Response to Referees' Comments:

Anonymous Referee #1

Received and published: 24 April 2018

(My ratings for both scientific and presentation quality are between "Good" and "Fair", so I give one "Good" and one "Fair".)

General Comments:

The authors performed 4 month-long field measurements across 53_N-53_S over the Atlantic Ocean from 2011-2012 and reported convincing source apportionment based on adequate and well-processed datasets obtained from HR-ToF-AMS and other techniques. Due to few number of similar studies that covered long time series and/or oceanic regions, the findings in this paper certainly provide valuable insights into the sources and origins of marine submicron atmospheric aerosols. Overall, the paper discussed relevant scientific questions within the scope of ACP journal with novel methods and datasets, and the results are generally (but not all) supportive to the interpretations and conclusions, in spite of some technical concerns and vague presentation or expression that need to be further supported, examined, or re-phrased. Therefore, I would recommend this paper be accepted for publication once the following specific comments are completely addressed.

Reply:

Thank you very much for your encouraging comments. We tried our best to improve the weak parts on both technical and language aspects. The detailed comments are responded point-to-point in the following text.

Suggestions for major improvements and revision:

1. The author(s) should have made best use of their valuable datasets as well as the

previously published studies, and emphasized the significance of their findings, if they also agree that they haven't done this enough in the abstract and the in the introduction. Besides, the author(s) should also, on one hand, carefully refer to previous studies that used similar techniques for marine aerosol, and on the other hand, include necessary comparisons (if available) in their own discussions. For example: The authors should add proper references to the sentences ended in: Page 10 Line 5; Page 11, Line 25; Page 12, Line 27; Page 12, Line 34; Page 13, Line 6; Page 16, Line 24 (Might be useful: Charlson et al., 1987, Nature; Bonsang et al. 1992, GRL; Yassaa et al., 2008, Env. Chem.; Shaw, Gantt, and Meskhidze, 2010, Advances in Meteorology).

Reply:

Thank you very much for your kind comments. According to referees' comments and co-authors' suggestion, we changed the title of this paper to "Organic aerosols over the Atlantic Ocean from 53°N to 53°S: similar contributions from ocean and long-range transport". The abstract and introduction have been re-written to better stress 1) the key findings on Atlantic organic aerosol sources; 2) the motivation of this study; and 3) previous studies on the same topic or field.

We added the references to the sentences mentioned in examples, as well as in the not mentioned but necessary places. However, the number of references in the original version reached 144, which is too many as pointed out by the other referee. So we removed unnecessary references during re-organizing the whole manuscript (shrinking to 87 references). The detailed revisions to each mentioned sentence are showed below:

Page 10 Line 5: (Now in Page 8 Line 24) "A similar seasonal variation of the marine biogenic tracer MSA was also observed (Huang et al., 2017), suggesting the biogenic sources (i.e. phytoplankton) contributed significantly to sulfate (Charlson et al., 1987; Hoffmann et al., 2016)"

Page 11 Line 25: (Now in Page 10 Line 4) "This factor is well correlated with the marine tracer MSA ($R^2 = 0.83$, Figure 3) and is consequently linked to the oxidation of DMS emitted by phytoplankton (Charlson et al., 1987; Gondwe et al., 2003)."

Page 12, Line 27: The original sentence “The diurnal cycle of MOA might have been weakened by averaging because the biological activities in autumn are usually lower than in spring.” is subjective and not well supported by the chlorophyll a satellite map offered by the referee. We deleted the sentence and replaced it by the new one in Page 10 Line 32: “To focus on the atmospheric behavior of MOOA and exclude the influence from other chemical composition, a “MOOA dominating period” is selected for a case study (about 57 h from 19:40, 18.11.2012 to 04:20, 21.11.2012).”

Page 12, Line 34: (Now in Page11 Line 7) “Similar diurnal cycles are observed for MSA and sulfate, suggesting that MOOA, MSA and sulfate are formed via the same secondary pathway (Charlson et al., 1987; Gondwe et al., 2003; von Glasow and Crutzen, 2004).”

Page 13, Line 6: This sentence was deleted when re-organizing the whole paragraph.

Page 16, Line 24: The original sentences were: “In addition, the particles measured in the range from ~15°N to 15°S (close to the west and middle Africa) showed external mixing state by the HTDMA measurements (details in an accompany paper by Wu et al., in preparation). It is the typical property of BB emissions.” Considering the mentioned paper will provide more detailed explanation and it is also arbitrary to define the “typical property of BB emissions”, we deleted these two sentences in the end of paragraph.

2. Conclusions discussing causality or reasoning must be carefully examined. Just give a few examples: Page 9, Line 5: The authors attributed “insufficient offline samples” to the weak correlation between AMS and offline sea salt. Actually this might not be a reasonable explanation especially if they used AMS data collected from the exactly same periods of time during the offline filter sampling. The data size itself should not affect the R2, and the authors should also examine p-value of correlation for “meaningfulness”. Furthermore, in this case, the authors should also clarify how they measured sea salts using the individual techniques and why they applied the method

from Ovadnevaite et al. (2012). For example, what ions were included as sea salts? Did they count Na+, Cl-, SO42-, K+, Mg2+, etc. in both? If NaCl accounted for different fraction from that in Ovadnevaite et al. (2012), was the scaling factor of 51 still suitable? Otherwise, the “therefore” in Line 6, did not explain why the same scaling factor was applied, considering the correlation and the coverage of time (“full year measurements in the reference”) discussed above was not supportive, or not relevant.

Reply:

Thank you for your comments and suggestions. We reorganized the paragraph about sea salt estimation and added more technical details including:

1) We agree that the “insufficient offline samples” was not a reasonable explanation for the weak correlation. According to referee’s suggestion, we performed the significance test (Spearman’s correlation test because of non-normal distribution of the data) and the resulting p-value is 0.009, indicating the sea salt concentrations from two techniques (AMS and offline) are significantly correlated, that is, the correlation is meaningful. Now relative sentence is in Page 7 Line 29: “the p-value of the regression of AMS-derived sea salt with offline results is 0.009 (Spearman's correlation test), indicating that sea salt concentrations from AMS and offline methods are correlated significantly.”

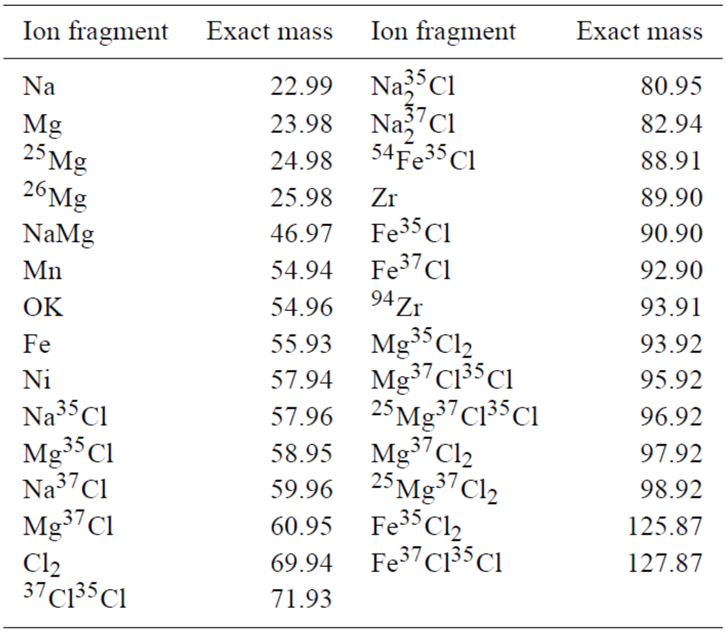
2) For the sea salt estimation based on PM_1 filter measurements, we use Na^+ and Cl^- ions to derive the sea salt concentration as applied in previous studies (Bates et al., 2001; Quinn et al., 2001): sea salt [μg m^{-3}] = Cl^- [μg m^{-3}] + Na^+ [μg m^{-3}] x 1.47 ; where the factor of 1.47 is the seawater ratio of $(Na^+ + K^+ + Mg^{2+} + Ca^{2+} + SO_4^{2-} + HCO_3^-)/Na^+$. So this estimation method can prevent the inclusion of non-sea-salt K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-} and HCO_3^- in the sea salt mass, and also allow for the loss of chloride mass through chloride depletion processes (Bates et a., 2001). The estimation method was added to the caption of Figure S6.

3) For the sea salt estimation using HR-ToF-AMS, we use the method from Ovadnevaite et al. (2012). It is the first reported studies of sea salt estimation using AMS containing both laboratory calibrations using artificial sea salt and ambient

measurements, and the later studies (e.g. Schmale et al., 2013) followed the method (applied the similar scaling factor). The sea salts certainly include many ions once fragmentized by AMS, e.g. Na+, Cl^-, SO_4^{2-}, K^+, Mg^{2+}, $NaCl^+$, Na_2Cl^+ and so on (see details in Table 1 from Schmale et. al, 2013, shown below). However, the particulate sea salt mass concentration cannot be the simple sum of the ions on the list, because most of them could be contributed by non-sea-salt sources (e.g. Cl^-, SO_4^{2-} and K^+ can be from continental transport) and some of the ions have too low intensity to be detected in ambient situation (e.g. metals and isotopes). Also, one of the main ions, Na^+, can vary significantly with the AMS vaporizer temperature (Ovadnevaite et al., 2012; Schmale et al., 2013). Therefore, Ovadnevaite et al. (2012) only used the $NaCl^+$ (m/z 57.95) as a surrogate of sea salt rather than the sea salt family ions, and we followed it for the same reason. In our study, the correlation slope between offline sea salt and AMS $NaCl^+$ ion was 62 (± 6), not very far from the reference value, but with a mild correlation coefficient ($R^2 = 0.38$). We still prefer to use the scaling factor of 51 from the literature for several reasons: first, this factor could lead to better coherence (slope = 1.01) of estimated sea salt concentration between filter and AMS; second, most scattering dots (with factor of 51) are distributed within the uncertainty range derived from literature (Figure S6); and third, the factor of 51 is not too far from the slope derived in this study (62 ± 6) but can make our study consistent with the previous studies. Of course, the estimated sea salt mass concentration should be used and discussed with caution and we need to always be aware of its uncertainty.

According to the comments, we re-organized the paragraphs and removed the improper conjunction phrase “therefore”. The revised sentence is now in Page 7 Line 25: “To be consistent with the literature (Ovadnevaite et al., 2012; Ovadnevaite et al., 2014; Schmale et al., 2013), the scaling factor of 51 from the reference is applied to the sea salt surrogate ($NaCl^+$) to estimate the sea salt mass concentration in this study.”

Table 1. Ion fragments considered within the sea salt family (Schmale et. al, 2013)



Ion fragment	Exact mass	Ion fragment	Exact mass
Na	22.99	$Na_2^{35}Cl$	80.95
Mg	23.98	$Na_2^{37}Cl$	82.94
^{25}Mg	24.98	$^{54}Fe^{35}Cl$	88.91
^{26}Mg	25.98	Zr	89.90
NaMg	46.97	$Fe^{35}Cl$	90.90
Mn	54.94	$Fe^{37}Cl$	92.90
OK	54.96	^{94}Zr	93.91
Fe	55.93	$Mg^{35}Cl_2$	93.92
Ni	57.94	$Mg^{37}Cl^{35}Cl$	95.92
$Na^{35}Cl$	57.96	$^{25}Mg^{37}Cl^{35}Cl$	96.92
$Mg^{35}Cl$	58.95	$Mg^{37}Cl_2$	97.92
$Na^{37}Cl$	59.96	$^{25}Mg^{37}Cl_2$	98.92
$Mg^{37}Cl$	60.95	$Fe^{35}Cl_2$	125.87
Cl_2	69.94	$Fe^{37}Cl^{35}Cl$	127.87
$^{37}Cl^{35}Cl$	71.93		

Page 10, Line 18: The author stated "The ammonium concentrations didn't follow a clear seasonal trend, although its precursor ammonia could be emitted from ocean (Ikeda, 2014; Johnson et al., 2008). The absence in seasonality suggests particulate ammonium during Polarstern cruises was contributed by both anthropogenic and biogenic sources." The deduction did not support their conclusion.

Reply:

Yes the causality of the sentences was not clear. We replaced them with the new ones: "The ammonium concentrations did not exhibit a seasonal difference between spring and autumn. The highest median value was found over the tropic Atlantic, followed by the North Atlantic, while the lowest median value was in the South Hemisphere. Both continental emissions via long-range transport and marine organism could be the origin of the ammonium or its precursor ammonia in the MBL (Adams et al., 1999)." (Now in Page 9 Line 9).

Page 13, Line 29: "The diurnal variation of NOA shows clear peak in the afternoon, reaching the maximum while the global radiation starts decreasing (Figure 4), indicating that the NOA factor is certainly composed of secondary organic products." The evidence is weak, and the authors should specify "global radiation" and cite papers that observed the similar diurnal trends of such a NOA factor, if available.

Reply:

We made major revision of the NOA part (now its name is changed to MNOA). Although the diurnal variation of NOA is very likely to be attributed to the secondary formation, it is hardly to find a NOA factors with similar diurnal pattern in previous studies. Sun et al., (2011) reported a NOA factor related to secondary transformation of amines from marine and industry sources but the factor showed a noon peak, comparable to our case (afternoon peak around 16:00UTC). Due to the limited amount of AMS measurements in the MBL, the comparison of specific marine factor become difficult so we can only make the speculation. New sentences started in Page 12 Line 3 "…and the diurnal variation of MNOA shows a broad afternoon peak with maximum at 16:00 UTC (Figure 4), similar to that of the amines-related secondary factor in the New York City showing a diurnal pattern with maximum at noon time (Sun et al., 2011)." Besides, "global radiation" was defined in Page 9 Line 29 "… with global radiation (the sum of the direct solar radiation and diffuse radiation)". We have to use the global radiation because the solar radiation data was not available during the cruises.

Page 13, Line 20: The authors suggested "This can be useful for better estimation of marine DMS related SOA both in field measurements and in models". However, MSA as a fraction of SOA can vary largely and different from time to time (especially between summer and winter). In addition, MOA in this case might not be equivalent to SOA.

Reply:

We agree that MSA as a fraction of SOA may vary between different seasons, especially between summer and winter in which our measurements did not cover.

Considering that AMS-PMF is an often-used method for distinguishing SOA and few other methods can provide more robust estimation of SOA, we think our result can at least provide a hint on, not the whole marine SOA, but the SOA formed from DMS-oxidation in the measuring seasons, especially in spring. Of course, MSA cannot trace the portion of SOA which is formed from other pathways, e.g. secondary formation from gaseous amines. According to referee's comments and the explanation above, we revised the sentences in manuscript to be more cautious, emphasizing the season (spring) and SOA portion (DMS-related SOA) in/for which the MSA and scaling factor 1.79 can be applicable. The new sentence is now in Page 11 Lines 26: "We therefore infer that the relation between MSA and its concomitant (DMS-related) SOA is roughly stable over the Atlantic, and suggest estimating MOOA mass concentration as the product of the MSA concentration multiplied by a factor of 1.79, which may be useful for a better estimation of marine DMS-related SOA both in field measurements and in models." Further analysis of data from other oceans/seasons are needed in future to examine this correlation coefficient.

3. For better presentation quality and reading experience, the English language and scientific writing in this paper can be more precise and largely improved. Just give a few examples: Page 11, Line 9: "These S/C ratios derived from the PMF analysis tool contain however certain estimation uncertainties and have therefore to be used with caution." This seems to be a grammatically wrong sentence.

Reply:

Thank you very much for the comments. The authors of this paper have tried best to improve the language. During the period after authors' reply, we finally had the manuscript improved by a professional company (American Journal Expert) for a standard editing. Now the words and grammar mistakes are already eliminated.

The sentence in Page 11, Line 9 is removed when re-organizing the text. This sentence is now changed to: "Note that the S/C ratios derived from the PMF analysis tool have to be used with caution because of calculation uncertainties (Aiken et al., 2007), but they can still provide an indication of the significance of sulfur when calculated with the same tool among the factors from the same dataset." (Page 10 Line 9)

Page 12, Line 24: "The minimum of the diurnal variation (0.04 μg m^{-3}) appears around 09:00, probably linking to the increase of mixing layer in morning." This sentence needs to be re-phrased and also supported with references.

Reply:

Based on the re-analysis of the MOOA diurnal variation, we think it is insufficient to attribute the minimum to the dilution effect of the rising boundary layer. Because the drop of the MOOA concentration was not found at the similar time point during the MOOA-dominating period. So, this sentence is removed.

Page 10, Line 27: I think it is more precise to say "57 hours" rather than "about 2 consecutive days", unless there was an interruption.

Reply:

Thanks for the suggestion. This has been done.

Page 13, Line 6: "the this OA component". Despite the grammatical error and lack of references, "OA component" was vague in the context.

Reply:

Thanks for reminding this. We reorganized this paragraph and deleted the mentioned sentence.

Page 17, Line 17: In this paragraph, the author said "still questionable" and then "This suggests… could be not correlated". This led to confusion due to the inappropriate English or logical expression.

Reply:

We apologize for the unclear causality here. We improved the sentences as (now in Page 13 Line 21): “This trend does not conflict with the speculation that MHOA is related to marine primary emissions because the mass fraction of organics in the sea spray aerosol was found to be size-dependent: increasing with decreasing particle size (Gantt et al., 2011; Quinn et al., 2015). The enrichment factor of organic compounds, i.e., the ratio between organic carbon in sea spray aerosols and that in sea water, is also largely influenced by particle size (Quinn et al., 2015). In addition, the transfer of organic matter from seawater to the particles is chemoselective and more complicated than it is for inorganic sea salt ((Schmitt-Kopplin et al., 2012)”.

Other technical and specific comments to be addressed:

1. Generally when discussing seasonality, the difference between “spring & autumn” might not be as distinct as that between “summer & winter”, in term of many factors such as meteorological parameters and marine bioactivity. Besides the “spring vs. autumn” comparison, the authors may also want to look into “spring/autumn vs. tropic”. In addition, their measurements on board was changing with time and location at the same time, so this will be different from those studies took place at a ground site over seasons. I wonder if the authors would like to make some comments on these.

Reply:

Thanks for the comments. Yes, the meteorological parameters such as temperatures and RH were not very different between spring and autumn as between summer and winter. We added the description on tropical case and compared the species mass concentrations in spring, autumn and tropic (Session 3.1.2). Although no big difference was found between spring and autumn for organics, sea salt, nitrate and so on, sulfate showed very discrepant average or median mass concentration in spring and autumn, maybe related to different biological activities. This may suggest even with the similar temperatures and RH, the seasonal events such as biological activities may still influence the aerosol chemical composition.

Considering the comparability between the mobile platform and stationary site, we admit there could be big difference caused by marine biomass distribution, e.g. more dense phytoplankton group near the coastal region than the remote ocean. But because of very limited amount of the mobile measurements over the ocean, it is quite difficult to find records for the similar regions. So we collected the aerosol chemical composition in several regions covering the ship tracks, and checked if they were comparable to our results. In future it would be helpful to have more information of submicron aerosols over the ocean based on satellite data.

2. The authors should try to clarify the influences from the "open oceans", "marine", and "coastal" when interpreting results in the discussions, even though the boundaries might be blurry. For example, on Page 11, Line 30, the author stated "The S/C ratio of the MOA factor is also over twice that of marine factor observed in Paris (0.013, Crippa et al., 2013b), implying a stronger influence from marine phytoplankton on aerosol particles over the ocean than those in the coast city.", but actually the abundance of phytoplankton can be much higher in the coastal areas. See https://earthobservatory.nasa.gov/GlobalMaps/view.php?d1=MY1DMM_CHLORA

Reply:

Thanks for the comments and website link. Due to the limited on-board measurements, we did not find the S/C ratios from offshore sites or open oceans in previous studies. So the S/C ratio from coastal measurements in Paris was used as a reference for comparison. We noticed that the comparison is not sufficient to support the conclusion of "stronger influence … over the ocean than those in the coast city", and the S/C ratio should be used with caution because of calculation uncertainties. So this conclusion is removed and we only compare the S/C ratios among the OA factors in this study. Now in Page 10, Line 8: "This leads to a high S/C ratio (0.030), which is 10 to 30 times higher than that of other factors (Figure 3)." Nevertheless, it is important to stress that organosulfates with biogenic sources may not correlate with chlorophyll a level, as the former is produced from the secondary pathway and the latter is the indicator of the primary biogenic mass (Huang et al., 2017).

3. The authors are suggested to add discussions for organosulfates, since they can make a considerable contribution to continental SOA masses at certain locations, and also derived from the same biogenic precursors over the oceans. For example, how is this class of compounds measured using AMS? Was it included in organics or sulfate, or neither?

Reply:

Thanks a lot for the suggestion. Organosulfates (except MSA) are also one of the important components of the marine SOA transformed from the precursors such as isoprene, monoterpenes and so on (Claeys et al., 2010; Surratt et al., 2007). We added small discussion on the organosulfates in the revised manuscript to stress the existence of organosulfates (Page 10 Line 28): It is well known that isoprene and monoterpene oxidation also leads to the formation of organosulfate compounds (Claeys et al., 2010; Fu et al., 2011; Iinuma et al., 2007; Surratt et al., 2008; Surratt et al., 2007), which can contribute to the $C_xS_y^+$ fragments observed in the MOOA factor." We hesitated to discuss more about the organosulfates in this paper because a parallel paper focusing on the organosulfates is in preparation, which included detailed analysis on a sub-dataset of Polarstern measurements. The paragraph below may answer referee's questions:

Our MOA (now changed to MOOA) mainly includes MSA fragments (as shown in Figure 1), while the contribution of organosulfates to MOOA may be tiny as found in previous marine study (Claeys et al., 2010). Using AMS, the fragments of organosulfate (e.g. MSA) are recognized as sulfate and organics (Figure 1). The quantification of organosulfates requires the laboratory calibrations using standard chemicals of known organosulfates (Huang et al., 2015; Huang et al., 2017).

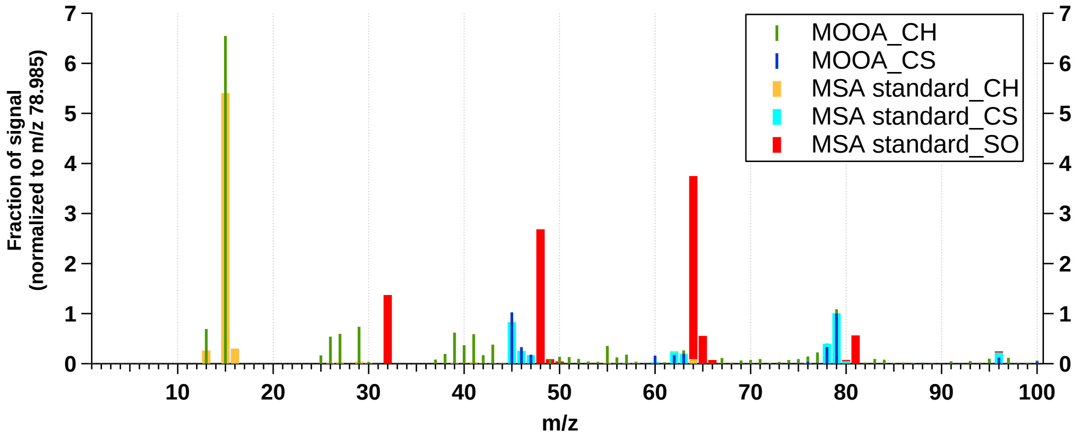


Figure 1 Mass spectra of MOOA factor (CH and CS ions) and pure MSA (CH, CS and SO ions)

4. Last but not least, the authors should revise the manuscript carefully by their own. Just give a few examples: 1) Page 12, Line 34: “Figure 4” – should this be Figure 5?

Reply:

Thanks for the detailed comments! In original sentence “Figure 4” was mentioned for “the average case”. In order to be more precise, the sentence is changed to “ The diurnal pattern for this specific period (Figure 6b), with a minimum of 0.11 µg m^{-3} (MOOA mass concentration) at 07:00 and a maximum of 0.25 µg m^{-3} at 16:00, was more noticeable than the average case (Figure 4b).” (Page 11 Line 6).

2) Acronym: define before use. For example, “SOA” was not defined but used in the abstract; “OA” was firstly defined on Page 10, Line 30 in the main text; “biomass burning” was defined but not used in many places.

Reply:

We checked the manuscript and corrected the use of acronyms. The definition of acronyms was added to the abstract: Page 1 Line 16 for OA, Page 2 Line 1 for SOA. Biomass burning (BB) was defined in Page 12 Line 21 and the abbreviation is mainly used in the section 3.2.5 Combustion oxygenated organic aerosol (Comb-OOA), e.g. Page 15 Line 2, "…the average BB organic aerosols…", Line 15 "The absence of these BB tracers…".

3) Please be consistent when using terms such as "fPeak" or "fpeak", "CxHyO" or "CxHyO1". 4) Please be consistent about adding a "_" between numerical values and their units. 5) Please specify "CxSj+" on Page 12, Line 21.

Reply:

We went through the text and uniform the terms: e.g. fPeak, $C_xH_yO^+$ and $C_xS_y^+$. We also uniform the format of values and units: put a blank between them.

References

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Response to Referees' Comments:

Anonymous Referee #2

Received and published: 22 May 2018

The technical aspect of the current paper is very good, and the data of very high quality. Being able to collect so many cruises with HR-ToF-AMS data is a really valuable contribution to the field. The paper is very suitable for ACP, but unfortunately major (big major) revision are needed:

Reply:

We thanks very much for referee's positive and constructive comments. The point-to-point responses are shown below:

- Introduction. Decide if you want to focus on the study area, or on the techniques, decide one flow and report it. At the moment there is confusion.

Reply:

Yes, the introduction part was confusing. We have rewritten the introduction to focus on the motivation of this study (referring to mainly the study area rather than the techniques). Also, we reorganized the abstract according to both referees' comments, in order to emphasize the key findings of this paper. According to referees' comments and co-authors' suggestion, we changed the title of this paper to "Organic aerosols over the Atlantic Ocean from 53°N to 53°S: similar contributions from ocean and long-range transport".

- There are 144 references, really there is no need to add all these references, suggestion to cut to 60 max.

Reply:

Thanks a lot! Indeed the amount of references is big. Considering that the other referee suggested to refer to more previous studies, we added some comparisons with historical studies and removed the less useful references. Finally we shrank the references amount from 144 to 87 now. The existing references are considered to be necessary for better explaining the key findings of this paper.

- Figure S8. Factors F1-F4 and F1-F6 in PMF analysis need to be better described and named accordingly to the names of Factor 5 solution. Report also correlations among factors so the reader can understand how the factors evolve.

Reply:

To keep the focus of the manuscript, we added the description of factor evolution in the supplementary. In Figure S8, we put annotations for each factor to note the similarity between factors from 4- and 6-factor solutions and the selected solution, for example, the factor similar to MOOA was named as MOOA-like factor in 4- or 6- solutions. An additional plot following Figure S8 showed correlations among factors (Figure S9) to explain the reason of naming and the changing of the factors.

- The paper is very descriptive, and many papers are cited and referenced. There is no need. For example the whole section of Page 13 can be cut

Reply:

The authors went through the whole manuscript and tried best to remove the sentences which were descriptive and less useful for the key findings. In Page 13 (of original version), we reorganized the manuscript and removed most of the description of both MOA (now MOOA) and NOA (now MNOA) factors and shortened the discussion on them.

- pg 14 delete all topic of aminoacid, it creates confusion. These markers used are not unique of aminoacids.

Reply:

We agree with the comment and this is done.

- naming. perhaps you want to simplify the naming, for example the aPOA may simply be anthropogenic organic aerosol (surely there will be a component that is secondary) and perhaps clearly stat that MOA POA and NOA are marine. NOA is marine, produced via secondary productions. Maybe start with "marine" or "anthopogenic" then "primary" or "secondary" then if it is Organic, nitrogen, MSA containing. Just a suggestion.

Reply:

We rethought about the naming of the OA factors and revised them for better indicating marine or anthropogenic sources. The MOA is now marine oxygenated OA (MOOA), NOA is changed to marine nitrogen-containing OA (MNOA), POA becomes marine hydrocarbon-like OA (MHOA), OOA is anthropogenic oxygenated OA (Anthr-OOA), and aPOA becomes combustion oxygenated OA (Comb-OOA).

- Overall it is advised that the senior scientists co-authoring this paper suggest how to improve the flow of the current manuscript.

Reply:

Thanks a lot for the suggestion. The senior scientists in the co-author list have read the manuscript and gave advices and suggestions on how to revise the paper. As you may see we reorganized the whole manuscript and rewrote many paragraphs in order to make the paper more clear and logical. Hope the efforts made the manuscript better.

I congratulate to the authors (both corresponding authors in particular) for the impressive dataset collected - once the flow of this paper is improved, it will make a very important contribution in the field.

Reply: Thank you very much for your encouraging comments!

~~Source apportionment of the submicron organic~~Organic aerosols over the Atlantic Ocean from 53°N to 53°S~~ using HR-ToF-AMS~~: similar contributions from ocean and long-range transport

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Abstract. ~~The marine~~Marine aerosol ~~is one of the most~~particles are an important part of the natural aerosol systems and ~~can~~might significantly impact the global climate ~~as well as~~and biological cycle. ~~A series of measurements during~~ It is widely accepted that truly pristine marine conditions are difficult to find over the ocean. However, the influence of continental and anthropogenic emissions on the marine boundary layer (MBL) aerosol is still less understood and nonquantitative, causing uncertainties in the estimation of the climate effect of marine aerosols. This study presents a detailed chemical particle characterization of the MBL aerosol as well as the source apportionment of the organic aerosol (OA) composition. The data set covers the Atlantic Ocean from 53°N to 53°S, based on four open-ocean cruises in 2011 and 2012~~ over the Atlantic from 53 °N to 53 °S were conducted to reveal the physical and chemical properties of the marine boundary layer (MBL) aerosol and its seasonality. Chemical composition of the submicron particles~~. The aerosol particle composition was ~~obtained using the on-line techniques High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) as well as from offline high-volume PM$_1$ filter samples with a sampling time of 24 hours. Our measurements show that the MBL aerosol particle mass is controlled by sulfate~~ measured with a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS), which indicated that Atlantic submicrometer aerosol particles are mainly composed of sulfates (50~~%), followed by~~% of the particle mass concentration), organics (21~~%),~~%) and sea salt (12~~%), ammonium (9%), Black Carbon (BC, 5%) and nitrate (3%). Only sulfate exhibits pronouncedly seasonal dependency, while no such trend was observed in other species. Source apportionment of the organic fraction was performed using Positive Matrix Factorization (PMF). Five~~%). OA have been apportioned into five factors~~ were identified~~, including three factors linked to marine sources and two ~~non-~~with continental/anthropogenic origins.

The marine oxygenated OA (MOOA, 16% of the total OA mass) and marine nitrogen-containing OA (MNOA, 16%) are identified as marine secondary products with gaseous biogenic precursors dimethyl sulfide (DMS) or amines. Marine hydrocarbon -like OA (MHOA, 19%) were attributed to the primary emissions from the Atlantic Ocean. The factor for the anthropogenic oxygenated OA (Anthr-OOA, 19%) is related to continental outflow. Represented by the combustion oxygenated OA (Comb-OOA), the aged combustion emissions from maritime traffic and wild fires in Africa contributed the largest portion of the total OA mass on average (30%). This study provides an important finding that long-range transport emissions were found to contribute averagely 49% of the submicron OA mass over the Atlantic Ocean. This is almost equal to that from marine sources~~. Marine sources are linked to primary production (19% of total organic aerosol (OA) mass), marine dimethylsulfide (DMS) oxidation (16%), and amine-related secondary formation (16%). The other two OA components are attributed to continental outflow (19%) and aged ship exhausts - biomass burning emissions (30%). Our study indicates that, on average, non-marine sources nearly have the equal importance to the Atlantic aerosols comparing with the marine sources, respectively contributing 49% and~~ (51~~% to the total OA mass loadings. The South Atlantic atmosphere is found to be less polluted than the North according to our source analysis. Detailed~~%). Further, a detailed latitudinal distribution of OA ~~sources~~source contributions showed that DMS oxidation ~~contributes remarkably~~contributed markedly to the ~~MBL aerosol~~OA over the South Atlantic during spring, while continental ~~pollutants~~emissions largely ~~contaminate~~contaminated the marine atmosphere ~~when~~ near Europe and the west and middle of Africa (15°N~~∼~~ to 15°S~~) as well as Europe. Based on our measurements, SOA produced from~~). In addition, supported by a solid correlation between marine tracer methanesulfonic acid (MSA) and the DMS~~-~~-oxidation OA (MOOA, $R^2 > 0.85$), this study suggests that DMS-related secondary organic aerosols (SOA) over the Atlantic ~~can~~Ocean could be estimated ~~as~~by MSA ~~mass concentration times~~and a scaling factor of 1.79~~ for~~, especially in spring~~ season, which is derived from the strong correlation (R^2 >0.85) between MSA and DMS-oxidation OA component~~.

1 Introduction

As one of the most important natural aerosol systems at the global level, the marine aerosol plays a significant role in the global radiation budget through both direct and indirect climate ~~effect~~effects, as well as playing a role in biogeochemical cycling (O'Dowd and De Leeuw, 2007; Saltzman, 2009). ~~The marine aerosol in~~In pristine conditions, ~~includes the~~marine aerosols consist of primary products~~, *i.e.*~~ and secondary products. Primary products, usually referring to sea ~~spray aerosol (SSA),~~salt-containing particles, are mechanically generated via sea/air interaction (Andreas, 2002)~~ and secondary particles, which~~. Secondary marine aerosols are chemically produced from atmospheric reactions of gases emitted ~~from the~~by organisms in the ocean (Charlson et al., 1987)~~. The nucleation events were observed in the boundary layer in coastal measurements, e.g. Mace Head~~. As one of the most well-known biological gases, dimethyl sulfide (DMS), emitted by marine phytoplankton, can be oxidized to eventually form sulfate and methanesulfonic acid (MSA) in the particulate phase (Ayers and Gillett, 2000; Bates et al., 1987; Charlson et al., 1987; Gondwe et al., 2003; Ole Hertel 1994; Shiro Hatakeyama, 1985; von Glasow and Crutzen, 2004)~~, and the Arctic Ocean (Leck and Bigg, 2010). However, over the open "warm" ocean, the new particle formation in the marine boundary layer (MBL) was not found. It is believed to take place in the free troposphere, in which the resulting new particles (with diameter 3 to 10 nm) grow to Aitken mode (10 – 100 nm) size range by condensation, and then are entrained to the MBL (Heintzenberg et al., 2004). For a long time, the focuses of marine aerosol research have been put on the sea salt (de Leeuw et al., 2011; de Leeuw et al., 2000; Geever et al., 2005; Grythe et al., 2014; Lewis and Schwartz, 2004; Ovadnevaite et al., 2012; Sofiev et al., 2011; White, 2008), and on sulfate (Ayers and Gillett, 2000; Bates et al., 1987; Charlson et al., 1987; Gondwe et al., 2003; Ole Hertel 1994; Shiro Hatakeyama, 1985; von Glasow and Crutzen, 2004). Recently, ambient measurements found that organics could be a dominating component of submicron marine aerosol particles, contributing up to 77% of the total particle mass concentration during phytoplankton bloom periods (O'Dowd et al., 2004; Ovadnevaite et al., 2011). Also, Quinn and Bates (2011) pointed out that organic aerosols are a considerable source of the cloud condensation nuclei (CCN), challenging the hypothesis that MBL cloud process is only controlled by the sulfate from dimethylsulfide (DMS)(Charlson et al., 1987). However, the chemical and physical characteristics of the organic component in the marine aerosol are still less understood.~~

~~The marine organic aerosols have been found to generally contain carboxylic acids, organic hydroxyl groups, alkane groups, as well as organosulfate~~ . Other volatile organic compounds, such as isoprene and monoterpenes, can also be produced by marine organisms (Bonsang et al., 1992; Shaw et al., 2010; Yassaa et al., 2008) and transformed to secondary particles (Fu et al., 2011). However, the chemical and physical characteristics of marine aerosol are still poorly understood.

For a long time, non-sea-salt sulfate (nss-SO_4) has attracted substantial research attention because it has been recognized as the major source of cloud condensation nuclei (CCN) over the ocean, consequently influencing the cloud albedo (Charlson et al., 1987). This biological regulation of climate has been referred to as the CLAW hypothesis (Charlson et al., 1987). Recently, this hypothesis was challenged because of the possible importance of non-DMS sources in the marine boundary layer (MBL) CCN, specifically sea salt and organics (Quinn and Bates, 2011). On the one hand, sea salt has been found to be a major component (60%) in the residual particles of dried cloud droplets (Twohy and Anderson, 2008). On the other hand, sea surface water is a reservoir of organic matter that can be injected into the air and enriched in the particles (Aller et al., 2005; Kuznetsova et al., 2005; Russell et al., 2010; Schmitt-Kopplin et al., 2012; van Pinxteren et al., 2017). Organics have been observed to dominate the particle mass (up to 77%) during phytoplankton bloom periods at a coastal station in Ireland (O'Dowd et al., 2004; Ovadnevaite et al., 2011)~~. Carboxylic acids could compose nearly 30% of the total submicron organic mass over the ocean, as important as alkane group and organic hydroxyl~~ . However, many marine aerosol studies were based on observations on islands or in coastal areas, where biological activities are much higher than the remote ocean (as illustrated by global maps of chlorophyll-a (Chl-a): https://earthobservatory.nasa.gov/GlobalMaps/view.php?d1=MY1DMM_CHLORA). Hence, more measurements aboard ships are required to provide details of the chemical composition and physical properties of marine aerosol over the open ocean far from the coast.

Aerosols over the ocean can be influenced by many nonmarine sources, including continental and ship emissions (Andreae, 2007; Simpson et al., 2014)~~. Yet, there are still a large fraction of the oxygenated compounds remaining unidentified (Decesari~~

~~et al., 2011). Methanesulfonic acid (MSA) is one of the few compounds that can be identified and quantified. MSA is almost exclusively formed from the oxidation of DMS that is emitted from phytoplankton in the ocean (Becagli et al., 2013; Gondwe et al., 2004). This makes MSA a good indicator for secondary organic aerosols (SOA) with marine origin. Besides DMS, several biogenic volatile organic compounds such as isoprene and monoterpenes have been recognized as possible precursors for marine SOA (Fu et al., 2011; Hu et al., 2013), though their significance in SOA formation remains unclear because inconsistent conclusions were drawn in different studies~~. It is difficult to find pristine conditions over the ocean. Significant impacts from ship and continental emissions were observed over the Pacific and Atlantic (63% of the sampling time) (Frossard et al., 2014), the Arctic (Chang et al., 2011) and the North Pacific between South Asia and North Japan (Choi et al., 2017). Nevertheless, there are still some regions with little anthropogenic impact on marine aerosols, such as the station on the coast of Ireland in the northeast Atlantic (Ceburnis et al., 2011; O'Dowd et al., 2014). ~~It is, however, difficult~~Due to ~~distinguish~~ the ~~primary and secondary marine organic aerosols~~ paucity of ship-based ~~on chemical characteristics. For example, carboxylic acids could be~~measurements, the ~~highly oxygenated products via secondary pathway, but also have been recognized as a distinct component in the marine primary organic matters (Hawkins and Russell, 2010); amines can contribute up to 14% of the submicron OA mass in the fresh sea spray aerosols (Quinn et al., 2014; Russell et al., 2010), and can also serve as precursor of marine SOA (Facchini et al., 2008; Ge et al., 2011; Müller et al., 2009).~~

~~Although certainly contributed by the ocean, the~~ nonmarine influence on MBL aerosols ~~can be influenced by many non-marine sources, including continental pollutants and ship emissions (Andreae, 2007; Heintzenberg et al., 2000; Saltzman, 2009; Simpson et al., 2014). Frossard et al. (2014) observed that organic matters~~is still unknown, especially for a large area of the oceans. Additionally, previous studies were ~~impacted by ship and continental pollutants during 63% of the sampling time in a series of measurements over the Pacific and Atlantic. Over the central Arctic Ocean, the identified continental contribution is comparable to the marine biogenic sources (36% vs 33%), and the rest 31% of the sampled ambient aerosol mass can possibly be influenced by multiple sources including aged continental emissions (Chang et al., 2011). Also, the~~often based on offline measurements~~ on ship transects between the South Asia and Northern Japan indicate heavy contaminations from non-marine sources in MBL aerosols, and the OA is mainly contributed by biomass burning (BB) emissions and anthropogenic pollution (Choi et al., 2017). Nevertheless, there are still some regions with little anthropogenic impact on the marine aerosol. For example, Ceburnis et al.(2011) found 80% organic aerosol matter of biogenic origin related to marine plankton emissions over the northeast Atlantic. O'Dowd et al.(2014) pointed out that the anthropogenic and coastal effects can be sufficiently minimized with the selection criteria to ensure the predominant marine contribution to the measured aerosols at Mace Head, a research station in the coast of the northeast Atlantic.~~

~~So far, the source apportionment of the MBL aerosols has been performed with multiple indicators or methods such as isotopes (Ceburnis et al., 2011; Seguin et al., 2011; Seguin et al., 2010), transmission electron microscope (e.g. Bigg and Leck, 2008; Leck and Bigg, 1999; Leck and Bigg, 2005), cluster analysis (Frossard et al., 2014; Rebotier and Prather, 2007), principal component analysis (Decesari et al., 2011), and positive matrix factorization (PMF) method (Chang et al., 2011; Choi et al., 2017; Schmale et al., 2013a). But, many details of the source contribution to the MBL aerosol are still unknown at both~~ , which could hardly provide variation of aerosol chemical properties at high temporal and spatial ~~scales. This is because the observations over the open ocean are few (Choi et al., 2017; Dall'Osto et al., 2010; Zorn et al., 2008) and most of the marine aerosol measurements were conducted on coastal or island stations (e.g. Crippa et al., 2013b; Ovadnevaite et al., 2014; Rinaldi et al., 2010; Schmale et al., 2013a).~~ resolution. In this study, aerosol measurements were conducted on board the German research vessel (R/V) Polarstern based on ~~4~~four cruises ~~over~~in the Atlantic Ocean in 2011 and 2012, covering the range from 53°N to 53°S. The detailed chemical characteristics of the Atlantic aerosols were measured by a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS). Based on this unique data~~-~~ set, sources of the organic aerosol particles over ~~the~~a major part of the Atlantic were investigated ~~in~~at a high temporal and spatial resolution to provide a latitudinal distribution of ~~OA~~organic aerosol (OA) source contributions in spring and autumn~~.~~ in both the Northern and Southern Hemispheres.

2 Methods

2.1 Ship-board campaigns measuring submicrometer marine aerosols over the Atlantic Ocean

~~The~~ This study is based on aerosol measurements ~~were~~ conducted by the Leibniz Institute for Tropospheric Research (TROPOS) during four cruises on ~~board of RV~~the R/V Polarstern in 2011 and 2012.~~-~~ Expedition details and ship tracks of the cruises are shown in Table 1 and Figure 1. All cruises were part of transfer voyages between Bremerhaven, Germany (53°33′N, 8°35′E~~)~~), and the German Antarctic research station~~,~~ via either Cape Town, South Africa (33°55′S, 18°25′E~~)~~), or Punta Arenas, Chile (53°10′S, 70°56′W). ~~In~~During each cruise, the ship ~~shortly~~briefly (and only) moored at Las Palmas, Spain (28°9′N, 15°25′W~~)~~), for ~~a supply~~resupply. The cruises can be divided into two groups according to the~~ campaign~~ period of the year: Cruise 1 (CR1) and Cruise 3 (CR3) correspond to spring in the Northern Hemisphere (NH), while Cruise 2 (CR2) and Cruise 4 (CR4) correspond to autumn in the NH. In terms of the spatial range, CR1, CR2 and CR4 followed almost the same route, while CR3 had ~~the~~ different ~~track~~tracks in ~~South~~the Southern Hemisphere~~,~~ but followed the same route ~~than~~as the other three cruises from ~ 15~~-~~°N to 53~~-~~°N (Figure 1).

During all ~~four~~4 cruises, the instruments were deployed inside (and on the roof) of an air-conditioned laboratory container, which was located on the first deck of the vessel, approximately 30 m above the ocean surface (Figure 1). The whole-air sampling inlet of the container was made of a stainless-steel tube (6 m long, 40 mm diameter, with an inclination angle of 45° to the container roof). A vacuum system ~~kept~~maintained a stable total aerosol flow rate of ~~approximately~~ 15 ~~liter per minute (l~~L min^{-1}~~)~~ through the inlet. The inlet loss due to diffusion and deposition was calculated ~~by the tool Particle Loss Calculator (von der Weiden et al., 2009). According to this tool, the container inlet completely excluded particles with mobility diameter larger than about 3 µm. In submicrometer size range (10 nm – 1000 nm),~~ (Figure S1), suggesting that the average inlet efficiency ~~is~~was nearly 100~~%,~~% in the particle size range between 10 nm and 1000 nm but ~~decreases~~decreased rapidly for particles smaller than 2 nm and larger than 1500 nm~~ (Figure S1).~~. Therefore, the inlet could be considered a PM$_{1.5}$ inlet.

An isokinetic splitter was used downstream of the aerosol inlet to distribute the aerosol flow to different online instruments for analysis of aerosol physicochemical properties, as mentioned below. Particle size distributions from 10 nm to 3 µm (mobility diameter, equal to volume equivalent diameter for spherical particles) were provided by a combination of one TROPOS-type mobility particle size spectrometer (MPSS, 10 nm - 800 nm, TROPOS custom-built, see Wiedensohler et al., 2012)~~,~~ and one Aerodynamic Particle Size Spectrometer (type TSI APS model 3321, 500 nm - 10 µm, TSI Inc., Shoreview, MN, USA). The particle hygroscopicity at 90–% relative humidity (RH) was measured by a Hygroscopicity Tandem Differential Mobility ~~Analyser (HTDMA, see details in e.g. Massling et al., 2011; Wu et al., 2011).~~Analyzer (HTDMA, TROPOS custom-built, e.g. Wu et al., 2011). A Differential Mobility ~~Analyser~~Analyzer – Cloud Condensation Nuclei Counter ~~(DMA-CCNc, see e.g. Henning et al., 2014)~~ (DMA-CCNc, TROPOS custom-built, e.g. Henning et al., 2014) was used for size-resolved measurements of cloud condensation nuclei. Optical properties including light scattering and absorption coefficients of particles were provided by an ~~Integrating Nephlometer~~integrating nephelometer (Model 3563, TSI Inc., Shoreview, MN, USA), a ~~Multi Angle Absorption Photometer (MAAP, Model 5012, Thermo Inc. USA)~~multi-angle absorption photometer (MAAP, Model 5012, Thermo Scientific, Waltham, MA, USA; see Müller et al., 2011) and a ~~Particle Soot Absorption Photometer~~particle soot absorption photometer (PSAP, Radiance Research, Inc., Seattle, WA, USA). Particle chemical properties were investigated using a HR-ToF-AMS (Aerodyne Research, Inc., Billerica, MA, USA), which is the central instrument for the present study. In parallel, ~~an offline particulate matter (diameter < 1 µm, i.e., PM_1)~~a high volume PM_1 sampler (Digitel, DHA-80, Digitel Elektronik AG, Switzerland) ~~that~~ was fixed on the roof of the aerosol container and provided daily (24 h) ~~particle chemical composition.~~filter samples. Before each campaign, all instruments in the aerosol container were synchronized to UTC ~~time~~ (Coordinated Universal Time).

2.2 Measurements

2.2.1 Particle chemical analysis

2.2.1.1 HR-ToF-AMS

~~HR-ToF-AMS (referred to as AMS in the following text) can directly distinguish the elemental composition of ions having the same nominal mass (DeCarlo et al., 2006). The instrument principle and field deployment have been described in detail in previous publications (e.g. Canagaratna et al., 2007; DeCarlo et al., 2006; Drewnick et al., 2005; Jayne, 2000; Zhang et al., 2007). The particles drawn into AMS impact onto a thermal vaporizer plate (600°C) where the non-refractory (NR) part of the particles were detected. The AMS provides size resolved chemical composition of aerosol particles in submicrometer size range(Canagaratna et al., 2007). Its size cut is within the range of nearly unity transmission efficiency of the main container inlet during Polarstern cruises (Figure S1). The inlet flow rate of AMS was approximately 0.08 l min^{-1}. To minimize the inlet loss between the AMS and MPSS, the AMS was located next to the MPSS and the inlet of AMS was connected direct in front of the MPSS inlet. The two instruments shared a Nafion dryer to maintain relative humidity (RH) lower than 40 %. The AMS was operated alternatively between V- and W-modes associated with PToF and/or MS modes at a time resolution of 2 min.~~

~~Collection efficiency (CE) of 0.7 was determined based on inter-comparisons between: (1) AMS and MPSS, (2) AMS and offline measurements (Huang et al., 2017).~~

The HR-ToF-AMS (referred to as AMS in the following text) can provide the size-resolved chemical composition of nonrefractory submicron particles (Canagaratna et al., 2007; DeCarlo et al., 2006). Its size cut is within the range of near unity transmission efficiency of the main container inlet during R/V Polarstern cruises (Figure S1). To minimize the inlet loss between the AMS and MPSS, the AMS was located next to the MPSS, and the inlet of AMS was connected directly in front of the MPSS inlet. The two instruments shared a Nafion dryer to maintain relative the humidity (RH) of the sampling flow below 40%. The AMS was operated alternatively between V- and W-modes at a time resolution of 2 min. Regular calibration was performed according to reported methods (Jimenez et al., 2003). Collection efficiency (CE) of 0.7 was applied based on intercomparisons between the (1) AMS and MPSS and (2) AMS and offline measurements, as already described in Huang et al. (2017).

The default components measured by the AMS include organics, sulfate, nitrate, ammonium and chloride. ~~Particularly,~~ In particular, the marine biogenic tracer MSA was quantified ~~with~~by the AMS based on standard calibrations and validated by collocated offline measurements (Huang et al., 2017). ~~The relative ionization efficiencies (RIE) of the above species were calibrated by the standard tests using pure ammonium nitrate, ammonium sulfate and MSA weekly during the measurements. In order to better~~To reduce the signal noise, AMS data ~~in~~with a 20-min average are calculated and used in the following analysis except as noted. Table 2 provides the detection limits (~~DL~~DLs) of detected AMS species ~~for~~at 20-min resolution (for calculation details, see Huang et al., 2017). ~~Besides~~In addition, a total uncertainty of ~ 30% is estimated for AMS measurements, including 10% for the inlet system, 20% for the ionization efficiency calibration and 20% for the collection efficiency ~~(Crippa et al., 2013a; Freutel et al., 2013; Poulain et al., 2014)~~ (Poulain et al., 2014).

The AMS data measured during R/V Polarstern ~~measurements~~cruises were analyzed using the software Squirrel v1.54 for the unit resolution and Pika v1.13 for the high-resolution, both downloaded from the ~~Tof~~ToF-AMS webpage (http://cires1.colorado.edu/jimenez-group/wiki/index.php?title=ToF-AMS_Main~~).~~). The software was based ~~in~~on Igor Pro (version 6.22A, WaveMetrics Inc., ~~version 6.22A~~Portland, OR, USA).

2.2.1.2 Offline measurements

A PM_1 high volume Digitel filter sampler was deployed to sample aerosol particles at a 24-hour time resolution (midnight to midnight, UTC) during R/V Polarstern CR1, CR2 and CR3, ~~working~~operating at a flow rate of 500 l min^{-1}. The daily aerosol masses were collected on quartz fiber filters (150 mm, Munktell, MK 360, Bärenstein, Germany), which were ~~pre-treated~~pretreated at 105 °C for 24 h before ~~the measurement.~~being measured. All filter samples were ~~stored in the fridge~~refrigerated at -20 °C until ~~being analysed~~analysis. The total aerosol particle mass was determined by the weight of the clean and particle loaded filter, and the loaded filter was separated ~~in~~into several aliquots for different ~~analysis~~analyses. Inorganic ions and oxalate were measured after aqueous filter extraction (25% of the filter in 20 mL, filtered with a 0.45 µm syringe) with ion chromatography (IC, ICS3000, Dionex, Sunnyvale, CA, USA). Organic carbon (OC) and elemental carbon (EC) were analyzed by a ~~thermographic method (C-mat 5500, Ströhlein, Germany) using~~thermo-optical method with a Sunset

Laboratory Dual-Optical Carbonaceous Analyzer (Sunset Laboratory Inc., Tigard, OR, U.S.A.) using the EUSAAR 2 protocol ~~(see more details in van Pinxteren et al., 2017). In total 86 ambient samples from CR1 (25 samples), CR2 (30 samples) and CR3 (31 samples) were analysed, while 45 effective samples were used in this study due to exclusion of filters contaminated by ship exhausts and sea-water contact under stormy conditions.~~ (van Pinxteren et al., 2017). In total, 86 ambient samples from CR1 (25 samples), CR2 (30 samples) and CR3 (31 samples) were analyzed, while 45 effective samples were considered in this study due to the exclusion of filters contaminated by ship exhausts and/or sea water.

2.2.2 Other measurements and data sources

~~During the Polarstern measurements, the particle number size distribution in the range between 10nm and 800nm was measured by a TROPOS-type MPSS, described in detail in previous literatures (e.g. Birmili et al., 1999; Birmili et al., 1997; Wiedensohler et al., 2012).~~ In this study, ~~only~~the MPSS ~~was~~and MAAP were used as external ~~instrument~~instruments to evaluate the data quality of the AMS ~~due to~~or provide supplementary information for the ~~similar measuring range of~~total particle ~~size (smaller than 1μm). This~~mass. The MPSS was operated at a time resolution of 8 min (CR1, CR2) and 5 min (CR3, CR4~~) with condition of RH < 40 %.~~), following recommendations from Wiedensohler et al. (2012). The resulting particle number size distribution was corrected for internal particle losses. Generally, an uncertainty of approximately 10 % can be considered, as shown by ~~inter-comparison~~intercomparison experiments (Wiedensohler et al., 2012).

The particle mass concentration of equivalent black carbon (~~BC~~eBC) was converted from the particle light absorption coefficient provided by ~~a~~the MAAP. ~~Detailed instrument description is available in previous articles (Müller et al., 2011; Petzold et al., 2002; Petzold and Schönlinner, 2004). The instrument measures the aerosol particle light absorption coefficient at 637 nm and reports the BC mass concentration by applying BC mass absorption coefficient 6.6 m^2 g^{-1}.~~ To be combined with the particle concentration measured by the AMS, ~~BC~~eBC mass concentration in the submicrometer size range is required. Here, the MAAP was connected to the main inlet of the aerosol container, which mostly collected particles no larger than 1.5 µm. Additionally, Poulain et al. (2011b) reported that ~~BC mass concentration in PM$_1$ is approximately~~ eBC particles are mainly (90% of ~~that in PM$_{10}$~~mass) distributed in the submicrometer size range according to ~~the~~a comparison between the data from 2 MAAPs with ~~PM$_1$~~upper size cuts of 1 µm and ~~PM$_{10}$ inlet in the central European background station of~~ 10 µm inlets in Melpitz (Germany). ~~However, here the MAAP was connected to the main inlet of the aerosol container which had significant particle loss when particle diameter was larger than 1500nm.~~ Thus, we suppose that the measured ~~BC~~eBC particles are almost in the submicrometer size range. In total, a global uncertainty of ~~5~~10% was ~~counted for~~attributed to MAAP measurements taking the uncertainties of the instrument, size cutting, density and mass absorption efficiency into consideration.

All meteorological parameters on R/V Polarstern cruises were measured by an ~~on-board~~onboard German Weather Service (~~Deutscher Wetterdienst,~~ DWD) station. Air mass back trajectories along the ship track in 12-hour time resolution (00:00 and 12:00 UTC ~~everyday~~every day) were also retrieved ~~by~~from the DWD~~,~~ using a global meteorological model GME ~~(Global Model of the Earth, Majewski et al., 2002).~~(Global Model of the Earth). Air masses at 950 hPa (approximately 500 m) were selected and considered as a well-~~mixing~~mixed situation~~;~~, and backward trajectories ~~in~~over the last five days (120 h) were investigated in this study. ~~Air mass back trajectory data were directly obtained from the DWD.~~ Navigation parameters together with meteorological parameters were supplied by the R/V Polarstern central data acquisition system (https://dship.awi.de/).

2.3 Positive matrix factorization (PMF)

~~PMF is frequently used for organic aerosol (OA) mass spectra analysis from AMS data, dividing OA into several factors with different origins or oxidation state~~ The source apportionment of OA measured on the R/V Polarstern was analyzed using the PMF method (Paatero, 1997; Paatero and Tapper, 1994). ~~The principle of this statistical model is described in the Equation 1 (Paatero, 1997; Paatero and Tapper, 1994):~~

~~$x_{ij} = \sum_p g_{ip} f_{pj} + e_{ij}$ (1)~~

~~In this study, the x_{ij} is the element of the matrix of the measured AMS~~High resolution (HR) organic ~~data to be fit (whose columns are time series of each *m/z* and rows are~~ mass spectra ~~with signal intensity at *m/z* from 12 to 120). The g_{ip} and f_{pj} are the elements of the matrices presenting the variability (time series) and the profile (mass spectra) for *p* factors according to the model solution, and values in these two matrices are constrained to be positive. The e_{ij} is the element of the matrix of the residuals. The subscripts *i*, *j* and *p* correspond to the row or column indices in the matrices.~~

~~To fit the data, the model uses a weighted least-squares algorithm based on the known standard deviations (σ_{ij}) of the elements of the data matrix to minimize a parameter *Q*, as well as minimizing the residuals (Equation 2) (Paatero, 1997; Ulbrich et al., 2009).~~

~~$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} (e_{ij}/\sigma_{ij})^2$ (2)~~

~~The advantages of PMF method are: (1) the measurement errors are considered in statistical calculation, and (2) the solutions of PMF are physically meaningful for ambient aerosol since the matrix elements are constrained to be positive.~~ ~~For Polarstern AMS data, PMF analysis was run for a 4-cruise~~and their uncertainties over the four cruises were combined ~~HR organic dataset using the PMF2 algorithm in~~and input into the Igor Pro-based PMF Evaluation Tool (PET, v2.06, Ulbrich et al., 2009). Before running the PMF model, the HR organic mass matrix and its error matrix were examined to remove ~~ship contamination periods,~~ incorrect signals (e.g~~.~~., organic fragments influenced by strong sulfate signal~~) and~~), very low signals (e.g~~.~~., C_x group, isotopes and *m/z* > 120~~).~~), and ship contamination periods. According to the instructions from Ulbrich et al. (2009), a minimum error estimate of one measured ion was calculated; the “bad” data with ~~Signal~~signal-to-~~Noise Ratio~~noise ratio (SNR) less than 0.2 were removed, and the “weak” data with SNR between 0.2 and 2 were ~~down-weighted~~downweighted by a factor of 2; signals for *m/z* 44 (CO_2^+) and related ions (O^+, HO^+, H_2O^+ and CO^+) were also ~~down-weighted~~downweighted by a factor of 2 ~~in order~~ to avoid overestimating the importance of CO_2^+. To find the best solution, PMF was run between 1 and 7 factors for (1) rotational forcing parameter fPeak between -1 and 1 (step of 0.2) and (2) seeds with random starts between 0 and 50 (step of 2). Based on a comprehensive evaluation of solutions with different factor numbers (regarding both time series and mass spectral pattern), a 5-factor solution was selected with fPeak = 0 and Q/Q_{exp} = 0.9246. The elemental analysis of PMF factors was performed ~~by~~using the ~~tool Analytical Procedure~~analytical procedure for ~~Elemental Separation~~elemental separation (APES light v1.06) tool detailed by Aiken et al. (2008) and Canagaratna et al. (2015). ~~To find the best solution, PMF was run between 1 and 7 factors for (1) rotational forcing parameter fpeak between -1 and 1 (step of 0.2), and (2) seeds with random starts between 0 and 50 (step of 2). The PMF analysis is detailed below~~Detailed PMF analysis results are shown and interpreted in section 3.2.

3 Results and discussions

3.1 Particle chemical composition

3.1.1 AMS data quality assurance

Ship contamination exclusion. During all four cruises, the ship's own exhausts (including emissions from the engine and kitchen) from the main chimney occasionally affected the measurements, especially when the wind came from behind the ship. ~~In this study, the detailed contaminated~~The specific contamination periods are identified based on extremely high ~~concentration~~concentrations of combustion tracers (e.g~~. BC~~., eBC and organics) and meteorological parameters (e.g~~.~~., wind direction~~)~~), as illustrated in Figure S2 and Figure S3. Accordingly, ~~a~~the ship contamination range of the relative wind direction (RWD) was determined ~~as~~to be between 135° and 250°. With this criterion, 85.2% of ambient AMS data (2-min resolution) remained as "clean" data during all 4 cruises. In the following text, all the data ~~analysis is~~analyses are performed on the "clean" data ~~except as noted~~.

Intercomparisons between AMS and PM$_1$ offline. Prior to investigating the particle chemical composition during the R/V Polarstern measurements, ~~the inter-comparisons~~intercomparisons between AMS and parallel measurements were performed to assure the AMS data quality (Figure S4 and Figure S5). ~~The total particle mass concentration from AMS is calculated as the sum of the mass concentrations of default AMS species (i.e. organics, sulfate, nitrate, ammonium) completed by estimated sea-salt and BC. It is compared to the calculated particle mass concentration derived from the particle number size distribution. Taking sea salt into the consideration can slightly improve the correlation between two different techniques (slope varies from 0.81 to 0.85; R^2 varies from 0.72 to 0.77, Figure S4). Also, the~~The mass concentration of the individual species from the AMS ~~is~~was compared to that from the offline measurements (Figure ~~S5~~S4). Organic matter (OM) provided by AMS measurement is correlated with ~~organic carbon (~~OC~~)~~ from filter measurements (R^2 = 0.53). The slope of 1.75, i.e~~.~~., the OM/OC ratio, is similar to those found in ~~the coastal cities as well as~~ offshore areas, e.g~~. 1.7 – 1.9 in Pasadena (Hayes et al., 2013),~~., 1.8 in the Gulf of Mexico (Russell et al., 2009)~~, and 1.66 – 1.72 in Paris (Crippa et al., 2013b). The~~ . An excellent linear correlation ~~is~~was found for sulfate (slope = 1.16, R^2 = 0.94), and the correlation for ammonium ~~is~~was moderate (slope = 0.80, R^2 = 0.63). No correlation ~~is~~was found for nitrate and chloride. A ~~part~~few values of nitrate ~~concentrations~~ from the AMS are higher than those from offline measurements, probably ~~attributed~~due to the evaporative ~~losses~~loss of nitrate ~~especially under low mass concentration conditions and the unidentified~~ . The contribution of ~~the~~ organic nitrates~~.~~ remains unknown but might not be negligible. Chloride is underestimated by the AMS because this instrument partly detects ~~the~~ sea salt, which is the main source ~~for~~of the chloride measured during R/V Polarstern cruises. Considering that nitrate and chloride account for only a tiny fraction of the measured particle mass concentration and the sea salt is estimated specifically, the ~~comparisons above ensure the data quality~~AMS can still properly detect a major part of ~~AMS~~ MBL aerosols in our measurements.

Mass closure with MPSS. The ~~inter-comparisons~~total particle mass concentration from the AMS is calculated as the sum of the mass concentrations of default AMS species (i.e., organics, sulfate, nitrate, ammonium) completed by estimated sea salt and eBC. This concentration is compared to the calculated particle mass concentration derived from the particle number size distribution (Figure S5). Taking sea salt into consideration can slightly improve the correlation between the two different techniques (the slope varies from 0.81 to 0.85; R^2 varies from 0.72 to 0.77, Figure S5). The intercomparisons also demonstrated that a constant ~~Collection Efficiency (~~CE~~)~~ of 0.7 for AMS measurements could achieve better agreement between AMS and external measurements, whereas the ~~Composition Dependent Collection Efficiency~~composition-dependent collection efficiency (CDCE) introduced by Middlebrook et al. (2012) does not seem appropriate for R/V Polarstern measurements because of the high acidity and low ammonium nitrate content of the MBL aerosol particles~~. A detailed explanation has been given in the previous paper~~ (Huang et al., 2017).

Sea salt estimation. The important primary marine product, sea salt, was estimated using the method from Ovadnevaite et al. (2012)~~ who successfully quantified the sea salt aerosol concentration with the sea salt typical ion NaCl$^+$ (m/z 57.95) and applying a scaling factor of 51. Although NaCl$^+$ ion could be well identified by the high resolution mass spectrometer of the AMS, the correlation between NaCl$^+$ ion and sea salt derived from PM$_1$ filter samples in Polarstern measurements showed a mild relationship with R^2 of 0.38 (Figure S6). The possible reasons for this might be, first, the slightly different sampling (inlet) location of the two samples; and second, the small amount of the available offline data during Polarstern cruises. The effective samples (45 samples) may be insufficient to provide meaningful correlation between offline and AMS sea salt in 4 Polarstern cruises, especially when comparing to the full year measurements in the reference. Therefore to be consistent with the literatures (Ovadnevaite et al., 2012; Ovadnevaite et al., 2014; Schmale et al., 2013a), the scaling factor of 51 from the reference is applied to the sea salt surrogate (NaCl$^+$) to estimate the sea salt mass concentration in this study.~~

, who successfully quantified sea salt aerosol concentration with HR-ToF-AMS in Mace Head. The reported method is based on the typical sea salt ion NaCl$^+$ (m/z 57.95) and a scaling factor of 51 derived from laboratory calibration using artificial seawater (Ovadnevaite et al., 2012). In R/V Polarstern measurements, NaCl$^+$ fragment was well identified by the high-resolution mode. Nevertheless, the linear correlation between NaCl$^+$ from the AMS and sea salt derived from PM$_1$ filter samples showed a mild relationship with R^2 of 0.38 and yielded a scaling factor of 62 (± 6). To be consistent with the literature (Ovadnevaite et al., 2012; Ovadnevaite et al., 2014; Schmale et al., 2013) the scaling factor of 51 from the reference is applied to the sea salt surrogate (NaCl$^+$) to estimate the sea salt mass concentration in this study. With this factor, the AMS estimated sea salt concentrations are quite close to those measured by the offline method, showing a slope of 1.01, and the main scattering points are located within the uncertainty range of the Mace Head measurements (Figure S6). Additionally, the p-value of the regression of AMS-derived sea salt with offline results is 0.009 (Spearman's correlation test), indicating that sea salt concentrations from the AMS and offline methods are correlated significantly. The uncertainties of this estimation method in R/V Polarstern measurements probably link to the different sampling (inlet) locations as well as the discrepant analysis methods between the AMS and offline measurements.

3.1.2 Chemical composition of the aerosol over the Atlantic Ocean

~~Based on the data quality control in steps above, an~~An overview of the chemical composition of Atlantic aerosol particles during 4 cruises is given ~~by~~in Figure 2~~, including~~ and includes AMS default species (organics, sulfate, nitrate and ammonium), ~~estimated~~ specially quantified marine products MSA and sea~~-~~ salt, as well as ~~BC. Since~~eBC. Because the ship tracks on latitude are nearly monotonic to the cruise time, particle chemical composition as a function of latitude ~~gives~~shows both temporal variation and ~~latitude~~latitudinal distribution. Air mass back trajectories indicate that the air masses captured ~~by the aerosol container~~ during R/V Polarstern cruises ~~came~~ either came from the ocean or were influenced by the continents (Europe, Africa or South America~~). These two air mass categories, marine air mass and mixed air mass with continental influence, are also~~), as marked in Figure 2. ~~The classification into five air mass groups (three for marine, two with continental influence) is briefly described in Table S1, which is consistent with those in previous on-board studies over the Atlantic Ocean (Maßling et al., 2003; Norman and Leck, 2005; Virkkula, Aki et al., 2006; Virkkula, A. et al., 2006).~~ Additionally, the statistics of seasonal variation of PM$_1$ chemical composition over the North (>5°, i.e~~.~~., 5°N) and South (<-5°, i.e~~.~~., 5°S) ~~of the~~ Atlantic are provided in Table 3. ~~Since~~Because there is no clear seasonal difference ~~of~~in the chemical composition of measured PM$_1$ in the area near the equator, the average, median, standard deviation and percentage in total were calculated for the region from ~5°S to ~5°N ~~(-5° ~ 5°) on~~ in latitude (defined as ~~tropic~~tropical in this study) regardless of the season~~, which~~ and are also shown in Table 3. Over all measurements, the total measured submicron particle mass concentration ~~varies~~varied over a large range from 0.22 µg m^{-3} to 14.15 µg m^{-3}~~. Its~~ with a median ~~is~~of 1.83 µg m^{-3}~~,~~. The reported concentrations sit between the clean marine case (from 0.27 to 1.05 µg m^{-3}) measured ~~over~~at the ~~Northeast Atlantic~~coastal station Mace Head, Ireland (Ovadnevaite et al., 2014)~~,~~ and the case of mixed marine-continental air masses (from 3.69 to 4.17 µg m^{-3}) over the North Atlantic (Dall'Osto et al., 2010). This difference suggests that the detected ~~aerosol~~aerosols during the R/V Polarstern cruises ~~was~~were from mixed sources as ~~hinted~~evidenced by the air mass origins. ~~On~~The average~~,~~, chemical composition of the measured ~~particle mass during 4 cruises is contributed half by~~particles indicated that sulfate was the major contributor to the total particle mass concentration (50 ± 13~~ %), which is~~%), followed by organics (21 ± 9 %), sea salt (12 ± 11 %), ammonium (9 ± 4~~ %), BC~~%), eBC (5 ± 4%) and nitrate (3 ± 2%). ~~However, the~~The mass concentrations of total ~~particle as well as~~ particles and individual species ~~show~~showed large ~~variation~~variations associated with ~~the~~ time and were obviously ~~they are~~ not distributed normally. Hence, the median rather than average of the mass concentration is used below.

During all ~~4~~four cruises, sulfate dominated the particle mass most of time, showing the highest median ~~of~~ mass concentration (0.78 µg m^{-3}) ~~in~~of all six species. ~~It~~Sulfate could contribute up to 85~~ % to~~% of the total particle mass concentration. Seasonal ~~discrepancy is~~discrepancies were found for sulfate mass concentration (a higher level in spring than in autumn), especially over the South Atlantic (Table 3). ~~Similar~~A similar seasonal variation of the marine biogenic tracer MSA was also observed

(Huang et al., 2017), suggesting ~~the~~that biogenic sources (i.e., phytoplankton) contributed significantly to sulfate~~.~~ (Charlson et al., 1987; Hoffmann et al., 2016). In the tropical Atlantic, sulfate appeared at a slightly lower value than that in spring but was still much higher than that in autumn. Nonetheless, anthropogenic sources of sulfate cannot be ruled out and can even be important, considering that long-range transport has been found to be a major source of sulfate (more important than DMS) over the tropical Pacific (Simpson et al., 2014).

Organics (here including MSA) are the second most abundant species (median: 0.26 µg m^{-3}). ~~The dominance of sulfate and organic is similar to other observations over the Atlantic Ocean (Dall'Osto et al., 2010; Zorn et al., 2008). Different from sulfate and MSA which have clear seasonal pattern, organics~~Organics did not show pronounced variation associated with ~~season,~~seasons but ~~more~~did vary with location. The mass concentration of organics was elevated ~~with~~in air masses under continental influence. During CR2 and CR4, organics ~~even~~ dominated the total measured particle mass concentration (up to 59%) in the region between 0° and 15°N. ~~Meanwhile, the non-marine~~This resulted in substantial organic aerosols over the tropical Atlantic (median: 0.34 µg m^{-3}). Moreover, the nonmarine species ~~BC, despite tiny contribution to the total particle mass, was tending~~BC tended to increase together with organics~~. It~~, especially near the equator, although taking up only a tiny portion of the total particle mass in the whole measurements, which indicates that anthropogenic emissions may be a significant contributor to the organics in this part of the Atlantic Ocean.

The marine primary product, sea salt~~ is~~, was found to play a minor role (6% ~ 17% in different regions) in the measured submicron particles during R/V Polarstern cruises. However, ~~associated with the elevated wind speed,~~ the mass concentration of sea salt ~~can~~could reach 1.63 µg m^{-3} while taking up to 66% of the total particle mass loading ~~(Figure 2). It is still~~ associated with elevated wind speed. This finding is comparable to the ~~sea salt's~~ importance of sea salt reported ~~in winter~~ over the Northeast Atlantic (66~~-~~ – 84%) (Ovadnevaite et al., 2014) and in the sub-Antarctic ~~island~~islands (47%) ~~(Schmale et al., 2013a) when winds were~~(Schmale et al., 2013) for high~~-~~ wind speed (> 10 m s^{-1}).

The ammonium concentrations ~~didn´t follow~~did not exhibit a ~~clear~~ seasonal ~~trend, although~~difference between spring and autumn. The highest median value was found over the tropical Atlantic, followed by the North Atlantic, while the lowest median value was in the Southern Hemisphere. Both continental emissions via long-range transport and marine organisms could be the origin of the ammonium or its precursor ammonia ~~could be emitted from ocean~~in the MBL ~~(Ikeda, 2014; Johnson et al., 2008). The absence in seasonality suggests particulate ammonium during Polarstern cruises was contributed by both anthropogenic and biogenic sources.~~(Adams et al., 1999). Nitrate ~~also~~ showed ~~no seasonal pattern during all cruises and~~ low mass concentration (0.04 µg m^{-3}~~). The absence of nitrate~~), which is not surprising~~,~~ because ~~on the one hand~~ it both has no marine sources~~,~~ and ~~on the other hand, nitrate~~ would mainly occur in supermicron particles~~. That is because~~ - nitrate would react with sulfuric acid and escape from submicron particles in the form of gaseous nitric acid, which will relocate to larger particles, e.g.~~.~~., sea salt particles (Saltzman, 2009).

3.2 Source apportionment for ~~organics aerosol (OA)~~organic aerosols

Source ~~identification and~~ apportionment ~~for~~of the MBL organic aerosol particles ~~are~~is necessary for a better understanding of ~~their chemical characteristics and transformations. Organics are one of the main constituents of aerosol particles and contain hundreds of compounds from various origins. Analysing the source of organics may provide hints for evaluating origins and processes of other components. For the source apportionment of organics~~both the factors contributing to the OA and their distribution over the Atlantic Ocean. For the OA source apportionment, PMF analysis was performed on the dataset of high-resolution ~~organic aerosol (OA)~~OA mass spectra ~~following the construction from Ulbrich et al. (2009). Based on a comprehensive evaluation of different number of factors (regarding both time series and mass spectral pattern) and the rotational forcing parameters fPeak, a 5-factor~~. Eventually, the best solution was ~~selected~~obtained with ~~fPeak =0 and Q/Q$_{exp}$ = 0.9246~~five factors. A summary of the model validation of ~~the model~~ and selection of the five-factor ~~PMF~~ solution is provided in ~~the~~ Figure S7~~. The mass spectra and time series of the chosen solution did not change pronouncedly with the different fPeak as well as different seed (Figure S7). For the 4-factor solution, the nitrogen-containing OA (NOA) factor was missing, while oxygenated OA (OOA) factor split into two factors in the 6-factor solution (~~, Figure S8~~). More details of both mass spectral profile and time series of 4- and 6-factor solutions can be found in Figure S8. To sum up, the 5-factor solution can properly explain the total OA with physical meanings for each factor.~~

and Figure S9 with captions. Among the five OA factors~~, four secondary (SOA) and one primary (POA) organic aerosol particle components were found in the Polarstern measurements.~~ of the selected solution, three marine factors and two nonmarine factors were identified. Their temporal variation and mass spectral profiles are shown in Figure 3. The ~~SOA components include: (1) marine organic aerosol (MOA) with the highest S/C ratio (0.030), correlated well with the~~ marine ~~tracer MSA (R^2 = 0.83). These S/C ratios derived from the PMF analysis tool contain however certain estimation uncertainties and have therefore to be used with caution (Aiken et al., 2007); (2) nitrogen-containing organic aerosol (NOA) with the highest N/C ratio (0.124); (3)~~ factors included (1) marine oxygenated organic aerosol (MOOA), (2) marine nitrogen-containing organic aerosol (MNOA), (3) marine hydrocarbon-like organic aerosol (MHOA), and the primary OA factors. The remaining two factors related to nonmarine origins were anthropogenic oxygenated organic aerosol (Anthr-OOA) and combustion oxygenated organic aerosol (Comb-OOA~~) correlated with continental tracer NO_3 (R^2 = 0.52); (4) aged primary organic aerosol (aPOA) with highest O/C ratio (1.35), varying temporally with BC (R^2=0.68). The only primary organic aerosol (POA) factor is characterized by abundant C_xH_y ions consequently with lowest O/C ratio (0.23) of all five factors.~~).

~~Figure 4 shows (a) the mass fraction of all 5 factors in total measured organics, as well as the functional groups composition and (b) the diurnal variation of each factor. Note that the mass fraction pie represents the average mass fraction of each factor derived from PMF analysis, and the “residuals” part of 0.4% is ignored in the pie chart but existing. The residuals correspond to the unexplained organics by PMF.~~ Table 4 summarizes all comparisons for ~~the~~source identification of the five OA factors, including~~:~~ (1) correlations of time series between the OA factors and the measured tracers~~;~~ and (2) correlations of mass spectral ~~pattern~~patterns between the OA factors and the identified OA sources in the ~~literatures. Details on~~literature. The average mass fraction of all five factors in the total measured OA, the functional group composition and the diurnal variation of each factor with global radiation (the sum of the direct solar radiation and diffuse radiation) are shown in Figure 4. As a final summary, Figure 5 provides the latitude distribution of five OA factors (mass fraction in the total OA mass) during the four R/V Polarstern cruises. Note that the residuals correspond to the unexplained organics by PMF. They are negligible in the average case (Figure 4) but can be recognized in the latitude series (Figure 5). Details on the characteristics of each OA component, including mass spectral profile, temporal variation, and associations with different sources and processes, are discussed in the following sections.

3.2.1 Marine oxygenated organic aerosol (~~MOA~~MOOA)

The ~~MOA~~MOOA factor contributes an average of 16% to the total OA mass, with a median mass concentration of 0.04 µg m^{-3}. This factor is well correlated with the marine SOA tracer MSA ($R^2 = 0.83$, Figure 3~~); it~~) and is consequently ~~can be~~ linked to the oxidation of DMS emitted by phytoplankton~~.~~ (Charlson et al., 1987; Gondwe et al., 2003). One characteristic of the ~~MOA~~MOOA factor is a high contribution from $C_xS_y^+$ ions (7–%), which mainly include ~~mainly~~the MSA identified ions $CH_3SO_2^+$ (*m/z* 78.985), $CH_2SO_2^+$ (*m/z* 77.978), $CH_4SO_3^+$ (*m/z* 95.988), CHS^+ (*m/z* 44.980), and CH_2S^+ (*m/z* 45.988~~). This results in~~) (e.g. Huang et al., 2017). This leads to a high S/C ratio (0.030), which is 10 to 30 times higher than that of other factors (Figure 3). ~~Despite the previously mentioned caution, the S/C ratios~~Note that the S/C ratios derived from the PMF analysis tool have to be used with caution because of calculation uncertainties (Aiken et al., 2007), but they can still provide an indication ~~on~~of the significance of sulfur when calculated with the same tool~~. The S/C ratio of the MOA factor is also over twice that of marine factor observed in Paris (0.013, Crippa et al., 2013b), implying a stronger influence from marine phytoplankton on aerosol particles over the ocean than those in the coast city. Moreover, the mass spectral pattern of the MOA factor is in positive agreement with reported marine origin factors (Table 4).~~

~~The MOA factor contributes averagely 16% to total OA mass, with the median of mass concentration as 0.04 µg m^{-3}. The enhancement of MOA mass concentration was observed to be independent on the air mass categories and most MOA peaks were in association with marine air mass. This supports the MOA is mainly from the ocean. Although~~ among the factors from the same dataset. For instance, the S/C ratio of the MOOA factor is 10 to 30 times higher than the other four OA factors (Figure 3). Even though organic sulfur species play a remarkable role, oxygenated organic ~~ions~~fragments are still the major species, accounting for 52~~-~~% of ~~the MOA~~MOOA mass loading (~~$C_xH_yO_1$~~$C_xH_yO^+$ 30~~-~~%, $C_xH_yO_z^+$ 22~~-~~%, Figure 4a). ~~They~~These fragment families are followed by hydrocarbon ~~ions, taking~~fragments, making up 30~~-~~% of the ~~MOA~~MOOA mass loading. CH_3^+ is the most abundant ion of the $C_xH_y^+$ family, contributing 43% to the total $C_xH_y^+$ group mass loading in the ~~MOA~~MOOA. As a result, ~~MOA~~MOOA shows the highest H/C ratio (1.73) of all five OA factors, similar to those reported previously: 1.57 (~~MOA)~~ marine OA) in Paris during summer ~~(Crippa et al., 2013b)~~ (Crippa et al., 2013) and 1.8 (MOOA) ~~in the~~on Bird Island~~,~~ in the Sub-Antarctic ~~(Schmale et al., 2013a).~~ region (Schmale et al., 2013). This suggests that a high level of hydrocarbon ions, in particular CH_3^+ together with C_xS_y~~$^+$ ions~~$^+$, could be an important characteristic for marine source SOA.

~~Comparing to the standard MSA mass spectral profile (only organics signals), MOA~~The MOOA includes almost all organic ~~ions~~fragments observed in ~~pure ~~MSA~~ and~~, as well as some ~~extra~~additional oxygenated ~~ions~~fragments, which ~~are absent or negligible in MSA. It ~~indicates that the ~~MOA~~MOOA factor consists of not only MSA but also other organic components either emitted from the same source or ~~process~~produced via similar processes as MSA. This finding is also proved by the relationship between the mass concentration of ~~MOA~~MOOA and MSA (slope = 2.19, R^2 = 0.83). Significant oxygen-~~contained~~containing ions, such as CO_2^+ (m/z 43.990) and $COOH^+$ (m/z 44.998~~)~~), could be related to carboxylic acids, which are ~~an ~~important in the composition of secondary marine aerosol (Decesari et al., 2011; Fu et al., 2011)~~. The plausible contributors~~. The possible precursors of these carboxylic acids could be isoprene and monoterpenes emitted by marine phytoplankton~~,~~ (Bonsang et al., 1992; Shaw et al., 2010; Yassaa et al., 2008), which can be easily oxidized ~~by OH radical and NO_3 radical ~~to form highly oxygenated products such as 2-methylglyceric acid, 2-methyltetrol and pinic acids (Claeys et al., 2010; Fu et al., 2011). ~~Marine-origin~~It is well known that isoprene and ~~monoterpenes could be the precursors of carboxylic acid as well as ~~monoterpene oxidation also leads to the formation of organosulfate ~~in SOA~~compounds (Claeys et al., 2010; Fu et al., 2011; Iinuma et al., 2007; Surratt et al., 2008; Surratt et al., 2007)~~. They may offer CO_2^+ and C_xS_j~~, which can contribute to the $C_xS_y^+$ fragments observed in the ~~MOA~~MOOA factor. ~~As shown in Figure 4, the~~

The secondary origin of MOOA was supported by its diurnal cycle ~~of the MOA suggests photo-oxidation is a main process. It shows ~~(Figure 4), showing a small but clear elevation in the afternoon, reaching the maximum (0.05 µg m^{-3}) at 16:00, almost when ~~the ~~global radiation started declining~~, which reflects the accumulation of photochemical production. The minimum of the diurnal variation (0.04 µg m^{-3}) appears around 09:00, probably linking to the increase of mixing layer in morning.~~

~~The diurnal cycle of MOA might have been weakened by averaging because the biological activities in autumn are usually lower than in spring. Thus~~. To focus on the atmospheric behavior of MOOA and exclude the influence of other chemical compositions, a "~~MOA~~MOOA dominating period" ~~is~~was selected for a case study (~~about 2 consecutive days~~approximately 57 h from 19:40, 18.11.2012 to 04:20, 21.11.2012). As shown in Figure ~~5~~6, the ~~MOA plays~~MOOA played an important role in the total OA during the selected period, ~~taking averagely~~constituting an average of 78% (up to 100%) of the total OA mass concentration. The ~~MOA has consistent variation~~MOOA had strong covariation with MSA~~ in time series~~, resulting in a quite stable MSA/~~MOA~~MOOA ratio of 52% ± 9%. ~~Also~~During this period, NO_3, NH_4 and ~~BC~~eBC showed low mass concentrations (median: 0.04 µg m^{-3}, 0.08 µg m^{-3} and 0.05 µg m^{-3}, respectively) close to their DLs, indicating a negligible impact from anthropogenic emissions during this period. The diurnal pattern for this specific period~~,~~ (Figure 6b), with a minimum of 0.11 µg m^{-3} (MOOA mass concentration) at 07:00 and a maximum of 0.25 µg m^{-3} at 16:00, ~~is~~was more noticeable than the average case (Figure ~~4~~4b). Similar diurnal cycles are observed for MSA and sulfate, suggesting that ~~MOA~~MOOA, MSA and sulfate are formed via the same secondary pathway~~.~~ (Charlson et al., 1987; Gondwe et al., 2003; von Glasow and Crutzen, 2004). Model studies found that the DMS is mainly (84% globally) removed via ~~the ~~photo-oxidation by OH ~~radical~~radicals (Kloster et al., 2006)~~. Also, the~~ or oxidized by O_3 in aqueous-phase ~~oxidation of DMS is dominant by O_3 during the cloud process, and ~~reactions to yield ~~significantly~~a significant amount of MSA (Hoffmann et al., 2016). These findings ~~support~~suggest that ~~the ~~DMS oxidation is controlled by photochemical ~~process~~processes and that its products should show a daytime maximum associated with ~~the solar radiation. Besides, isoprene and monoterpenes can also react with oxidants especially OH radical to form oxidation products (Claeys et al., 2004), consequently contributing to the this OA component.~~ solar radiation (as well as global radiation, as shown in Figure 6b).

The enhancement of MOOA mass concentration was observed to be independent of the air mass categories, and most MOOA peaks were associated with marine air masses (Figure 3). This finding also supports that MOOA originate mainly from the ocean. Related to the DMS oxidation, the MOOA factor shows prominent seasonality and higher contributions to the total OA mass in spring than in autumn; moreover, it shows higher contributions over the South Atlantic than the North in spring (Figure 5). In particular, the MOOA could be the exclusive contributor to the OA at approximately 16°S in spring, linked to the high biological activity fueled by the Benguela upwelling system, which is a northward-flowing ocean current along the west coast of southern Africa from Cape Point (Nelson and Hutchings, 1983) bringing ~~Since the MOA~~up the nutrients from deep cold waters.

Because the MOOA component is successfully traced by MSA, the relationship between the MSA and ~~MOA~~MOOA should be applicable to estimate DMS-related ~~organic aerosols~~SOA over the Atlantic Ocean. The correlations between MSA and ~~MOA~~MOOA in spring, autumn and ~~tropic~~tropics (with unclear seasonal variation, 5~~-~~°N to 5~~-~~°S~~ of~~ latitude) are shown in Figure ~~6~~7. The scattering points are fitted using linear orthogonal distance regression (ODR). Overall, the correlations between MSA and ~~MOA~~MOOA in three cases are robust (R^2 = 0.85, 0.53, 0.88), ~~and~~ consistent (slope = 0.57, 0.56, 0.56~~) when not considering the spatial difference. We~~), and independent of regions and seasons (for spring and autumn). We therefore infer that the relation between MSA and its concomitant ~~secondary organic components (MOA in this study) is generally~~(DMS-related) SOA is roughly stable~~, only showing tiny discrepancy in different regions. In spring, the slope is slightly smaller in the South Atlantic (0.52) than in the North Atlantic (0.66), with excellent correlations in both hemispheres (R^2 = 0.87 $\sim$ 0.92). In tropical region, the MSA-MOA relationship is similar as that in the average case in spring, but both components show lower level (MSA <0.1μg m^{-3}, MOA <0.16μg m^{-3}) than those in spring (MSA < 0.2μg m^{-3}, MOA < 0.32μg m^{-3}). The lowest amount of both MSA and MOA was observed in autumn probably due to the low biological activities. This also weakens the linear correlation especially in the south hemisphere (R^2 = 0.22). On average, a slope of 0.56 between MSA and MOA is obtained for the whole Atlantic. Accordingly, the MOA mass concentration could be estimated as the production of the MSA~~ over the Atlantic and suggest estimating MOOA mass concentration ~~time~~as the product of the MSA concentration multiplied by a factor ~~(i.e.,~~of 1.79~~ for average, 1.52 for the North Atlantic while 1.92 for the South). This can~~, which may be useful for a better estimation of marine DMS~~-~~-related SOA both in field measurements and in models.

3.2.2 ~~Nitrogen~~Marine nitrogen-containing organic aerosol (~~NOA~~MNOA)

The ~~nitrogen-containing OA (NOA)~~ MNOA component showed a unique time series ~~with~~and poor correlation with the other four factors (all R^2 ~~are~~were below 0.13). ~~It~~The mass concentration of MNOA varied ~~up~~from below the DL to 0.47 μg m^{-3}~~, but with~~ (median ~~of~~ 0.03 μg m^{-3}~~ which is quite close~~) and contributed to ~~the detection limit~~16% of ~~organics. Similar to the MOA,~~ the ~~variation of NOA mass concentration shows independence of the different air masses, suggesting that the NOA may be of~~

~~an oceanic origin. The NOA~~OA. The MNOA is characterized by a remarkable contribution from organonitrogen ~~(ON), mainly $C_xH_yN^+$~~ fragments (17~~%~~%, Figure 4), mainly $C_xH_yN^+$-related, such as $C_2H_6N^+$ (accounting for 5.3% of total m/z 44 intensity), $C_2H_7N^+$ (2.6% of m/z 45) and CH_4N^+ (2.7% of m/z 30), which are at least one order of ~~the total NOA mass loading, Figure 4), showing the highest N/C atom ratio (0.124,~~ magnitude higher (intensity fraction in the located m/z) than in other factors (Figure 3). Nevertheless, ~~the NOA~~this factor is still dominated by oxygenated fragments including $C_xH_yO^+$ (30%) and $C_xH_yO_z^+$ (28%, Figure 4~~). The~~), and the diurnal variation of ~~NOA~~MNOA shows ~~clear peak in the~~a broad afternoon~~, reaching the~~ peak with maximum ~~while the global radiation starts decreasing~~at 16:00 UTC (Figure 4), ~~indicating~~similar to that of the ~~NOA factor is certainly composed of~~amine-related secondary ~~organic products.~~ factor in New York City showing a diurnal pattern with maximum at noon (Sun et al., 2011). Both of these findings may indicate that secondary formation could be one of the possible pathways for MNOA generation.

~~Nitrogen~~N-containing OA ~~component has~~(NOA) factors from PMF analysis have been ~~identified~~found in ~~several previous~~many studies ~~using AMS-PMF method,~~and can be related to various ~~sources~~origins highly dependent on ~~the~~ local ~~situation, for example,~~ sources, such as Gentoo ~~penguins~~penguin hatching activities ~~(Schmale et al., 2013b), local coffee roastery (Carbone et al., 2013), and local primary (industry~~ (Schmale et al., 2013) and local primary (industrial) emissions (Aiken et al., 2009). ~~In MBL, gaseous amines emitted by marine phytoplankton have been recognized as an important SOA source (Dall'Osto et al., 2012; Facchini et al., 2008; Jickells et al., 2013; Müller et al., 2009). This is because~~During the R/V Polarstern campaign, the MNOA is correlated with neither eBC ($R^2 = 0.17$) nor NO_3 ($R^2 = 0.06$), excluding the possibility of combustion and anthropogenic (continental) sources. Meanwhile, high similarity ($R^2 = 0.70$) of the mass spectral profile is found between the R/V Polarstern MNOA and the NOA in Sun et al. (2011), who attributed that factor in New York City to marine and local industry emissions and stressed the possibility of gas-to-particle conversion via the reactions of acidic gases and the gaseous amines. It is worth noting that the characteristic $C_xH_yN^+$ fragments are actually different in these two studies: $C_3H_8N^+$ (m/z 58) and $C_2H_4N^+$ (m/z 42) dominated the $C_xH_yN^+$ group in the New York study, while $C_2H_6N^+$(m/z 44), $C_2H_7N^+$ (m/z 45) and CH_4N^+ (m/z 30) played a more important role in R/V Polarstern measurements. These C1-C3 $C_xH_yN^+$ fragments may originate from low molecular weight aliphatic amines such as methylamine (CH_5N), dimethylamine (C_2H_7N) and trimethylamine (C_3H_9N~~) can be excreted by marine organisms as products of metabolic processes~~), which have been regarded as the main species in organonitrogen fragments from marine sources (Gibb et al., 1999; Müller et al., 2009)~~. During the Polarstern measurements, the NOA factor is well correlated with ON fragments, e.g. $C_2H_7N^+$ ($R^2 = 0.86$), $C_2H_6N^+$ ($R^2 = 0.77$), and CH_4N^+ ($R^2 = 0.65$), which could be generated from amines (McLafferty and Tureček, 1993). The N/C ratio of the NOA factor (0.124) is close to the one used in a global 3D chemistry-transport model in the paper from Kanakidou et al.~~ as well as important biogenic SOA precursors over the ocean (Dall'Osto et al., 2012; Facchini et al., 2008; Müller et al., 2009). In addition, a large number of $C_xH_yN^+$ fragments results in the highest N/C atom ratio (0.124) among all five OA factors, and this N/C ratio is close to the one used in a global 3D chemistry-transport model by Kanakidou et al. (2012) to trace the ~~ON from ocean sources (0.15) and different from the ratio for BB and anthropogenic sources (0.3). The NOA factor also shows similarity ($R^2 = 0.70$) of mass spectral profile as that reported by Sun et al. (2011) who found the NOA factor in the New York City might~~

~~be related to marine emissions and local industry emissions. The characteristic ions such as $C_2H_7N^+$ and $C_2H_6N^+$ may be attributed to the dimethylamine (C_2H_7N), which has been found as characteristic and abundant amines in marine emissions in previous studies (Facchini et al., 2008; Gibb et al., 1999; Müller et al., 2009).~~ organonitrogen from ocean sources (0.15), while it is different from the ratio for biomass burning (BB) and anthropogenic sources (0.3). This may also support the idea that the MNOA originates from the ocean, likely transformed from phytoplankton-emitted gaseous amines.

~~Meanwhile, the NOA is neither correlated with BC (R^2 = 0.17) nor NO_3 (R^2 = 0.06), excluding the possibility of combustion and anthropogenic (continental) sources. This factor~~The MNOA shows ~~different temporal variation from~~no correlation with marine secondary product tracer MSA (R^2 = 0.01~~) as well. However, this is consistent with findings~~). This absence of correlation has already been reported in ~~the previous~~several marine measurements ~~which related the NOA to~~ of particulate amines with biogenic ~~amines~~origins (Facchini et al., 2008; Miyazaki et al., 2011; Müller et al., 2009), although acid-base reactions were considered a key process of gas-to-particle conversion for amines over the ocean (Facchini et al., 2008; Sun et al., 2011). Given that gaseous amines can enter the particle phase in different ways (Ge et al., 2011), other pathways, including oxidation, nucleation and condensation, should also be considered.

During each cruise, the MNOA had a low mass concentration with no clear seasonality. However, its high significance can be found when the total OA mass concentration was extremely low, generally below 0.5 µg m^{-3} (Figure 5), e.g., 20°S to 20°N in CR1 and CR3. It is interesting that during CR3, the MNOA contributed to nearly half of the total OA between the equator and 20°S in association with very clean air masses from the open ocean, which may confirm its marine origin. We also noticed that the MNOA had a similar variation trend during all four cruises, slowly increasing and then decreasing broadly between 20°S and 20 °N. This variation was generally coincident with the change in the water temperature (Figure S10). The covariation might be explained by the biogenic sources of the MNOA - temperature could positively affect metabolism rate, including N excretion of marine microorganisms (Ikeda, 2014).

3.2.3 Marine hydrocarbon-like organic aerosol (MHOA)

The only true primary factor identified, MHOA, is related to marine primary emissions. It is characterized by a high contribution of hydrocarbon ions (64% of total factor mass concentration, Figure 4), which is usually considered a feature of primary emissions. One-fourth of the MHOA mass was identified as oxygenated organic compounds ($C_xH_yO^+$, $C_xH_yO_z^+$). This finding is not surprising because carboxylic acids can also be supplied via the primary pathway and have been identified as a distinct type of primary marine organic matter (Hawkins and Russell, 2010). ~~. Moreover, the NOA contains two characteristic makers for amino acids, i.e. CH_4N^+ (*m/z* 30) and $C_2H_4N^+$ (*m/z* 42) recognized by Schneider et al. (2011), although the NOA shows poor similarity of mass spectra (partly shown in Table 4) to 15 pure amino acids (Schneider et al., 2011). The possibility cannot be completely excluded that amino acids (proteins) from marine primary organic components (Hawkins and Russell, 2010) are transformed (e.g. photo-oxidized, or decarboxylated) and contribute to this factor. Although the NOA mass concentration has similar trend with the water temperature (Figure S9), the reason for this coincidence is still unclear. It might be related to the positive effect of temperature on metabolism rate including N excretion of marine microorganisms (Alcaraz~~

~~et al., 2013; Ikeda, 1985; Ikeda, 2014; López-Urrutia et al., 2006). Therefore, we speculate that the NOA component is mainly related to marine amines emitted from phytoplankton via gas-to-particle conversion. The contribution of amino acids (proteins) is not recognized but cannot be fully ruled out.~~

A small but pronounced portion (5%) of $C_xH_yN^+$ fragments was observed in total MHOA mass loadings, consistent with the findings in previous measurements that amines also existed in primary marine OA (Frossard et al., 2014; Quinn et al., 2015). The time series of MHOA mass concentration was spiky and varied from <DL to 0.67 µg m^{-3} with a median of 0.04 µg m^{-3}. It contributed 19% to the total OA mass, comparable to two marine secondary factors (MOOA 16%, MNOA 16%). No clear diurnal pattern was found for the MHOA, indicating that the contribution of photooxidation could possibly be ignored for this factor.

Considering that the ship contamination periods have been eliminated and the MHOA was not correlated with eBC (R^2 = 0.04), fresh ship emissions were unlikely to have been a contributor to this primary factor. The primary emissions from the ocean were considered a main source of the MHOA because of the similarity (R^2 = 0.61) in the mass spectral profile between this factor and primary marine OA during high biological activity at Mace Head, Ireland (Ovadnevaite et al., 2011). For the entire measurement period, the MHOA was not correlated with sea salt (R^2 = 0.01) or the wind speed (R^2 = 0.01), even though a similar variation trend (but no strong linear correlation, $R^2 < 0.4$) was found in several periods, such as the southern parts (from 33°S to 0°) of CR2 and CR4 (Figure S11). This trend does not conflict with the speculation that MHOA is related to marine primary emissions because the mass fraction of organics in the sea spray aerosol was found to be size-dependent: increasing with decreasing particle size (Gantt et al., 2011; Quinn et al., 2015). The enrichment factor of organic compounds, i.e., the ratio between organic carbon in sea spray aerosols and that in sea water, is also largely influenced by particle size (Quinn et al., 2015). In addition, the transfer of organic matter from seawater to the particles is chemoselective and more complicated than it is for inorganic sea salt (Schmitt-Kopplin et al., 2012). During all four cruises, the MHOA factor did not show any location dependence but played a more prominent role in regions with extremely low OA mass concentrations, e.g., the southern part of CR1 and the whole period in CR3. This finding could support the hypothesis that the MHOA originates from the ocean.

3.2.4 Anthropogenic oxygenated organic aerosol (Anthr-OOA) ~~3.2.3 Oxygenated organic aerosol (OOA)~~

~~Though measuring over the ocean, 19 % of~~Although measured over the ocean, 19% of the organic aerosol mass was contributed by ~~the long-range transported~~continental emissions from human activities, presented by the Anthr-OOA factor with a similar median ~~of~~ (0.04 µg m^{-3} ~~for mass concentration.~~) but the highest maximum (2.70 µg m^{-3}) compared to the other OA factors. The Anthr-OOA factor was identified by anthropogenic tracer NO_3 regarding time series (R^2 = 0.52, Figure 3) and resemblance of mass spectral ~~profile~~profiles to ~~the~~several reported continental OOA factors (Table 4). ~~For instance, the~~ The Anthr-OOA in this study ~~is~~was in excellent agreement (R^2 = 0.98) with a continental organics factor observed over the central Arctic Ocean (Chang et al., 2011). It ~~is~~was also similar (R^2 = 0.67) to the average OOA factor based on nine urban measurements (Ng et al., 2011). ~~The~~ As shown in Figure 4, the Anthr-OOA factor ~~is~~was dominated by $C_xH_yO^+$ fragments (contributing 40% to the total factor mass), followed by $C_xH_yO_z^+$ (26~~ %) as shown in Figure 4.~~%). Significant contributions ~~are~~were observed from CO_2^+ (m/z 44, 21% of total Anthr-OOA mass loading) and $C_2H_3O^+$ (m/z 43, 6%), comparable ~~with~~to values in previous studies in urban ~~or~~and rural areas (e.g. Ng et al., 2011; Poulain et al., 2011a). Another carboxylic acid fragment, CO^+ (m/z 28, 21% of total Anthr-OOA mass loading~~) is~~), was estimated according to the CO_2^+ ion, and thus CO^+ is not ~~particularly~~specifically discussed in the present work. There ~~is~~was no clear diurnal pattern for the Anthr-OOA factor (Figure 4). The Anthr-OOA mass concentration dropped in the early morning from 05:00, ~~reaching~~reached a minimum at ~10:00, then ~~being~~stayed stable until midnight. This change may be explained by the rising mixing layer in the morning, which dilutes the particle concentration, and/or increasing temperature after sunrise, which drives volatile species from particles into the gas phase. Hence, the Anthr-OOA is ~~not likely~~unlikely to be contributed by ~~locally~~local photochemical formation~~. Moreover, as shown in Figure 3, significant elevation of OOA and NO_3 mass concentrations (up to 2.70 μg m^{-3} and 0.45μg m^{-3}) was mainly associated with the mixed air mass with continental influence especially when close to Africa and Europe. This also supports the~~ , but continental outflow ~~is the main source of the OOA factor~~from anthropogenic activities via long-range transport.

Significant elevation of Anthr-OOA mass concentrations (up to 2.70 μg m^{-3}) was associated mainly with continental air masses (Figure 3). The median value of the Anthr-OOA mass concentration in marine air masses was 0.03 μg m^{-3} and higher (0.08 μg m^{-3}) during periods influenced by continental air masses. Additionally, the contribution of Anthr-OOA to the total OA significantly increased, even when close to Africa and Europe (Figure 8). This confirms that the continental outflow is the main source of the Anthr-OOA factor.

3.2.5 Combustion oxygenated organic aerosol (Comb-OOA) ~~3.2.4 Aged primary organic aerosol (aPOA)~~

Of all five factors, the ~~aPOA~~Comb-OOA is the only one correlated with ~~BC~~eBC ($R^2 = 0.69$, Figure 3~~).~~), pointing to combustion sources. It ~~is~~was the most abundant component of ~~organic aerosols~~the measured OA on average, contributing 30% of the total OA mass. The median ~~of aPOA~~Comb-OOA mass concentration ~~is~~was 0.07 μg m^{-3} (<DL to 1.38 μg m^{-3}). Similar to the Anthr-OOA, ~~the aPOA factor~~most Comb-OOA peaks ~~usually~~ appeared together with continental ~~influence~~ air masses~~, pointing to non-marine sources~~ (Figure 3), indicating a nonmarine source. One significant characteristic of the ~~aPOA~~Comb-OOA factor ~~is~~was its highly oxygenated level. Oxygenated ~~ions~~fragments including $C_xH_yO^+$ and $C_xH_yO_z$~~.$^+$ account~~$^+$ accounted for 73% of the total ~~aPOA~~Comb-OOA mass (Figure 4~~), hence aPOA exhibits~~). This factor contained remarkably high CO_2^+ (CO_2^+/total Comb-OOA = f_{44} = 32%), indicating a possible origin from organic acids. As a result, the Comb-OOA exhibited the highest O/C ratio (O/C = 1.35~~),~~) and lowest H/C ratio (H/C = 0.94) of all ~~the~~ OA factors. The Comb-OOA was also contributed to by pronounced N-containing fragments: $C_xH_yN^+$ (4%) and $C_xH_yO_zN_w^+$ (2%). Despite the small contribution to the Comb-OOA mass concentration, $C_xH_yO_zN_w^+$ fragments were primarily distributed in this factor (46% of total $C_xH_yO_zN_w^+$ mass).

~~Since correlated~~The Comb-OOA factor was attributed to aged aerosol particles from combustion emissions mainly because of its highly oxygenated level and covariance with combustion tracer ~~BC, this factor can be considered to connect with various burning sources and processes, such as ship exhausts, cooking, and burning with biomass. Given that~~ eBC. Additionally, this factor had a similar mass spectrum to the OA below clouds measured by a flight impacted by ship emissions ($R^2 = 0.73$)

(Coggon et al., 2012) and the photooxidation products of diluted diesel generator exhaust (R^2 = 0.46) (Sage et al., 2008), rather than any fresh combustion emissions, e.g., the fresh ship emissions factor (R^2 = 0.00) (Chang et al., 2011), the average BB organic aerosols BBOA (R^2 = 0.09) (Ng et al., 2011), and the average HOA factor (R^2 = 0.01) (Ng et al., 2011). This finding is reasonable because the influence of direct ship emissions from the R/V Polarstern ~~(including the kitchen exhausts using the same chimney)~~ has been removed~~, the own ship exhausts as well as cooking emissions could be left out of consideration. Moreover, the mass spectral profile of aPOA factor shows no similarity with any fresh combustion emissions, including 1) the fresh ship emissions factor (R^2 = 0.00) (Chang et al., 2011) , 2) the average BB organic aerosols BBOA (Ng et al., 2011) with R^2 = 0.09, and 3) the average HOA factor (R^2 = 0.01) (Ng et al., 2011), supporting the conclusion above. Because most of the time Polarstern travelled along the main water way (Figure S10), a likely source of aPOA could be the transported ship exhausts from other ships.~~. Sage et al. (2008) found that SOA could be quickly formed from fresh diesel exhausts, and the aged products were increasingly oxidized with time~~ resembling the profile of atmospheric aged OA within a few hours of oxidation. The aPOA factor in this study has very similar mass spectrum (R^2 = 0.73) to the OA below clouds measured by a flight impacted by ship emissions (Coggon et al., 2012). The aPOA mass spectral profile is also correlated with the photo-oxidation products of diluted diesel generator exhaust (R^2 = 0.46) (Sage et al., 2008). Thus, the aged ship emission should be one of the~~, resembling the profile of atmospheric aged OA within a few hours of oxidation. Given that most of the time, the R/V Polarstern travelled along major shipping routes (Figure S12), a possible source of the Comb-OOA could be the transported ship exhausts from other ships.

The BB emissions via long-range transport are likely to be the other important source of the Comb-OOA, indicated by good correlation with $C_xH_yO_zN_w^+$ fragments (from AMS, R^2 = 0.83) and potassium (K^+, from offline measurements, R^2 = 0.61), as shown in Figure 8. The $C_xH_yO_zN_w^+$ ions have been related to the photooxidation product of m-cresol, a typical wood burning emission (Iinuma et al., 2010; Poulain et al., 2011a), ~~contributors of the aPOA component. The mass concentration of aPOA increased when the ship was in the English Channel where the marine traffic is very busy (Figure S10).~~ and potassium is commonly regarded as an unreactive tracer of BB emissions. Nevertheless, some often used BB tracers, $C_2H_4O_2^+$ and $C_3H_5O_2^+$ (Capes et al., 2008; Cubison et al., 2011), were extremely low in our Comb-OOA factor ($C_2H_4O_2^+$/total Comb-OOA = f_{60} = 0.06%, $C_3H_5O_2^+$ /total Comb-OOA = f_{73} = 0%), even though the f_{60} increased to 0.18% during the high Comb-OOA period (the factor mass concentration and mass fraction in total OA reached 1.02 µg m^{-3} and 47%). The absence of these BB tracers may be caused by decay in the aging process during long-range transport. Fresh BB emissions can be quickly photochemically aged (in several hours), resulting in the formation of new OA with a higher degree of oxygenation and a significant decrease in BB tracers as well as saturated hydrocarbon compounds. This change has been observed in both laboratory (Bertrand et al., 2018; Grieshop et al., 2009) and field measurements (Capes et al., 2008; DeCarlo et al., 2010).

The significance of the Comb-OOA, i.e., the aged particles from combustion emissions, are dependent on regions and seasons (Figure 5). More than 50% of the total OA was contributed by aged particles from combustion emissions, especially during the two November cruises (CR2 and CR4) between 15°N and 15°S, when the ship was near West and Central Africa. It is well known that Africa is the single biggest continental source of BB emissions with strong seasonality (Roberts et al., 2009). In

West and Central Africa, more intense fires occurred in November than in April/May according to the fire maps (Figure S13), consistent with higher mass concentrations of Comb-OOA in CR2 and CR4, than during the other two cruises. In addition, the mass concentration of the Comb-OOA increased when the ship was near the English Channel, where marine traffic is very busy (Figure S12).

~~4 SummaryThe ship traffic, however, can hardly explain the remarkable seasonal elevation of aPOA in November near the equator. Thus, the other plausible source of the aPOA, the aged BB emissions, should be considered. It is well known that Africa is the biggest single continental source of the BB emissions with strong seasonality (Cooke et al., 1996; Giglio et al., 2006; Roberts et al., 2009). The fire maps (Figure S11) showed that in the west and middle Africa, there were more intensive fire points occurred in November than in April/May, consistent with higher mass concentration of aPOA in the CR2 and CR4 (both covering the November) than other two cruises. In this study, the aPOA factor contains extremely high oxygenated ions (especially m/z 44, CO_2^+, its relative amount to the total aPOA mass, i.e. f_{44}, is 32%), while nearly no BB tracer ions at m/z 60 and m/z 73 (Bertrand et al., 2017; Capes et al., 2008; Cubison et al., 2011), i.e., $C_2H_4O_2^+$ (f_{60} = 0.06%) and $C_3H_5O_2^+$ (f_{73} = 0%). The f_{60} in the aPOA factor is much lower than the background level without apparent BB influence (0.3% ± 0.06%) provided by Cubison et al. (2011); but it increased up to 0.18% during the high aPOA period when the aPOA average mass concentration and mass fraction (in total OA) reached 1.02 ±0.14 μg m^{-3} and 47% ± 3%. The absence of these BB tracer ions could be reasonable if taking the aging process during long-range transport into the consideration. Fresh BB emissions can be quickly photochemically aged (in several hours), resulting in formation of the new OA with higher degree of oxygenation and a significant decrease of BB tracers as well as saturated hydrocarbon compounds. This has been observed in both laboratory (Bertrand et al., 2017; Bertrand et al., 2018b; Grieshop et al., 2009a; Grieshop et al., 2009b) and field measurements (Capes et al., 2008; DeCarlo et al., 2010). During the Polarstern cruises, the BB tracers in aPOA factor decayed severely, possibly due to the chemical aging in long-range (i.e. long-period) transport and dilution effect of clean marine air masses.~~

~~Another evidence for aged BB emissions is: the aPOA is well correlated with $C_xH_yO_zN_w^+$ fragments (from AMS, R^2 = 0.83) and potassium ion (K^+, from offline measurements, R^2 = 0.61) as shown in Figure 7. The $C_xH_yO_zN_w^+$ ions have been related to the photo-oxidation product of m-cresol, a typical wood burning emission (Iinuma et al., 2010; Poulain et al., 2011a), while potassium is commonly regarded as an unreactive tracer of BB emissions. In addition, the particles measured in the range from ~15°N to 15°S (close to the west and middle Africa) showed external mixing state by the HTDMA measurements (details in an accompany paper by Wu et al., in preparation). It is the typical property of BB emissions. Therefore, aPOA is possibly contributed by aged combustion emissions from both ship traffic and biomass burning. Aged BB emissions may be the dominant source, leading to a spatial and seasonal dependence.~~

~~3.2.5 Primary organic aerosol (POA)~~

~~The only true identified primary factor, POA, is related to marine primary emissions. It is characterized by high contribution of hydrocarbon ions (64 % of total factor mass concentration, Figure 4), which is usually considered as a feature of primary emissions. Also, the diurnal profile of POA (Figure 4) indicates there is no photo-oxidation contribution to this factor. The time series of POA mass concentration is spiky and varies from <DL to 0.67 µg m^{-3} with the median of 0.04 µg m^{-3}. The POA shows no synchronicity with continental influenced air masses, implying plausibly marine sources for the POA. It averagely contributed 19% to the total OA mass, comparable to two marine SOA factors (MOA 16 %, NOA 16 %). Since the ship contamination periods have been eliminated and the POA is not correlated with BC ($R^2 = 0.04$), fresh ship emissions are not likely to be a contributor to this primary factor. The primary emissions from the ocean are considered as a main source because of the similarity ($R^2 = 0.61$) on mass spectral profile between this factor and primary marine organic aerosol during high biological activities in Mace Head Ireland (Ovadnevaite et al., 2011). Moreover, CHN fragments take pronounced portion (5%, Figure 4) in total POA mass loadings, only smaller than its portion in the NOA factor. They may be related to amines which have been observed in primary marine organic aerosols in recent measurements (Frossard et al., 2014; Quinn et al., 2014; Quinn et al., 2015).~~

~~There are one fourth of POA mass identified to be oxygenated organic compounds ($C_xH_yO^+$, $C_xH_yO_z^+$). It is worth noting that carboxylic acids can also be supplied via primary pathway and have been identified as a distinct type of marine primary organic matters (Hawkins and Russell, 2010). Sea water is a pool of dissolved organic matters contributed by direct algal release, metabolism of marine heterotrophs, bacterial and viral lysis, and cell senescence (Hansell and Carlson, 2002). The sea spray aerosol is mechanically generated from the bubble bursting processes, in which the chemoselective transfer occurs and results in the enrichment of organic compounds in the primary marine aerosol particles (Aller et al., 2005; Kuznetsova et al., 2005; Russell et al., 2010; Schmitt-Kopplin et al., 2012).~~

~~Overall, the POA is not correlated with the sea salt ($R^2 = 0.01$), nether the wind speed ($R^2 = 0.01$), even if similar variation trend was found in several periods, such as the south parts (from 33°S to 0°) in CR2 and CR4, and the middle part (5°N to 20°N) in CR3 (Figure S12). However, whether the primary marine organics should be proportional to the sea salt is still questionable. On one hand, several studies observed that the production mass flux of the sea salt exponentially enhanced with increasing surface wind speed, and the strong wind usually produces the sea spray particles in the supermicrometer size range (Grythe et al., 2014; Ovadnevaite et al., 2012). On the other hand, the mass fraction of organics in the sea spray aerosol was found to increase with the decreasing particle size (Gantt et al., 2011; Quinn et al., 2015). This suggests that the ocean-source primary organic aerosol could be not correlated with the sea salt. Due to the resemblance between mass spectral profile of POA and reported primary marine organic aerosol, we speculate that the POA factor could be attributed to the mechanically generated ocean products.~~

4 Summary ~~and conclusions~~

The present study reports the physicochemical measurements of Atlantic aerosols conducted during 4 open-ocean cruises for a total of 17 weeks in 2011 and 2012 and covering 53°N to 53°S in the Atlantic Ocean. Based on this unique dataset, especially the part obtained with HR-ToF-AMS, the aerosol chemical composition and OA sources were investigated in detail.

~~In this study, chemical composition of the submicron aerosols was investigated based on a unique dataset during 4 open-ocean cruises over the Atlantic in 2011 and 2012.~~ PM$_1$ composition ~~varies~~varied dynamically during the cruises, ~~averagely composed~~with an average composition of sulfate (50%), organics (21%), sea salt (12%), ammonium (9%), ~~BC (5%) and nitrate (3%). Organics~~BC (5%) and nitrate (3%). Sulfate was found to be the dominant species of submicron aerosol particle over the open Atlantic Ocean. Sulfate also showed noticeable seasonality, suggesting a major contribution of marine biogenic sources. Considering that organics are an important constituent of PM$_1$ and contain a large number of compounds from different sources~~. The PMF analysis~~, source apportionment of OA was therefore performed ~~to~~using the ~~high-resolution mass spectra matrices of OA and~~ PMF method. Five OA factors were identified ~~five factors~~and linked to ~~the~~ distinct sources~~. Figure 8 illustrates the latitudinal distribution~~, including three marine factors, 1) an MOOA factor related to marine DMS oxidation (16% of ~~OA source contributions associated with the~~the total OA mass concentration), 2) an MNOA factor from the secondary formation of biogenic amines (16%), and 3) an MHOA factor from primary marine emissions (19%), and two nonmarine factors, 1) an Anthr-OOA factor from continental outflow (19%) and 2) a Comb-OOA factor attributed to aged aerosol particles from combustion emissions mainly from biomass burning in Africa and maritime traffic over the Atlantic~~, which also gives a summary of OA source apportionment. Related the DMS oxidation, the MOA~~ Ocean (30%). The MOOA factor shows prominent seasonality, with a higher contribution to the total OA mass in spring than in autumn; moreover, it shows a higher contribution over the South Atlantic than the North ~~in spring. Especially, the MOA could be the exclusive contributor of the OA at around 16 °S in spring, linked to the high biological activity fuelled by the Benguela upwelling which is a northward~~ Atlantic in spring. This seasonality is, however, not observed for the other two marine factors. The MNOA and MHOA~~flowing ocean current along the west coast of southern Africa from Cape Point (Nelson and Hutchings, 1983) bringing the nutrients from the deep cold water. This seasonality is, however, not observed for the other two marine factors, i.e., the NOA factor with precursors of biogenic amines, and the POA from primary marine emissions. They~~ both played a significant role in the clean regions with low particle mass concentration (e.g~~.~~., in CR3 when the ship started from Punta Arenas). ~~The continental influence is clearly recognized in Figure 8~~Continental influences on Atlantic aerosols were latitude-dependent during the R/V Polarstern measurements, represented by the Anthr-OOA and ~~aPOA~~Comb-OOA factors. Both factors ~~took~~had dominant, even overwhelming, mass fractions when close to ~~the~~ land~~. The impact of wild fires in the~~, e.g., Europe and West and ~~Middle~~Central Africa ~~to the open-ocean OA could be inferred from the significance of aPOA~~, especially between 15°N and 15°S~~, where aPOA contributed more than 50% to the total OA (e.g. in CR2 and CR4).~~.

~~The main findings of this study support that the sulfate is the dominant species of submicron aerosol particles over the open-ocean of Atlantic. Sulfate is significantly contributed by the biogenic sources (e.g. DMS) due to the noticeable seasonality of~~

~~its mass concentration. The prominence of organics mass concentration has been found when the ship track was near the Europe or Africa. This is mainly linked to the continental outflow including anthropogenic pollutants and biomass burning emissions which can bring abundant organic aerosols. Moreover, the maritime traffic density is higher when closer to the continents, so the ship emissions would also contribute to MBL organic aerosols. Despite the marked continental influence on organics over some regions of the Atlantic, the detailed source apportionment of~~ During the R/V Polarstern cruises, marine sources contributed 51% to the total OA mass concentration, close to that of the nonmarine emissions (49%), reflecting the fact that continental emissions/human activities have a large influence on aerosols in the MBL even over the open ocean. However, the latitudinal source contribution shows that ocean-source OA ~~displayed that oceanic OA is~~are ubiquitous and, in a great part of cruising areas, ~~dominates the total OA mass loadings. On average, marine sources (represented by POA, MOA, and NOA) contributes 51% to the total OA mass concentration, nearly equal to that of the non-marine emissions (OOA and aPOA, 49%). One of the marine factors, MOA, is highly controlled by seasonal phytoplankton blooming (DMS production) and~~ dominate the total OA mass loadings. DMS oxidation could even be the sole source of the OA in some regions, e.g., with ~~high biological activities~~upwelling, while the ~~other two represent~~marine primary OA and amine-related organics represented a background oceanic contribution and ~~are~~were more visible in the clean marine areas.

~~The results from this work also suggested that the South Atlantic is less polluted by the continental transport and human activities (such as ship traffic) than the North Atlantic regarding the OA. Nevertheless, the OA could also be dominant by the marine sources in some regions over the North Atlantic, e.g. ~40° N in CR3, while the opposite situation was found in CR1 in the same season. This shows that the discrepancy of OA source contributions in the same regions exists, requiring more future studies with multiple techniques as well as analysis methods.~~ Finally, as a ~~co-product~~coproduct of the source apportionment, a solid linear correlation has been found between ~~MOA~~MOOA and MSA, which enables the estimation of marine SOA with DMS origin in the spring as MSA mass concentration times a factor of 1.79. This may be applicable in both field measurements and model ~~study~~studies with a focus on ~~the~~ marine ~~aerosol.~~ aerosols.

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Table 1. The description of 4 cruises

Expeditions	Starting point and destination	Duration	Season (in NH)
Cruise 1 (ANT-XXVII/4)	Cape Town - Bremerhaven	20.04 -20.05.2011	Spring
Cruise 2 (ANT-XXVIII/1)	Bremerhaven - Cape Town	28.10 -01.12.2011	Autumn
Cruise 3 (ANT-XXVIII/5)	Punta Arenas -Bremerhaven	10.04 -15.05.2012	Spring
Cruise 4 (ANT-XXIX/1)	Bremerhaven - Cape Town	27.10 -27.11.2012	Autumn

Table 2. The 20-min detection limits during 4 Polarstern cruises (μg m^{-3})

	CR1	CR2	CR3	CR4
Organics	0.024	0.025	0.017	0.022
Sulfate	0.011	0.018	0.014	0.012
Nitrate	0.004	0.006	0.008	0.005
Ammonium	0.021	0.020	0.021	0.018
Chloride	0.005	0.006	0.005	0.007
MSA	0.002	0.003	0.002	0.006

Table 3. Seasonal chemical composition of measured PM_1 over the Atlantic (μg m^{-3})

		Spring				Autumn			
		average	median	σ	%	average	median	σ	%
North Atlantic (>5°)	SO_4	1.38	1.02	1.09	51%	0.76	0.63	0.55	42%
	Org	0.53	0.38	0.52	20%	0.47	0.27	0.51	26%
	SS	0.27	0.17	0.26	10%	0.16	0.10	0.16	9%
	NH_4	0.29	0.19	0.31	11%	0.20	0.15	0.15	11%
	NO_3	0.09	0.06	0.08	3%	0.07	0.06	0.04	4%
	~~BC~~eBC	0.10	0.06	0.10	4%	0.13	0.08	0.14	7%
	MSA	0.04	0.03	0.03	1%	0.01	0.01	0.01	1%
	Total	2.71				1.79			
South Atlantic (<-5°)	SO_4	1.23	1.11	0.70	57%	0.33	0.28	0.17	47%
	Org	0.23	0.18	0.16	11%	0.17	0.15	0.09	24%
	SS	0.37	0.33	0.22	17%	0.09	0.07	0.08	13%
	NH_4	0.15	0.08	0.12	7%	0.07	0.07	0.04	10%
	NO_3	0.04	0.04	0.02	2%	0.02	0.01	0.01	2%
	~~BC~~eBC	0.07	0.05	0.07	3%	0.02	0.01	0.03	3%
	MSA	0.05	0.04	0.04	2%	0.01	0.01	0.00	1%
	Total	2.14				0.71			
Tropic Atlantic (-5°~5°)	SO_4	1.03	0.93	0.65	50%				
	Org	0.46	0.34	0.33	23%				
	SS	0.13	0.12	0.08	6%				
	NH_4	0.23	0.22	0.13	11%				
	NO_3	0.04	0.03	0.02	2%				
	~~BC~~eBC	0.14	0.10	0.12	7%				
	MSA	0.02	0.02	0.02	1%				
	Total	2.05							

(σ = standard deviation; SO_4 = sulfate, Org = organics, SS = sea salt, NH_4 = ammonium, NO_3 =nitrate)

Table 4. Summary of correlations of time series and mass spectra for the five-factor PMF solution

	~~MOA~~MOOA	~~NOA~~MNOA	Anthr-OOA	~~aPOA~~Comb-OOA	~~POA~~MHOA
Time series (R^2)	particulate MSA **(0.83)**	$C_2H_7N^+$ **(0.86)**	particulate NO_3 **(0.52)**	particulate BC **(0.68)**	
Mass spectra (R^2)	~~MOOA[1] in Bird Island (Schmale et al., 2013a)~~MOOA in Bird Island (Schmale et al., 2013) **(0.71)**	NOA in New York (Sun et al., 2011) **(0.70)**	Continental organics (Chang et al., 2011) **(0.98)**	~~Beech smoldering (Weimer et al., 2008)~~Below the clouds along the ship track (Coggon et al., 2012) **(0.~~68~~73)**	Marine primary organic matter in Mace Head (Ovadnevaite et al., 2011) **(0.61)**
	~~MOA in Paris summer (Crippa et al., 2013b)~~MOA in Paris summer (Crippa et al., 2013) **(0.68)**	Alanine (Schneider et al., 2011) **(0.50)**	~~LVOOA[2] Paris winter (Crippa et al., 2013a)~~Average OOA (Ng et al., 2011) **(0.~~91~~67)**	~~Fir smoldering (Weimer et al., 2008)~~Oxidation products of diesel generator exhausts (Sage et al., 2008) **(0.~~68)~~46)**	
	Marine organics over Arctic (Chang et al., 2011) **(0.54)**		Average ~~OOA~~ LVOOA[1] (Ng et al., 2011) **(0.~~67~~66)**	Ship track (Coggon et al., 2012)~~Oak smoldering (Weimer et al., 2008)~~ **(0.~~62~~40)**	
			~~Average LVOOA (Ng et al., 2011)~~ ~~**(0.66)**~~	~~Ship track (Coggon et al., 2012)~~ ~~**(0.40)**~~	

[1] ~~MOOA: marine oxygenated organic aerosols~~

~~2~~ LVOOA: low-volatility oxygenated organic aerosols

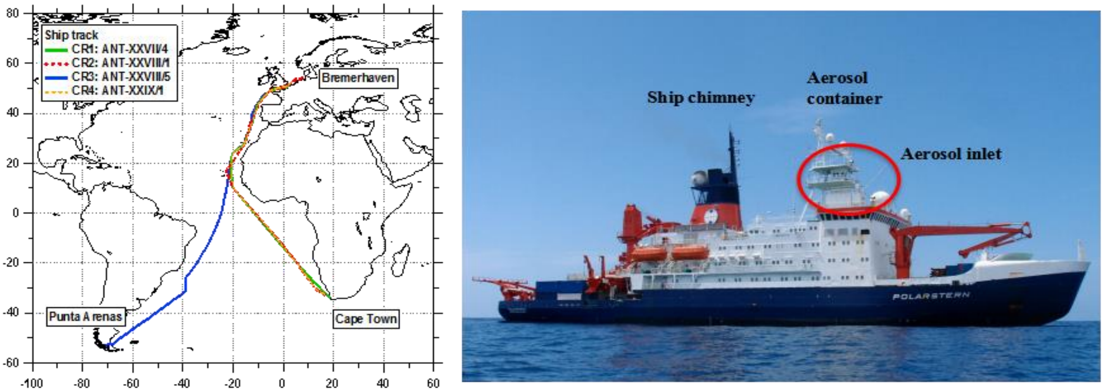
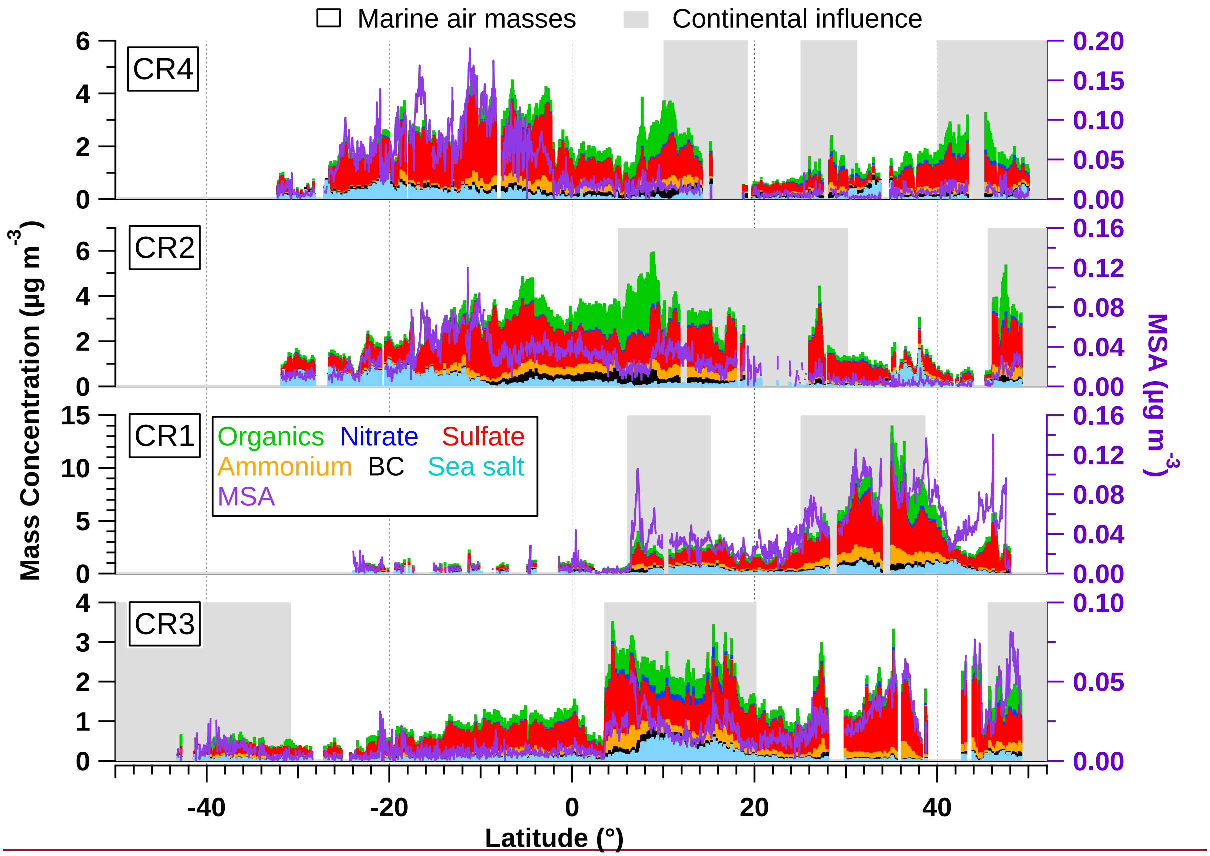


Figure 1. (a) Ship tracks of 4 cruises; (b) The position of the container during Polarstern cruises.



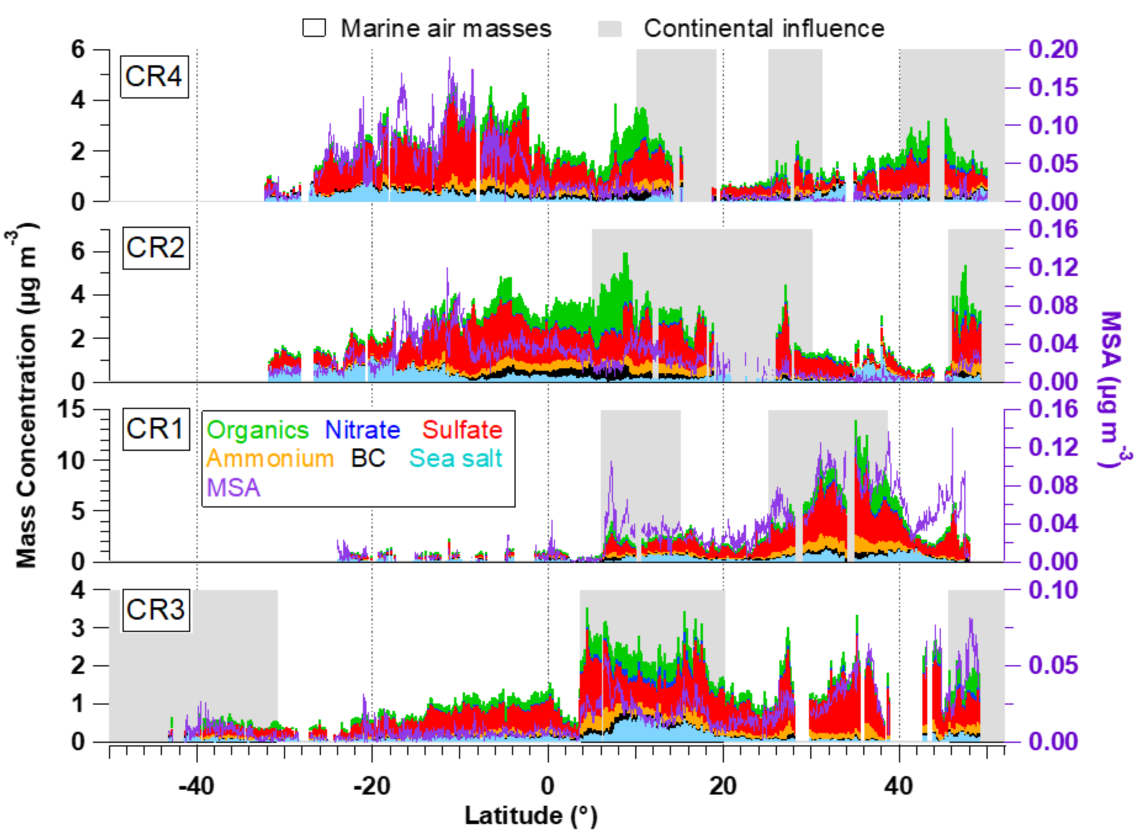
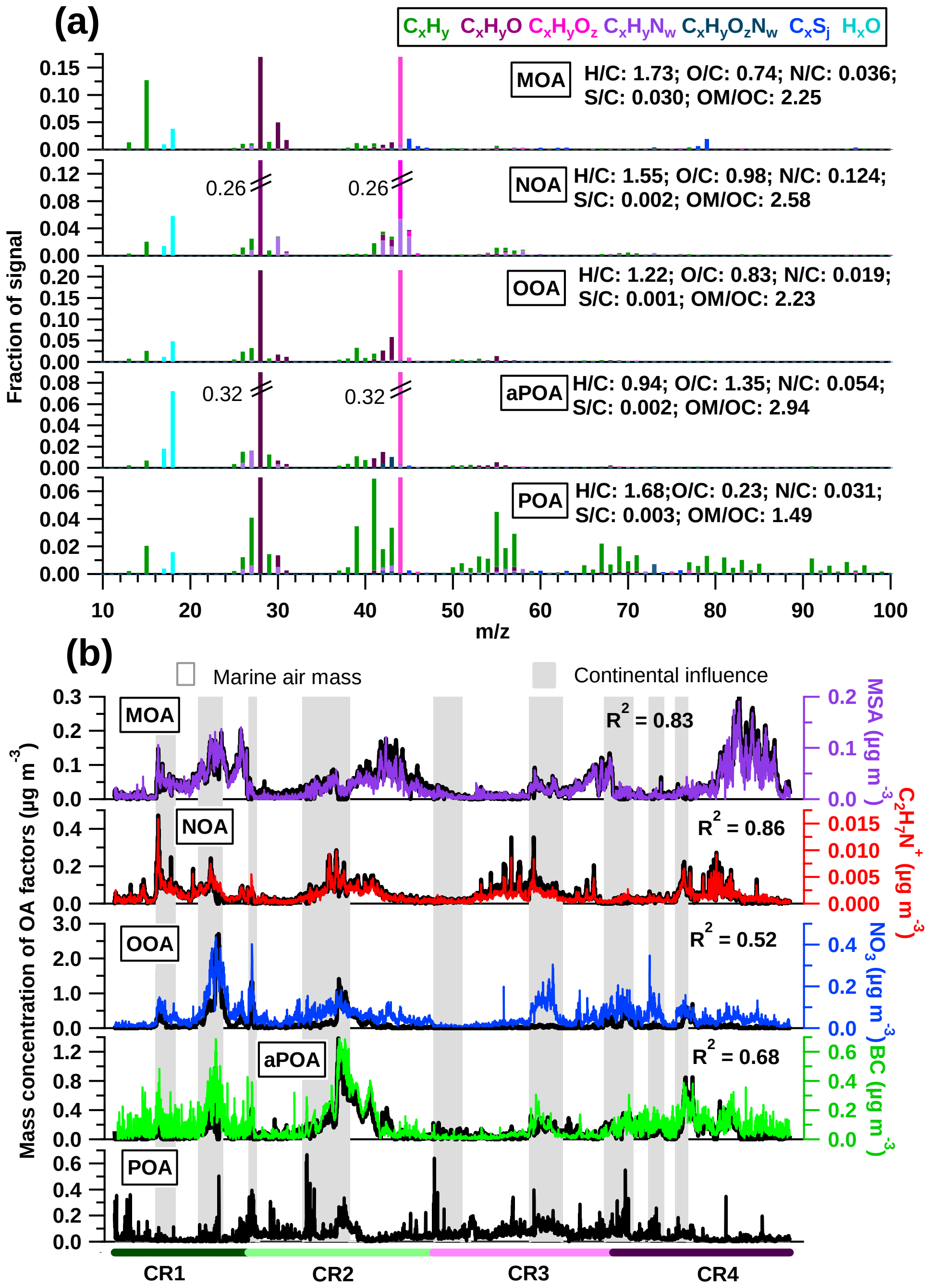


Figure 2. Latitudinal variation of organics, nitrate, sulfate, ammonium, ~~BC~~eBC, sea salt (left axis) and MSA (right axis) ~~in~~during the ~~four~~4 Polarstern cruises. Air masses with continental influence (grey) and originated from the ocean (blank) are marked on background. Note that CR1, CR2, and CR4 followed almost the same ship track between Bremerhaven and Cape Town, while the route of CR3 was different (from 15°N) since starting from Punta Arenas.


(a)
C$_x$H$_y$ C$_x$H$_y$O C$_x$H$_y$O$_z$ C$_x$H$_y$N$_w$ C$_x$H$_y$O$_z$N$_w$ C$_x$S$_j$ H$_x$O
MOA
H/C: 1.73; O/C: 0.74; N/C: 0.036; S/C: 0.030; OM/OC: 2.25
NOA
H/C: 1.55; O/C: 0.98; N/C: 0.124; S/C: 0.002; OM/OC: 2.58
0.26
0.26
OOA
H/C: 1.22; O/C: 0.83; N/C: 0.019; S/C: 0.001; OM/OC: 2.23
aPOA
H/C: 0.94; O/C: 1.35; N/C: 0.054; S/C: 0.002; OM/OC: 2.94
0.32
0.32
POA
H/C: 1.68;O/C: 0.23; N/C: 0.031; S/C: 0.003; OM/OC: 1.49
Fraction of signal
m/z
10 20 30 40 50 60 70 80 90 100
(b)
Marine air mass
Continental influence
MOA
R^2 = 0.83
MSA (μg m^{-3})
NOA
R^2 = 0.86
C$_2$H$_7$N$^+$ (μg m^{-3})
OOA
R^2 = 0.52
NO$_3$ (μg m^{-3})
aPOA
R^2 = 0.68
BC (μg m^{-3})
POA
Mass concentration of OA factors (μg m^{-3})
CR1
CR2
CR3
CR4

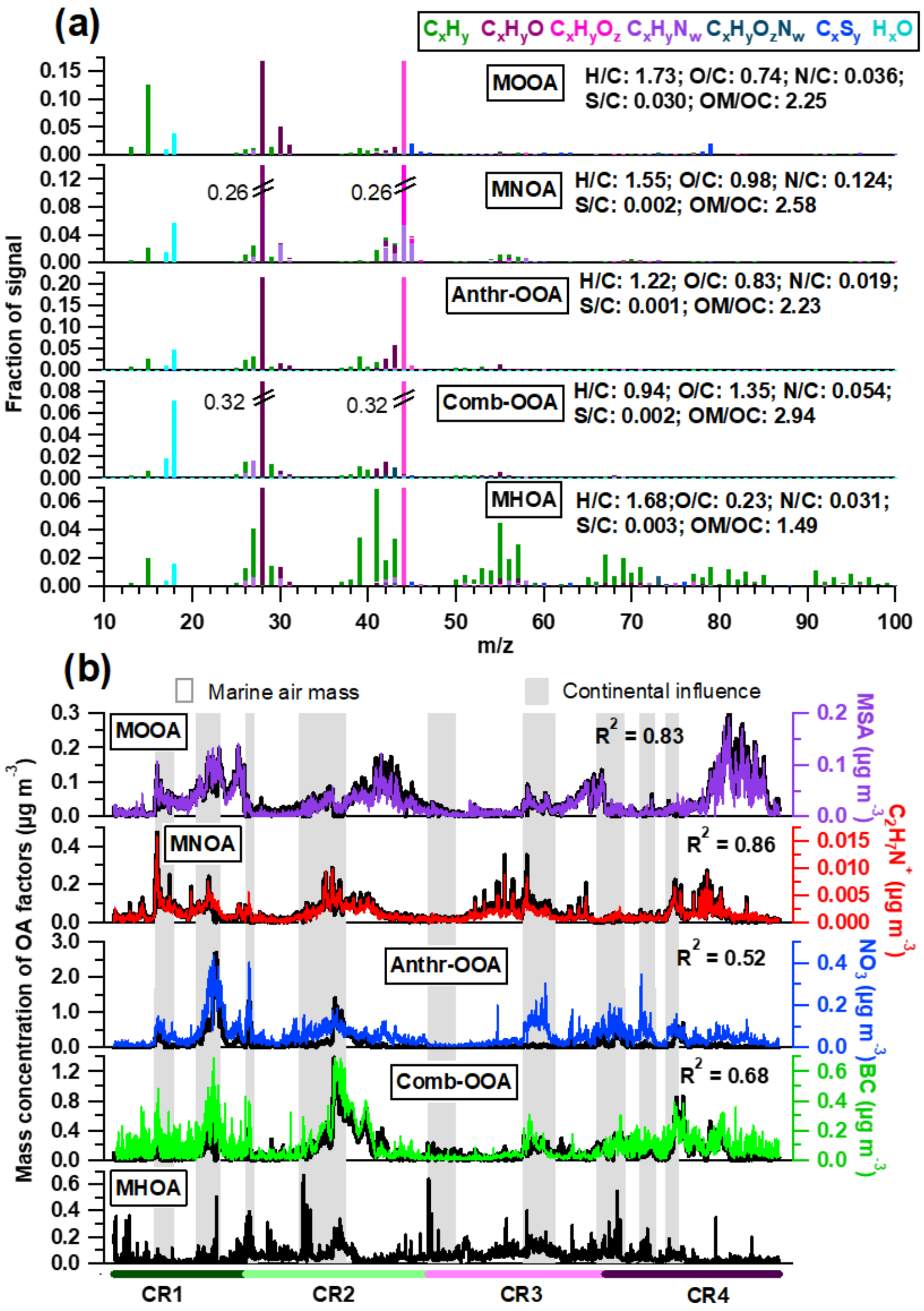
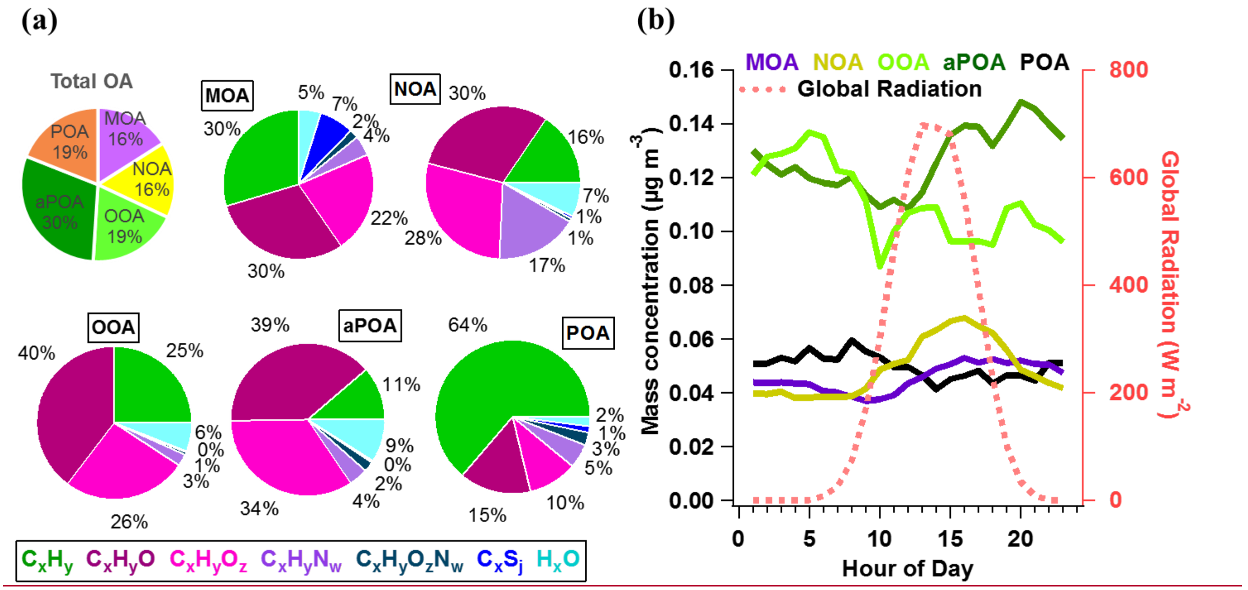


Figure 3. (a) High resolution mass spectra and (b) time series of 5 OA components. Also shown are simultaneous variation of tracer compounds on the right axes with marine (blank) and continental influenced (grey) air masses.



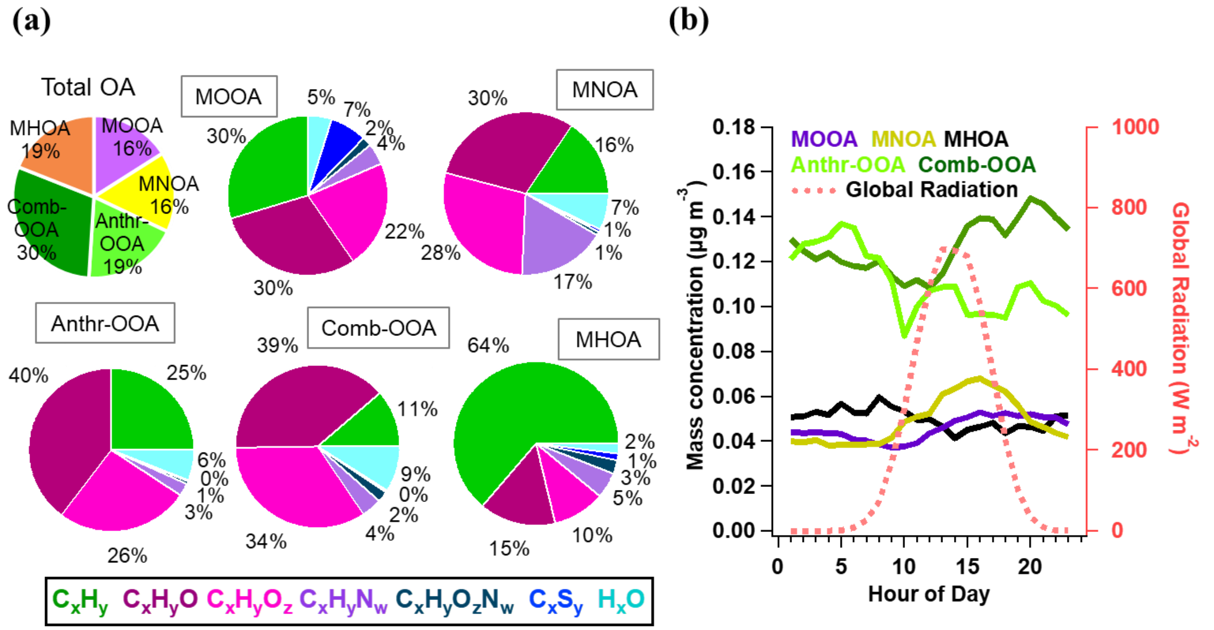
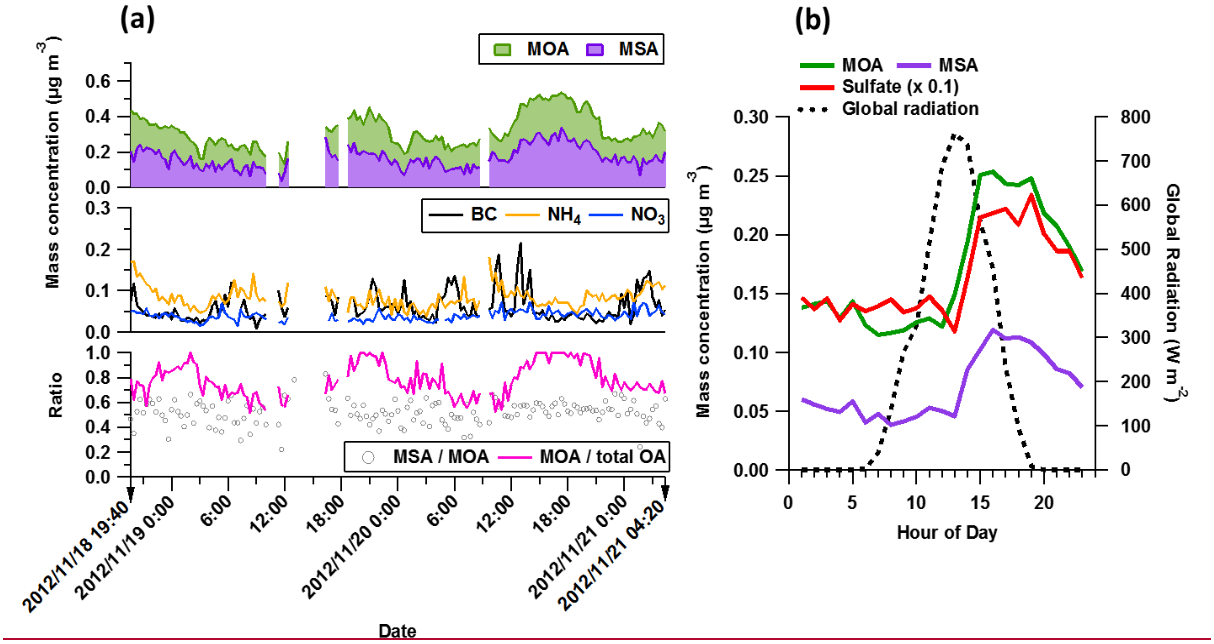


Figure 4 (a) ~~average~~Average mass fraction of each component in the total OA mass concentration, and the functional groups composition of each OA factor, and (b) diurnal variations of 5 OA factors with global radiation.


(a)
MOA
MSA
Mass concentration (µg m-3)
0.6
0.4
0.2
0.0
0.3
0.2
0.1
0.0
BC
NH4
NO3
Ratio
1.0
0.8
0.6
0.4
0.2
0.0
MSA / MOA
MOA / total OA
2012/11/18 19:40
2012/11/19 0:00
6:00
12:00
18:00
2012/11/20 0:00
6:00
12:00
18:00
2012/11/21 0:00
2012/11/21 04:20
Date
(b)
MOA
MSA
Sulfate (x 0.1)
Global radiation
Mass concentration (µg m-3)
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Global Radiation (W m-2)
800
700
600
500
400
300
200
100
0
0
5
10
15
20
Hour of Day

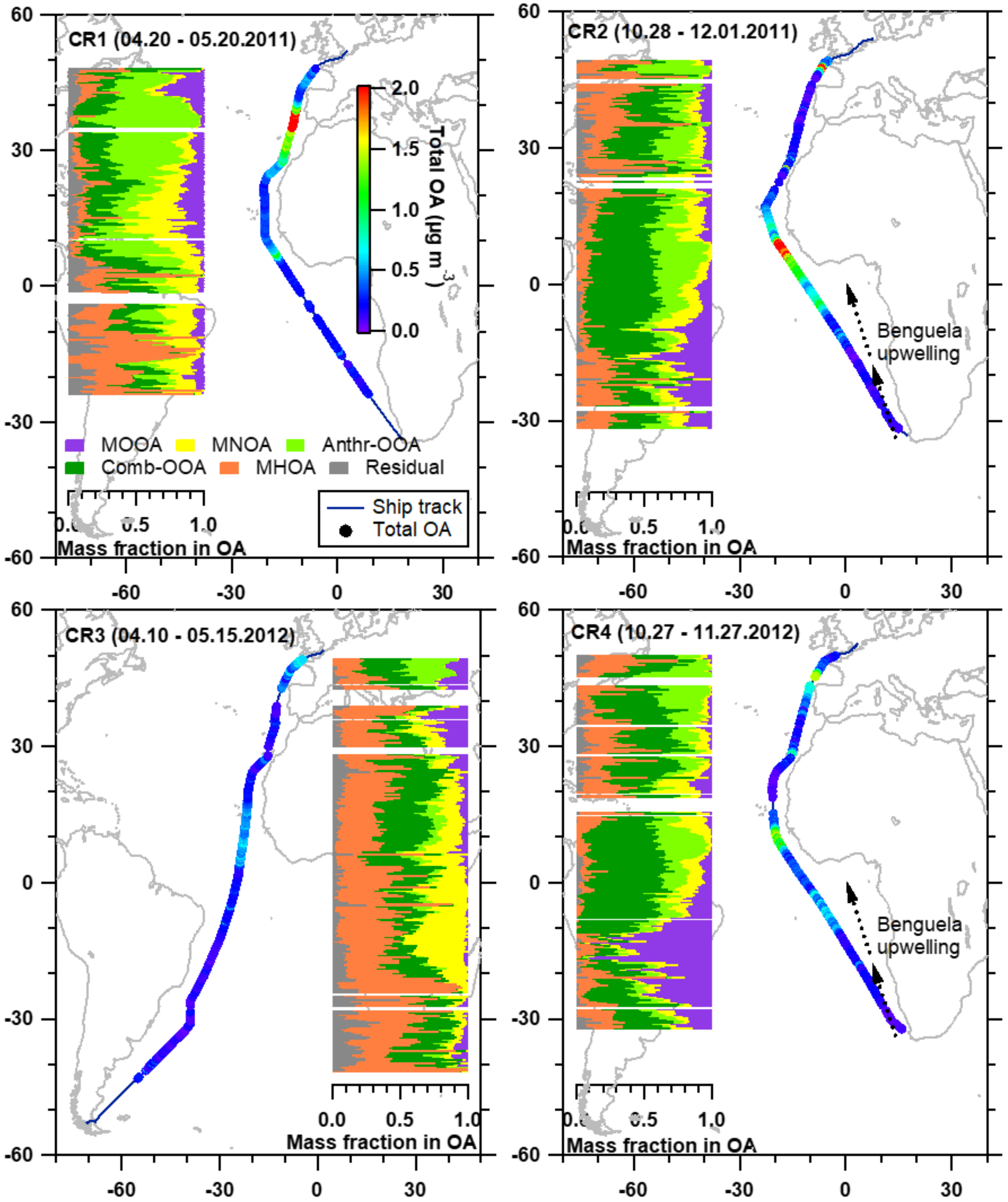
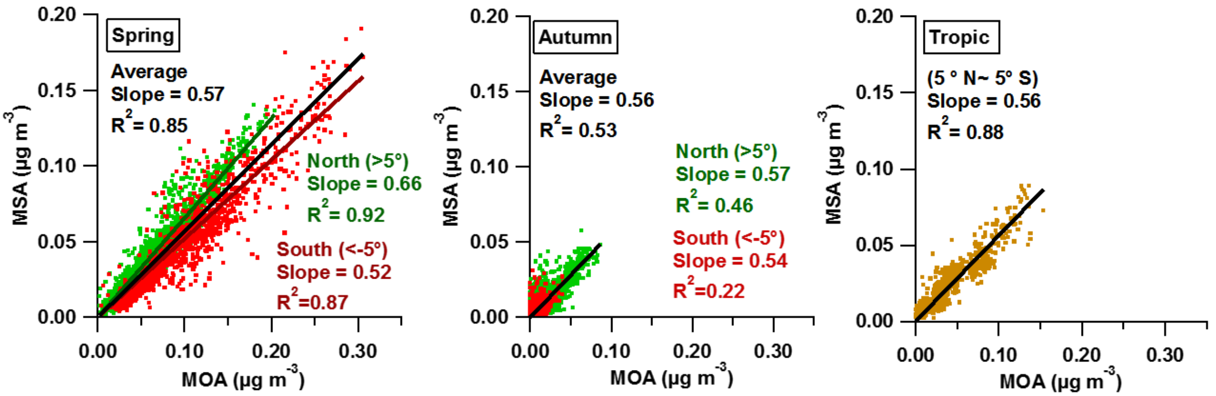
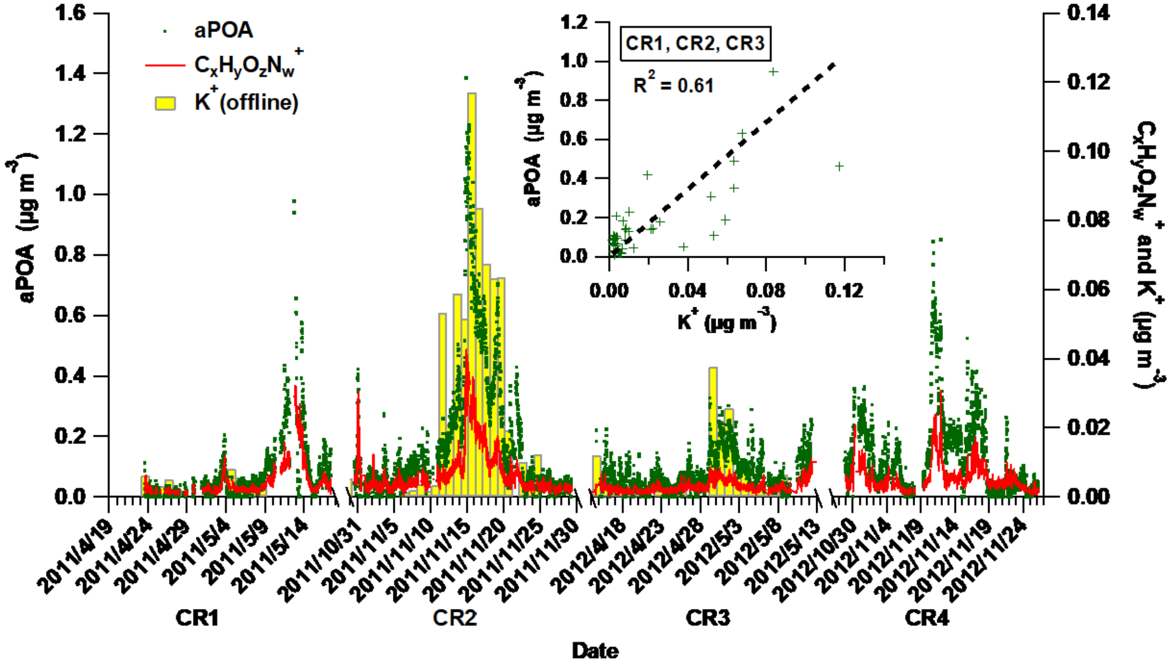


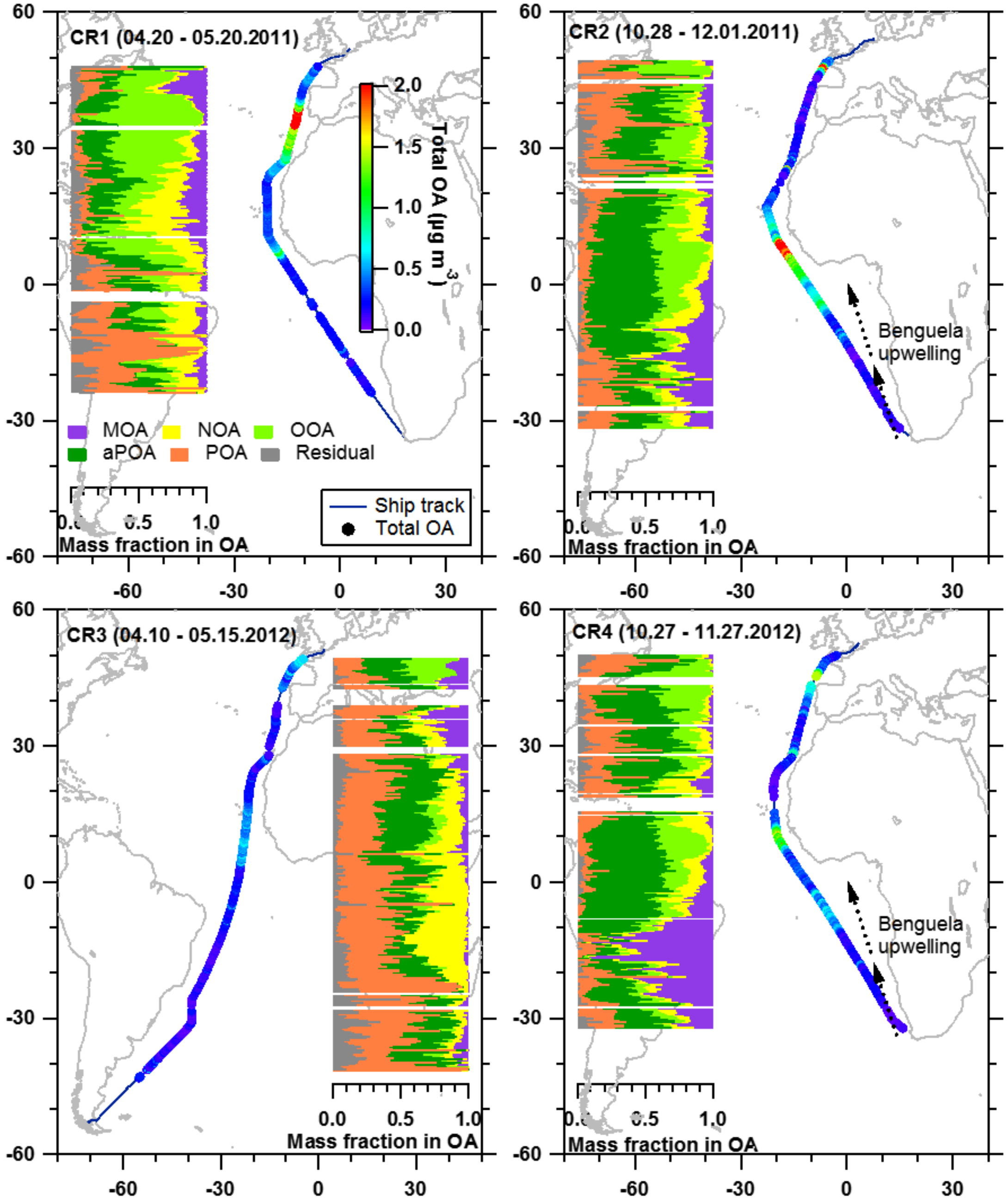
Figure 5- Latitude distribution of 5 OA factor mass fractions in the total OA with total OA mass concentration along the ship track during 4 cruises. The Benguela upwelling is marked in the figures for CR2 and CR4, while not displayed (but still exists) in CR1 and CR3.



~~**Figure 6 Correlation between the MOA factor and MSA in spring and autumn over different regions of the Atlantic**~~



~~**Figure 7 The time series of aPOA (green dots), $C_xH_yO_zN_w^+$ fragments (red line) and potassium (K^+, the yellow bar with grey box) during Polarstern cruises. Note that the daily mass concentration of K^+ is obtained from offline measurements only performed in the first three cruises. The scattering plot in the sub-window provides the correlation between daily average mass concentration of aPOA from AMS and potassium from offline measurements.**~~



~~Figure 8 Latitude distribution of 5 OA factor mass fractions in the total OA with total OA mass concentration along the ship track during 4 cruises. The Benguela upwelling is marked in the figures for CR2 and CR4, while not displayed (but still exists) in CR1 and CR3.~~

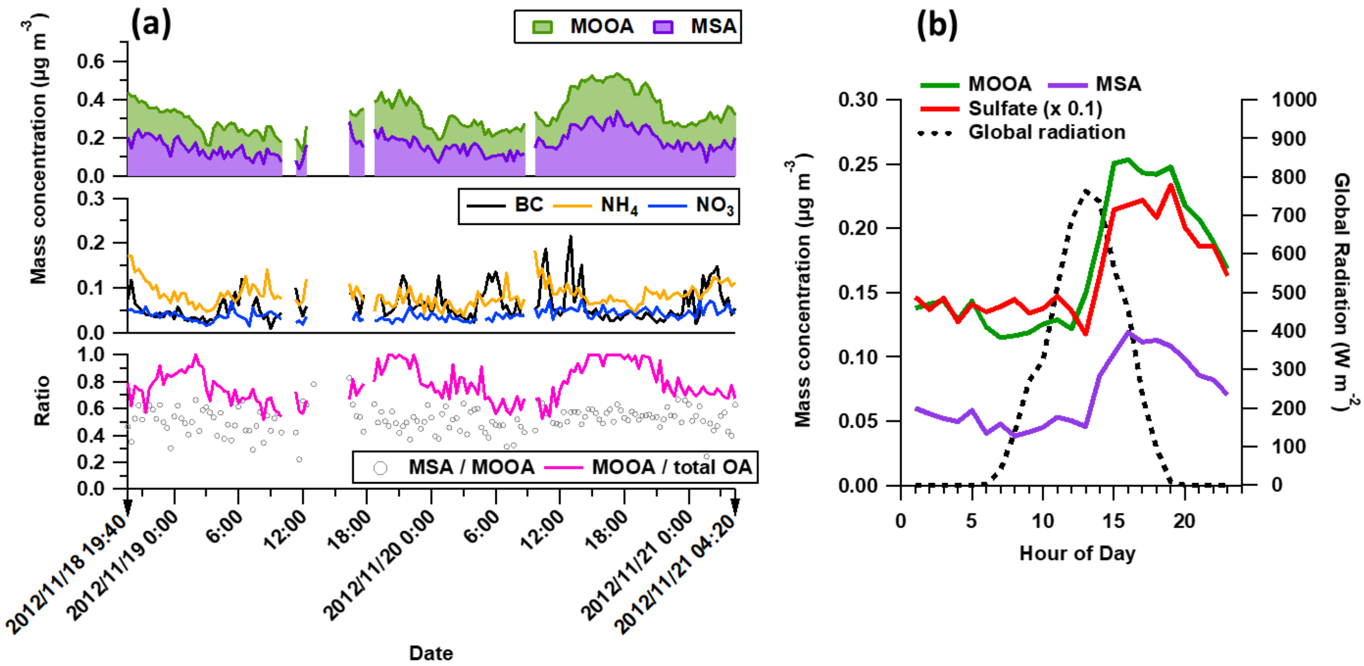


Figure 6 The characteristics of the MOOA dominating period: (a) time series of MOOA and MSA (top), possibly non-marine species (eBC, NH_4, NO_3; middle figure), as well as the ratio between MSA and MOOA, and the mass fraction of MOOA in the total OA (bottom); (b) the diurnal variation of MOOA, MSA, Sulfate (reduced to one tenth for comparison) and the global radiation.

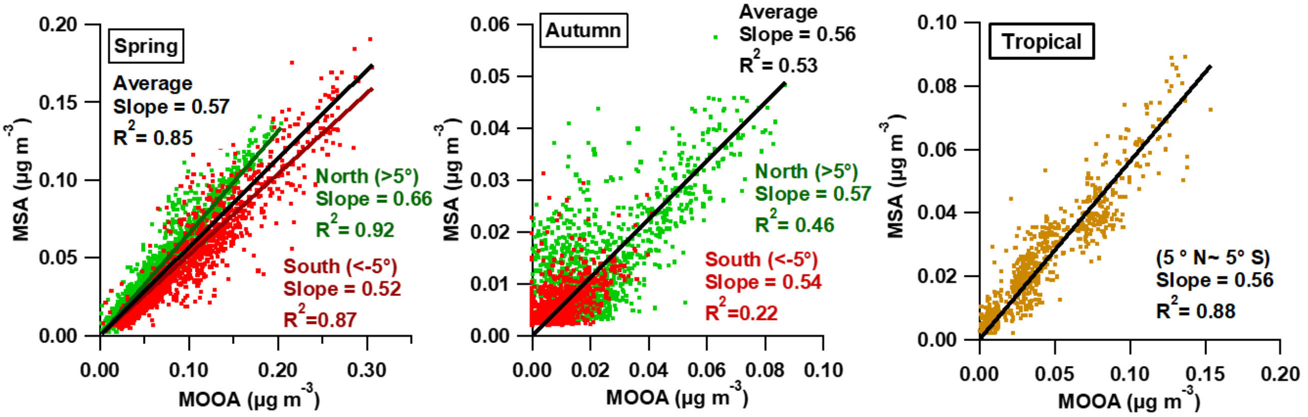


Figure 7 The correlations between the MOOA factor and MSA in spring and autumn over different regions of the Atlantic

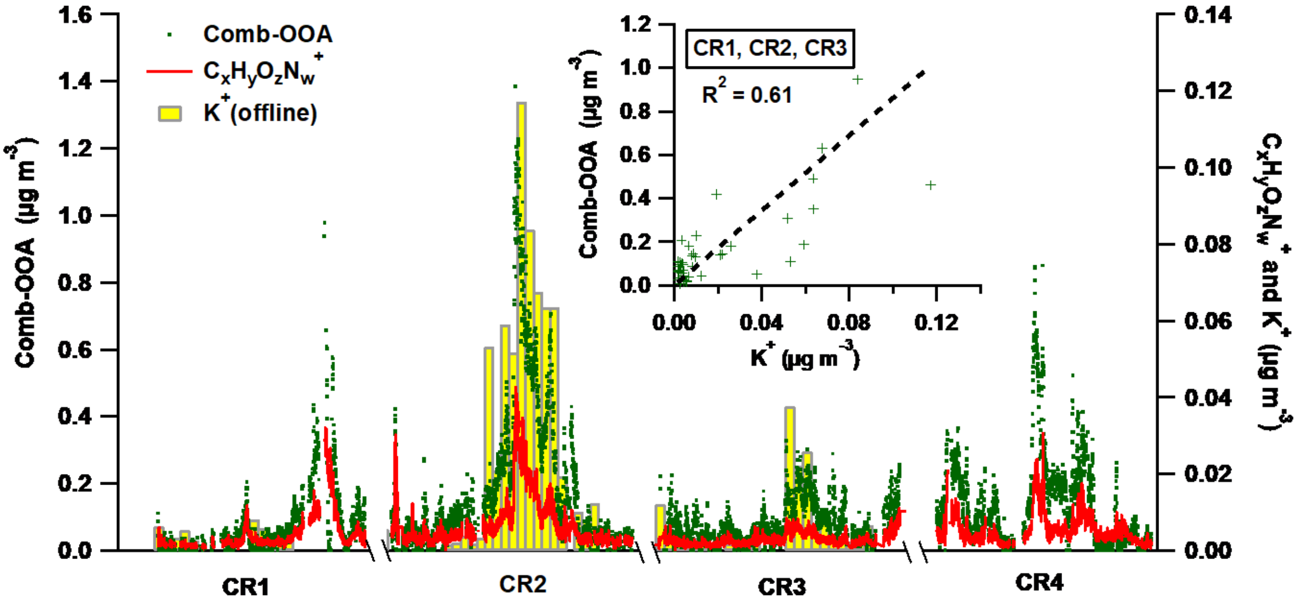


Figure 8 The variation of Comb-OOA (green dots), $C_xH_yO_zN_w^+$ fragments (red line) and potassium (K^+, the yellow bar with grey box) during Polarstern cruises. Note that the 24h-average mass concentration of K^+ is obtained from offline measurements only performed during the first 3 cruises. The scattering plot in the sub-window provides the correlation between 24h-average mass concentration of Comb-OOA from AMS and potassium from offline measurements.

Supplementary

Source apportionment of the submicron organic aerosols over the Atlantic Ocean from 53°N to 53°S using HR-ToF-AMS

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~~**Table S1** The boundary of latitude for each air mass group in the four cruises (unit: °).~~

~~**Air mass group**~~	~~**CR1**~~	~~**CR2**~~	~~**CR3**~~	~~**CR4**~~
~~Continent Europe **(Ec)**~~	~~25< Ec≤38.5~~	~~45.5< Ec≤51~~	~~45.5< Ec≤51~~	~~40 < Ec≤51~~
~~Marine Europe **(Em)**~~	~~38.5< Em≤48~~ ~~15< Em≤25~~	~~30< Em≤45.5~~	~~20< Em≤45.5~~	~~31< Em≤40~~ ~~19< Em≤ 25~~
~~Continent Africa **(Ac)**~~	~~6< Ac≤15~~	~~5< Ac≤30~~	~~3.5< Ac≤20~~	~~25< Ac≤31~~ ~~10< Ac≤19~~
~~Marine Africa **(Am)**~~	~~-25< Am≤6~~	~~-32< Am≤5~~	~~-31< Am≤3.5~~	~~-33< Am≤10~~
~~Continent South Africa **(SAc)**~~	~~-~~	~~-~~	~~-55< Am≤ -31~~	~~-~~

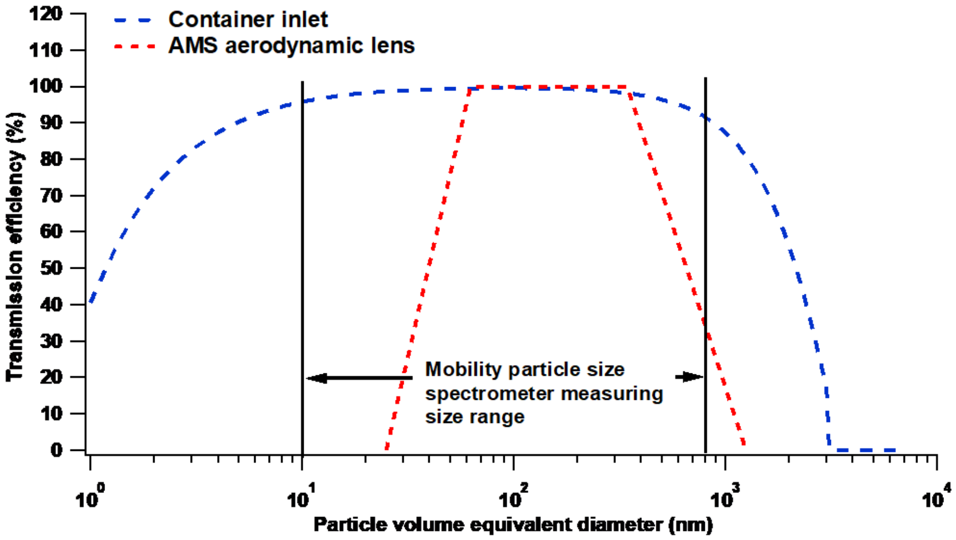


Figure S1 The transmission efficiency as a function of particle volume equivalent diameter for: the Aerosol container inlet (blue dashed line) derived by the Particle Loss Calculator (von der Weiden et al., 2009), and AMS aerodynamic lens (red dashed line) shown as an average of of transmission efficiency curves in several studies (Bahreini et al., 2008; Jayne, 2000; Takegawa et al., 2009; Zhang et al., 2004). The measuring size range of the mobility particle size spectrometer is depicted.

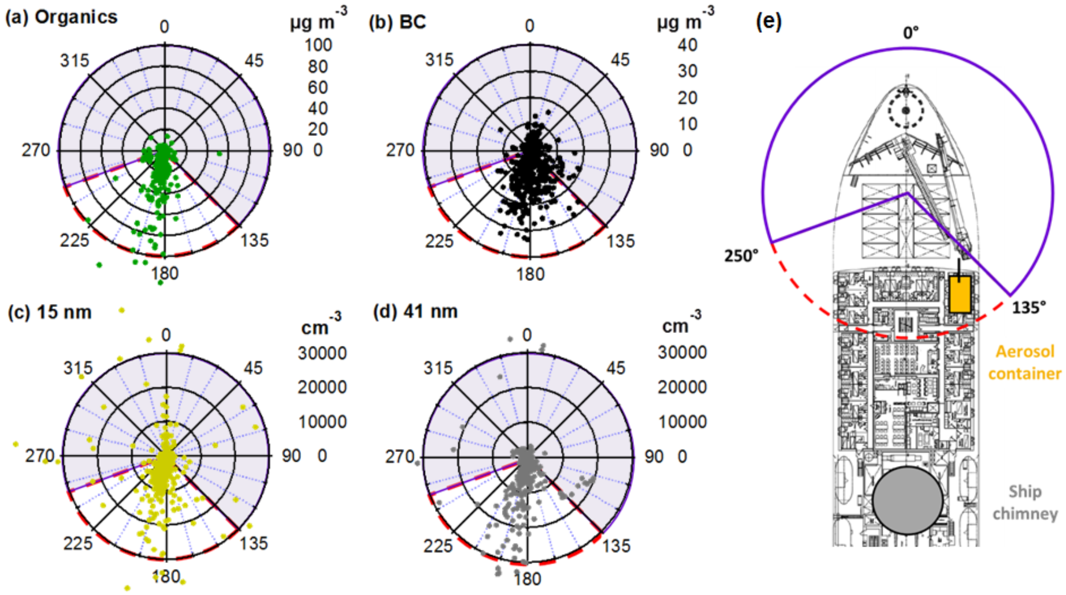


Figure S2 Wind rose (on relative wind direction, RWD) of mass concentration of (a) organics and (b) BC, as well as particle number concentration at size of (c) 15nm, and (d) 41nm. Data points are for CR4 at 20-min time resolution. (e) Location of Aerosol container and ship chimney, as well as the identified ship contamination range from 135° to 250° of RWD.

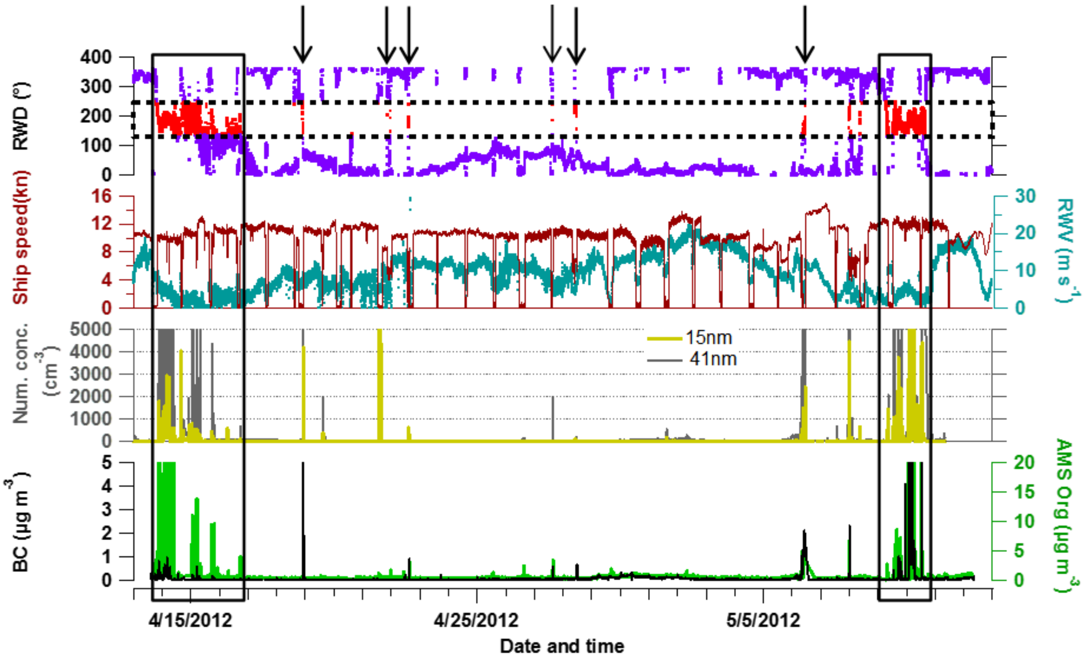
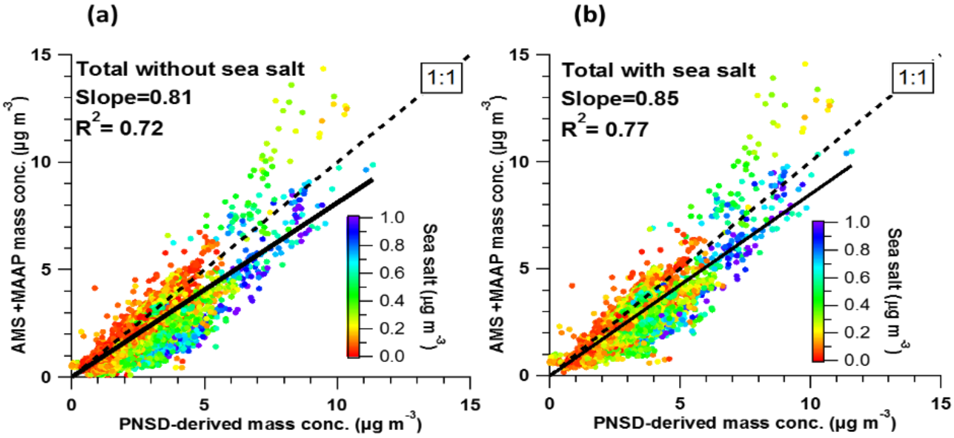


Figure S3 Example of CR3: unfiltered time series for mass concentration of organics (AMS) and BC (MAAP) and particle number concentration (Num. conc.) of 15 nm and 41 nm particles, together with relative wind direction (RWD), relative wind velocity (RWV) and ship speed.



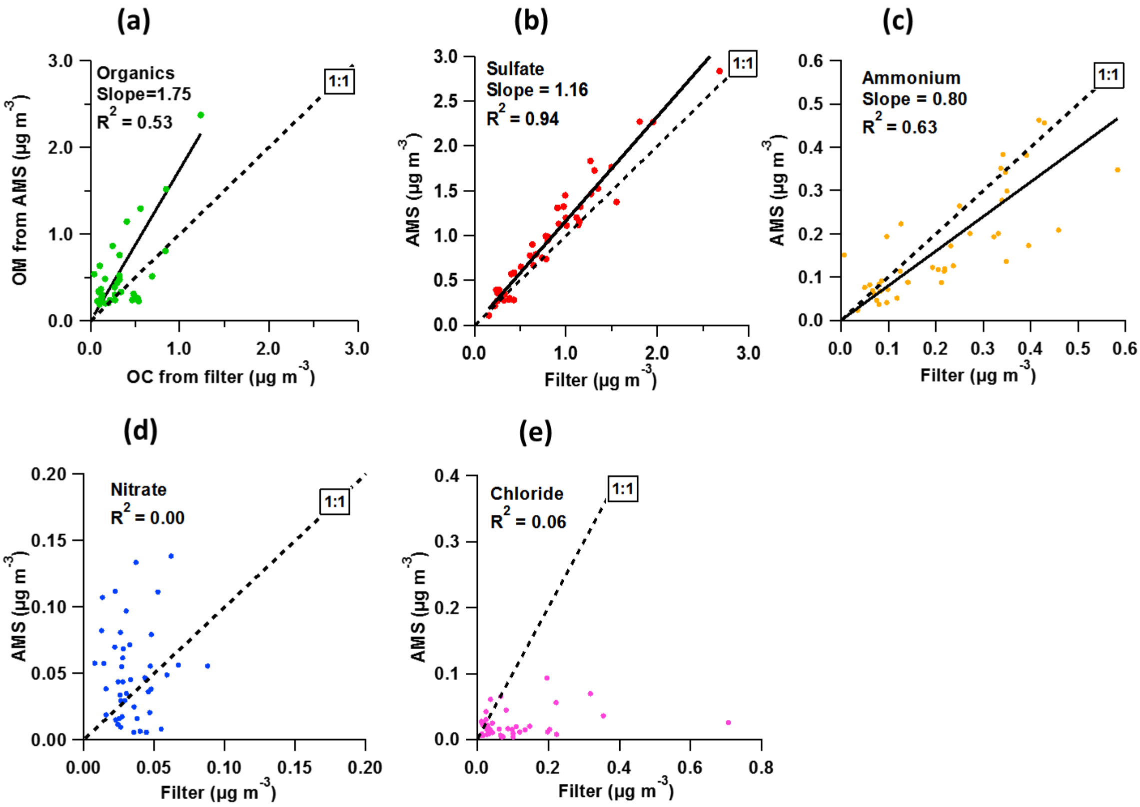


Figure S4 Comparison between AMS measurements and filter measurements for (a) organics (organic matters, OM, vs organic carbon, OC), (b) sulfate (c) ammonium (d) nitrate and (e) chloride during Polarstern cruises.

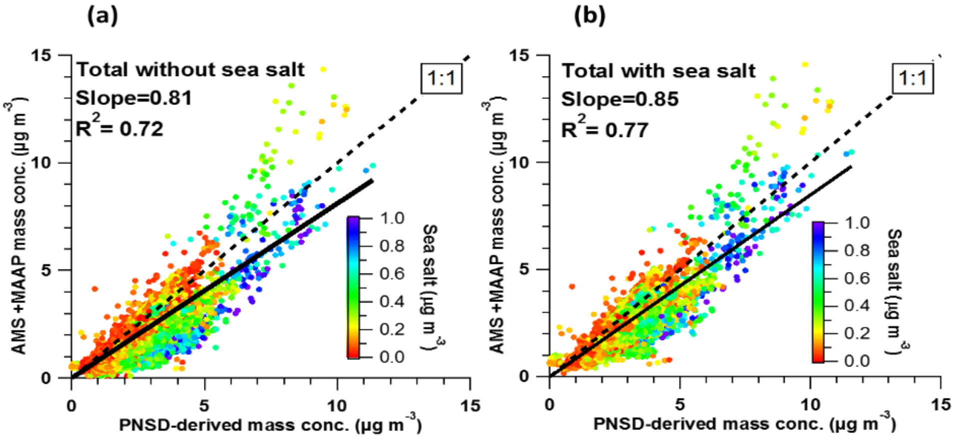
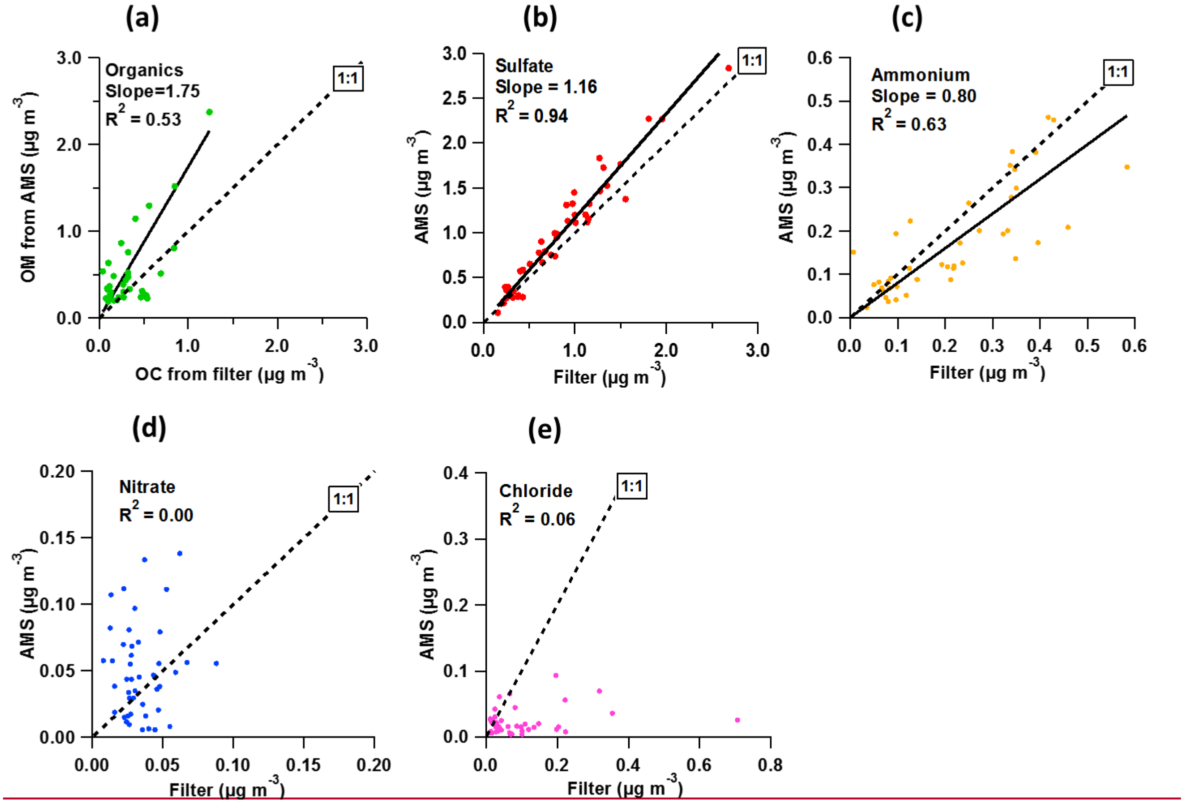


Figure S5 Correlation between total particle mass concentration from AMS + MAAP (a) without sea salt and (b) with sea salt to that derived from particle number size distribution (PNSD), coloured by mass concentration of sea salt. Note that to derive the density of the particles the following densities have been used for individual species: 1.75 g cm^{-3} for sulfate, nitrate and ammonium, 1.4 g cm^{-3} for organics, 1.52 g cm^{-3} for chloride, 1.77 g cm^{-3} for BC and 2.17 g cm^{-3} for the sea salt. CE = 0.7 is chosen and applied.



~~**Figure S5** Comparison between AMS measurements and filter measurements for (a) organics (organic matters, OM, vs organic carbon, OC), (b) sulfate (c) ammonium (d) nitrate and (e) chloride during Polarstern cruises.~~

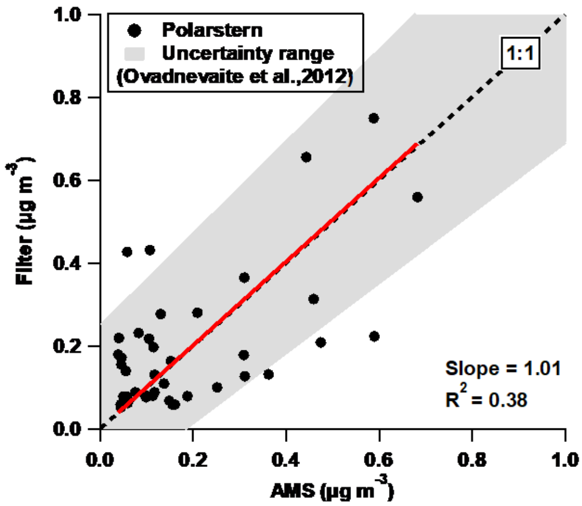
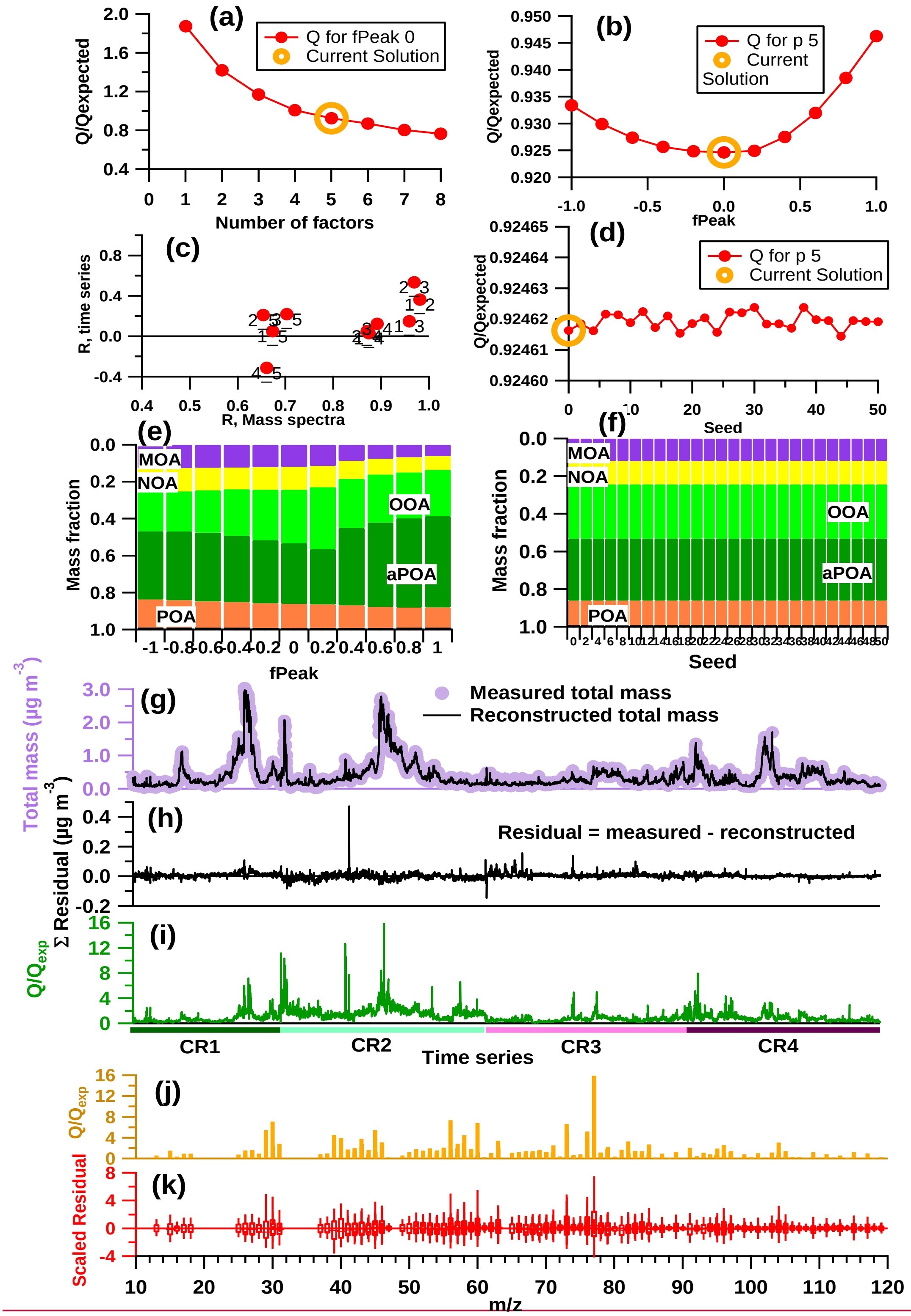


Figure S6 Comparison between sea salt mass concentrations from filter measurements and AMS measurements during Polarstern cruises. The grey shadow presents the uncertainty range of the similar comparison at Mace Head, adapted from Ovadnevaite et al. (2012). Offline sea salt mass concentration is calculated according to the method from Bates et al. (2001) with the equation: sea salt (μg m^{-3}) = Cl$^-$ (μg m^{-3}) + Na$^+$ (μg m^{-3}) x 1.47, the factor of 1.47 is the seawater ratio of (Na$^+$ +K$^+$ +Mg^{2+} + Ca^{2+} +SO$_4^{2-}$ + HCO$_3^-$)/Na$^+$.


(a)
Q for fPeak 0
Current Solution
Q/Qexpected
Number of factors
(b)
Q for p 5
Current Solution
Q/Qexpected
fPeak
(c)
R, time series
R, Mass spectra
(d)
Q for p 5
Current Solution
Q/Qexpected
Seed
(e)
MOA
NOA
OOA
aPOA
POA
Mass fraction
fPeak
(f)
MOA
NOA
OOA
aPOA
POA
Mass fraction
Seed
(g)
Measured total mass
Reconstructed total mass
Total mass (µg m^{-3})
(h)
Residual = measured - reconstructed
Σ Residual (µg m^{-3})
(i)
Q/Q$_{exp}$
CR1
CR2
CR3
CR4
Time series
(j)
Q/Q$_{exp}$
(k)
Scaled Residual
m/z

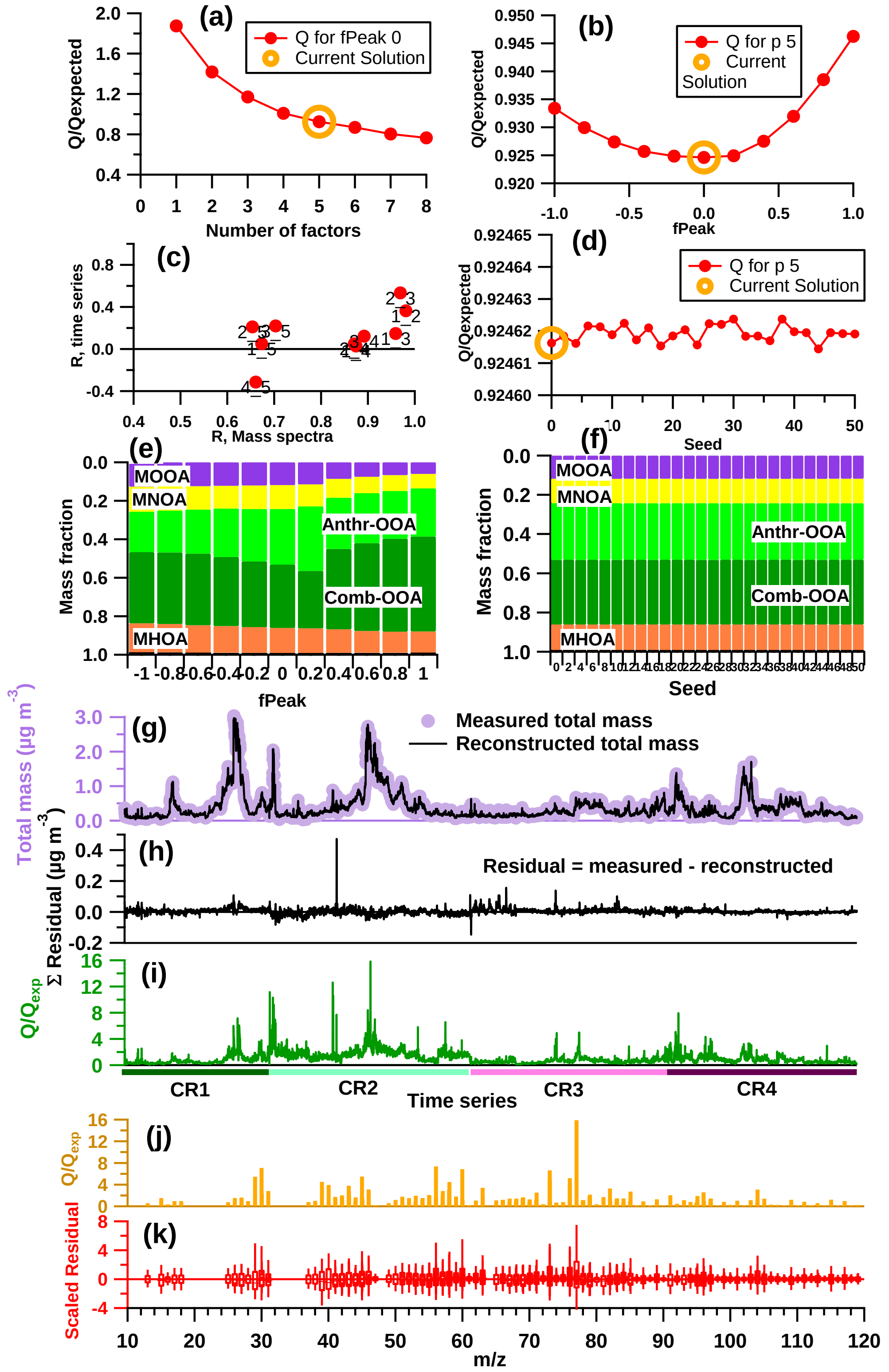
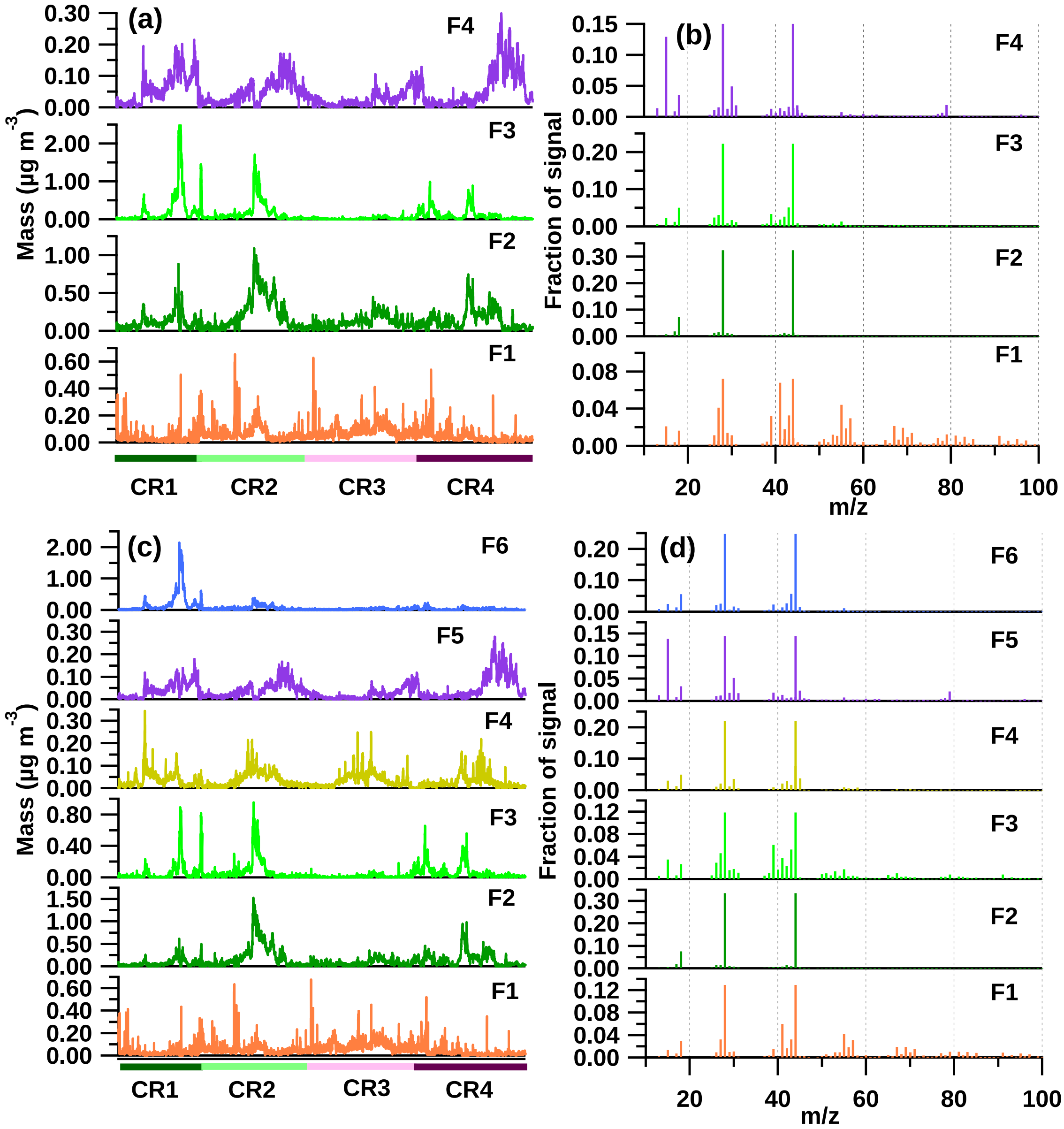


Figure S7 Diagnostic plots: (a) Q/Q_{exp} ratio vs. number of factors, (b) Q/Q_{exp} vs. fPeak between -1 and 1 in step of 0.2 for 5-factor solution, (c) Pearson's correlation coefficient R for time series and mass spectra among 5 factors, (d) Q/Q_{exp} vs. seeds between 0 to 50 in step of 2, (e) variation of mass fraction of each factor as a function of fPeak, (f) variation of mass fraction of each factor as a function of seeds, (g) comparison of total measured mass and reconstructed mass, (h) sum of the residuals of the fit, (i) Q/Q_{exp} in time series, (j) Q/Q_{exp} for each m/z, and (k) scaled residuals for each m/z, with horizontal bars for median, boxes for interquartile and sticks for 95% and 5% of points.



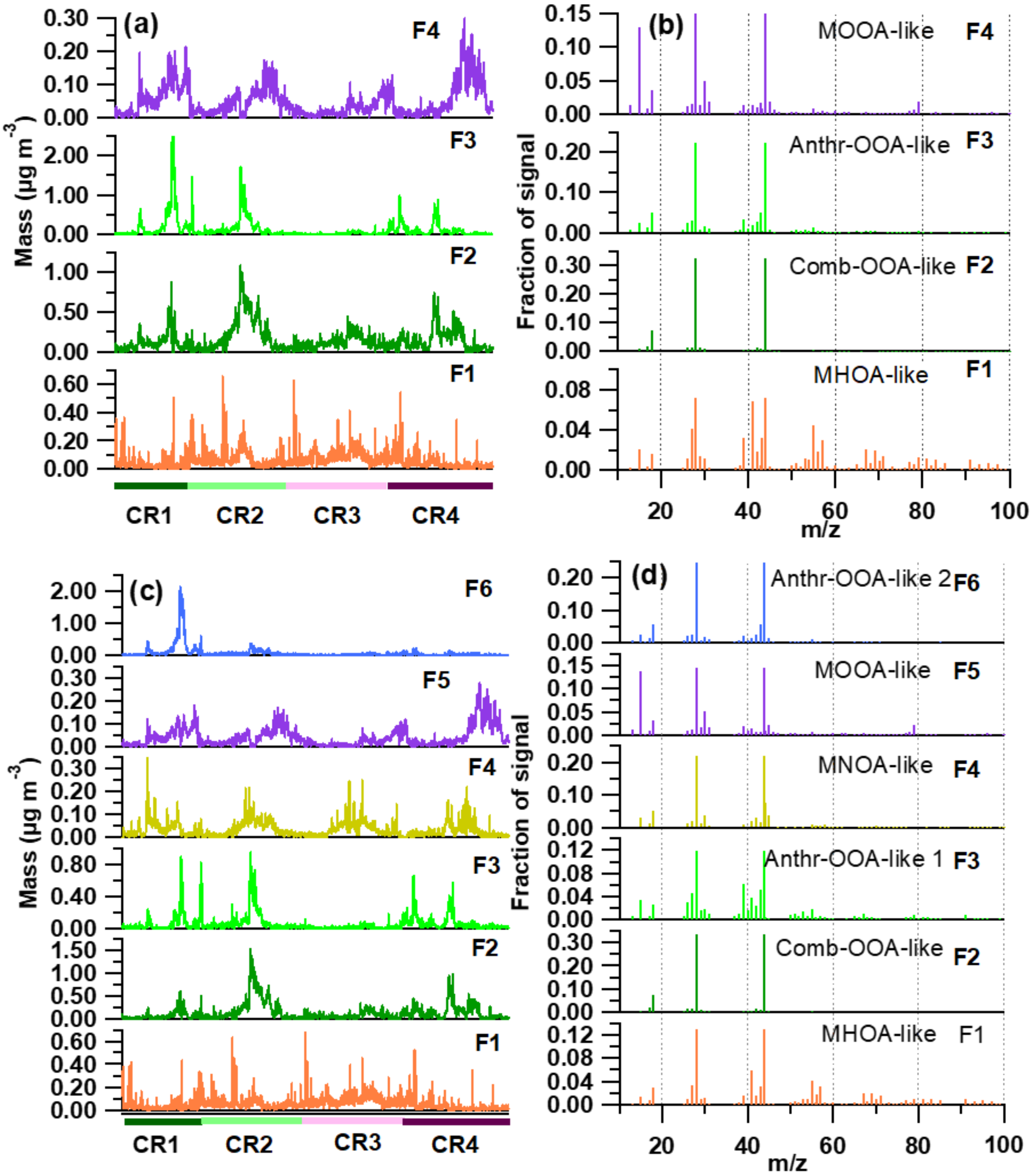
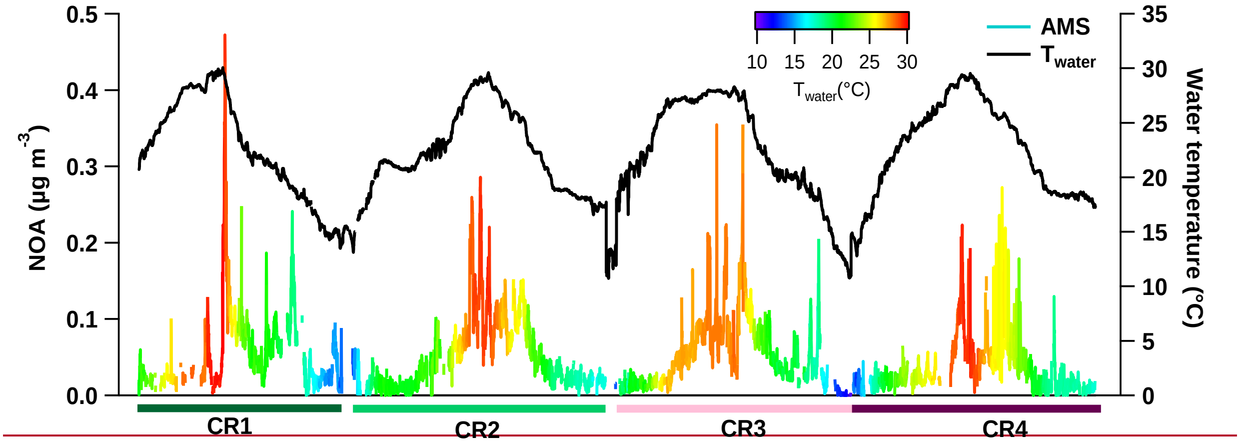


Figure S8 Time series and mass spectra for OA components of (a, b) 4-factor solution, (c, d) 6-factor solution. (More explanation see Figure S9)



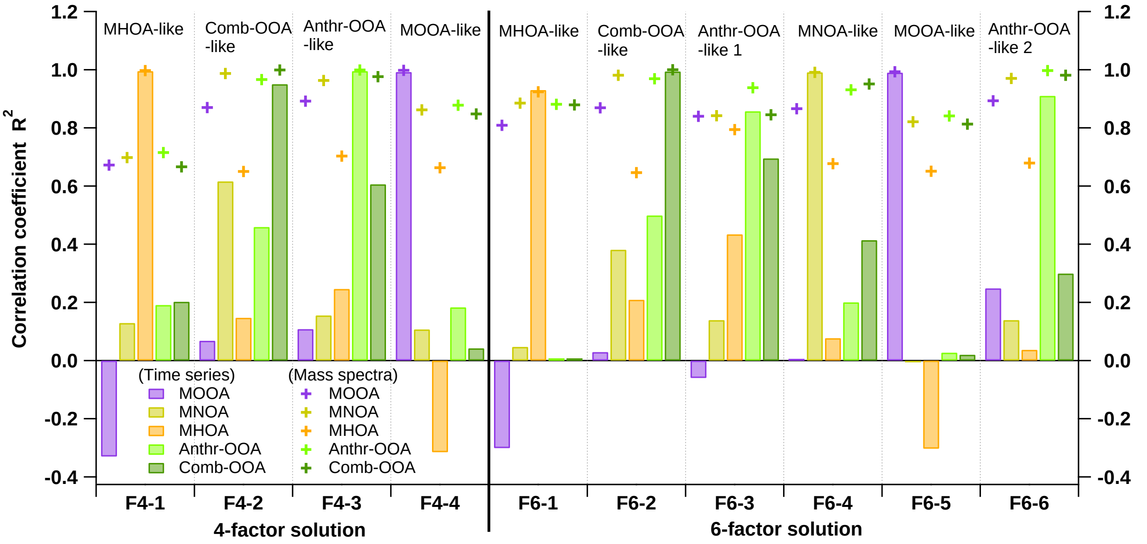


Figure S9 Correlation coefficients of time series and mass spectra for OA components of 4-factor solution and 6-factor solution comparing to 5-factor (selected) solution. The correlations among factors on time-series are shown in bars, while regarding mass spectra shown in cross with the same color code. Correlation coefficients reveal the evolution of the factors when the factor number changes: 4-factor solution already has stable MHOA-like, Comb-OOA-like, Anthr-OOA-like and MOOA-like factors, but MNOA factor is not identified; 6-factor solution keeps stable MHOA-like, Comb-OOA-like, MNOA-like and MOOA-like factors, while Anthr-OOA factor is separated into two parts. Note that the mass spectra of all factors show general resemblance due to high CO$^+$ and CO$_2^+$ ions. This results in higher R^2 on mass spectra than on time-series.

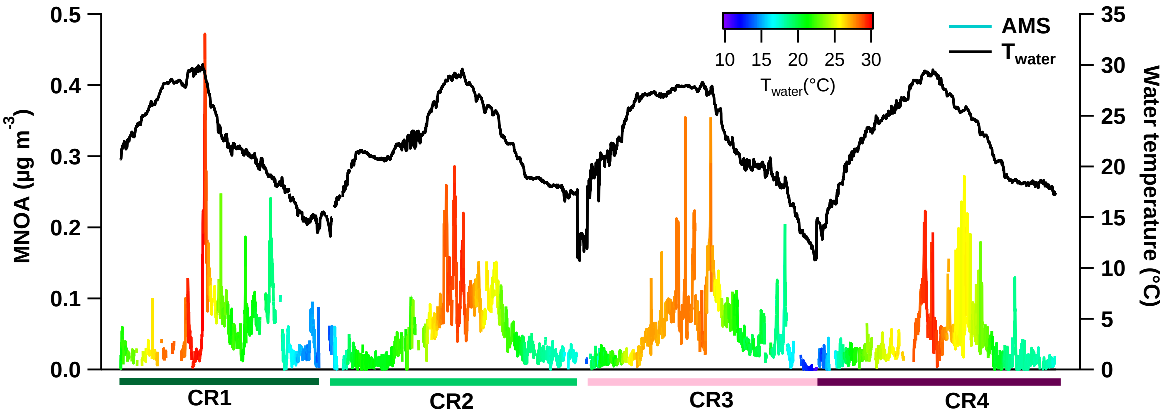
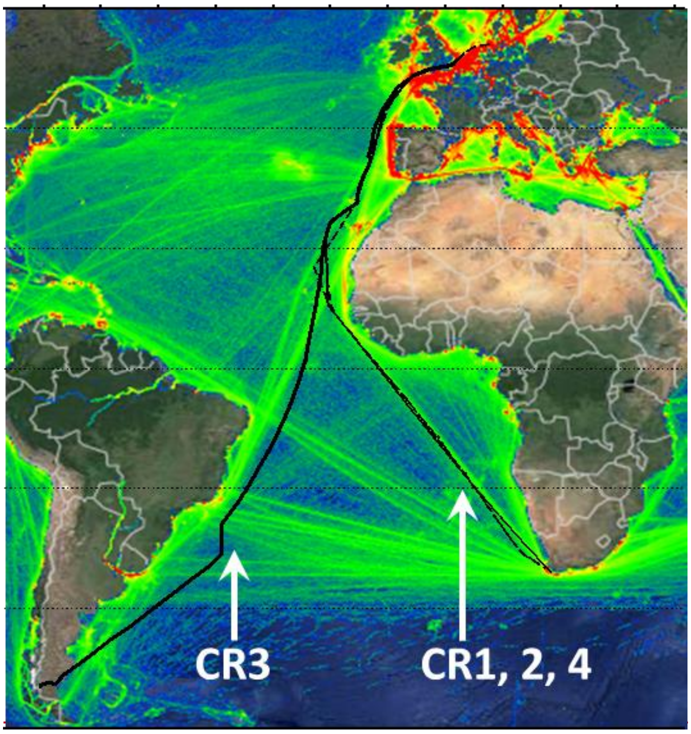


Figure S10 Similar variation between water temperature and ~~NOA~~MNOA (also colored in water temperature) during 4 cruises.



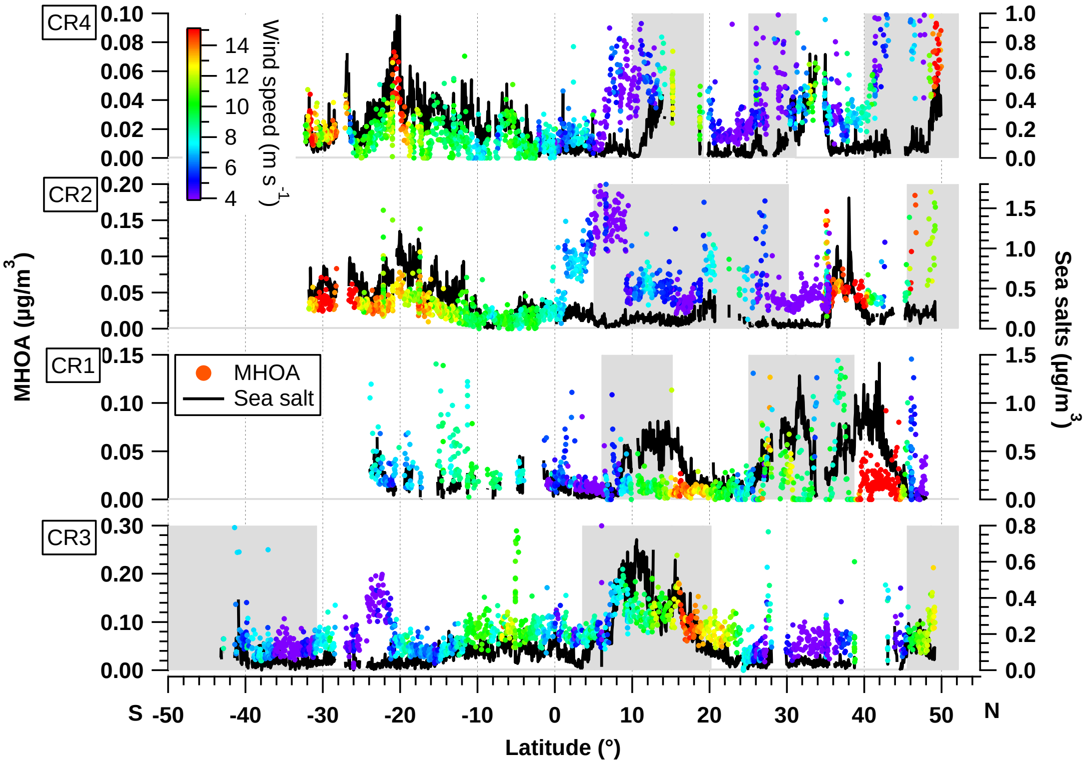


Figure S11 Latitude distribution of MHOA mass concentration (left axis), comparing to the sea salt particle mass concentration (right axis). The MHOA is colored by wind speed (true wind speed). Red boxes mark the cases in which the MHOA and estimated sea salt show similar variation. Grey background indicates continental air masses, white one for marine air masses.

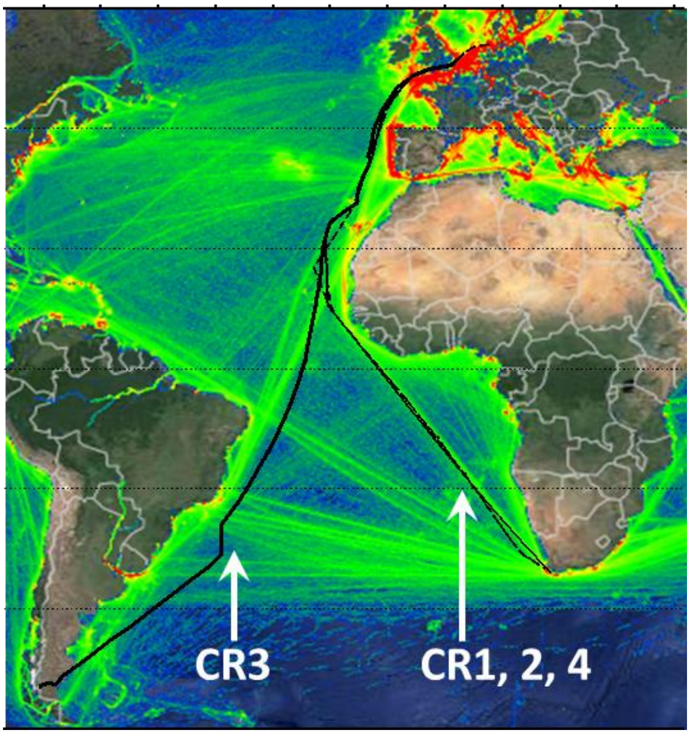
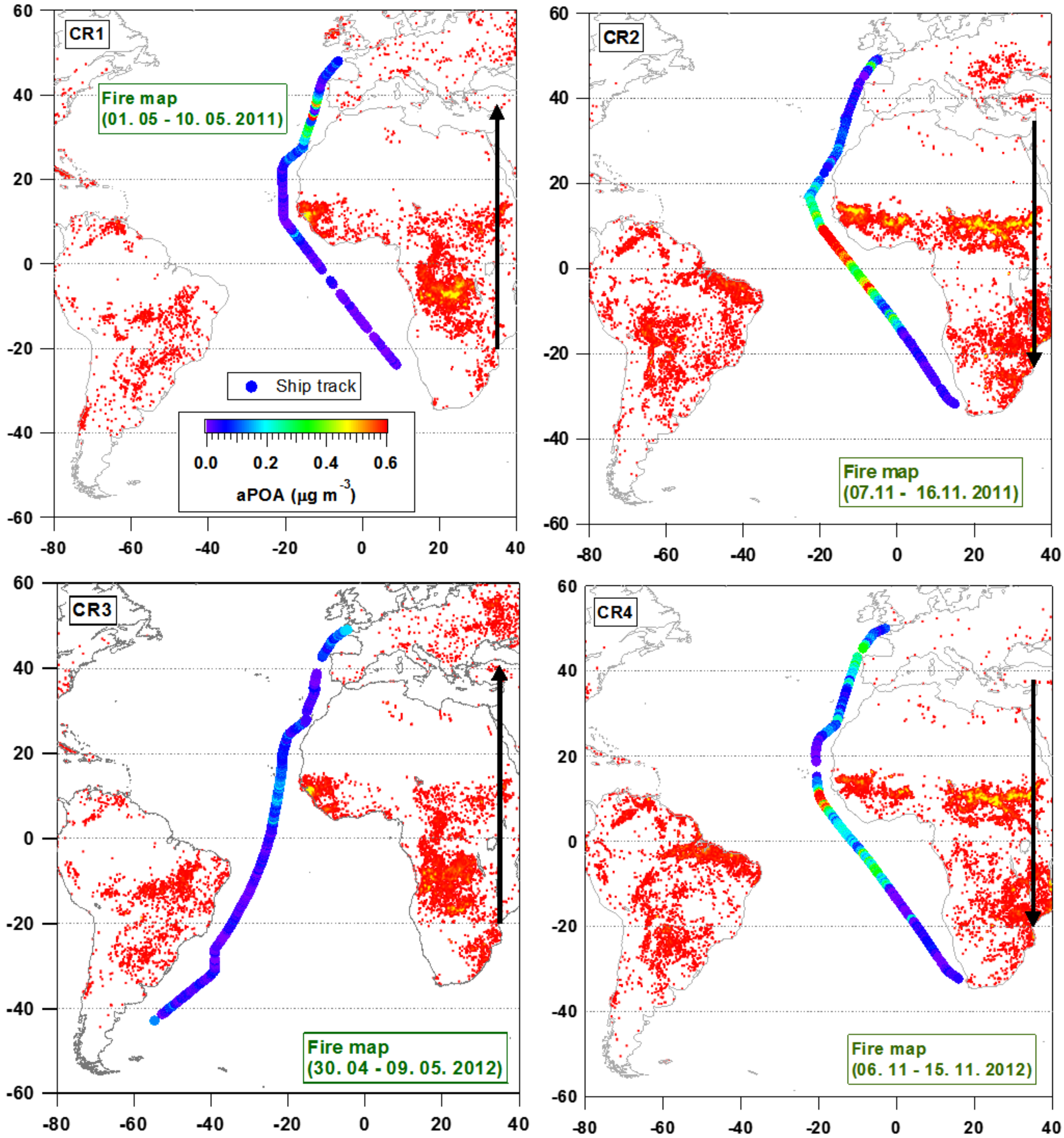


Figure S12 Density map of the maritime traffic with Polarstern cruise tracks (black lines). The background snapshot was taken from https://www.marinetraffic.com/en/ on May 2014 and assumed to be similar to the situation in 2011 and 2012.


CR1
Fire map
(01. 05 - 10. 05. 2011)
Ship track
0.0
0.2
0.4
0.6
aPOA (μg m^{-3})
CR2
Fire map
(07.11 - 16.11. 2011)
CR3
Fire map
(30. 04 - 09. 05. 2012)
CR4
Fire map
(06. 11 - 15. 11. 2012)
60
40
20
0
-20
-40
-60
-80
-60
-40
-20
0
20
40

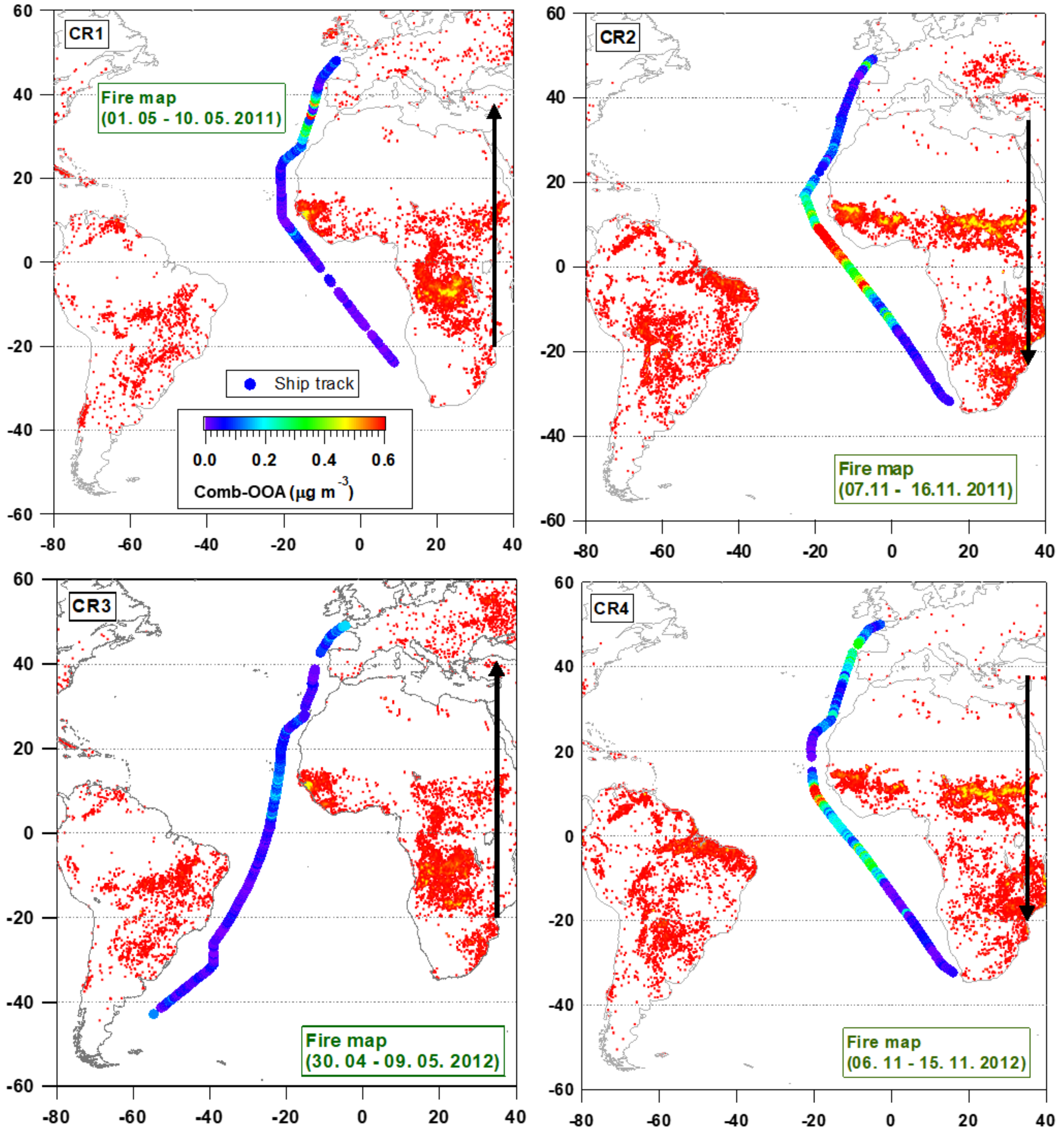
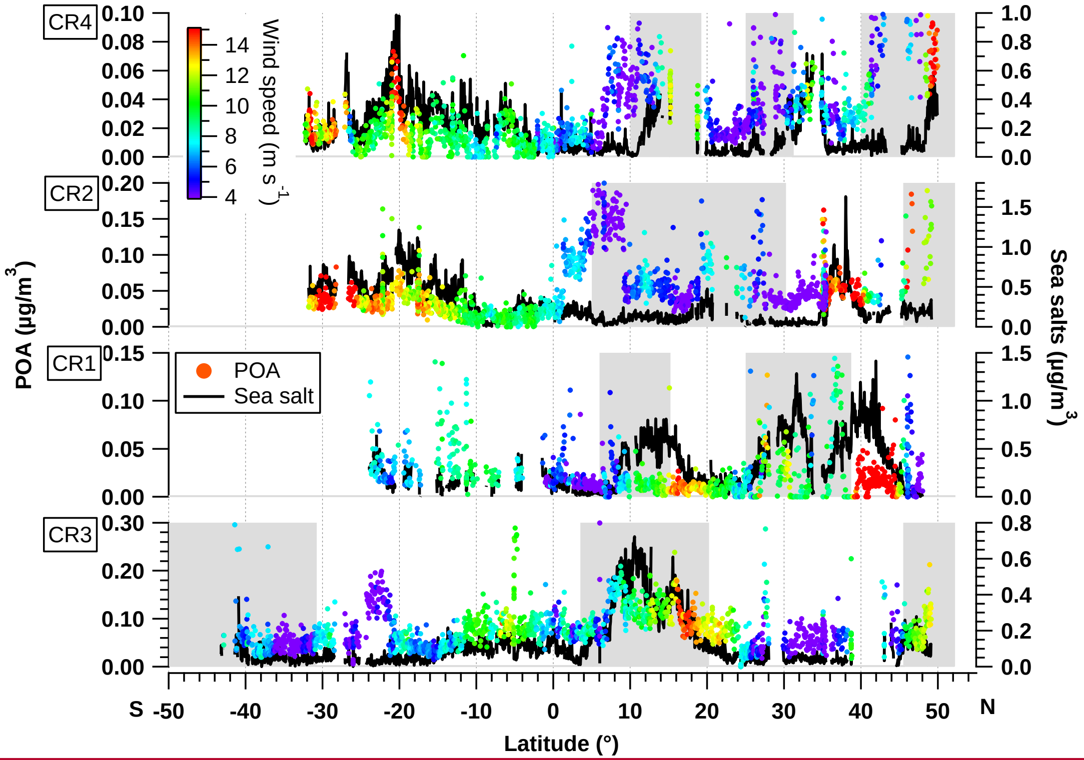


Figure S13 Fire maps obtained from an online database of MODIS satellite (http://rapidfire.sci.gsfc.nasa.gov/firemaps/) , colored by ~~aPOA~~Comb-OOA mass concentration during Polarstern cruises. The black arrows show the ship direction.



~~**Figure S12** Latitude distribution of POA mass concentration (left axis), comparing to the sea salt particle mass concentration (right axis). The POA is colored by wind speed (true wind speed). Red boxes mark the cases in which the POA and estimated sea salt show similar variation. Grey background indicates continental air masses, white one for marine air masses~~

References

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Ovadnevaite, J., Ceburnis, D., Canagaratna, M., Berresheim, H., Bialek, J., et al. (2012). On the effect of wind speed on submicron sea salt mass concentrations and source fluxes. J. Geophys. Res., 117(D16), D16201.

von der Weiden, S. L., Drewnick, F., & Borrmann, S. (2009). Particle Loss Calculator – a new software tool for the assessment of the performance of aerosol inlet systems. Atmos. Meas. Tech., 2(2), 479-494.