### Response to anonymous Referee#1: Zábori et al., 2013.

The authors thank anonymous referee#1 for insightful comments on the manuscript. The reviewer provided several suggestions for improving the readability and quality of the manuscript. We have followed the suggestions, and our detailed response is outlined below.

### 1. Comment:

Zábori et al., ACP, 12, 10405-10421, 2012 paper (when talking about the winter experiments) claims that most of the variation in particle number concentration originates from the sea water temperature changes and not from a depletion of organic substances from the sea water. Is this the same case for the summer experiments?

# 1. Reply:

The conclusion about the dominating effect causing the change in particle number concentration was based on conducting both warming and cooling experiments for water sampled during wintertime (Zábori et al., 2012a). During summertime only one cooling experiment was conducted, but unfortunately problems with the stability of the water level in the bottle where the aerosols were produced occurred. Therefore, for the summer experiments, we cannot use both cooling and warming experiments to rule out any influence of organics in the same way as we did for the winter experiments. An important point is that for water temperatures above 6°C the trend of a decreasing particle number concentration with increasing temperature diminishes. Thus, despite a missing set of experiments, we are pretty confident that at sea water temperatures > 6 °C the temperature trend on primary marine aerosol number emissions is small.

# 2. Comment:

Figure 4+5: why is there this sudden peak at  $\sim$  120 nm during winter, but not during summer?

# 2. Reply:

We do not know what caused the sudden peak at about 265 nm during wintertime experiments, but it is very likely that it is an artifact as this was not observed by the DMPS measurements, overlapping the same size range.

Tests with the GRIMM 1.109 OPC have shown that its counting efficiency decreases considerably for particle diameters smaller than 300 nm and reaches a counting efficiency as low as about 15 % for the smallest diameter (265 nm) (Heim et al., 2008). This would imply for our results that the particle number concentration would be even higher with about 1000 particles cm<sup>-3</sup> when assuming a counting efficiency of 50% for particles with a Dp of 265 nm. This more or less immediately increase of particle number concentration from one size bin to the next seems to be biased, especially as this pattern is not observed for the overlapping DMPS measurements. The OPC is more sensitive to optical properties of the aerosols compared to the DMA. Because the RH in the sampling line was less than 30% and the sampling inlet was the same for the DMPS and the OPC, these can be excluded as reasons for the difference between the particle number concentrations.

# 3. Comment:

Why is there so great difference in the measurement time (P31161 L26-27 and P31162 L5-6)?

### 3. Reply:

The total measurement time depends on how often experiments were repeated. This was different for different water types. For example, seven experiments were conducted with water sampled close to the glacier (summertime) but the experiment with deep sea water was only repeated once. Additionally, the repeating experiments didn't always cover the whole water temperature range. Water temperatures at the lowest and upper most temperature scale were usually less covered by all experiments of a certain water type.

#### 3. Revision:

To clarify the difference in the total measurement times the sentences "**The large variation** in total measurement times is explained by the different numbers of repeating experiments for different water types. In addition, it should be mentioned that the repeating experiments did not always cover exactly the same water temperature range." is added after the sentence: "The total average measurement time for which the medians of the size distributions are based on is 2 h 13 min, with 5 min as the shortest measurement time and 6 h 52 min as the longest." (lines 4-6, page 31162)

### 4. Comment:

### The section on 'Future implications'/Figure 9:

This section (and figure) would need some improvements: the figure could be more illustrative and clear, e.g. by adding colours. In the text, add the expected Arctic Ocean temperature increase and discuss the feedbacks with respect to that. It would improve the figure, if also DMS and marine VOCs were included and discussed. Likewise, salinity changes due to decreased sea ice and glacial extent should be included and discussed as well. Discuss the figure with respect to the future expected winter vs the summer situation. In the paper you show that the temperature increase shifts the PMA size distribution which will affect the CCN prediction, which should also be addressed here. P31170 L16-20 "Assuming a change of Tw in the lower water temperature range (below 6 C), the net resulting change in PMA production due to the two factors (increasing Tw and increasing source area) is currently not know (since they have opposite signs on the PMA production) and should be studied in the future, for example with the help of modeling tools". It would strengthen your figure to make a back-of-the-envelope calculation on this (use your results from your paper, expected future sea ice extent and water temperature).

#### 4. Reply:

We thank the reviewer for the constructive criticism on Fig.9 and the chapter "Future implication". We prefer not adding additional parameters except BVOC (biogenic volatile organic compounds) into Fig.9, as this would result in a decrease of the figure's clarity. Our intention is not to provide a picture of all possible feedbacks involved, but instead focus on those which are linked closely to the presented results. But, we agree that additional factors are important to discuss and therefore the discussion of the future implications was extended. However, we do not agree, that a back-of-the-envelope calculation would strengthen the manuscript. We can come up with a multitude of other parameters that may in addition alter the PMA production (for example the parameters mentioned in the revised form of the chapter "Future implication"). These should be considered in a calculation as well and the outcome will rely completely on the given assumptions and parameters.

4. Revision:

The revision based on Comment 4, also includes changes made based on comments by Referee2.

Fig. 9 was changed by highlighting the research focus of the paper using the colour red. The path considering BVOC is added in green. Based on a comment by reviewer 2 more figures were added to the manuscript and Fig. 9 was renamed to Fig. 12.



**Fig. 12.** Potential feedback loop resulting from a warming in the Arctic. Plus signs indicate increases and minus signs indicate decreases. Question marks indicate that the direction of the change is not clear. **The focus of this study is marked by the red colour. The green colour indicates the path related to changes in BVOC emissions.** 

The text in chapter 5 "Future implication" was revised completely based on both reviewer's comments:

# **5** Future implications

The decrease in Arctic sea ice extent due to climate warming, will be followed by changes in a number of different processes, which eventually will lead to different feedbacks. Figure 12 displays a potential feedback loop focused on processes closely related to PMA production and changes in sea ice cover (marked in red). For the sake of completeness we have also included one BVOC emission process loop (biogenic volatile organic compounds; which also include DMS) in the figure (marked in green). It is worth reiterating that our results are based on laboratory experiments and therefore lack the interdependencies that may occur in the Arctic environment. However, to our knowledge no existing in-situ measurements have been reported in the literature. As such we feel it appropriate to base our discussion on possible Arctic feedbacks on our laboratory measurements. With this caveat in mind it should be noted that Fig. 12 only serves to exemplify key pathways and does not represent all possible feedback processes related to aerosol direct and indirect effects that may be affected by climate change in the region. Following discussion of the feedback loop, analysis of those parameters which are expected to alter with climate change is conducted. However, these parameters are not included in the figure to retain clarity. The decrease in Arctic sea-ice extent, which follows from a warming of the Arctic, will influence parameters controlling the production of primary and secondary marine aerosols (Fig. 12). These factors are the increase of the PMA source region, an increase in sea surface temperature (with subsequent effects on PMA production as presented within this study), and an increase in BVOC emissions, those precursor gases responsible for secondary marine aerosol production.

If sea surface temperature changes in the region  $Tw > 6^{\circ}C$ , no sea ice will be present and no change of PMA due to a change in source area will occur. If the results of our laboratory studies are correct there will also be little effect of sea surface temperature changes on PMA production at these temperatures as effects here are minimal (cf., Sect. 3.1). Assuming a change of Tw in the lower water temperature range (Tw <  $^{\circ}6^{\circ}C$ ), the net resulting change in the PMA production due to the two factors (increasing Tw and increasing source area) is currently unknown (due to their opposing sign on PMA production). This issue therefore merits further studies, for example using modeling tools, as well as including additional parameters other than Tw that may impact on PMA production. It is likely that there will be a region that experiences sea surface temperature changes in the range between seawater ice formation and Tw< $^{\circ}6^{\circ}C$ . In a scenario with no or rather limited sea ice extent PMA production will mainly be affected by the temperature trend.

The change in PMA production has important implications for the number of available cloud condensation nuclei (CCN) in the Arctic region. An increase in water temperature below ~6 °C will likely decrease the PMA number concentration, and subsequently the amount of potential CCN (cf., Zábori et al., 2012a). Further to this, our results highlight that the temperature dependent relative PMA number size distribution is changing in the same direction for the accumulation mode but in different directions for the Aitken and coarse mode for aerosols produced by water sampled during wintertime and summertime. An increase in water temperature (from 5 to 13 °C for summer experiments and from -1 to 9 °C for winter experiments) reduces the relative particle number concentration in the accumulation mode i.e. those particles that are most efficient as CCN. The different changes for the Aitken and coarse mode for the different seasons may affect the particle dynamics and consequently the amount of CCN which can be activated into cloud droplets. Besides primary marine aerosols, the importance of secondary marine aerosols as CCN is currently being discussed extensively in the literature. Conclusions on the role of DMS for CCN production are ambiguous. Charlson et al. (1987) showed that the CCN number was affected by DMS emissions however, other studies have found only sporadic or no correlation between DMS and CCN (e.g. Bates et al., 1992 and Berresheim et al., 1993 in Kloster et al., 2006). Gabric et al. (2005) modeled the DMS production in the Arctic Ocean as a result of a  $CO_2$  tripling up to the year 2080. DMS emissions were shown to increase considerably, mainly due to the decrease of the sea-ice extent and the resulting decrease in the ocean-atmosphere exchange barrier. Besides DMS, other BVOCs are suspected to be precursors of secondary aerosols, e.g. isoprene (Vaattovaara et al., 2006). A study modeling the Arctic Ocean has highlighted the importance of both DMS and other BVOCs for new particle formation (Karl et al., 2012). Despite these hints it is our opinion that the factors influencing BVOC emissions in the Arctic Ocean are not well enough constrained to

discuss the potential influence of climate change (see Shaw et al., 2010 for a review of marine isoprene and monoterpene emissions).

Our limited understanding of Arctic CCN characteristics and their potential response to a changing climate affects our ability to predict future aerosol related changes in cloud cover. The supersaturation of water vapour in the atmosphere, atmospheric dynamics and the availability, size, and composition of CCN determines if and where cloud droplets and clouds form. The amount of water vapour in the Arctic atmosphere is dependent on sea ice cover, sea surface temperature and air temperature. Lower sea ice cover coincident with an increase in sea surface temperature should result in an increased transport of water vapour to the atmosphere given that the sea ice represents an evaporation barrier for the water and higher sea surface temperatures will increase evaporation rates. As the air temperature increases more water vapour can remain in the atmosphere before condensation occurs consequently intensifying Arctic warming.

A further parameter besides PMA source area, sea surface temperature, BVOC emissions, and water vapour that is influenced by a decreasing sea ice extent is the surface albedo, which decreases with decreasing sea ice cover. This decrease in surface albedo, coincident with increases in water vapour, an unknown change in PMA production and the subsequent unknown change in cloud properties close the feedback loop and impact on the warming of the Arctic. Both the decrease in surface albedo and the increase in water vapour are expected to have a positive feedback on the warming of the Arctic. It is impossible to assess the net sign and magnitude for all the feedbacks in the warming Arctic linked to changes of sea ice coverage and PMA production at this point. Nevertheless we can speculate that the non-linear relation between PMA production and increasing sea surface temperatures in concert with changes in sea ice cover have a strong potential to contribute to the evolution of the Arctic climate and deserve future attention.

As previously mentioned, the feedback loop presented in Fig. 12 only considers a small fraction of those factors important for marine aerosol production in the Arctic. What follows is a discussion of other parameters that may impact on PMA production in the Arctic Ocean.

The salinity of the Arctic Ocean is expected to decrease in future for a number of different reasons; at local scales a negative mass balance of glaciers has been observed (Nuth et al., 2010). This results in a decrease in the salinity of ocean surface water. It has also been suggested that an interplay between wind fields, melting sea ice and river runoff may lower salinities in the Arctic Ocean (Giles et al., 2012; MacDonald et al., 2002). The effect of salinity on PMA is unclear. Zábori et al. (2012a) did not observe a clear trend of particle number concentrations with salinity changes between 26 and 36‰ when conducting experiments with Arctic Ocean water. However, a number of other studies have shown that higher salinities can result in higher particle number concentrations (Mårtensson et al., 2003; Tyree et al., 2007; Hultin et al., 2011). Nevertheless these case experiments were conducted outside the Arctic.

An increase in water temperature affects the production of gas bubbles in the water. These gas bubbles produce aerosols when rising and bursting on the ocean surface. Thorpe et al. (1992) concluded that the temperature related decrease in gas solubility and the temperature related increase in molecular diffusivity cancel out and that the net effect of a temperature increase is a decrease in bubble concentrations due to a reduction in viscosity. However, a water temperature independent change in oxygen saturations in the water occurs due to a change in photosynthesis rates. Since altered environmental conditions caused by climate change may impact the flora and fauna in the Arctic (Wassmann and Reigstad, 2011; Tremblay et al., 2011), a future change in oxygen saturation is likely to take place. Zábori et al. (2012a) did not observe a change in PMA number production with a change in oxygen saturation between 72 and 83% for Arctic Ocean conditions. Hultin et al. (2011) observed for Baltic Sea water an anti-correlation between particle production and oxygen saturations in the range 90 to 100 %. Thus, it is not possible to derive a clear conclusion on the role of oxygen saturation on PMA production.

The concentration of organic substances in the water is known to impact PMA production. Depending on the substance used, differences in total particle number concentrations and shifts in particle number size distributions have been observed. Experiments with dissolved organic carbon and colloidal organic matter (exudates of algae) have produced a shift of the size distribution towards smaller particle sizes relative to artificial inorganic seawater (Fuentes et al., 2010b). Tyree et al. (2007) observed an increase in total particle number concentration with an increase in the concentration of oleic acid. Zábori et al. (2012b) observed a decrease in total particle number concentration with an increase in the concentration of succinic acid. Clearly the influence of organic substances on PMA is complex and there is a need for further well designed experiments to aid understanding. Another important parameter for PMA production that is impossible to assess in laboratory experiments using water jets is the wind speed. It has been shown that PMA production is a non-linear function of wind speed (Lovett, 1978; Nilsson et al., 2001). Struthers et al. (2011) simulated the sea salt emissions in a future Arctic climate, where the emissions were dependent on sea ice extent, sea surface temperature and the 10m wind speed. An increase in sea salt emissions was observed with the effect driven predominantly by the decrease in sea ice extent and changes in sea surface temperature rather than from a change in wind speed. However, a change in wind speed is likely to change the organic composition of PMA. Gantt et al. (2011) developed a conceptual model describing the organic mass fraction of sea spray aerosols as a function of wind speed. As the wind speed exceeds 3-4 ms<sup>-1</sup> the surface microlayer (a tens of nanometers to about 100 µm thick layer on the ocean surface consisting of organic substances (Lion and Leckie, 1981; Cunliffe et al., 2013) starts to get mixed with subsurface water and at wind speeds larger than 8 ms<sup>-1</sup> a homogeneous water column is expected, resulting in lower organic mass fractions of sea spray aerosols. Transferred to our experiments, this means that possible PMA organic fractions in the aerosols are not only dependent on the production of the organic substances in water, but also on the mixing in the water column. Additional factors potentially important for the climate feedback loop shown in Fig. 12 are an increase in the maritime transportation, tourism, and oil exploration activity as a result of an increasingly ice-free Arctic Ocean. These will result in increasing anthropogenic aerosol emissions and the release of substances into the Arctic Ocean water. Our attempt is to present a rather simplified scheme of possible feedbacks linked to PMA production from the Arctic Ocean and sea water properties. There are numerous other processes influencing the ocean-atmosphere interactions. Some of them were discussed in the text and some of them not at all, like impact of broader scale processes outside the Arctic linked to the atmospheric and ocean general circulation.

Minor Comments:

Comment: *P31177 Table 1: Maybe add water surface temperature.* Reply: Unfortunately, no surface water temperature data in Kongsfjorden were available by the Norwegian Meteorological Institute.

All other minor comments by the reviewer have been considered and the paper has been changed accordingly. A native speaker proofread the manuscript and the language was corrected accordingly.

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