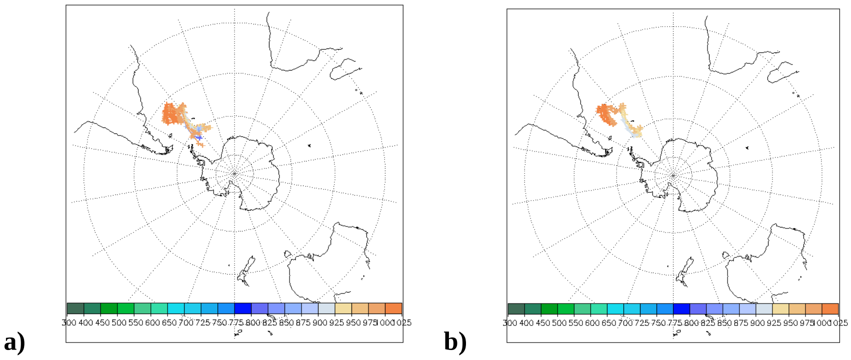

Fig. 7: Five day air mass back trajectories 30th January 2007 (a) and 31th January 2007 (b), during Episode-A. The colored code indicates the pressure level (hPa).

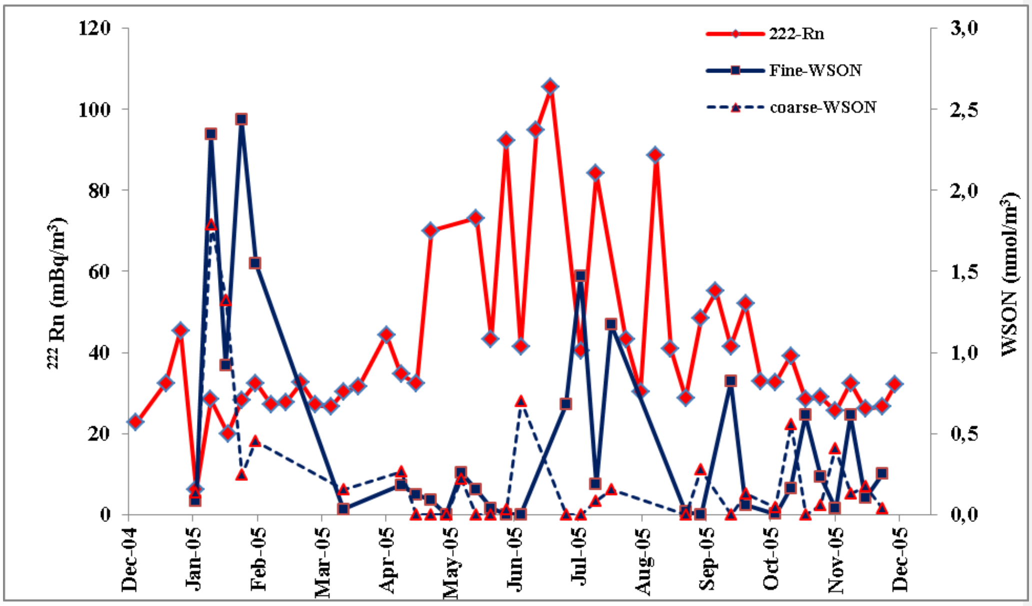

Fig.8: Seasonal variation of fine & coarse mode WSON with Radon at Amsterdam Island. Austral Summer is defined from December to April & winter from May to November.

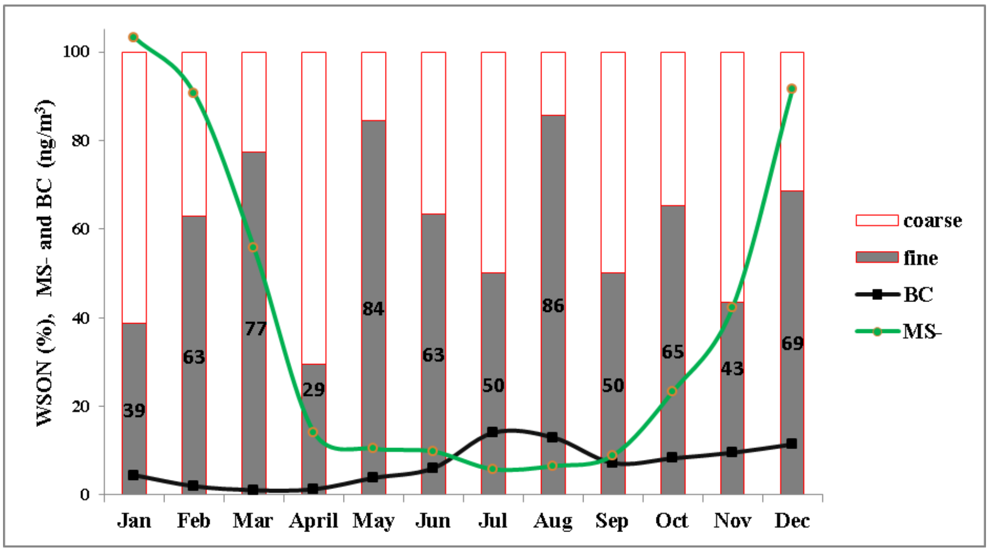

Fig.9: Average monthly concentration of bulk MS^- and BC together with the percentage contribution of WSON in fine and coarse mode at Amsterdam Island (Indian Ocean) during 2005.

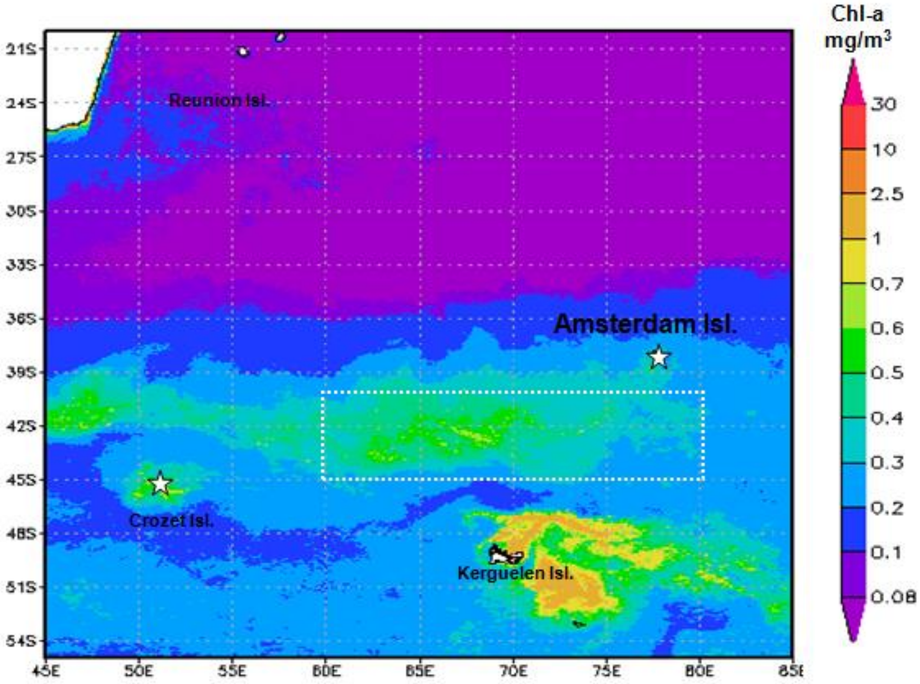

Fig.10: Chlorophyll map obtained for January (SeaWiFS data) for the Indian sector of the Austral Ocean. The white frame corresponded to the source region which could contribute to the levels of marine organics at Amsterdam Island.

Table 1:Average concentration of WSON and percentage contribution to TDN for fine and coarse particles in both Hemispheres. The discrimination between high and low biogenic activity in marine atmosphere was based on the concentration levels of DMS; Higher biogenic activity was considered in cases with DMS concentration higher than 3 nmol m^{-3}.

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**
			Northern Hemisphere					
E. Mediterranean*	Marine with anthropogenic influence	2005-2006 (n=65)	$PM_{1.3}$	11.6±14.0	13	$PM_{1.3-10}$	5.5±3.9	13
Tropic Atlantic Ocean	Marine with Sahara dust influence	16 Jul–4 Aug 2006 (n=18)	<2	0.9±1	5	>2	6.3±3.8	14
			Southern Hemisphere					
S. Atlantic Ocean	marine with the high~~hest~~ biogenic activity~~Chl-a~~	30-31 Jan 2007(n=4)	$PM_{2.5}$	11.3±3.3	84		-	-
middle S. Atlantic	~~Pristine~~ remote marine with low biogenic activity	26-29 Jan 2007 (n=5)	$PM_{2.5}$	1.3±0.~~.~~8	51		-	-
Indian Ocean (Amsterdam Isl.)	~~Pristine~~ remote marine	2005 (n=42)	$PM_{2.5}$	0.8±1.4	32	$PM_{2.5-10}$	0.2±0.4	35

*Violaki and Mihalopoulos (2010b)

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