Contribution of water soluble organic matter from multiple marine geographic eco-regions to aerosols around Antarctica

Matteo Rinaldi[1], Marco Paglione[1], Stefano Decesari[1],

Roy M. Harrison[2†], David C.S. Beddows[2,]

Jurgita Ovadnevaite[3], Darius Ceburnis[3], Colin D. O'Dowd[3],

Rafel Simó[4], Manuel Dall´Osto[4*]

[1]Institute of Atmospheric Sciences and Climate, National Research Council, Bologna, Italy.

[2]National Centre for Atmospheric Science, University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom

[3]School of Physics and Centre for Climate and Air Pollution Studies, Ryan Institute, National University of Ireland Galway, University Road, Galway, Ireland

[4]Institute of Marine Sciences, Passeig Marítim de la Barceloneta, 37-49. E-08003, Barcelona, Spain;
corresponding author to Email: dallosto@icm.csic.es,

[†]Also at: Department of Environmental Sciences / Center of Excellence in Environmental Studies, King Abdulaziz University, PO Box 80203, Jeddah, 21589, Saudi Arabia

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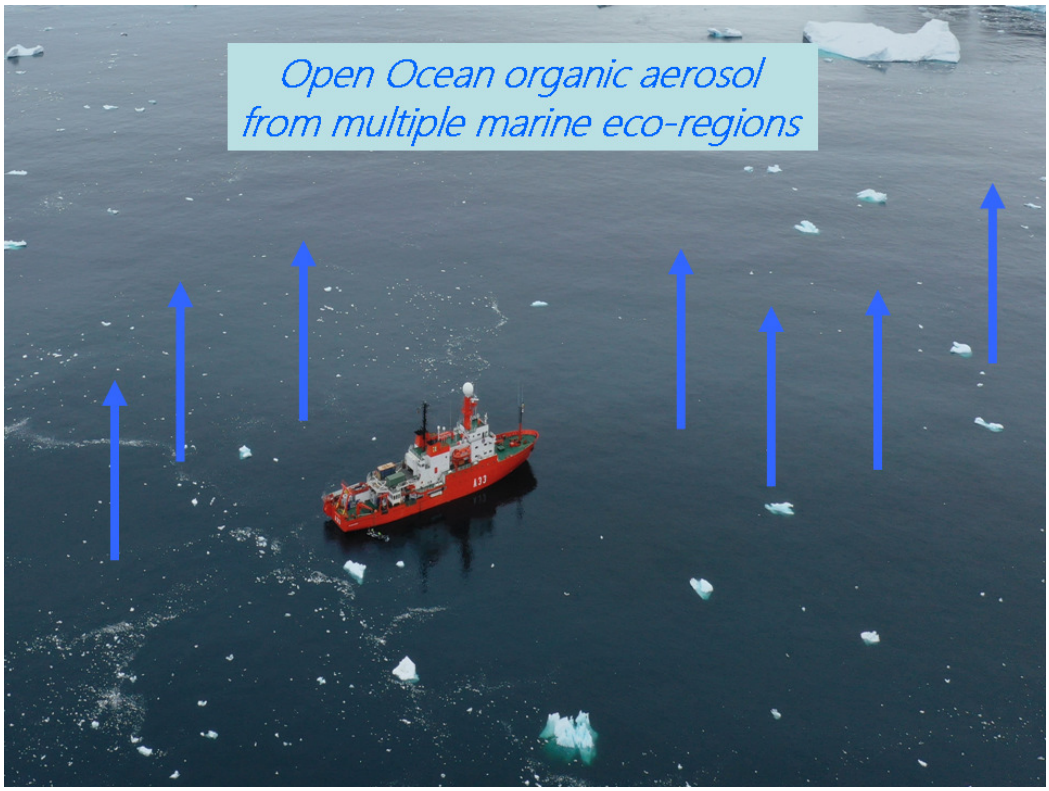
Open Ocean organic aerosol
from multiple marine eco-regions

Abstract

We present shipborne measurements of size-resolved concentrations of aerosol components across ocean waters next to the Antarctic Peninsula, South Orkney Islands and South Georgia Island, evidencing aerosol features associated to distinct eco-regions. Non-methanesulfonic acid Water Soluble Organic Matter (WSOM) represented 6-8% and 11-22% of the aerosol PM_1 mass originated in open ocean (OO) and sea ice (SI) regions, respectively. Other major components included sea salt (86-88% OO, 24-27% SI), non sea salt sulfate (3-4% OO, 35-40% SI), and MSA (1-2% OO, 11-12% SI). The chemical composition of WSOM encompasses secondary organic components with diverse behaviors: while alkylamine concentrations were higher in SI air masses, oxalic acid showed higher concentrations in the open ocean air. Our online single-particle mass spectrometry data exclude a widespread source from sea bird colonies, while the secondary production of oxalic acid and sulfur-containing organic species via cloud processing is suggested. We claim that the potential impact of the sympagic planktonic ecosystem on aerosol composition has been overlooked in past studies, and multiple eco-regions act as distinct aerosol sources around Antarctica.

1. Introduction

Remote from most human influences, the Southern Ocean (SO) is one of the most pristine regions on Earth, and a window to the preindustrial atmospheric conditions and processes[1-5]. It is the stormiest of all oceans, and its atmospheric and oceanic circulations impact the entire Southern hemisphere and beyond. The surface of the ocean closer to the Antarctic continent undergoes an annual freezing cycle, forming a layer of sea ice that generally extends over an area ranging from 4 x10^6 km^2 in the summer to approximately 19 x 10^6 km^2 in late winter[1]. This large area increases surface albedo and controls the air-sea gas exchange. Sea ice ecosystems are also one of the largest biomes on earth, providing a stable habitat for diverse microbial assemblages[2,3].

Currently, many unknowns remain about atmospheric and oceanographic processes in this region, and their linkages. Climate models are prone to large biases in the simulation of clouds, aerosols and air-sea exchanges[4]. This is largely due to the poor understanding of aerosol sources and processes in this region. Overall, two natural sources largely govern the aerosol population, sea spray (primary) and non sea salt sulfate ($nssSO_4^{2-}$; secondary). Sea spray (mostly composed of sea salt) generated by breaking waves is often reported as the main source of supermicron aerosols in marine areas[6,7]. Recently, blowing snow over pack ice has been suggested to contribute sea salt aerosol in similar amounts to breaking waves[8-10]. The other major component of Antarctic aerosols, $nssSO_4^{2-}$, is mainly derived from atmospheric oxidation of dimethylsulfide (DMS), a trace gas produced by marine plankton. The marine sulfur biogeochemical cycle received much attention after the proposal by Charlson et al. (1987)[12] that the principal source of cloud condensation nuclei (CCN) in the marine environment is DMS-derived $nssSO_4^{2-}$ [13]. Such a hypothesis of a central role for DMS was questioned by Quinn and Bates (2011)[14] as the large variety of ocean-emitted

126 aerosol components was being disclosed, but mounting evidence has been
127 collected thereafter that DMS emission chiefly contributes to aerosol formation,
128 growth and activation as CCN over the oceans[15-18]. In the atmosphere, DMS
129 is oxidized also into aerosol-prone methanesulfonic acid (MSA), which peaks
130 in the summer and is found predominantly as methanesulfonate in the
131 submicron size range[19]. Unlike $nssSO_4^{2-}$, which may originate also from
132 anthropogenic and lithogenic sources, MSA has been proposed as a proxy for
133 oceanic DMS emissions. However, the overall interpretation of MSA and
134 $nssSO_4^{2-}$ is far less straightforward than initially thought[20], given complex
135 ecological and biogeochemical processes controling the DMS marine
136 emissions[21] and variable MSA oxidation yields[22].
137 The relative roles of secondary aerosols produced from biogenic sulfur versus
138 primary sea-spray aerosols in regulating cloudiness above the SO is still a
139 matter of debate[23-27]. Mc Coy et al. (2015)[25] reported observational data
140 indicating a significant spatial correlation between regions of elevated Chl-a
141 and particle number concentrations across the SO, and showed that modeled
142 organic mass fraction and sulfate explain 53 ± 22% of the spatial variability in
143 observed particle concentration, suggesting that primary marine organic
144 aerosols are important in this region, similarly to other remote marine
145 regions[28]. Despite the increasing awareness of their importance,
146 measurements of organic components in SO aerosols are scarcer than
147 inorganic measurements, and the overall apportionment of primary versus
148 secondary marine aerosol in the southern hemisphere is not known. First
149 observations of organic carbon (OC) in size-segregated aerosol samples
150 collected at a coastal site in the Weddell Sea (Virkkula et al., 2006)[29] showed
151 that MSA represented only a few % of the substantial amount of OC observed
152 in the submicron fraction. However, Zorn et al (2008)[30] showed that MSA
153 dominated Antarctic OC, whereas non-MSA organic compounds dominated
154 SO OC. Recent measurements over the SO (43°S–70°S) and the Amundsen
155 Sea (70°S–75°S) showed that Water Insoluble Organic Carbon (WIOC)
156 accounted for 75% and 73% of aerosol total organic carbon in the two regions,
157 respectively[31]. In the Amundsen Sea, WIOC concentrations correlated with
158 the relative biomass of a phytoplankton species (*Phaeocystis antarctica*) that
159 produces extracellular polysaccharide mucus. Whilst sympagic and pelagic

160 plankton biomass controls biological productivity and the organic mass budget
161 of the Southern Hemisphere[2,3], including organic emissions to the atmosphere,
162 insular terrestrial biomass emissions contain large amounts of OC[32-34].
163 Here, we report atmospheric measurements during a 42 day cruise in the SO
164 near Antarctica. We previously showed that the microbiota of sea ice and the
165 sea ice-influenced ocean can be a source of atmospheric organic nitrogen
166 (ON), specifically low molecular weight alkylamines[35]. In a follow-up paper, we
167 reported a specific analysis of the primary ON aerosol detected by bubble
168 bursting chamber experiments on board, and also showed that alkylamines
169 form in the ambient aerosol by secondary processes involving volatilization
170 from the ocean surface and re-condensation onto acidic aerosol particles[36].
171 Using valuable high time resolution data from the same campaign, and
172 selecting 12 pseudo-steady state periods (where aerosol microphysical
173 properties varied less than 20% over eight hours), Fossum et al (2018)[27]
174 evaluated the relative contributions of primary and secondary aerosols to SO
175 cloud condensation nuclei, and concluded that both sea salt and non-sea-salt
176 sulfate were major CCN components. In the selected cases studied, non MSA
177 organics contributed in the range 2-10% of aerosol mass.
178 In the present work, we (1) report the aerosol water soluble fraction
179 composition for the whole campaign; (2) report the size-resolved
180 concentrations of oxalic acid and alkyl amines in PM_{10} aerosols; (3) discuss
181 the mixing state of oxalic acid by means of single particle mass spectrometry;
182 and (4) discuss the processes and sources responsible for the measured
183 patterns, stressing that multiple eco regions govern the aerosol population
184 numbers and composition. Such detailed chemical characterization of the
185 water soluble fraction of marine aerosol, including tracers of secondary
186 aerosol formation processes, has never been achieved before close to the
187 Weddell Sea region. We highlight that water soluble aerosol components
188 contribute to aerosol hygroscopicity and influence the ability of particles to
189 activate into cloud droplets, therefore being climate relevant. The role of
190 water-soluble organics in these processes in the Antarctic atmosphere is far to
191 being understood, mainly due to the lack of quantitative observations.
192

2 Methodology

The Cruise.

We conducted extensive aerosol measurements on board of the RV Hesperides from January 2 to February 11, 2015 under the project PEGASO (Plankton-derived Emissions of trace Gases and Aerosols in the Southern Ocean). Different air masses were sampled, including the regions of Antarctic Peninsula, South Orkney, and South Georgia Islands.

Aerosol offline measurements.

Off-line aerosol samples were collected on the upper deck by using a 5-stage Berner impactor (hereafter BI5; type LPI80, Hauke; cut-offs at 0.06, 0.14, 0.42, 1.2, 3.5 and 10 μm) and a high volume PM_1 sampler (hereafter HIVOL; TECORA). Ion chromatography was used for the quantification of water-soluble inorganic ions, oxalic acid and low molecular weight alkyl-amines (methyl-, ethyl-, dimethyl-, diethyl- and trimethylamine)[37] in the BI5 water extracts, while an elemental analyzer (Shimadzu TOC-5000A) was used to quantify the water-soluble organic carbon content both of the impactor stages and of the HIVOL filters. The water soluble organic carbon content was measured on both kinds of samples to assess the impact of the sampling technique upon the measured value. Indeed, impactor samples may be subject to negative artifacts due to loss of semi-volatiles at the low operating pressure and to bouncing, while HIVOL samples on quartz filters may be affected by positive artifacts[38].

Sampling was allowed only when the samplers were upwind the ship exhaust with a relative wind speed threshold of 5 m s^{-1}. Due to the necessity of collecting sufficient amounts of samples for detailed chemical analyses, sampling time was of the order of ~50 h for each sample. Samples were stored at –20 °C until the chemical analyses. One field blank per sample was collected during the cruise and the concentrations were corrected for the blank values, which resulted negligible for amines and oxalate. A carbon-to-mass conversion factor of 2 was used to estimate the WSOM from organic

carbon measurements. This value is in line with state-of-the-art marine organic aerosol measurements[39]. The non-sea-salt fraction of aerosol chemical components was derived based on the standard seawater chemical composition using Na^+ as the sea-salt tracer.

Aerosol online measurements.

The online instruments[34] were kept inside the bow of the ship, sampling was done with an purposely designed inlet, 9m in length followed by a cyclon with a cut-off of approximately 5um at a flow rate of 5 L min−1. All downstream online instruments were isokinetically subsampling from it and dried to below 40% relative humidity. The ATOFMS (model 3800-100, TSI, Inc.) allowed collection of mass spectra (both positive and negative) of single particles roughly between 500 and 1500 nm. The ATOFMS mass spectra were imported into Yet Another ATOFMS Data Analyzer (YAADA), and adaptive resonance theory neural network, ART-2a (learning rate 0.05, vigilance factor 0.85, and 20 iterations) was run[40]. The size resolved non-refractory chemical composition of submicron aerosol particles was measured with an Aerodyne High Resolution Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne, Billerica, MA)[41], hereafter indicated as AMS.

Bioregion classification

We collected aerosol data in the areas of the Antarctic Peninsula, South Orkney, and South Georgia Islands. We ran 117 air mass back trajectories (6h resolution, 42 days) and classified them into two broad source regions according to the characteristics of the overflown areas: “open ocean” (OO) and “sea ice” (SI). Out of the 6 samples analyzed, PE24, PE28 and PE06 were assigned to OO, and PE09, PE13 and PE18 were assigned to SI[35]. A detailed characterization of the air mass history, ground type contribution and water soluble organic features of each sample have been presented in Decesari et al.[42], where a map of the sampling locations can also be found. As we have previously showed[35,36,42], SI samples are influenced by aerosol

precursors emitted by the peculiar microbiota thriving in sea ice and sea ice-influenced waters, while OO samples are representative of the open Ocean biota. This results in distinct chemical compositions, which we will investigate in detail below.

3 Results

3.1 Overall aerosol chemical composition

Six shipborne aerosol filters are reported in this study. Figure SI1 and SI2 show the remarkable similarity among the sub-micron OO and SI samples (within the same group).

The average concentrations of the PM_1 aerosol water soluble fraction in the OO and SI samples are shown in Figure 1 and reported in Tables SI1. Sea salt dominates the PM_1 water soluble fraction in OO samples, with average concentrations of 2.39±2.36 µg m^{-3} (n=3; min, max: 0.79-5.1 µg m^{-3}) representing on average 87% of the mass. In the SI region, sea salt concentrations were ten fold lower, average of 0.198±0.056 µg m^{-3} (n=3; min, max: 0.143-0.254 µg m^{-3}), representing on average only 25% of the aerosol water soluble mass. By contrast, in the SI region the dominant species was $nssSO_4^{2-}$, with average concentrations of 0.295±0.061 µg m^{-3} (n=3; min, max: 0.228-0.348 µg m^{-3}) representing on average 37% of the water soluble fraction. This was the third lowest species in OO air masses, with average concentrations of 0.099±0.014 µg m^{-3} (n=3; min, max: 0.087-0.114 µg m^{-3}) representing on average only 4% of the aerosol water soluble mass.

As expected, MSA exhibited similar patterns to $nssSO_4^{2-}$. Higher concentrations were seen from the SI region, with average concentrations of 0.088±0.032 µg m^{-3} (n=3; min, max: 0.061-0.123µg m^{-3}) representing on average 11% of the water soluble fraction. High MSA concentrations over the Weddell Sea were previously attributed to emissions from the marginale ice zone biota[35,36,42] in agreement with the global MSA climatology[43]. In the OO region, average concentration was 0.043±0.012 µg m^{-3} (n=3; min, max: 0.036-0.057µg m^{-3}), representing on average 2% of the aerosol water soluble mass.

293 Minor concentrations of ammonium were found for the SI region, average of
294 0.068±0.017 μg m^{-3} (n=3; min, max: 0.055-0.087 μg m^{-3}), which represented
295 on average 9% of the water soluble fraction (n=3; min, max: 7-10%). These
296 were much lower in the OO region, as previously discussed in Dall´Osto et al.
297 (2017)[35]: average of 0.027±0.005 μg m^{-3} (n=3; min, max: 0.022-0.031 μg m^{-3}),
298 representing on average 2% of the water soluble mass (n=3; min, max: 0-3%).
299 Low ammonium concentrations made the submicron aerosol particles rather
300 acidic as in many other remote regions.
301 A key observation was that non-MSA organic compounds (see Methods)
302 represented an important aerosol component. The average non-MSA WSOM
303 concentration from the BI5 was 0.083±0.022 μg m^{-3} (n=3; min, max: 0.058-
304 0.10 μg m^{-3}) and 0.17±0.02 (n=3; min, max: 0.15-0.19 μg m^{-3}) in SI and OO
305 regions, respectively, while from the HIVOL samplers concentrations as high
306 as 0.19±0.05 (SI, n=3; min, max: 0.21-0.22 μg m^{-3}) and 0.21±0.05 (OO, n=3;
307 min, max: 0.17-0.26 μg m^{-3}) were obtained. Consequently, non-MSA-WSOM
308 accounted for 11% (n = 3; min, max: 9-16%) and 6% (n=3; min, max: 3-13%)
309 of total sub-micrometer water soluble mass in SI and OO regions, respectively,
310 when considering the BI5 results, and 22% (n=3; min, max; 18-27%) and 8%
311 (n=3; min, max: 4-15%), using the HIVOL data. Although the concentration
312 differences between the two datasets are notable (particularly for the Si
313 region), the non-MSA WSOM was the third most abundant component in SI,
314 and the second in OO, independent of the sampling technique.
315 Parallel AMS measurements performed during the cruise[27,35] were averaged
316 over the filter sampling times in order to provide a further evaluation of the
317 organic aerosol concentration over the two regions. An excellent agreement
318 was observed for MSA concentrations between AMS and BI5 samples (n = 6;
319 slope: 1.04; R: 0.66), while more significant differences were reported for the
320 total organics. Comparing the non-MSA organic aerosol concentration by
321 AMS with the non-MSA-WSOM measured on the BI5 samples, we got a slope
322 of 0.53 (n=6; R: 0.74, OM/OC = 2, see Par. 2.), indicating at least a factor two
323 overestimation of the organic fraction on the BI5 samples with respect to AMS
324 measurements. The overestimation was obviously higher if we compare the
325 AMS with the HIVOL samples (n=6; slope: 0.33, R: 0.56). Accordingly, if we
326 assume that all the organics measured by the AMS contribute to the WSOM

measured offline, a reduction of the average non-MSA WSOM contribution over the SI region is obtained, from the range 11-22% by offline measurements, down to 8%.

This discrepancy between the sub-micrometre non-MSA organic aerosol quantification by offline and online techniques is consistent with the existing literature. Virkkula et al. (2006)[29] reported a high contribution of non-MSA organics in Antarctic samples (~50% of PM_1 mass) by offline chemical analyses, while Zorn et al. (2008)[30] reported a negligible non-MSA organic contribution in sub-micrometre Antarctic aerosol through online AMS measurements. Although the existing measurements are too scarce to derive any sound conclusion, the evidenced tendency is worthy of investigation and proves the necessity for further organic aerosol characterization studies over Antarctica.

Considering the PM_{10} size range (Table SI2), sea salt dominated in both OO and SI samples, with average concentrations of 7.93±3.99 µg m-3 (n=3; min, max: 5.20-12.51 µg m-3) and 2.17±0.83 µg m-3 (n=3; min, max: 1.22-2.77 µg m-3) respectively, representing on average 94 and 78% of the aerosol water soluble mass.

Whilst the speciation of individual organic compounds was treated in a separate paper[42], the next section discusses two chemicals of interest as markers of secondary aerosol sources.

3.2 Alkylamine and oxalate measurements

In this Section, we present the atmospheric concentrations of selected secondary aerosol formation process tracers: alkyl amines and oxalic acid. The former have been associated to secondary aerosol formation based on acid-base reactions[37], including new particle formation[35]. The latter was identified as one of the most abundant single oxygenated compounds in many marine aerosol studies at different latitudes[44-48]. All the tracers were characterized by high quantification precision even at the low aerosol concentrations typical of Antarctica.

3.2.1. Aerosol size-resolved mass concentrations

Figure 2 shows that alkylamines were 5 times higher (t-test, significantly different, $p<0.01$) in aerosols from the SI region (n=3; 9.1±4.5 ng m^{-3}) than from the OO regions (n=3; 1.8±1.1 ng m^{-3}). In a previous paper[35] we had reported alkylamines only in PM_1 aerosols, here we present the PM_{10} concentrations. Contrasting with the amines, oxalate concentrations were 9 times higher (t-test, significantly different, $p<0.05$) in OO (n=3; 1.98±1.44 ng m^{-3}) than in the SI (n=3; 0.20±0.09 ng m^{-3}) region (Figure 2a).

Concerning their size distributions, clear differences were seen (Figure 2b). Whilst amines occurred mainly in the fine mode, the oxalate size distribution was different between regions. In SI samples, the sub-micron oxalate concentration was below detection limit in two samples out of three, while non-negligible concentrations were always detected in the 1.2-3.5 µm size range, resulting in the coarse-mode dominated distribution of Figure 2. In OO samples, the oxalate distribution peaked in fine particles (0.42-1.2µm). Very few measurements of oxalate in the SO exist. Xu et al (2013)[49] reported low concentrations, 3.8 ± 3.8 ngm^{-3} (range: 0 to 9.1), over the SO, and 2.2 ± 1.5 ngm^{-3} (range: 0 to 4.6) over coastal Antarctica. These results were in line with data collected in Aboa Station[29] and in the region of >50°S,130°E–150°E[49]. In this latter study, oxalate size distributions over the SO were bimodal, with peak at <0.49 µm and 0.95–1.5 µm, whereas over coastal East Antarctica oxalate concentration peaked at 0.56–1.8 µm.

3.2.2 Mixing state of oxalate containing particles

In this section we investigate the aerosol mixing state, broadly defined as the distribution of the chemical component within the aerosol population. In Dall´Osto et al., (2019)[36] we compared ATOFMS spectra of particles generated by bubbling melted sea ice with those produced by bubbling surface sea water. Here, we only consider the mass spectra of ambient aerosols. We expanded the analysis by running ART-2a on mass spectra containing a peak (m/z -89, $[(C_2O_4H)H]^-$, approximately 1,300 single particle mass spectra) representative of oxalic acid[51]. The small peak at *m/z* 179 is attributed to the oxalic acid dimer $[(C_2O_4H)_2H]^-$, which is commonly observed

in the spectra of oxalic acid standards. Unfortunately, the temporal trends of the ATOFMS particles detected did not allow differentiation of the SI and OO regions due to low counts and poor statistic. Nevertheless - broadly - three particle types were seen:

(a) *ATOFMS Na-OX* (about a quarter of the total mass spectra identified): Sea spray particles containing organic carbon including oxalic acid. Peaks at *m/z* 23 (Na^+), *m/z* 24 (Mg^{++}), *m/z* 39 (K^+) (positive mass spectra) and *m/z* -16 $[O]^-$, -17 $[OH]^-$, -35 (Cl^-), -46 $[Na_2]^-$, 62 $[Na_2O]^+$, and 63 $[Na_2OH]^+$ consistent with sea salt in sea spray (Figure 3a). The negative ion mass spectrum shows prominent peaks at *m/z* -26 $[CN]^-$ and *m/z* -42 $[CNO]^-$, indicating that all particle types presented were internally mixed with organo-nitrogen species. In the negative spectra, putative peaks of oxalate (m/z -89) are seen also with larger mass peaks, likely due to unidentified large chemical compounds. This particle type likely corresponds to degraded primary marine organic aerosols internally mixed with sea spray.

(b) ATOFMS biogenic-OX (about a quarter of the total mass spectra identified). Peaks due to Na^+ (m/z 23), K^+ (m/z 39) and phosphate (*m/z* -63 $[PO_2]^-$ and *m/z* -79 $[PO_3]^-$) characterize this particle type (Figure 3b). The ATOFMS has already proved to be a good tool to separate dust (mainly Ca-rich or Al-Si rich) and biological particles[52,53]. Briefly, biological mass spectral signatures can be differentiated from crustal dust on the basis of abundant organic and phosphorus ions, as well as a lack of key dust markers, such as aluminium and silicates. Additionally to the peak of oxalate (m/z -89) a strong peak at *m/z* 114 can be seen, previously demonstrated to be preserved in particles that contain amine salts and that have undergone photo-oxidation[54,55]. This particle type may correspond to biogenic material in general, but not enough mass spectra (about a dozen) were collected to obtain more information.

(c) ATOFMS SOA-OX (about half of the total mass spectra identified). This particle type was seen associated with secondary organic components in both positive and negative mass spectra (Figure 3c). Beside the previously described peaks associated with amines and oxalic acid, a unique peak at m/z 59, ($[N(CH_3)_3]^+$) is attributed to trimethylamine (TMA). Previous studies showed that cloud/fog processing can increase gas-to-particle partitioning of TMA[56], and potentially form non-salt organic aerosols[57]. The unique mass

series of m/z –81, –97 and m/z –111 is due to species $[HSO_3]^-$, $[HSO_4]^-$ and $[HOCH_2SO_3]^-$. ATOFMS particle spectra of this type have previously been shown to arise from hydroxymethanesulphonate in both laboratory studies and field experiments[58,59]. Minor peaks can also be seen at m=z 58, 74, and 128, which were previously attributed to alkyl ammonium nitrate salt particles formed by reaction of nitric acid and amines[60].

Our ATOFMS mixing state results confirm that a complex mixture of oxalate containinig particles contributes to the chemical composition of Antarctic aerosol, including primary Na-containing aerosols and non-MSA marine secondary organic particles.

4 Discussion

WSOM was found present in non-negligible concentration during our study, although with significant uncertainty due to its dependence on the measurement technique. Even though alkylamines and oxalic acid altogether represented a minor fraction of the total water soluble organic mass (see Tables SI1 and SI2), these compounds can be used as proxies to discuss processes and sources of secondary organic aerosols in the study area.

4.1 Multiple processes driving the observed aerosols patterns

4.1.1 Amines

Aliphatic amines are known important organic compounds in the marine atmosphere. An important contribution of biogenic amines to marine organic aerosol was first reported by Facchini et al. (2008)[37], pointing to a secondary formation pathway for alkylammonium salts. Indeed, in our study the size distribution peaked in the accumulation mode and exhibited a good correlation with $nssSO_4^{2-}$, NH_4^+ and MSA, which is indicative of an acid-base reaction of gaseous amines with sulfuric or sulfonate acids. In our previous study[35] we demonstrated that the microbiota of sea ice and the sea ice-influenced ocean

462 is a source of atmospheric organic nitrogen, including low molecular weight
463 alkylamines. In a follow up study[36], thermodynamic equilibrium calculations
464 suggested that the alkylamine shift from seawater to atmospheric secondary
465 aerosol is driven by the very low pH expected in fine and ultrafine particles.
466 Furthermore, a detailed analysis of single particle mass spectra of sea-spray
467 (primary) aerosols artificially generated by bubbling seawater samples
468 showed that in ambient aerosol the fingerprint of primary alkylamine-rich
469 particles represents only a minor percentage (11-25%). Here we report an in-
470 depth analysis of total aerosol mass as well as the size distribution of
471 alkylamines, which show that these compounds occur in different aerosol
472 modes from oxalic acid.
473 It should be kept in mind that ammonia and organic nitrogen in general -
474 including alkylamines - may also be important contributors to new particle
475 formation and growth in the SO. Indeed, using an unprecedented suite of
476 instruments, Jokinen et al. (2018)[61] showed that ion-induced nucleation of
477 sulfuric acid and ammonia, followed by sulfuric acid–driven growth, is the
478 predominant mechanism for new particle formation and growth in eastern
479 Antarctica a few hundred kilometers from the coast[61]. Dall´Osto et al (2017)[35]
480 suggested that the microbiota of sea ice and sea ice-influenced ocean were a
481 significant source of atmospheric nucleating particles (size of 1-3nm). It must
482 be noted, though, that new particle formation and growth is a key process that
483 governs particle number concentrations but does not play an important role in
484 governing aerosol mass.
485
486 **4.1.2 Oxalate**
487
488 Our study supports the existence of a natural source of oxalic acid to the
489 marine atmosphere[62,63]. Previous studies[44,62,63, 64, 65] showed that oxalate was
490 distributed along a wide aerosol size range, including the sub-micrometer and
491 a super-micrometer mode. This suggests that oxalate of marine origin must be
492 produced through a combination of processes. These may include:

493 (1) Cloud processing - from oxidation of gaseous glyoxal and mediated by
494 particulate water, occurring over remote oceanic regions, which may
495 contribute oxalate to submicrometer aerosols[44,45, 46, 66, 67].
496
497 (2) Photochemical degradation of fatty acids of biological origin at the ocean's
498 surface, giving rise to oxalic acid and other LMW dicarboxylic acids; these
499 may be transferred with sea-spray particles to the atmosphere and
500 subsequently degraded[46, 48, 65, 68].
501
502 (3) Neutralization of gaseous oxalic acid (which may originate from points (1)
503 or (2)) onto sea-salt particles[44].
504
505 The broad size distributions of oxalate in the OO region strongly points to
506 multiple atmospheric processes, in agreement with previous open sea
507 observations[6]. By contrast, the oxalate size distribution found in the SI region -
508 centered in the coarse mode at 1.2-3.5 µm – could be due to the degradation
509 of primary biogenic organic matter, emitted with sea spray[62,63]. According to
510 this hypothesis, the limited importance of sea-spray emissions over the
511 Weddell Sea[35,36] may explain the lower oxalate concentrations observed in SI
512 samples with respect to OO ones. On the other hand, in Dall'Osto et al.
513 (2019)[36] we have shown that sub-micron aerosol over the Weddell Sea is
514 extremely acidic, because of the persistent fine-mode sulfate and
515 methanesulfonic acid particles and the low liquid water content (LWC) (pH_SI
516 = 1.4; pH_OO = 6.6). The coarse size distribution of oxalate in this region may,
517 therefore, be driven by the fine aerosol acidity, which would favour the
518 accumulation of oxalate in the more alkaline coarse mode[69]. This is the
519 simplest explanation, which probably accounts for much of the best known
520 mechanism pattern in the oxalic acid size distribution.
521 It is also possible that alternative pathways exist, including cloud and fog
522 processing, as discussed in point (1) above. An example of a real time event
523 of this process was recorded in the evening of the 14th January 2014 and it is
524 presented in Figure SI4. The two aerosol size distribution modes indicative of
525 cloud processing[70] can be observed during the event. This event occurred in

526 the marginal sea ice region, the research vessel was about 75Km from the
527 closest coast of the little island of Coronation (South Orkneys). Figure SI5
528 shows that all air masses were travelling over open ocean and not terrestrial
529 zones before arriving at the ship. Furthermore, the case study was seen in air
530 masses that were the most affected by sea ice and the marginal sea ice zone
531 (Fig. SI5). A clear growth of the smaller mode from 38nm to 43nm was seen
532 over five hours (1 nm h^{-1}; not shown), in concomitance with an increase of
533 Relative Humidity due to foggy-cloudy conditions. By contrast, the decrease of
534 the larger mode (from 105 nm to 87 nm) was likely due to the higher activation
535 of large aerosol due to higher RH. Immediately after the onset of fog, the
536 number of ATOFMS counts attributed to the SOA-OX particle type increased.
537 After the event, the two size modes returned to about 38-40 nm and 181-190
538 nm. The latter mode was likely due to cloud processing (Hoppel mode[70]),
539 which transforms organic and inorganic compounds and shifts the size
540 distribution to large accumulation mode sizes. After about 4-7am on the 15th
541 January 2015 air masses changed, shifting towards West Pacific air masses,
542 hence different aerosols were sampled and the event track was lost.
543 Recently, Kim et al., (2019)[71] demonstrated that aqueous reactions in
544 atmospheric droplets can significantly modify aerosol composition and
545 contribute to the formation of oxygenated and nitrogen-containing organic
546 compounds in atmospheric aerosol particles. Our study shows that chemical
547 reactions involving organic compounds of biogenic origin (acid-base
548 neutralization and oxidation reactions) - likely related to marginal sea ice
549 zones - are also occurring in the Antarctic region, and aerosol chemical
550 composition may be more complex than solely sulfate and sea spray.
551
552 **4.2 Marine vs terrestrial inputs of ammonia, amines and organic aerosol**
553
554 According to our previous studies[35,36], elevated alkylamine concentrations
555 originate from melted sea ice and sea-ice-influenced waters. These could
556 result from degradation of quaternary amine osmolytes, which we also found
557 in sympagic plankton. Regarding oxalate, the higher abundance in OO
558 samples suggests that this aerosol component is less related to the coastal
559 and marginal sea-ice zone.

An important open question for Antarctic aerosol is the relative role of marine versus terrestrial sources of organic matter (including organic nitrogen) and ammonia, whose answer is obscured by the scarcity of existing measurements. Recently, Liu et al (2018)[34] showed that atmospheric aerosol natural organic matter (OM) from a coastal location was 150 times higher in summer than in winter. Natural sources that included marine sea spray and seabird emissions contributed 56% OM in summer but only 3% in winter. The "marine source" was identified by high hydroxyl group fractions, and the "seabird source" was related to ammonium and an organic nitrogen peak associated with coastal penguin emissions[34]. In Bird Island, South Georgia, Schmale et al. (2013)[33] also showed strong influence of sea bird colonies. Legrand et al. (2012)[72] reported oxalate enrichment in aerosols at Dumont d'Urville Station, which was associated with the high levels of gaseous ammonia in the atmosphere. It was suggested that seabirds and mammals in coastal Antarctica could be sources of aerosol oxalate. This idea had also been discussed in Legrand et al. (1998)[61], where ornithogenic soil was proposed to be a source of oxalate in aerosols. Therefore, oxalate would be produced and released together with ammonia upon bacterial decomposition of uric acid. However, it was also stressed that the relationship between gaseous nitrogen (or carbon)-derived species and emitted oxalate aerosol was likely a complex one[73-74]. Legrand et al. (1998)[32] and Jourdain and Legrand (2002)[675] proposed nssK^+ and nssCa^{2+} as tracers for ornithogenic soil (defined as guano-enriched soil) emissions. Based on the proposed metrics, we can exclude any significant contribution from bird colony emissions in SI and, more obviously OO, samples. In fact, the K^+/Cl^- weight ratio in Si and OO samples is 0.021±0.003 and 0.020±0.002, respectively, much closer to the seawater value (0.021) than to the proposed values for ornithogenic soils (0.23-1.4). Similarly, the Ca^{2+}/C^{l-} weight ratio is 0.026±0.002 and 0.026±0.0003, against a seawater reference value of 0.021 and an ornithogenic soil value of 0.045. Finally, the formula for calculating the amount of potassium related to ornithogenic soil emissions (Kor), proposed by Jourdain and Legrand (2002)[75], yielded negative values in both SI and OO samples, demonstrating a tendency for K^+ depletion and certainly not an enrichment.

The results presented in this study, together with our previous works from the same sampling cruise[35,36,42] show that alkylamines and oxalic acid have different spatially located sources in the investigated area, with the former being more related to sympagic emissions connected with sea-ice melting and sea-ice influenced waters, and the latter being more related to pelagic emissions. This suggests that aerosol chemical composition, and likely physical properties, is strictly related to the biological environment characterizing the source region[35,36,42]. Aerosol samples reported in this study showed no major relation with seabird emissions, even though this does not exclude that this source may be significant in other Antarctic coastal environments (eco-regions).

4.3 Considerations under a changing climate perspective

The Antarctic region possesses a substantial spatial heterogeneity across marine, terrestrial and freshwater biomes, with productivity and biodiversity patchiness superimposed on strong environmental gradients[76] .Warming climate is posing one of the greatest threats to the Antarctic environment. The Antarctic Peninsula has experienced one of the most rapid temperature rises in the Southern Hemisphere[77]. Antarctic terrestrial productivity and biodiversity occurs almost exclusively in ice-free areas that cover less than 1% of the continent, although these could increase under a strongest forcing scenario[77,78]. Changes in the Antarctic environment will feed back to climate by biosphere and cryosphere exchanges with the atmosphere. Antarctica harbors extreme physical gradients such as those of incident solar radiation, UV intensity, ice cover, ocean circulation and temperature, which change over time as a consequence of global warming. The impacts of these changes on marine and terrestrial life through nutrient availability, ecophysiological adaptations, duration of the productivity and breeding seasons, migrations and location of refugia will affect biogenic emissions to the atmosphere, aerosol formation and aerosol-cloud interactions. Also physicochemical transformations of organic matter, as through exposure of snow and the sea surface microlayer to solar radiation[79] will impact the emission of climate-active substances to the atmosphere. Future interdisciplinary studies using

emerging chemical and statistical analytical techniques are required to tease out processes across spatial gradients of key environmental factors.

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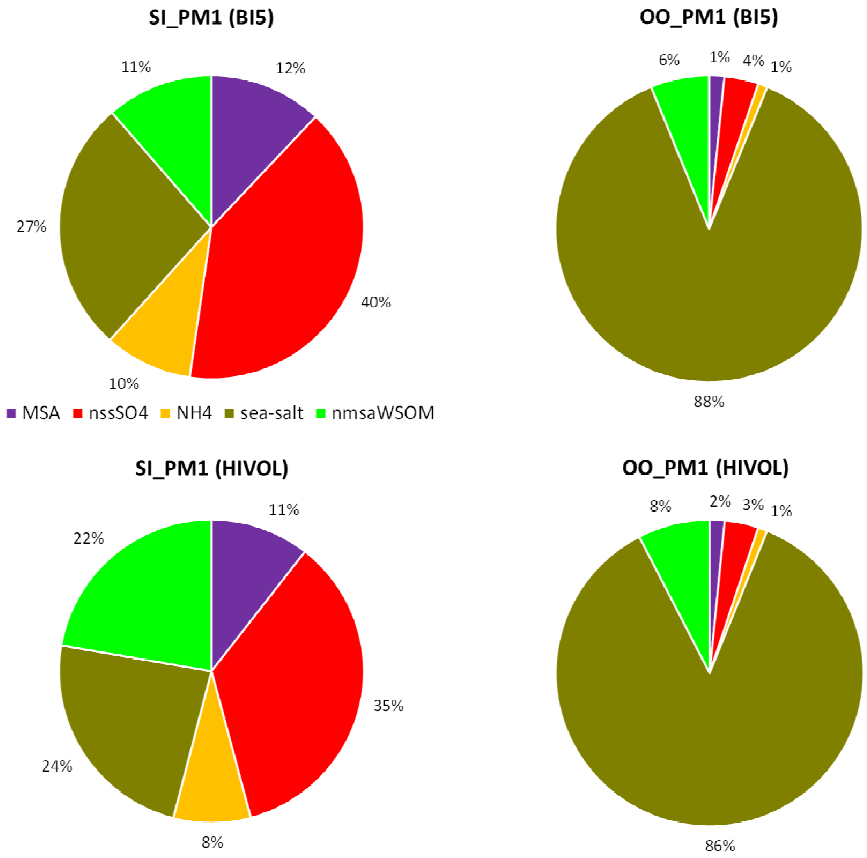


Figure 1. Composition of PM_1 aerosol water soluble fraction in the sea ice influenced region (SI) versus open ocean (OO). The "BI5" pies refer to measurements performed on Berner impactor, while the "HIVOL" pies refers to the WSOM measured on the high volume samples; nmsaWSOM stands for non-MSA-WSOM.

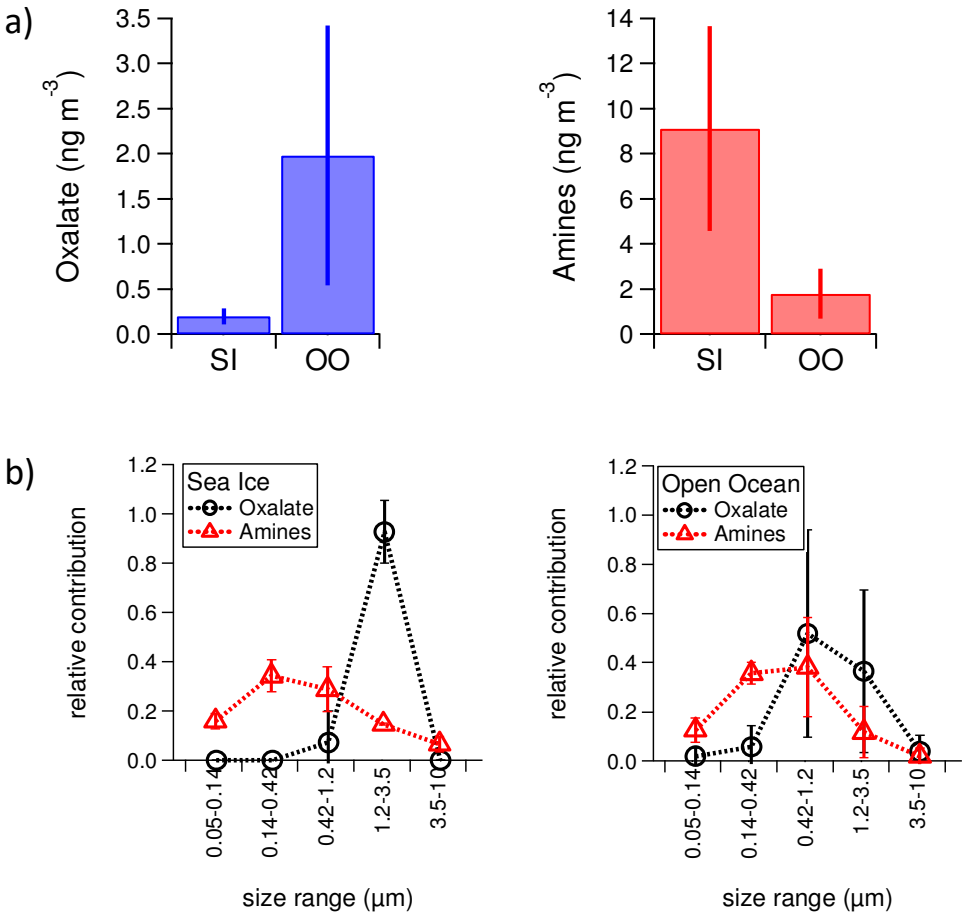
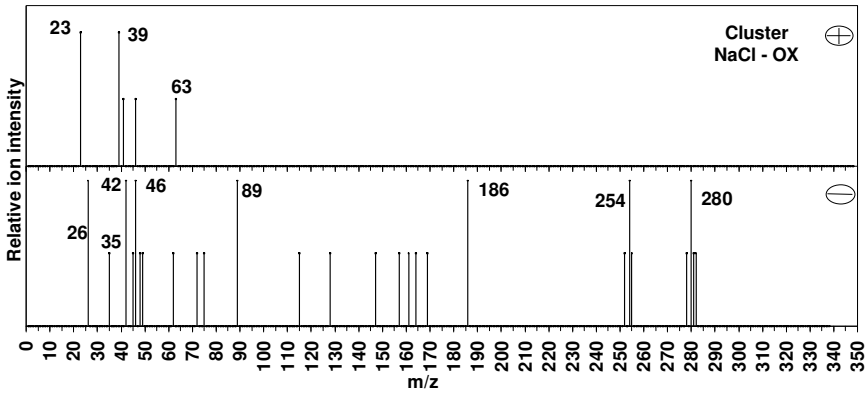
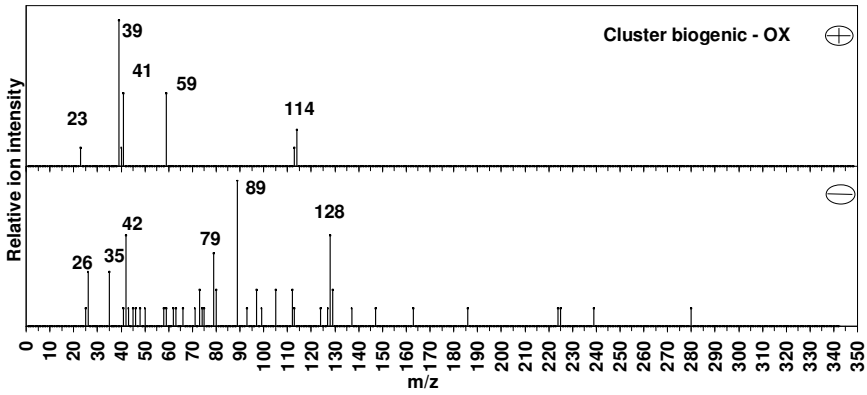


Figure 2. (a) PM_{10} concentrations of oxalate and amines in SI and OO samples (average and standard deviation). (b) Normalized size distributions of oxalate and amines for the 2 regions.



(a)



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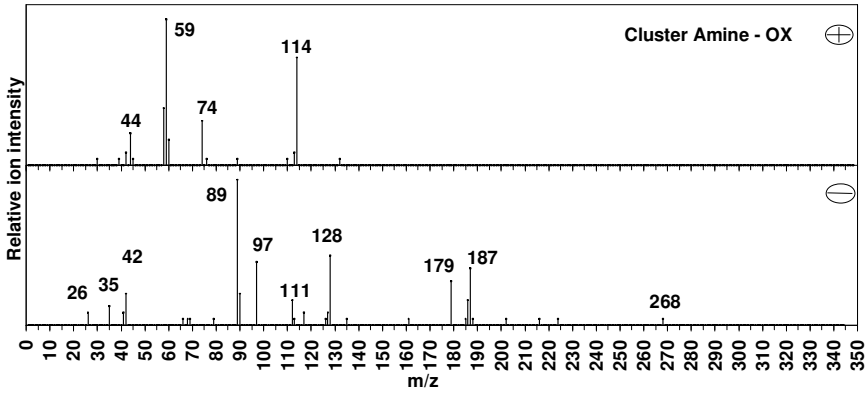

(c)

Figure 3 Average Art-2a positive and negative mass spectra for (a)ATOFMS oxalate internally mixed with sea spray, (b) ATOFMS oxalate in biogenic particles and (c) ATOFMS oxalate in secondary organic aerosols