

Response to Anonymous Reviewer #1

We thank the reviewer for the valuable and helpful comments. We believe that addressing the issues raised by the reviewer will considerably improve the manuscript.

Please see our reply to each comment below.

Note: All reviewer comments are in *italics*. All author responses are in normal format. The new text included in the manuscript is in bold face.

1. *Introduction and methods. Very well written sections and well presented. I would remove some of the references; at the moment they are more than 100!*

The research presented and explicitly the aim of ASCOS to understand sea/ice surface-aerosol-cloud interactions in the High Arctic covers a wide range of interconnected topics. Also, this study which deals with the mass spectrometric analysis of single particles represents the first of its kind in this location. Therefore, the authors' goal is to present a comprehensive overview/introduction to the covered and directly related topics. As a consequence, we would like to keep the reference list as is, providing the reader the opportunity to gather detailed auxiliary information if needed.

2. *Results. It is not clear if ENCHILARA or Art-2a were used. These two are very different methods. Additionally, I would try to simplify the 10 particles types presented, which are not described in details.*

„ENCHILADA“ is the software/platform developed by *Gross et al., 2011*, in which the analytical tool ART-2a is implemented. In Sect. 2.4, the altered text should make this clearer:

„For cluster analysis, the single particle mass spectra generated by the ATOFMS were imported into the software system ENvironmental CHEmistry through InteLligent Atmospheric Data Analysis (ENCHILADA; Gross, 2011). ENCHILADA enables the analysis of mass spectra by providing a variety of data mining and visualization tools. In ENCHILADA, the aerosol particle data were clustered based on the mass spectral peaks and intensities through an ART-2a algorithm.“

3. *It is not satisfactory not to present temporal trends and mass spectra of the particle types presented. Additionally, if the temporal trends of particles are similar, perhaps there is no room to keep 1a-b-d different. Can they be merged or are they really different? Are the temporal different? cluster 1c should be called exhaust and separated from figure 2 (which indeed is not presented!)*

Temporal trends and individual mass spectra are now presented and discussed in the supplementary information (see upload on ACPD). The temporal trend of the cluster type 1 particles (sum of 1a, b, d but averaged over 12h) remained in the main manuscript as is. Indeed, the similar temporal trends of type 1a and 1b are consistent with the chemical similarities between these two sub clusters, pointing to a generally common source and legitimate the aggregation into one time trace. Still, different origins of the types and internal mixing at the source/location of production location cannot completely be ruled out. Also, type 1d particles were not present during the IF-station, which makes a comparison of the time traces impossible. Thus, the differentiation into type 1a, b, and d was kept - all named type 1 - with the sub clusters notifying certain differences in the chemical composition. However, taking the reviewers comment into consideration, the potentially common source and mass spectrometric similarities between type 1a and b are now emphasized in the text. Herein, the individual time traces are now addressed in Sect. “Inorganic carbonaceous types” and Sect. 3.2.1 “Time series of inorganic ECOC type 1 particles”.

Cluster 1c is now assigned to the source “exhaust” but was already separated from Figure 2. As “exhaust” is a name of a source-type, but the clusters are named after their chemical components, the

nomenclature of “ECOC-PAH” was kept.

4. *Metal type and soil type needs to be also addressed. Are these simply particles coming from the ship or are the temporal trends related to something else?*

Individual spectra of metal type and soil type particles are now shown in the supplementary information. As the number of identified particles for these types were extremely small (22 and 21 at the ice floe station for metal and soil type, respectively), and the „clustering“ of these two groups was done manually, the authors refrain from presenting the temporal trends as the lack of statistics make a further analysis implausible (see also comment of/answer to reviewer #2). Both, the dust/soil dust and metal type particles did not occur during a confined time period, which is now mentioned in Sect. “Origin of the particles”:

“A detailed source characterization study for these small numbers of analyzed particles was not conducted as the lack of statistics made a further analysis implausible. The particles contained in both groups did not occur during a confined time period but were rather distributed over the entire IF measurement period. As a consequence, a source was not apportioned to type 4 and 5 particles.”

5. *NaCl. At the moment they are correctly separated from fresh, mixed and aged, but are the temporal trends different? Do they help in separate clean-polluted periods? Are NaCl fresh particles correlating more with 1b (biogenic) or KPOx?*

First, a general remark concerning the answers to the following questions 5-9 of the reviewer: The authors assume that by KPOx the reviewer is referring to the *K-CN-S* cluster type as a *KPOx* type is not discussed in the manuscript. In the following, the answers of question 5-9 are given in relation to the *K-CN-S* cluster type particles.

Temporal trends of all three NaCl types are now presented and discussed in the supplement. Based on the results, mixed and aged NaCl particles seem to originate from the same source or had a similar transport path before reaching the ship as the temporal trends correlate.

Based on the lack of statistics, a significant correlation analysis between type 1a (*pure NaCl*) with type 3 (*K-CN-Sulfate* / potentially biogenic) could not be performed. An interpretation only based on the low particle numbers revealed no similarities between the temporal trends of *pure NaCl* and *K-CN-S* particle counts which is stated in the supplementary. In the main manuscript, the following section was added relating to the correlation 2b vs. 2c (page 23):

„The temporal trends of type 2b (*mixed NaCl*) and type 2c (*aged NaCl*) particle counts show strong similarities (see supplementary information Fig. S5) indicating a common transport path and origin of the particles of both types before reaching the ship. The advanced “chemical age“ of type 2c suggests that these particles resided, thus aged for a longer time over the pack ice before detected at *Oden*.

6. *I would not be surprised if the biogenic mass spectra are different from typical Mg-rich ATOFMS marine biogenic particle types, given the geographical and biological differences of the ocean and marine biota.*

We agree with the reviewer that the chemical, mass spectrometric signatures from ocean-derived biological particles do not have to be universal. This is now mentioned in the text in Sect. 3.3:

„In general, the mass spectrometric tracers for ocean-derived biological particles as reported in literature do not necessarily have to be universal, taking the overall lack of single particle MS reference data from this measurement location of ASCOS into consideration.“

However, the analysis of the temporal trend of the potentially marine biogenic cluster type 3 as

suggested by the reviewer actually supports our conclusion on page 29: „... an assignment of these clusters to a biogenic, ocean-derived primary particle source is, however, rather unlikely and makes a clear-source apportionment of this type difficult.“ The time series of type 3 particles (supplementary material Fig. S6) peaks to some degree in correlation with those of the type 1 particles, i.e. they most likely were transported with or are „chemically connected“ to the inorganic carbonaceous type particles. This is now included by changing the end of Section 3.3 as follows:

„However, the similarities in biogenic marker ions compared to literature data are limited, indicated by the lack of Mg^{2+} , Na^+ , phosphate, oftentimes transition metals (Prather et al., 2013) and less intense organic ions as, e.g., observed by Gaston et al., 2011. Also, as outlined in the supplementary information, the temporal trend of the *K-CN-sulfate* type particles shows similarities with those of the type 1 particles (note that the temporal trend analysis is only based on 36 particles). Altogether, these findings make an assignment of these clusters to a biogenic, ocean-derived primary particle source rather unlikely and prevented us from a clear source-apportionment of this particle type.“

7. *What is the temporal of KPOx? Does it help to understand anything? Primary or secondary?*

The temporal trend of the *K-CN-S* type is now included in the supplement and discussed in the main body as outlined in question 6. Note that the temporal trend analysis of the *K-CN-S* type of only 36 detected particles during the IF station clearly lacks statistics for a detailed source-apportionment study.

8. *I would present the best single particle mass spectra of one particle describing the KPOx particles, and look at small peaks and to see if there is anything interesting.*

A single mass spec of a *K-CN-S* type particle is now presented and discussed in the supplement.

9. *There is an ATOFMS study (Dall’Osto et al., 2013 - JGR Doi:10.1029/2012JD017522, 2012) reporting Nitrogenated and aliphatic organic vapors as possible drivers for marine secondary organic aerosol growth. If you had an SMSP on board, can you compare the SMPS size distributions of the occurrence of KPOx? Do they occur during periods of primary production (NaCl ATOFMS) or nucleation events (SMPS size spectra).*

The temporal trend of *K-CN-S* is not correlated to nucleation events (only one major event was detected on the 2nd of September 2008. The temporal trend of *K-CN-S* is now included and discussed in the supplementary (cp. question 6 and 7 above). The size distribution showing the nucleation event is depicted below. The fact, that the occurrence of *K-CN-S* is not correlated with particle nucleation is now stated in the text as follows (end of Sec. 3.3. right after the text above (page 29)):

„Finally, we investigated the temporal trend of type 3 particles in the context of particle nucleation as, e.g., observed by Dall’Osto, 2012, for marine aerosol: The occurrence of type 3 particles did not coincide with the only nucleation event observed on 2 September (not shown; for details on the event please refer to Karl et al., 2012, 2013). This finding excludes the freshly nucleated particles being a direct source of the *K-CN-sulfate* type. However, nucleation mode particles cannot be seen by the ATOFMS due to their small size. Thus, only sufficiently large particles can be detected and indirectly linked to particle nucleation events after particle growth over a certain time span.“

The detailed analysis of the nucleation event is beyond the scope of this paper and discussed elsewhere (Karl et al., 2012, 2013).

10. *The most annoying part of the manuscript is to see in various part Vanadium called "Va", which I think is "V".*

Agreed and corrected.

11. Finally, given the "biogenic marine" factor of Chang et al (2011) - figure 3 and 4 of Chang et al 2011 - is rich in DMS-MSA, perhaps a query for MSA markers in the ATOFMS could be run and see what the mixing state of such particles are.

A query for MSA markers ($m/z = -95$; CH_3SO_3^-) was performed on all detected particles using the TSI-software MS-Analyze. Similar to Gaston et al., 2010, a threshold peak area > 300 was used for the identification of MSA containing particles. The analysis of the ASCOS data set revealed a fraction of approximately 30% of the IF-particles falling under that category, however, compared to Gaston et al., 2010, the peak at $m/z = -95$ was much less dominant and its peak area/height only exceeded that of $m/z = -97$ in a few cases. Compared to the AMS used in Chang et al., 2010, the unit-mass resolution of the ATOFMS makes, however, an unambiguous assignment of $m/z = -95$ to MSA difficult as the ion peaks of NaCl_2^- and PO_4^- potentially interfere at that mass-to-charge ratio. In our case, this mainly concerned fresh and mixed sea salt particles and phosphorus-containing type 1, 3, and 5 particles.

A detailed analysis of the MSA-containing particles as performed in Gaston et al., 2010, is beyond the scope of this paper, especially when accounting for the lack of statistic. The investigation of the mixing-state of the MSA-containing particles using MS-Analyze revealed that up to 85% of the queried particles showed BC-pattern in the positive ion mode (ion at $m/z +36$) and about 35% in the negative mode (ion at $m/z -36$) when using a threshold value for relative intensity of 2%. The most dominant peaks in the positive and negative stem from K^+ and HSO_4^- , respectively, thus the most prominent internally mixed components.

The occurrence of MSA in the mass spectra is now mentioned in the manuscript in Sect. 3.2.1 including the conclusions drawn from the internal mixing of type 1 particles with MSA:

“Some fraction of the type 1 particles contained methanesulfonic acid (MSA - indicated by a peak at $m/z -95$ (CH_3SO_3^-)), a photo-oxidation product of dimethyl sulfide (DMS). MSA has no known anthropogenic source making it a useful tracer for ocean-derived biogenic sulfur. MSA was also detected by Chang et al., 2011, with its mass mainly connected to a “marine biogenic factor” obtained from PMF-analysis (cp. Sec. 2.6). The internal mixing of MSA with the inorganic ECOC-types suggests that the measured air masses passed over biologically-active waters where it incorporated the MSA-precursor gases such as DMS. These were then oxidized to MSA and sulfate which subsequently condensed on the particles before detected at the location of the ship. The marine biogenic factor of Chang et al, 2011, was present for most of the time during the IF measurement period which is consistent with our findings (for a more detailed discussion please refer to the cited publication). Note that the assignment of $m/z -95$ to MSA is ambiguous as the ion peaks of NaCl_2^- and PO_4^- potentially interfere.”

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Response to Anonymous Reviewer #2

We thank the reviewer for the valuable and helpful comments. We believe that addressing the issues raised by the reviewer will considerably improve the manuscript.

Please see our reply to each comment below.

Note: All reviewer comments are in *italics*. All author responses are in normal format. The new text included in the manuscript is in **bold face**.

- 1. As I see one of the major contributions of this paper to be presentation of the data set itself, I recommend explicitly showing the mass spectra and time traces of all the cluster types. It lends credibility to show all such data, and in this specific case will show in detail the lack of statistics which make further analysis impossible for most of the cluster types. These data can also be shown in a supplementary material.*

A chapter “supplementary material” was produced presenting temporal trends/time traces of the individual clusters including mass spectra of cluster types, and, when necessary, of individual particles (see comments of reviewer no. 1) for the ice floe station. The only exceptions are time traces of the clusters 1c, 4 and 5 as the contained particles were sorted by hand (a reevaluation of all “unidentified” particles would be necessary to extract the corresponding time stamps) and represent a total fraction of only $\ll 2\%$. However, a screening showed that these three types did not occur during a confined time period (compared to cluster 1c “pollution” – see comment 3 to reviewer no.1).

Time traces are discussed in the supplementary, and the arising lack of statistics explicitly for the sparsely populated clusters is emphasized in the text, e.g. for type 4 and 5 particles (Sect. “Origin of the particles”):

“A detailed source characterization study for these small numbers of analyzed particles was not conducted as the lack of statistics made a further analysis implausible. The particles contained in both groups did not occur during a confined time period but were rather distributed over the entire IF measurement period. As a consequence, a source could not be apportioned to type 4 and 5 particles.”

- 2. Fig. 4: I find this figure very confusing for several reasons:*

- The y-axis shows a “median” concentration for three values based on percentiles. It would be more intuitive at least to me, if the y-axis showed concentration, and then three distributions were plotted, which showed the median together with the 25- and 75-percentiles, as is usually done. Presumably it turns out to show roughly the same results.

- The distributions should be colored with different colors, and the scaling removed, so that one could actually see the variability.

- The legend shows numbers like “2008x0.01” which is extremely confusing. The year 2008 should not be included here, as there are no other data presented in the paper, and should especially not be shown as a multiplication with some scaling constant.

The figure was modified according to point 2 and 3 of this comment (see manuscript). As the data were provided by our collaborators in the presented manner and taken from Heintzenberg *et al.*, 2012, the parameter “median concentration“ had to be kept. After discussion with the co-authors and as noted by the reviewer itself, the scientific information remained „roughly“ the same by doing so.

- 3. The use of the word “station” is a bit misleading, as typically stations are permanent structures. In case this terminology is in common use in previous publications, then it should stay, but if it is only used here, I suggest changing it to “site” or similar.*

The terminology “station“ is in common use in previous publications (see, e.g. *Tjernström et al., 2013*, or *Chang et al., 2011*) and thus we would prefer to keep the wording as is. Indeed, the argumentation of the reviewer is coherent, but I was told by oceanographers that the terminology “station” is common sense in their community.

4. Technical comments

Page 612, 18: “time series”

622, 9: “saccarides”

624, 6: “do not”

All done

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