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Discussions

Shipborne measurements of Antarctic submicron organic aerosols: an NMR perspective linking multiple sources and bioregions

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1 Abstract

2 The concentrations of submicron aerosol particles in maritime regions around Antarctica are influenced by
3 the extent of sea ice. This effect is two way: on one side, sea ice regulates the production of particles by sea
4 spray (primary aerosols) while, on the other side, it hosts complex communities of organisms emitting
5 precursors for secondary particles. Past studies documenting the chemical composition of fine aerosols in
6 Antarctica indicate various potential primary and secondary sources active in coastal areas, in offshore
7 marine regions as well as in the sea ice itself. In particular, beside the well-known sources of organic and
8 sulfur material originating from the oxidation of dimethyl-sulfide (DMS) produced by microalgae, recent
9 findings obtained during the 2015 PEGASO cruise suggest that nitrogen-containing organic compounds are
10 also produced by the microbiota colonizing the marginal ice zone. To complement the aerosol source
11 apportionment performed using online mass spectrometric techniques, here we discuss the outcomes of
12 offline spectroscopic analysis performed by nuclear magnetic resonance (NMR) spectroscopy. In this study
13 we (i) present the composition of ambient aerosols over open ocean waters across bioregions, and
14 compared it to the composition of (ii) seawater samples and (iii) bubble bursting aerosols produced in a sea
15 spray chamber on board the ship. Our results show that the process of aerosolization in the tank enriches
16 primary marine particles with lipids and sugars while depleting them of free aminoacids, providing an
17 explanation for why aminoacids occurred only at trace concentrations in the marine aerosol samples

18 analyzed. The analysis of water-soluble organic carbon (WSOC) in ambient submicron aerosol samples
19 shows distinct NMR fingerprints for three bioregions: 1) the open Southern Ocean pelagic environments, in
20 which aerosols are enriched with primary marine particles containing lipids and sugars; 2) sympagic areas in
21 the Weddell Sea where secondary organic compounds, including methanesulfonic acid and semivolatile
22 amines abound in the aerosol composition; and 3) terrestrial coastal areas, traced by sugars such as
23 sucrose, emitted by land vegetation. Finally, a new biogenic chemical marker, creatinine, was identified in
24 the samples from the Weddell Sea, providing another confirmation of the importance of nitrogen-
25 containing metabolites in Antarctic polar aerosols.

26

27 **1. Introduction**

28 The Antarctic continent is one of the last pristine areas of our planet but its natural ecosystems are now
29 threatened by an acceleration of the effects of global warming. Although at the beginning of the XXI
30 centuries the signals of climate change looked still weak in the region, the ice-sheet mass loss in Western
31 Antarctica has greatly accelerated in the last ten years as the Southern Ocean waters have experienced a
32 clear warming trend (Shepherd et al., 2018). The consequences for Antarctic maritime and coastal
33 environments encompass strengthening of westerly winds, reduction of summer sea ice extent, shifting
34 geographical ranges of bird communities, expanding terrestrial vegetation, increasing glacier melt and
35 freshwater formation over land, etc. (Rintoul et al.; 2018). As all these specific ecosystem impacts involve
36 factors deemed important for aerosol production in Antarctica (Davison et al., 2006; Schmale et al., 2013;
37 Kyrö et al., 2013; Barbaro et al. 2017), a significant effect of climate change on atmospheric concentrations
38 of aerosols and cloud condensation nuclei (CCN) must be expected to occur by the end of this century. The
39 field studies performed in maritime and coastal areas around Antarctica in the austral summer since the
40 90's (Davison et al., 1996) enable us to gather precious information on the multiple feedbacks between
41 atmospheric composition and ecosystems in a warming climate. In summer, the sea ice recedes allowing
42 wind stress over the oceanic surface and sea spray occur closer to the continent, hence increasing the
43 production of primary marine aerosols. At the same time, the thinning of sea ice in its marginal zone and
44 the increased intensity of solar radiation allow microalgae colonize the ice (Fryxell and Kendrick, 1988;
45 Roukaerts et al. 2016). The microbiota produce low-molecular weight metabolites as cryoprotectors and
46 osmoregulators, like dimethylsulfoniopropionate (DMSP) and quaternary nitrogen compounds (Dallosto et
47 al., 2017). Once released in seawater, such compounds become precursors of atmospheric reactive volatile
48 reactive compounds, such as dimethylsulfide (DMS) and methylamines, which eventually can lead to the
49 formation of secondary aerosols. Indeed, Davison et al. (1996) observed concentrations of DMS south of
50 60°S more than four times higher than in the Atlantic Ocean.

51 During the 2015 PEGASO cruise (Dall'Osto et al., 2017, 2019; Fossum et al., 2018), we conducted
52 continuous atmospheric observations for over 42 days, providing one of the longest shipborne aerosol
53 measurement records in this area of the world. We contrasted the composition of seawater north and
54 south of the Southern Boundary of the Antarctic Circumpolar Current (SBACC), which represents the
55 approximate boundary between the open Southern Ocean and the waters directly affected by sea ice
56 formation and melt around Antarctica. Dall'Osto et al. (2017) showed that not only DMSP and DMS
57 occurred in greater concentrations in sympagic waters (south of the SBACC), but so did quaternary nitrogen
58 compounds and methyl amines. By contrast, other biological parameters of seawater, like chlorophyll a,
59 total organic carbon (TOC) and transparent exopolymeric particles (TEP), showed higher concentrations
60 north of the SBACC, in the open Southern Ocean. These results indicate that not only the biological
61 productivity per se, but also the composition of the microbiota affect the production of aerosol precursors
62 in seawater. Indeed, the observations of organic nitrogen in the aerosol – carried out by both online and

63   offline chemical methods – pointed to strong sources in the area of the Weddell Sea which, at the time of
64   the field campaign, was heavily covered by sea ice.

65   These findings contribute to the growing observational dataset of aerosol chemical compositions for
66   coastal Antarctic and sub-Antarctic marine areas, which hosts reports of chemical analysis performed on
67   filter and impactor samples (Davison et al., 2006; Virkkula et al., 2006) as well as the results of online
68   aerosol mass spectrometric techniques acquired in the recent years (Zorn et al., 2008; Schmale et al., 2013;
69   Giordano et al., 2017). All the measurements performed so far agree in showing a reduction of sea salt
70   aerosols from the Southern Ocean to the coasts of Antarctica, while secondary species including non-sea
71   salt sulfate and methanesulfonate (MSA) occur in relatively higher concentrations at higher latitudes as a
72   result of the DMS emissions from marginal ice zone waters. Open questions remain about a) the amount of
73   non-MSA organic matter in Antarctic air masses, and b) its origin (either primary or secondary). Recent
74   studies also suggests that blowing snow at high wind speeds may be an important yet hitherto
75   underestimated source (Giordano et al, 2018; Frey et al., 2019), adding complexity onto the source
76   apportioning of organic aerosols. First observations of organic carbon (OC) in size-segregated aerosol
77   samples collected at a coastal site in the Weddell Sea (Virkkula et al., 2006) showed that MSA represented
78   only a few % of the total OC in the submicron fraction. In contrast with these findings, aerosol mass
79   spectrometric (AMS) measurements showed that the organic matter in submicron aerosols transported in
80   Antarctic air masses was almost totally accounted for by MSA, while non-MSA organic compounds were
81   associated to aerosols originating from highly productive waters in the Southern Ocean (Zorn et al., 2008).
82   Non-MSA OC can form also from insular terrestrial biomass emissions (Schmale et al., 2013). In particular,
83   organic particles emitted from seabird colonies contain large amounts of nitrogen with MS spectral
84   fingerprints overlapping with those of natural aminoacids. In the paper by Liu et al. (2018), FTIR
85   spectroscopy was employed to probe the sources of particulate organic compounds at another coastal
86   Antarctic site, and the results point to a contribution of marine polysaccharides transported in sea spray
87   aerosols. Finally, detailed organic speciation using offline analytical techniques with high sensitivity and
88   selectivity suggest further contributions from marine proteinaceous material, terrestrial lipids, and
89   secondary organic compounds (Bendle et al 2007; Barbaro et al., 2015; 2017), but it is unclear how much
90   the concentrations of compounds occurring at pg m^{-3} relate to that of bulk organic matter. We present here
91   the organic characterization of Antarctic aerosol employing proton nuclear magnetic resonance (^{1}H-NMR)
92   spectroscopy. NMR spectroscopy has been used for decades in several fields of biogeochemistry for its
93   ability to fingerprint several classes of biomolecules and natural organic matter in aquatic and terrestrial
94   environments (e.g., Pautler et al., 2012; Hertkorn et al., 2013). In this study, which focuses on the analysis
95   of samples collected during the PEGASO 2015 cruise, we contrast the NMR composition of submicron
96   aerosol samples with that of seawater samples and bubble-bursting aerosols. The results provide new hints
97   on the origin of non-MSA aerosol organic matter in fine aerosol particles in the Antarctic and sub-Antarctic
98   marine environment.

99

100   **2. Experimental**

101   **2.1. Ambient aerosol sampling on filters.**
102   The PEGASO (Plankton-derived Emissions of trace Gases and Aerosols in the Southern Ocean) cruise was
103   conducted on board of *RV Hesperides* in the regions of Antarctic Peninsula, South Orkney and South
104   Georgia Islands from 2 January to 11 February 2015 (Dall'Osto et al. 2017). A high volume sampler (TECORA
105   ECO-HIVOL, equipped with Digitel PM1 sampling inlet) collected ambient aerosol particles with Dp < 1 μm
106   on pre-washed and pre-baked quartz-fibre filters, at a controlled flow of 500 LPM. Sampling was allowed
107   only when the samplers were upwind the ship exhaust with a relative wind speed threshold of 5 m s^{-1}. Due

108   to the necessity of collecting sufficient amounts of samples for detailed chemical analyses, sampling time
109   was of the order of ~50 h for each sample. A total of eight PM1 samples were collected during the cruise
110   (Figure 1). The samples were stored at −20 °C until extraction and NMR analysis.
111   For HPLC-MS analyses, aerosol samples were collected on PTFE fiber filters (70 mm diameter, Pallflex
112   T60A20, Pall Life Science) with flow rates of 2.31 – 2.41 m^3/h through a PM2.5 inlet. Sampling times ranged
113   from 12 - 24 h, resulting sampling volumes of 28.1 – 56.1 m^3 of air. As outlined above, sampling was only
114   allowed when the sampler was upwind the ship exhaust.
115
116   **2.2. Seawater sampling and tank experiments.**
117   Seawater samples were collected from a depth of 4 m using either the uppermost Niskin bottle of the CTD
118   rosette casts or the ship's flow-through underway pumping system. The samples were filtered with a
119   Millipore filtration apparatus on quartz-fiber filters (Whatman, Ø= 47mm) after a previous cut off at 10 μm
120   performed with a polycarbonate filter (Millipore, Isopore, porosity=10 μm, Ø= 47mm). In total 45 samples
121   were collected for subsequent quantification of the Particulate Organic Carbon (POC) and 20 mL of the
122   filtrates were stored for subsequent analysis of Dissolved Organic Carbon (DOC). All the samples were
123   stored at −20 °C until the chemical analyses. Three samples of sea ice from the marginal ice zone in the
124   northern Weddell Sea were also collected using the methodology described in Dall'Osto et al. (2017). The
125   samples, once melted, were filtered and treated similarly to the seawater samples.
126   Seawater was pumped from a depth of 4 m to fill an airtight high grade stainless steel tank (200 L) designed
127   for aerosol generation experiment. Sea ice samples were also introduced and melted in the tank for
128   dedicated experiments. Water was dropped from the top of the tank as a plunging jet at a flow rate of 20 L
129   min^{-1}. The entrained air formed bubbles that, upon bursting, produced sea-spray aerosol, as reported in
130   O'Dowd et al. (2015). Particle-free compressed air was blown into the tank headspace (120 L min^{-1}), which
131   had outlet ports leading to samplers for the collection of filters and the subsequent off-line chemical
132   characterization of the produced sea-spray. In particular nine sea-spray aerosol samples were collected for
133   approximately 72h by a PM1 sampler (flow rate 40 lpm) equipped with pre-washed and pre-baked quartz-
134   fiber filters (PALL, Ø= 47mm). Sampling time was of the order of ~72 h for each sample.
135
136   **2.3. ^{1}H-NMR spectroscopy.**
137   Quartz-fiber filters from both ambient, POC filter samples and sea-spray generation experiments were
138   extracted with deionized ultra-pure water (Milli-Q) in a mechanical shaker for 1 h and the water extract was
139   filtered on PTFE membranes (pore size: 0.45 μm) in order to remove suspended particles. The water-
140   soluble organic carbon (WSOC) content was quantified using a TOC-TN thermal combustion analyser (Multi
141   N/C 2100 by Analytik Jena) (Rinaldi et al., 2007). Aliquots of the aerosol extract were dried under vacuum
142   and re-dissolved in deuterium oxide (D_2O) for organic functional group characterization by ^{1}H-NMR
143   spectroscopy, as described in Decesari et al. (2000). The ^{1}H-NMR spectra were acquired at 600 MHz in a 5
144   mm probe using a Varian Unity INOVA spectrometer, at the NMR facility of the Department of Industrial
145   Chemistry (University of Bologna). Sodium 3-trimethylsilyl-(2,2,3,3-d_4) propionate (TSP-d_4) was used as an
146   internal standard by adding 50 μL of a 0.05% TSP-d_4 (by weight) in D_2O to the standard in the probe. To
147   avoid the shifting of pH-sensitive signals, the extracts were buffered to pH ~ 3 using a deuterated-
148   formate/formic-acid ($DCOO^-$/$HCOOH$) buffer prior to the analysis. The speciation of hydrogen atoms bound
149   to carbon atoms can be provided by ^{1}H-NMR spectroscopy in protic solvents. On the basis of the range of
150   frequency shifts, the signals can be attributed to H-C containing specific functionalities (Decesari et al.,
151   2000, 2007). A total of eight HiVol PM1 ambient aerosol samples (+ one blank), four POC samples from
152   seawater and two POC samples from melted sea ice, and two samples from the tank experiments (from
153   aerosolization of one seawater sample and one melted sea ice sample) + one blank for the 47mm filters
154   were characterized by NMR spectroscopy.

155
156   **2.5. UHPLC-HESI-Orbitrap-MS.**
157   One half of each filter sample was extracted according to the following protocol: three times sonication in
158   1.5 mL, 1 mL, and 1 mL ACN/H2O (9:1, v/v) for 30 min. The extracts were filtered through PTFE membranes
159   (pore size: 0.45 μm), combined, dried at 50 °C under a gentle stream of N_2, resuspended in 200 μL
160   ACN/H2O (1:4, v/v), and stored at -20 °C until analysis. Samples were analyzed in triplicate by UHPLC-HESI-
161   HRMS using an Orbitrap mass analyzer (Q-Exactive hybrid quadrupole orbitrap mass spectrometer, Thermo
162   Scientific, Germany) equipped with an UHPLC-System (Dionex UltiMate 3000 UHPLC system, Thermo
163   Scientific, Germany) and a Hypersil Gold, C18, 50 x 2.0 mm column with 1.9 μm particle size (Thermo
164   Scientific, Germany). The injection volume was 20 μL and the eluents were ultrapure water with 2%
165   acetonitrile and 0.04% formic acid (eluent A), and acetonitrile with 2% water (eluent B). The gradient of the
166   mobile phase with a flowrate of 0.5 mL min-1 was as follows: starting with 2% B isocratic for 1 min,
167   increasing to 20% B in 0.5 min, isocratic for 2 min, increasing to 90% B in 2.5 min, isocratic for 4 min and
168   decreasing to 2% B in 0.5 min. Mass spectrometric analyses were performed using a ESI source under the
169   following conditions: 30°C ESI temperature, 4 kV spray voltage, 40 psi sheath gas flow, 20 psi auxiliary gas
170   flow and 350°C capillary temperature. Mass resolution was 70000 and the acquired mass range was m/z
171   80–550.
172
173   **2.5. Air mass back-trajectories.**

174   Five-day back trajectories arriving at the ship's position at 03:00, 09:00, 16:00 and 21:00 every day were
175   calculated using the HYSPLIT model (Draxler & Rolph, 2010) with GDAS data (or the BADC Trajectory
176   Service?). In total, 140 air mass back trajectories were obtained. A Polar Stereographic map was used to
177   classify 24x24 km grid cells as land, sea and ice. From this information we calculated the percentage of time
178   spent by each trajectory over each surface type, and particularly over sea ice. Daily maps of sea ice
179   percentage concentration measured on a 12.5 km grid were used for this calculation. Sea ice abundance
180   was derived from satellite microwave data (Ezraty et al., 2007) available at IFREMER. This analysis allowed
181   also assigning air mass trajectories (and percentages of surface type overflown) to the aerosol samples
182   collected on the filters (Figure 1).

183

184   **3. Results**

185   **3.1. Organic composition of seawater: POC samples.**
186   The composition of seawater in terms of pigments, metabolites, fluorescent organic matter and other
187   organic constituents from the PEGASO cruise has been characterized in great detail (Dall'Osto et al., 2017;
188   Nunes et al., 2019; Zamanillo et al., 2019). Marine organic substances occur in the ocean in dissolved and
189   particulate form. Particulate organic carbon (POC) is defined operationally by a filtration cutoff at 0.45 μm,
190   and recovers phytoplankton cells, bacteria and of the large colloids, such as transparent exopolymeric
191   particles ("TEPs") (Passow et al., 2002). Dissolved organic carbon (DOC) is mostly contributed by the excreta
192   and metabolites of the marine biota but it also accounts for a pool of refractory compounds, resistant to
193   microbial degradation, and well mixed in the water column (Hertkorn et al., 2013). Past studies have
194   extensively characterized the NMR features of labile and refractory organic constituents of marine organic
195   matter (Repeta 2015). However, the NMR characterization of the dissolved organic substances was limited
196   to desalted fractions of DOC isolated by solid-phase extraction or ultrafiltration (Koprivnjak et al., 2009).
197   Therefore, the NMR analysis of low-molecular weight polar organic constituents of marine DOC remains
198   elusive. In our study, we screened the NMR features of POC in phytoplankton bloom areas. In addition,
199   samples of aerosolized seawater and melted sea ice were used as a proxy of primary marine aerosol

200   (Dall'Osto et al., 2017). During the process of bubble bursting performed in the tank experiments, aerosol
201   particles became depleted in sea salt with respect to seawater and enriched in surface-active DOC
202   components and in buoyant POC substances.
203   Figure 2 shows the proton NMR spectra of three POC samples, one from seawater (POC W3101) and two
204   from melted sea ice (POC SeaIce-1, and POC SeaIce-3) as examples. It is worth reminding that the samples
205   were pre-filtered through a polycarbonate membrane of 10 μm porosity, hence the analyzed POC fraction
206   is only the fine one (between ~ 0.45 and 10 μm). The interpretation of the spectra was carried out by
207   comparison with the datasets and spectra provided by the literature on metabolomics (e.g., Bertram et al.,
208   2009; Matulova et al., 2014; Li et al., 2015; Upadhyay et al., 2016) as well as by means of NMR analysis of
209   commercial standard compounds. Characteristic patterns of NMR resonances for specific compounds (e.g.,
210   patterns in multiplicity) enabled an accurate identification, while only a tentative attribution of the most
211   simple NMR resonances (singlets) was attempted when standards were not available, because deviations
212   with respect to published NMR data are possible when different experimental conditions (e.g., in respect to
213   pH of the sample) are used. Nevertheless, the POC extracts show several NMR features overlapping with
214   typical ones for other biological matrices. In particular, the occurrence of most common aliphatic
215   aminoacids was observed in all three samples analysed and particularly in sample POC SeaIce-1. Acidic
216   aminoacids dominated over the basic ones, while aromatic residuals were detected only in trace amounts
217   (Figure S1). The identification of modified aminoacids among the most typical natural products of the
218   Antarctic microbiota, such as mycosporines (Oyamada et al., 2007), could not be carried out in detail
219   because of the lack of suitable spectral libraries. The presence of metabolites such as low-molecular weight
220   nitrogen-containing compounds (choline, betaine, etc.) is confirmed by the singlets in the chemical shift
221   range 3.1 – 3.3 ppm from methyls bound to nitrogen atoms (H_3C-N-). Resonances at higher chemical shift,
222   between 3.4 and 4.2, recovered the -NC$\underline{H}$RCO- groups of alpha-aminoacids and the H-C-O groups of sugars
223   and polyols: traces of glycerol were found in all three samples analyzed, while glucose was found in trace
224   amounts in samples POC W3101 and as a major component in sample POC SeaIce-3 (Figure S2). These
225   results confirm the potential of ^{1}H-NMR spectroscopy for the characterization of marine metabolites and
226   natural products. The small set of POC samples analyzed in this study is, however, mainly aimed to provide
227   spectral fingerprints useful for the interpretation of the results of the aerosol sample analyses discussed in
228   the following sections.
229
230   **3.2. Organic composition of bubble bursting aerosols.**
231   The natural process of sea spray – mimicked by the experiments carried out in the tank onboard *RV*
232   *Hesperides*– selectively transfers organic compounds from seawater into the aerosol depending on the
233   ability of the specific pools of organic substances to enrich in the surface microlayer and/or to be
234   scavenged by rising air bubbles. The selective nature of such process is witnessed by our NMR data,
235   showing that the seawater composition dominated by aminoacids, osmolytes and sugars/polyols differs
236   quite substantially from that of bubble bursting aerosols from the tank experiments (Figure 3, Figure S3).
237   Bubble bursting aerosol was characterized by the occurrence of low-molecular weight metabolites like
238   lactic acid and amines (dimethylamine, DMA and traces of monomethyl- and trimethyl- amines) which likely
239   originated from DOC components of seawater. The most characteristic feature of the spectra is, however,
240   the bands at 0.9 and 1.3 ppm of chemical shift. These correspond to aliphatic chains with terminal methyl
241   moyeties typical of lipids. Their occurrence in the aerosolized seawater and not in the POC samples can be
242   explained by an enrichment of surface-active compounds from DOC in the surface microlayer. Lipid
243   enrichment in aerosol from bubble bursting experiments has already been documented by the two
244   previous studies reporting NMR composition data (Facchini et al., 2008; Schmitt-Kopplin et al., 2012).
245   Nevertheless, our findings clearly show that, beside lipids, there are specific constituents of POC taking part
246   in the formation of primary aerosol particles in the tank experiments. In particular, the spectral region for

247 sugars and polyols in bubble bursting aerosols is completely consistent with the spectral features of POC
248 (Figure S4), although the contribution of the -NC<u>H</u>RCO- groups of aminoacids in the same spectral window
249 is clearly missing in the aerosol. The presence of nitrogen-containing metabolytes (betaine) is confirmed in
250 the aerosol samples from the tank. It is plausible that betaine, glycerol and other sugars are chemically
251 bond to lipids making glycolipids and phospholipids, which can explain their preferential enrichment during
252 the aerosolization process with respect to other POC constituents like the aminoacids. It is a matter of fact
253 that aminoacids could be detected only in very trace amounts (the doublet of alanine at 1.45 ppm is barely
254 visible) in the sea spray samples. Other molecular tracers found in previous sea-spray experiments in other
255 geographical regions, such as acrylic acid (Schmitt-Kopplin et al., 2012), which is also product of DMPS
256 degradation, were not found in our experiment.

3.3. Organic composition of ambient submicron WSOC samples.

259 The eight ambient PM1 HiVol samples analyzed for organic composition include six that were collected in
260 parallel to the impactor samples discussed in Dall'Osto et al. (2017). The proton NMR spectra of the eight
261 samples are reported in Figures S5-S7. Air mass origin varied largely during the cruise, with transport from
262 the Weddell sea prevalent during the first half of the cruise turning into open ocean prevailing air masses
263 during the second half (Fig. 1). Two samples (A-0701 and A-0102) of mixed origin had been omitted by
264 Dall'Osto et al (2017), who focused on the comparison between aerosols from the sympagic regions and
265 those from the open ocean. We applied hierarchical cluster analysis to investigate if a dual classification
266 also held with the NMR spectra (Figure 4). The original spectra were normalized to their integrals and
267 binned to 354 points before clustering. Two main clusters were indeed identified: a first one recovering
268 three samples collected downwind the Weddell Sea during the first half of the cruise, and a second cluster
269 with samples representative of a greater diversity of conditions, from the Drake Channel, to the Antarctic
270 Peninsula and to the productive waters around South Georgia. This second cluster corresponds to the
271 samples characteristic for the open ocean conditions in Dall'Osto et al. (2017) plus samples A-0701 and A-
272 0102. Unexpectedly, sample A-0701, whose air mass spent most of time over sympagic waters (Fig. 1)
273 clustered together with the samples from the open ocean according to NMR composition. It is noticeable,
274 however, that binned NMR spectra can only trace the distribution of the major organic functional groups
275 while the information carried by fine spectral features, which is critical to detect the presence of specific
276 molecular markers, is not taken into account in the cluster analysis. In the following sections, we will show
277 that sample A-0701 exhibits a peculiar NMR composition which must be put in relation to terrestrial
278 sources of organic compounds. On the basis of the back-trajectories (Figs. 1 and 8), the likely land sources
279 were located in the Antarctic Peninsula. In summary, the variability in the distribution of NMR functional
280 groups in ambient PM1 samples (Table 1) was primarily driven by the air mass origin over sympagic
281 (Weddell Sea) or pelagic waters, in agreement with the results on inorganic compounds, WSOC and amines
282 reported by Dall'Osto et al. (2017; 2019). Nevertheless, the analysis of fine NMR spectral features supports
283 the existence of a third source area over land. In the following discussion, we will provide an in-depth
284 description of the NMR compositions for these three source sectors.

3.3.1. Ambient aerosols from the Weddell Sea.

287 Sample A-0911 was collected in the marginal ice zone of the Weddell Sea. Its spectrum shows a complete
288 absence of aromatic compounds and alkenes (Figure S7). The aliphatic region (Figures 5, S8) exhibits broad
289 similarity to that of the primary marine particles generated in the sea spray tank, but with a major
290 difference in the chemical shift range between 1.7 and 3.0 ppm where the background broad NMR bands
291 are much more intense in the ambient sample. This is also the region recovering the signals from acyl
292 groups (RC<u>H</u>-(C=O)-) in aliphatic carboxylic acids and ketoacids, which are formed by VOC oxidation in the
293 atmosphere (Barbaro et al., 2017). The most abundant individual compounds detected in these samples

294   were, however, MSA (Fossum et al., 2018), and the low-molecular methylamines (MMA, DMA, TMA). The
295   predominance of semivolatile C_1-C_3 alkyl-amines (Ge et al., 2011) indicates that the amines form in the
296   ambient aerosol by secondary processes involving volatilization from the ocean surface and recondensation
297   onto acidic aerosol particles (Dall'Osto et al., 2019). The aliphatic bands at 0.9 and 1.3 ppm in sample A-
298   0911 show a partial overlap with the resonances of the lipids in the aerosolized seawater. However, the
299   bands at 1.6 ppm and 2.2-2.3 ppm which, in lipids, correspond to methylenes in beta and alpha position to
300   a C=O group, are much more intense in the spectrum of A-0911 than in BB SeaIce-3 (Figure S8), indicating
301   that aliphatic chains are shorter and more substituted in the ambient aerosol than in nascent primary
302   aerosol particles. The pattern of bands at 0.9, 1.3, 1.6, 2.2, 2.4 and 2.6 ppm follow the structure elucidated
303   by Suzuki et al. (2001) and attributed to C_7-C_9 aliphatic dicarboxylic acids and oxo-acids. This class of organic
304   compounds, clearly characterizing the aliphatic composition of the ambient samples in the Weddell Sea
305   area, can originate from degraded (oxidized) lipids (Kawamura et al., 1996), or from gas-to-particle
306   conversion of carbonyls produced by the photochemical oxidation of lipids at the air-sea interface (Bernard
307   et al., 2016; Alpert et al., 2017). Support to the latter hypothesis (secondary formation) is given by the fact
308   that the N-osmolytes (betaine, choline) present in the sea spray generated in the tanks were completely
309   absent in the ambient sample. Nevertheless, the resonances in the spectral window 3.5 − 3.8 ppm in
310   sample A-0911 are completely consistent with the occurrence of glycerol, indicating that in fact primary
311   aerosol particles contributed to the composition of the ambient aerosol in this region (Figure S9). There is
312   another one striking difference between the composition of the ambient aerosol and sea spray particles:
313   the former contains significant levels (1.65 ng m^{-3}) of creatinine. This compound is responsible to the two
314   singlets at 3.12 ppm and 4.27 ppm of chemical shift and was identified by the comparison with a standard
315   under identical NMR experimental conditions (Figure S11). The concentration of creatinine clearly follows
316   that of low-molecular weight amines (Figure 6) and shows a maximum in the three samples collecting most
317   of the air masses that travelled over the Weddell Sea. Creatinine was also determined by HPLC/-MS analysis
318   in a parallel set of filter samples collected onboard Hesperides during the PEGASO cruise (see Section 2.4).
319   Identification was based on MS/MS fragmentation patterns and retention time. Quantification was based
320   on chromatographic peak area. Figure 7 shows extracted ion chromatograms for m/z 114.0655-114.0667,
321   corresponding to creatinine, of the filter extract of sample 0119N obtained during the PEGASO campaign
322   and the neat creatinine standard. The HPLC/MS analysis indicate that creatinine occurred in concentrations
323   of 20 − 50 pg/m^3 in the samples from the Weddell Sea area (Table S1), much less than the concentrations
324   determined by ^{1}H-NMR spectroscopy (1.6 − 2.5 ng/m^3, Table 1). Such discrepancy can be due to the
325   different extraction protocols and to non-ideal chromatographic conditions in HPLC/MS for creatinine
326   quantification (elution close to the void volume). Nevertheless, our findings demonstrate that high-field
327   NMR methods can integrate HPLC/MS analysis for the identification of molecular markers in atmospheric
328   aerosol complex organic mixtures.
329
330   **3.3.2. Ambient aerosols in the open ocean.**
331   Sample A-2401 was collected during the northern transit of the cruise, *RV Hesperides* just west to South
332   Georgia (55° S) (Figure 1). During sampling, the air masses had a westerly component and can be
333   considered representative of Southern Ocean conditions. The ^{1}H-NMR spectrum of A-2401 shares
334   similarities with that of A-0901 described above: a) the resonances of MSA and methyl-amines are much
335   more intense than that of other low-molecular weight compounds (such as N-osmolytes); b) the spectral
336   region of acyls (1.8 − 3.0 ppm) accounting for unresolved carboxylic acids is clearly more intense than in the
337   spectrum of primary organic aerosols; c) the pattern of bands at 0.9, 1.3, 1.6 and 2.2-2.4 ppm highlights the
338   presence of linear aliphatic structures substituted with oxo- and carboxylic groups. Nevertheless, MSA and
339   the low molecular weight amines were less abundant in A-2401 than in the sample from the Weddell Sea
340   (Table 1). Also the ratio between acyl (C$\underline{H}$-C=O) and alkyl (C$\underline{H}$-CH) groups was smaller in A-2401 than in A-

341   0911 (Figure S8). The linear aliphatic structures involved longer methylenic chains in A-2401 than in A-0911,
342   so that in the former case they were more similar to the aliphatic structures of the aerosolized melted sea
343   ice (Figure S8). Another difference between the two ambient aerosol samples is that the one from the
344   Southern Ocean contains much more alcoxy groups (HC-O, in the chemical shift range 3.4 – 4.2 ppm) of
345   polyols than the one from the Weddell Sea (Figure 5; Table 1). When comparing the functional group
346   distributions of the ambient aerosol samples to that of the aerosol generated during the tank experiments,
347   clearly the samples from the Southern Ocean show a better match than the samples from the Weddell Sea
348   do. Other similarities between the composition of A-2401 and the aerosol in the tank can be found in the
349   fine structures of the spectra, especially in the ranges of aromatics, acetals and polyols (Figure S12). A-2401
350   clearly contains traces of organic markers of primary aerosols and specifically glycerol, N-osmolytes (Figure
351   S10) and aminoacids (alanine). Finally, contrary to A-0901, sample A-2401 contains only trace amounts of
352   creatinine.
353

354   **3.3.3. Ambient aerosols influenced by coastal land sources.**
355   Sample A-0701 was collected in the western sector of the Weddell Sea. The air masses showed several
356   overpasses on the Antarctic Peninsula. The ^{1}H-NMR spectrum shows unique features: isobutyric acid was
357   found in relatively high concentrations, together with an amine tentatively identified as cadaverine (Figure
358   5). The aliphatic chains occur in much lower amounts than in the samples described above, the band of
359   acyls is not as pronounced as in A-0901 (Figure S8), whereas alcoxyls are abundant, especially due to the
360   occurrence of sucrose at a remarkable concentration of 10 ng/m^3. Finally, no creatinine was found in this
361   sample. Clearly, the composition of A-0701 is drastically different from that of the other samples collected
362   in the Weddell Sea. The presence of sucrose (Figure S9) points to a contribution from primary biological
363   particles emitted from a terrestrial biota, not a marine one. Vegetation cover (scarce but existing) in the
364   Antarctic Peninsula can be responsible for such emissions. The NMR composition of A-0701 provides
365   evidence of the diversity of biogenic aerosol sources active in this area of the world.
366

367   **4. Discussion**

368   **4.1 Source apportioning of primary and secondary organic components in different regions**

369   The comparison of the NMR compositions of the ambient aerosol samples collected onboard *RV Hesperides*
370   (Figure 8) supports the distinction of aerosol sources between the sympagic and pelagic environments
371   already introduced by Dall'Osto et al. (2017). The higher abundance of alkyl (C-H) and alcoxy (H-C-O) groups
372   detected in the second half of the cruise points to a larger fraction of primary organic compounds rich in
373   lipids and polyols in the aerosols of the open Southern Ocean. Analogous compositions were obtained
374   using FTIR spectroscopy at Ross Island (Liu et al. 2018). In our study, the attribution of compound classes
375   and molecular markers (such as glycerol and N-osmolytes) to primary marine particles was supported by
376   the comparison with the analysis of tank-generated sea-spray particles. According to our NMR datasets,
377   primary marine organics were ubiquitous in the region as witnessed by the presence of glycerol in all
378   samples. However, glycerol accounted for almost the entire polyol content in the three samples from the
379   eastern/north Weddell Sea, while the samples from the open ocean contained much larger and more
380   complex mixtures of polyols/sugars. Sub-ng/m^3 levels of free aminoacids (alanine) and trace amounts of N-
381   osmolytes along with the greater abundance of linear aliphatic structures similar to lipids in the samples
382   from the Southern Ocean point to a major contribution of primary organics to submicron organic aerosols
383   in this environment. These findings provide further confirmation to the importance of sea spray as a source
384   of marine organic particles in oceanic regions characterized by high productivity and strong wind stress.
385

386 In sympagic waters, other mechanisms of aerosol formation take place. Sympagic waters are rich in S- and
387 N- osmolytes produced by the algal communities colonizing the sea ice. The osmolytes degrade to VOCs
388 which are then converted to SOA components, such as MSA (Davison et al., 1996) and low-molecular
389 weight methyl-amines (Facchini et al., 2008). Also the distribution of the oxygenated functional groups was
390 different between sympagic and pelagic regimes. If alcoxyl groups (H-C-O) from polyols and sugars
391 accounted for almost 50% of total alcoxyl (H-C-O) and acyls (H-C=O) in the samples from the Southern
392 Ocean, such fraction decreased to less than 30% in the three samples from the offshore areas of the
393 Weddell Sea (Fig. 8). The mixtures of organic compounds carrying acyls, like carboxylic and oxocarboxylic
394 acids, are not associated to primary marine aerosols and are likely components of SOA. Carboxylic acids can
395 form photochemically (Cui et al., 2019) during the austral summer. The nature of parent VOCs for
396 carboxylic acids in our samples is unknown, but the occurrence of linear aliphatic compounds containing
397 oxo- and carboxylic groups indicates that one of the possible sources stands in the oxidative degradation of
398 lipids - either in the aerosol or in the marine microlayer - as suggested by past studies in Antarctica
399 (Kawamura et al., 1996) and consistent with recent AMS observations in the Arctic marginal ice zone (Willis
400 et al., 2017).
401 In the Weddell Sea, under the influence of air masses that had travelled over the Peninsula (sample A-
402 0701), the contribution of the emissions from the land biota became evident, therefore supporting the
403 observations of Schmale et al. (2013) on the contribution of primary biological particles from the coastal
404 land ecosystems. Our data suggest that beside animal colonies, also the land vegetation (grasses, mosses,
405 lichens) of the Antarctic Peninsula can contribute to the emission of particles, and in particular to the
406 content of sugars. Other biological compounds of primary origin, the aminoacids, were not found in the
407 Weddell Sea in our study. These results contrast with the previous findings that a significant fraction of the
408 ambient PM1 mass was accounted for by proteinaceous material at an island site in the Southern Ocean
409 (Schmale et al., 2013). On the other hand, the observations of Schmale et al. (2013) were carried out under
410 the direct influence of the emissions of seabird colonies, while our observations were carried out offshore.
411 More research is needed to quantify the range and extent to which primary particles from the terrestrial
412 biota impact the marine aerosol composition in the Antarctic region.
413
414 **4.2 A new potential marker: creatinine.**

415 The sources of creatinine in the ambient aerosol is controversial. On the basis of its chemical structure, it is
416 water-soluble but clearly less volatile than the methyl-amines and, as a consequence, its Henry coefficient
417 must be much less favorable for transferring this amine out of seawater into the gas phase. A primary origin
418 via sea spray is also doubtful because creatinine is not a strong surfactant. On the other hand, Prather et al.
419 (2013) showed that sea-spray aerosols encompass several classes of organic particles, including some made
420 of biological material: POC particles and large colloids can be scavenged by rising bubbles and injected in
421 the atmosphere by jet drops. Jet drop emission represents a plausible mechanism to transfer primary
422 organic compounds which are not strong surfactants from seawater to the atmosphere. If this happened to
423 creatinine, it must have occurred in source areas other than the algal blooms where we conducted the tank
424 experiments, since we did not detect any creatinine in the aerosolized sea water and sea ice. Creatinine is a
425 common metabolite of mammals, therefore an alternative source via the excreta of sea lions in Antarctic
426 coastal areas can be postulated. However, a much more vast potential source in seawater is also possible
427 under the hypothesis that creatinine results from the enzymatic conversion of creatine, which is a known
428 metabolite of the urea cycle in marine animals (Whitledge and Dugdale, 1972) and phytoplankton (Allen et
429 al., 2011) that contributes to pelagic DOC across the world's oceans (e.g., Wawrik et al., 2017).
430
431
432 **5. Conclusions**

433   Our results demonstrate that, beside MSA, a complex mixture of biogenic organic compounds contributes
434   to the composition of submicron aerosol particles in the Antarctic atmosphere. Although individual organic
435   markers encompassing sugars, aminoacids and carboxylic acids have already been identified in past studies,
436   our results indicate that non-MSA biogenic organic compounds impact the bulk composition of organic
437   aerosol in this environment (Figure 8). The NMR analysis provides evidence for both secondary (more
438   important in sympagic regions) and primary marine (more important in pelagic areas) sources. A third
439   contribution from the terrestrial biota in the Antarctic Peninsula was also identified. The emission of sea-
440   spray organics in offshore areas was unambiguously demonstrated by the determination of molecular
441   tracers for lipids and polyols and by the comparison of the fine structures in the ^{1}H-NMR spectra of the
442   ambient samples and of the aerosol generated in the tank experiments. A new biogenic marker, creatinine,
443   was identified for the first time in the ambient aerosol, extending the list of reduced nitrogen containing
444   molecular tracers in the atmosphere. The discovery of creatinine also exemplifies the usefulness of
445   employing non-targeted analytical techniques like NMR spectroscopy for screening the organic composition
446   of the aerosol in remote environments where the sources of atmospheric particulate matter are still poorly
447   known. The complexity of the organic composition illustrated in this study calls for more research on
448   suitable methodologies – both online and offline and combinations of them – to investigate the nature of
449   non-MSA marine organic particles in off-shore regions around the Antarctic continent.
450

451   **Data Availability**

452   The NMR data sets are available on request to the corresponding author.

453

454   **Author Contribution**

455   SD wrote the paper; MDO and RS coordinated the experimental activities in the field; MP, MDO and SG
456   collected the aerosol samples; MDO, MP and DC collected the sea ice samples; COD, JO and DC set up the
457   bubble bursting tank; MR, MP, MR, NZ and FV performed the sample extraction and preparation for WSOC
458   and NMR analysis; NZ and MP performed the NMR analyses; SG and CJK carried out the HPLC/MS analyses;
459   SD, MP and ET elaborated the NMR data; MDO, RS and ET contributed to the interpretation of the analyses
460   of the seawater samples; SD, MP, MR, MDO, TH, CJK and ET contributed to the interpretation of the
461   analyses of the aerosol samples; all authors contributed to the general discussion and to work out the main
462   conclusions of this study.

463

464   **Acknowledgments**

472

473   **References**

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Table 1.

sample ID:	**A-0701**	**A-0901**	**A-1301**	**A-1801**	**A-2401**	**A-2801**	**A-0102**	**A-0602**
sampling times:	07 Jan 20:00 – 09 Jan 09:00	09 Jan 14:50 – 13 jan 13:50	13 Jan 19:20 – 18 Jan 12:20	18 Jan 13:30 – 21 jan 23:55	24 Jan 15:00 – 28 jan 05:15	28 Jan 13:30 – 31 jan 13:50	01 Feb 14:50 – 06 Feb 03:15	06 Feb 22:00 – 10 Feb 11:00
average air mass type:	Weddell Sea / Antarctic Peninsula	Weddell Sea	Weddell Sea	Weddell Sea	Open Ocean	Open Ocean	Open Ocean / mixed	Open Ocean
Water-soluble organic carbon ($\mu gC/m^3$):								
WSOC	0.14	0.07	0.12	0.13	0.09	0.14	0.05	0.11
^{1}H-NMR functional groups ($nmolH/m^3$):								
H-C	2.60	2.16	2.28	3.03	3.27	2.81	2.07	2.82
H-C-C=O	2.40	1.58	1.80	2.10	1.91	1.86	1.28	1.78
H-C-O	2.15	0.57	0.69	0.83	2.06	0.99	0.99	1.41
O-CH-O	0.20	0.07	0.05	0.04	0.08	0.09	0.07	0.09
Ar-H	0.12	0.05	0.00	0.10	0.09	0.10	0.11	0.07
MSA	2.13	1.95	2.63	4.54	1.72	2.90	2.22	1.53
Alkyl-Amines	0.30	0.79	0.53	1.32	0.34	0.49	0.13	0.15
Molecular markers (ng/m^3):								
MSA	68	62	84	145	55	93	71	49
methyl-amines	2.31	5.5	3.79	9.0	2.53	3.56	0.92	1.20
creati-nine	0.09	1.65	1.52	2.21	~0.05	1.00	0.29	0.41
glycerol	NA	1.1	0.7	0.7	3.0	0.8	0.7	1.3
sucrose	11							
alanine			traces[1]	traces[1]	0.6			0.7
betaine					traces[2]			

[1] below the limit of quantification (0.3 ng/m³); [2] below the limit of quantification (0.2 ng/m³)
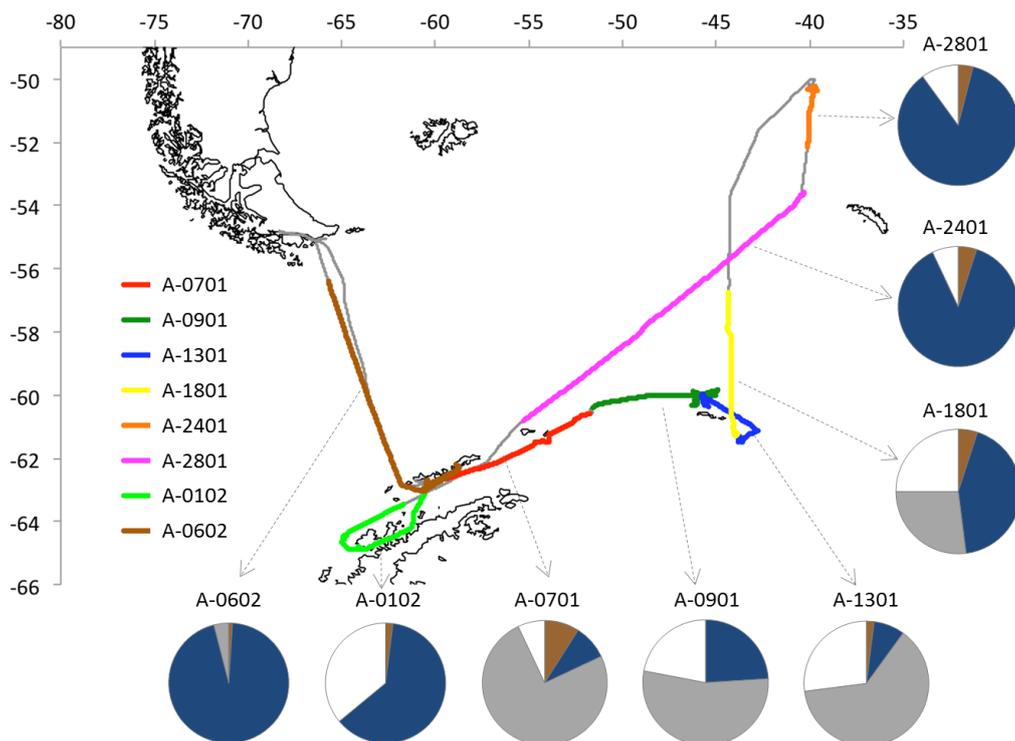
Figure 1. Cruise of RV Hesperides. The colors indicate the duration of the single aerosol samplings (short interruptions undertaken to avoid contamination from ship emissions are not indicated in the figure). The average time spent by air masses travelling over land (brown), marginal ice zone (1-99% surface coverage; grey), compact sea ice (100% coverage; white) and open ocean (dark blue) is indicated for each sample.
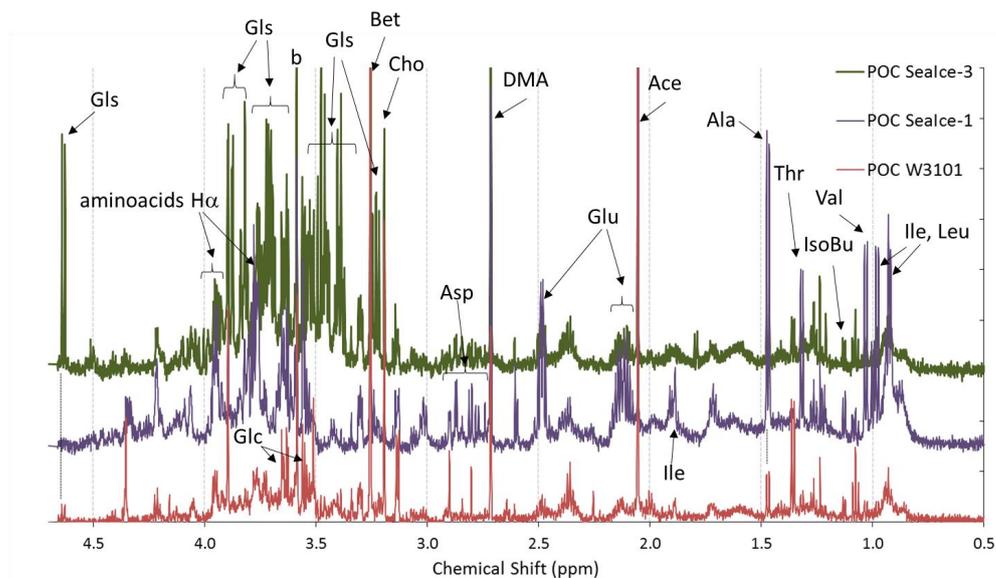
Figure 2. Aliphatic region of the ¹H-NMR spectra of three POC sample extracts: one for the seawater sample (POC W3201) and two from melted sea ice (POC SeaIce-1 and POC SeaIce-3). Specific NMR resonances were assigned to: the residuals of aminoacids (Ala, Thr, Val, Ile, Leu, Glu and Asp) and their alpha hydrogen atoms, isobutyric acid (IsoBu), acetic acid (Ace), dimethylamine (DMA), N-osmolytes (Bet: betaine; Cho: choline), glycerol (Glc) and to glucose (Gls).
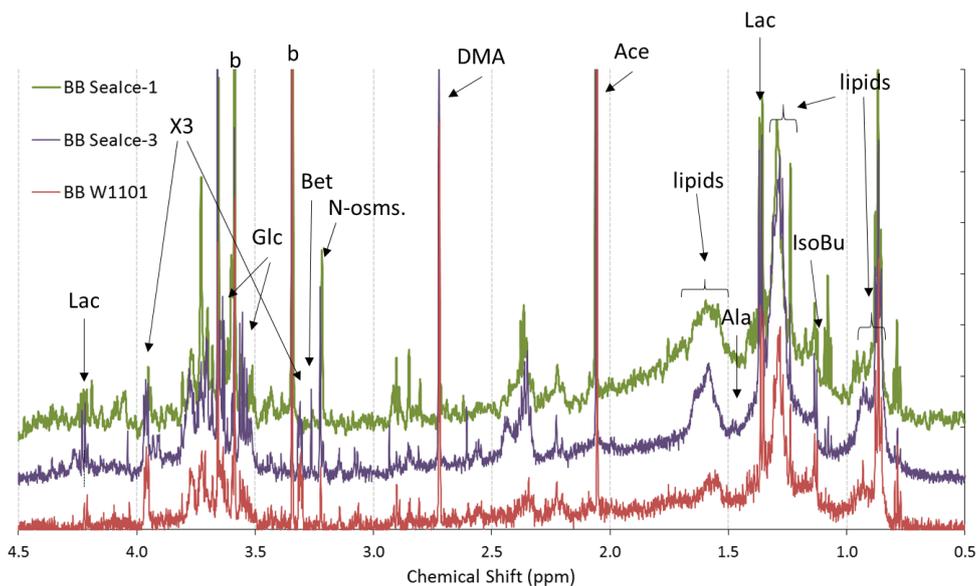
Figure 3. The same as Figure 2 but for the three bubble bursting aerosols: from seawater sample W1101 (BB W1101) and melted sea ice #1 and #3 (BB SeaIce-1 and BB SeaIce-3). Specific resonances were assigned to lactic acid (Lac), acetic acid (Ace), isobutyric acid (IsoBu), alanine (Ala), dimethylamine (DMA), glycerol (Glc), N-osmolytes (Bet: betaine;

"N-osms": unidentified, possibly phosphocholine) and to blank contaminations (b). Unresolved mixtures of aliphatic compounds were identified as lipids.
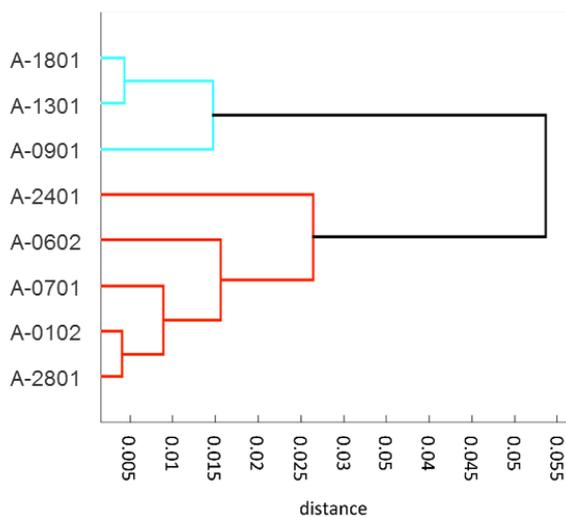

Figure 4. Cluster analysis of the ^{1}H-NMR spectra of the PM1 HiVol samples of ambient aerosol.
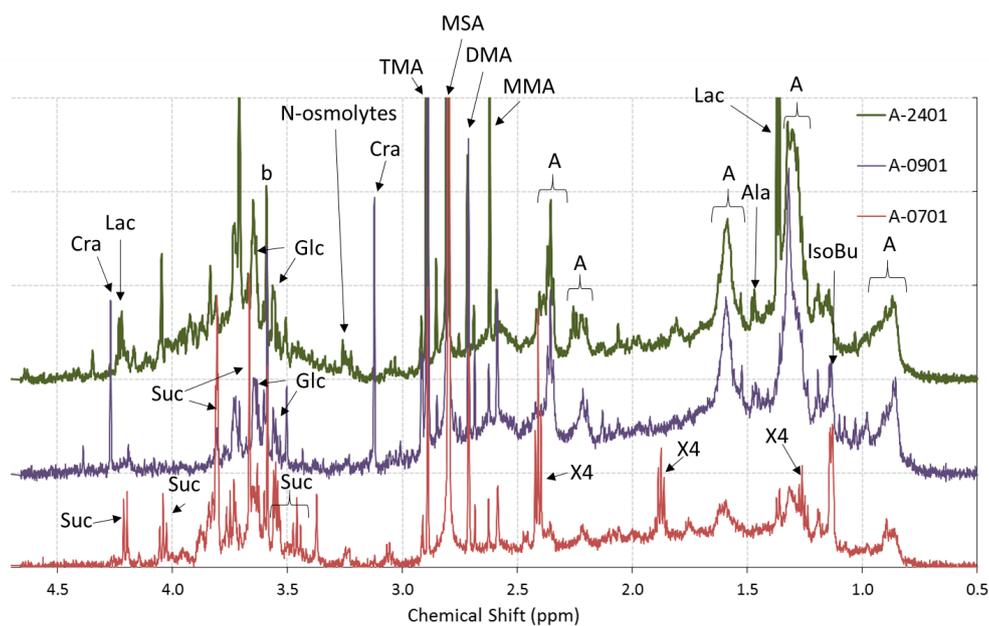

Figure 5. The same as Figure 2 but for the three ambient submicrometer aerosol samples. Specific resonances were assigned to lactic acid (Lac), isobutyric acid (IsoBu), alanine (Ala), monomethylamine (MMA), dimethylamine (DMA), trimethylamine (TMA), glycerol (Glc), sucrose (Suc), creatinine (Cra) and to blank contaminations (b). Unresolved

mixtures of linear aliphatic compounds (A), including possible contributions from lipids, are indicated in the spectra. Other NMR signals were only tentatively attributed to cadaverine (X4).
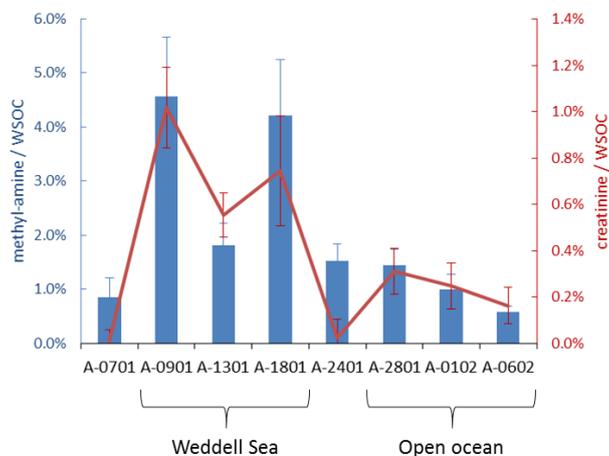

Figure 6. Concentrations of creatinine and methylamines in the PM1 samples. The concentrations are expressed as contributions to WSOC (mol% of carbon). "Weddell Sea" and "Open ocean" labels indicate the sampling periods identified by Dall'Osto et al. (2017) to characterize the aerosol composition in air masses travelling over sea ice and in the Southern Ocean, respectively.
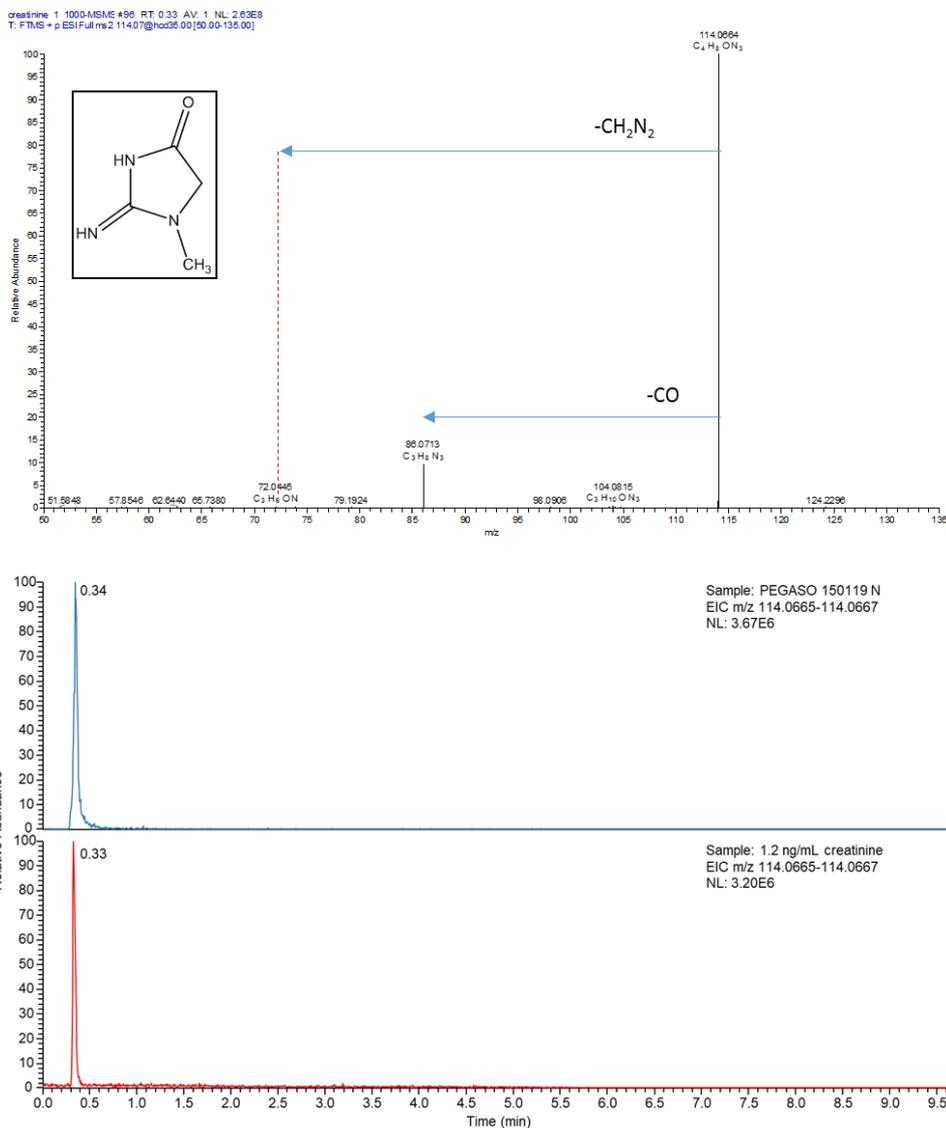
Figure 7. (top) MS spectrum of a creatinine standard. (bottom) Extracted ion chromatograms for m/z 114.0655-114.0667, corresponding to creatinine, of the filter extract of sample 0119n obtained during the PEGASO campaign and the neat creatinine standard. The retention time of creatinine was found to be 0.33 min using the conditions outlined in Section 2.4.
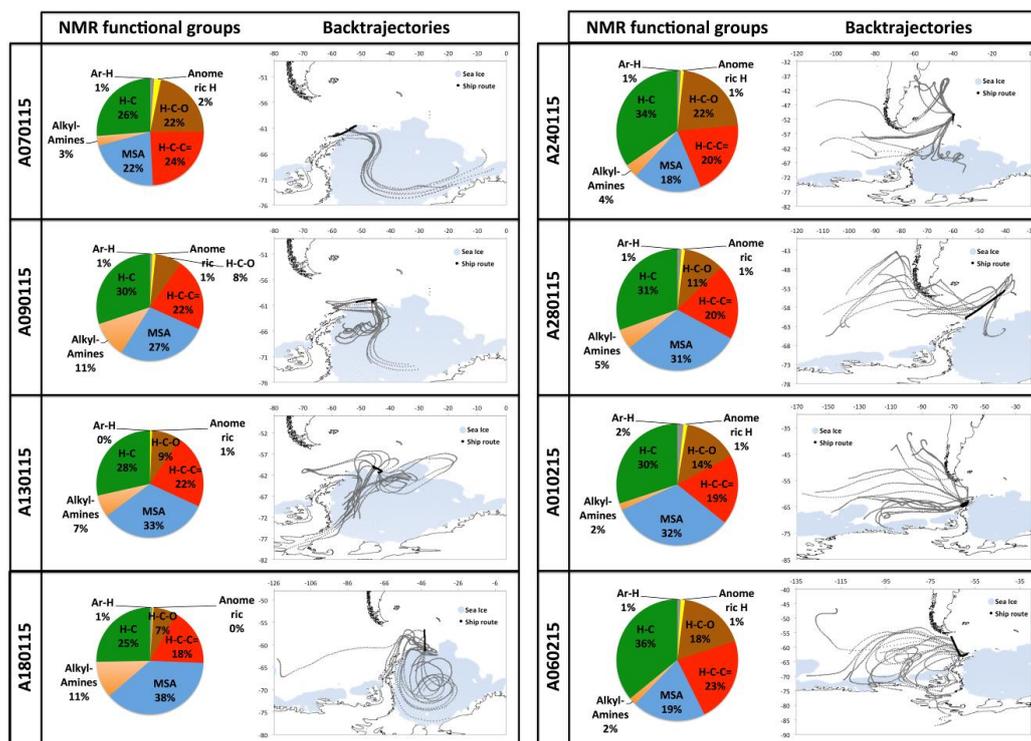
Figure 8. NMR functional group compositions of WSOC in the PM1 HiVol samples. Functionalities: H-C (alkyls), H-C-(C=) (acyls), H-C-O (alcoxyl), MSA, amines, anomeric, Ar-H (aromatic).