

REPLY to Anonymous Reviewer #1

We thank the Reviewer for the positive comments. We accept her/his invitation to integrate the Introduction highlighting the importance of organic marine aerosols along with a summary of Dall'Osto et al. 2017 reporting the first results of atmospheric and seawater measurements carried out during the PEGASO cruise.

The following text was added to the manuscript:

(After line 50 in the Introduction): “DMS and other reactive volatile species are known precursors to the secondary marine aerosol which contribute to the aerosol population in the marine boundary layer together with primary sea-spray particles. Marine aerosols impact global climate by reducing the amount of solar radiation reaching dark surface of the ocean, both directly (through scattering) and indirectly (by modulating cloud formation and life-time) (O’Dowd and de Leeuw 2007). Furthermore, in polar regions, cloud seeding by marine aerosols transported over glaciated regions also affects the longwave radiation budget (Willis et al. 2018).”

And lines 58 to 64 of the Introduction are rewritten with a more detailed summary of the Dall’Osto et al. (2017) study including information about the tank experiments which are key in this study:

“By contrast, other biological parameters of seawater, like chlorophyll a, total organic carbon (TOC) and transparent exopolymeric particles (TEP), showed higher concentrations in the open Southern Ocean north of the SBACC. Results of bubble bursting experiments conducted on nascent seawater as well as using melted sea ice showed that organic nitrogen and organic carbon were more abundant in the aerosol in the latter case. Moreover, the production of organic-rich particles was better traced by markers of the ice biota, such as mycosporines, than by macro-tracers of biological productivity (chlorophyll). These results indicate that not only productivity per se but also the composition and ecophysiological state of the microbiota affect the production of aerosol precursors in seawater. Indeed, the observations of organic nitrogen in the aerosol – carried out by both online and offline chemical methods – pointed to strong sources in the area of the Weddell Sea which, at the time of the field campaign, was heavily covered by sea ice.”

Replies to the specific Referee’s comments are provided below:

1-Are the nascent sea spray generation experiments running with the same seawater (closed loop) or continuously flushed with fresh seawater? If performed in a closed loop fashion, what impact on an eventual depletion of surfactant organics from the sample with time? I it said that 9 samples were performed but only one sample is analyzed by HNMR. It would be useful to state what was the spatial variability of the general chemical composition of these 9 samples, and how the one sample analysed with HNMR compared to the rest of the samples.

REPLY: The bubble bursting experiments with seawater were conducted in the tank continuously flushed with a fresh sea water provided by the ship’s underway pumping system resulting in the water residence time inside the tank of approximately 10-20min. The sea-ice experiments were instead performed in the tank in a closed loop fashion because of the limited amount of water volume available from the melted sea ice samples. We agree with the Referee that under such conditions, modifications in seawater can be induced by the forced aerosolization itself, with dependence on the technical characteristics of the apparatus for bubble bursting. During past sea-spray generation experiments with the same equipment and closed loop system, the online monitoring of organic aerosol concentrations did not show any decline with

time (O'Dowd et al., 2015) with no evidence of surfactant depletion effects of the film. Therefore, it is unlikely that the depletion could have occurred in a continuously flushed system. However, the focus of the present study is not organic enrichment factor of sea spray aerosol but rather its organic composition. We will insert a new short paragraph to comment the possible effects of the bubble bursting experimental conditions:

(appending after line 134 of Section 2.2) "In six cases, bubble bursting experiments were conducted in the tank continuously flushed with fresh seawater conveyed from the ship's pumping system. In the three sea-ice experiments instead bubble bursting was carried out in a closed loop system because of the limited amount of water volume available from the melted sea ice samples. In this case, the bubble bursting process could lead to chemical and biological modifications in the samples like a progressive depletion of surfactants on the film. Quantification of such artefacts is unavailable. Nevertheless, past studies carried out in different geographical region of North East Atlantic but with the same apparatus showed no evidence of decreasing organic enrichment in the generated sea spray when operated in a closed loop system (O'Dowd et al., 2015)."

The nine bubble bursting experiments conducted during the campaign included 6 carried out with seawater (in a continuously flushed tank) and 3 with melted sea ice (in a closed loop tank). The three sea ice samples are the same discussed in Dall'Osto et al. (2017). Two of the three experiments provided enough material for off-line chemical analysis by $^1\text{H-NMR}$ spectroscopy, and these are the samples discussed in the present manuscript (BB Sealce-1 and BB Sealce-3). All the samples of sea ice were collected at the northern edge of the Weddell Sea marginal ice zone, south of South Orkney islands. The other six samples from the tank were obtained by bubble bursting of seawater and a summary of the online aerosol measurements is also included in Dall'Osto et al. (2017). Water was collected mostly in highly productive oceanic regions from diverse geographical areas: from the blooms by the South Orkney, to those nearby South Georgia, and finally in the highly productive coastal areas of the Antarctic peninsula. Only during one of the bubble bursting experiment, more oligotrophic waters were collected during the transect from the South Georgia to the Antarctic Peninsula. The sample selected for NMR analysis (BB W1101) was obtained from seawater in a bloom area west and north of the South Orkney. We will include a short explanation in the new version of the paper:

(At line 231 at the beginning of Section 3.2): "The three primary marine aerosol samples collected in the tank and analysed by $^1\text{H-NMR}$ spectroscopy included the following samples. One sample was collected from bubble bursting of nascent seawater (BB W1101) obtained during almost four days of navigation west and north of the South Orkney Islands with seawater continuously flushed onboard the RV maintaining continuous sea spray production in the tank. The other two samples (BB Sealce-1 and BB Sealce-3) were obtained from two of the three sea ice samples melted in the tank and run in a closed loop system. Sea ice was collected from the marginal ice zone around 100 km south of the South Orkneys by using small inflatable boats and clean laboratory ware. The chemical information obtained for these bubble bursting aerosols is, therefore, representative for primary marine particles in the northern sector of the Weddell Sea."

2-In general, variability among samples is not discussed much neither for the seawater samples. What differences amongst the 45 POC samples of seawater? Is a comparison between bloom versus non bloom POC content possible?

REPLY: The four samples analysed by $^1\text{H-NMR}$ spectroscopy had a similar POC content: 10, 12, 9.8 and 11 $\mu\text{molC L}^{-1}$. This corresponds to ca. to the 75%-percentile of the POC distribution of the 45 POC samples (average \pm standard deviation for the full set was $8.7 \pm 4.1 \mu\text{molC L}^{-1}$). All four selected samples originated from bloom areas, where POC concentration ranged between 8 and 12 $\mu\text{molC L}^{-1}$ (with peaks above 15

$\mu\text{molC L}^{-1}$), while the oligotrophic areas of the Southern Ocean showed concentrations of about $4 \mu\text{molC L}^{-1}$. The text in section 3.1 (lines 203 to 207) was modified and integrated as follows:

“Figure 2 shows the proton NMR spectra of three POC samples, one from seawater (POC W3101) and two from melted sea ice (POC Sealce-1, and POC Sealce-3) as examples. It is worth noting that the samples were pre-filtered through a polycarbonate membrane of $10 \mu\text{m}$ porosity, hence the analyzed POC fraction represents only the fine fraction (between ~ 0.45 and $10 \mu\text{m}$). During PEGASO, the concentration of fine POC fraction ($0.45 - 10 \mu\text{m}$) ranged between 8 and $12 \mu\text{molC L}^{-1}$ in bloom areas. The sub-set of samples analysed by $^1\text{H-NMR}$ spectroscopy exhibited a concentration of $10.6 \pm 0.7 \mu\text{molC L}^{-1}$ ($n = 4$). Sample POC W3101 originated from the bloom area west of South Georgia island, while the two sea ice samples were collected in the marginal ice zone of the Weddell Sea. The interpretation of the spectra was carried out by comparison with the datasets and spectra provided in the literature on metabolomics...”

3-For comparing aerosol Organic carbon characteristics with those of organic carbon in the seawater, the results on the seawater DOC analysis should be known as both are expected to contribute to the aerosol organic matter. As these analysis are presumably not available, there should be a discussion on the fact that the POC 10-45micron composition does not represent the full organic matter present in the seawater. This has implications on the conclusions made on preferential organic transfer to the atmosphere.

REPLY: The concentrations of $\text{POC}_{0.45-10\mu\text{m}}$ determined in this study ($8.7 \pm 4.1 \mu\text{molC L}^{-1}$) represents a small amount with respect to the TOC concentrations reported in Dall’Osto et al. (2017) ($50 - 70 \mu\text{molC L}^{-1}$), and we agree with the Reviewer that a large fraction of TOC could not be characterized by our analytical techniques. Nevertheless, not all TOC components can contribute to sea spray composition. The pre-filtration of our seawater samples through $10 \mu\text{m}$ -pore membranes was carried out with the purpose of excluding POC particles that are too large to form primary marine aerosols. The DOC pool as well includes compounds, like marine refractory fulvic material, which are homogenously distributed in the water column with a small enrichments in the surface film (Hertkorn et al., 2013). We will specify the limitations of our methodology with respect to seawater sample analysis as follows:

(To append after line 202 in Section 3.1): “The chemical characterization of the smallest POC component ($0.45 - 10 \mu\text{m}$) aims to provide information about composition of the buoyant particles, while the contribution from DOC to the surface film composition could not be determined in this study.”

4- Again, there is only one sample or primary marine aerosol (PMA) generated the tank experiment, so we do not know the variability of the organic composition of PMA in this region. This should be discussed, especially when stating that creatinine was not detected in the PMA (this could be true for the one sample presented but not for the others..?).

REPLY: We agree with the reviewer. Nevertheless, the single PMA sample derived from bubble bursting in seawater shows very similar spectroscopic features with the other two PMA samples obtained by aerosolizing melted sea ice (Figure 3). Sample BB W1101 was obtained from sea water collected in an area west and north of the South Orkney islands, approximately 100 km north of the edge of the marginal sea ice zone where the ice samples were subsequently collected. Our data, though based on a small sample number (but sample BB W1101 corresponds to almost four days of navigation), indicate that sea spray aerosol in the northern sector of the Weddell Sea does not contain creatinine. However, little can be said about the PMA composition from other geographical regions of the Southern Ocean (South Georgia, etc.). This will be acknowledged in the revised version of the manuscript. We copy the proposed text from above in relation to Major comment #1:

(At line 231 at the beginning of Section 3.2): “The three primary marine aerosol samples collected in the tank and analysed by ^1H -NMR spectroscopy included the following samples. One sample was collected from bubble bursting of nascent seawater (BB W1101) obtained during almost four days of navigation west and north of the South Orkney Islands with seawater continuously flushed onboard the RV maintaining continuous sea spray production in the tank. The other two samples (BB Sealce-1 and BB Sealce-3) were obtained from two of the three sea ice samples melted in the tank and run in a closed loop system. Sea ice was collected from the marginal ice zone around 100 km south of the South Orkneys by using small inflatable boats and clean laboratory ware. The chemical information obtained for these bubble bursting aerosols is, therefore, representative for primary marine particles in the northern sector of the Weddell Sea.”

All minor Reviewer comments have been addressed accordingly.

References:

Dall’Osto et al., Antarctic sea ice region as a source of biogenic organic nitrogen in aerosols, *Scientific Reports*, 7, 6047, 2017.

Hertkorn et al., High-field NMR spectroscopy and FTICR mass spectrometry: powerful discovery tools for the molecular level characterization of marine dissolved organic matter, *Biogeosciences*, 10 (3), 1583–1624, 2013.

O’Dowd, C. D. & de Leeuw, G. Marine aerosol production: a review of the current knowledge. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 365, 1753, 2007.

O’Dowd et al., Connecting marine productivity to sea-spray via nanoscale biological processes: Phytoplankton Dance or Death Disco? *Scientific Reports*, 5, 14883, 2015.

Willis et al., Processes controlling the composition and abundance of Arctic aerosol. *Reviews of Geophysics*, 56, 621–671. <https://doi.org/10.1029/2018RG000602>, 2018.