Simultaneous organic aerosol source apportionment at two Antarctic sites reveals large-scale and eco-region specific components

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Abstract. Antarctica and the Southern Ocean are the most pristine areas of the globe and represent ideal places to investigate aerosol-climate interactions in an unperturbed atmosphere. In this study, we present PM1 (Particulate Matter < 1μm) source apportionment for two sample sets collected in parallel at two British Antarctic Survey (BAS) stations, namely Signy and Halley, during the austral summer 2018-2019. We find that Water Soluble Organic Matter (WSOM) is a major aerosol

20 component at both sites (average 25-33%). Remarkable differences between pelagic (open ocean) and sympagic (influenced by sea ice) air mass histories and related aerosol sources are found. The application of non-negative factor analysis techniques to H-NMR spectra of the samples allows the identification of five Organic Aerosol (OA) sources: two primary (POA) types, two secondary (SOA) types, and a fifth component of unclear origin possibly associated with the atmospheric ageing of primary emissions and dominating at Halley. Overall, the concentrations of primary and secondary organic aerosols are prevalently

25 dictated by the emissions in sympagic and pelagic marine regions, with atmospheric circulation causing to establish marked latitudinal gradients only for some of such aerosol components. Our results strongly indicate that various sources and aerosols processes are controlling the Antarctic aerosol population, with the emissions from sympagic and pelagic ecosystems affecting the variability of submicron aerosol composition both in maritime areas as in inner Antarctic regions.

1 Introduction

30 The Southern Ocean (SO) and Antarctica are considered a window to the preindustrial atmospheric condition and processes (Cavalieri et al., 1999; Arrigo et al., 2010; Carslaw et al., 2013; Arrigo et al., 2015; Hamilton et al., 2015) which impact the climate of the entire Southern hemisphere. During winter, a layer of sea ice is formed over the SO, extending up to

approximately 19 x 106 km^2, reducing by about 80% (4 x106 km^2) in the summer (Cavalieri et al., 1999). Climate models have large uncertainties in simulating clouds, aerosols and air-sea exchanges along with their effects on Earth's albedo in this area

35 of the globe (Carslaw et al., 2013). One of the main reasons of this uncertainty is that the aerosol source apportionment is poorly understood. The much diverse ecosystems stretching from the SO, the sub-Antarctic marine areas to the Antarctic coastal areas and ice shelves are schematically reduced to two large natural sources governing the aerosol populations: sea spray (primary, mostly composed of sea salt) and non-sea salt sulfate (nssSO$_4^{2-}$; secondary). The former - with mass size distributions peaking in the supermicron range - is produced by oceanic waves breaking. By contrast, the latter - secondary in

40 type and submicron in size - is obtained by atmospheric oxidation of dimethylsulfide (DMS), a trace gas produced by marine phytoplankton. However, a recent intensification in Antarctic aerosol measurements field campaigns is revealing that aerosol chemistry in the Southern high latitudes can be much more complex. For example, blowing snow over pack ice has been suggested to contribute sea salt aerosol in similar amounts to breaking waves (Legrand et al., 2017a; Giordano et al., 2018, Frey et al., 2020).

45 As regards of secondary (gas-to-particle formation) aerosols, the DMS-derived nssSO$_4^{2-}$ (Charlson et al., 1987; Vallina et al., 2007) is normally accompanied by organic sulfur species, the best known of which is methanesulfonic acid (MSA) (Rankin and Wolff, 2003; Legrand et al., 2017b). The role of aerosol sulfur species in regulating cloud condensation nuclei (CCN) concentrations in the marine environment is being challenged by a much larger varieties of poorly known ocean-emitted aerosol components (Quinn and Bates, 2011). The scientific question about the chemical nature and source identification of the

50 aerosols in the SO intercepts therefore the broader debate about the relative importance of secondary aerosols produced from biogenic sulfur versus primary sea-spray aerosols in regulating cloudiness in the marine environment.

Pioneering measurements of organic carbon (OC) in size-segregated aerosol (Virkkula et al., 2006) showed that MSA represented only a few percentages of the substantial amount of OC observed in the submicron fraction. Recent Antarctic measurements also suggest that the importance of organic components may have been overlooked. Saliba et al. (2021) found

55 that the large organic fraction of particles <0.1 mm diameter may have important implications for CCN number concentrations and indirect radiative forcing over the SO. Recent measurements over the SO (43°S−70°S) and the Amundsen Sea (70°S−75°S) showed that Water Insoluble Organic Carbon (WIOC) accounted for 75% and 73% of aerosol total organic carbon in the two regions, respectively (Jung et al., 2020). In the Amundsen Sea, WIOC concentrations correlated with the biomass of a phytoplankton species (Phaeocystis antarctica) that produces extracellular polysaccharide mucus which can be ejected by sea

60 spray into the aerosol.

Intensified observations using advanced aerosol instrumentation onboard research ships have highlighted a certain dependence of aerosol concentrations and composition on air mass type and atmospheric circulation patterns across latitudes. Humphries et al., (2021) identified three main aerosol source areas in the SO: northern (40-45 S), mid-latitude (45-65 S) and Southern sector (65-70 S), with different mixture of continental and anthropogenic, primary and secondary aerosols depending on the

65 studied region. During the same period of study, Sanchez et al (2021) found a weak gradient in CCN at 0.3% supersaturation

with increasing CCN concentrations to the south between 44° to 62.1° S, which may be caused by aerosol precursors from Antarctic coastal biological emissions.

At the same time, the study of the variability of aerosol sources in sub-Antarctic and Antarctic coastal areas has added complexity to the representation of aerosol concentrations based on latitudinal changes. Indeed, emerging recent literature

70　shows that within the polar Antarctic air masses (<60 S) aerosol populations of variable chemical composition can be observed. Lachlan-Cope et al. (2020) - by analyzing simultaneous aerosol size distributions measurements at three sites - showed that the dynamics of aerosol number concentrations and distributions are more complex than the simple sulfate–sea-spray binary combination, and it is likely that an array of additional chemical components and processes drive the aerosol population. Likewise, our previous results indicate that not only the marine productivity but also the biogenic taxa and ecophysiological

75　state of the microbiota affect the production of aerosol precursors in seawater (Dall´Osto et al., 2017; 2019).

Rinaldi et al. (2020) reported that non-methanesulfonic acid Water-Soluble Organic Matter (WSOM) represents 6−8% and 11−22% of the aerosol PM_1 mass originated in open ocean (OO) and sea ice (SI) regions, respectively. This study showed that the Weddell sea areas covered by open or consolidated packed sea ice is a strong source of organic nitrogen in the aerosol. Organic nitrogen compounds should be considered when assessing secondary aerosol formation processes in Antarctica beside

80　the known role played by sulfur aerosols (Brean et al., 2021). By means of chamber experiments simulating primary aerosol formation *on site*, we previously reported that the process of aerosolization enriches submicron primary marine particles with lipids and sugars while depleting them of amino acids. Overall, the potential impact of the sea ice (sympagic) planktonic ecosystem on aerosol composition were overlooked in past studies, and multiple eco-regions act as distinct aerosol sources around Antarctica (Decesari et al., 2020; Rinaldi et al., 2020).Decesari et al. (2020) found at least three main bioregions sources

85　of water-soluble organic carbon (WSOC): (1) open Southern Ocean pelagic environments dominated by primary Sea-Spray Aerosol (SSA) mainly constituted of lipids and polyols, (2) sympagic areas in the Weddell Sea, with secondary sulphur and nitrogen organic compounds and (3) terrestrial land vegetation coastal areas, traced by sucrose in the aerosol.

Here, we report atmospheric measurements during a three-months period (December 2018 - March 2019) simultaneously

90　carried out at two Antarctic research stations (Signy and Halley). To our knowledge, this is the first study attempting aerosol characterization and source apportionment at the synoptic scale by means of parallel measurements at two distant Antarctic stations. We stress that organic water-soluble aerosol components contribute to the aerosol population and to its most hygroscopic fraction, hence we claim their overlooked climate relevant importance. It is becoming clear that in order to address important research questions in the polar regions it is essential measuring at multiple stations with a strong international

95　scientific cooperation (Dall´Osto et al., 2019; Schmale et al., 2021).

2 Material and methods

2.1 Measurement field campaigns

The measurements reported here were made in the framework of PI-ICE (Polar Interactions: Impact on the Climate and
100 Ecology) study in the period December 2018 - March 2019 at the British Antarctic Survey's stations of Halley and Signy. BAS
Halley VI station (75°36'0" S, 26°11'0" W) is located in coastal Antarctica, on the floating Brunt Ice Shelf about 20 km from
the coast of the Weddell Sea. A variety of measurements were made from the Clean Air Sector Laboratory (CASLab), which
is located about 1 km south-east of the station (Jones et al., 2008). BAS Signy station at Signy Island (60°43'0" S, 45°38'0"
W) is located in the South Orkney Islands (Maritime Antarctic) and is characterized by a cold oceanic climate, with mean
105 annual air temperature of 3.5 C and annual precipitation ranging from 350 to 700 mm, primarily as summer rain.
Two high volume samplers (MCV Barcelona Spain, equipped with Digitel PM_1 sampling inlet) at Signy and Halley collected
ambient aerosol particles with Dp<1 μm on pre-washed and pre-baked quartz fiber filters, at a controlled flow of 500 L min^{-1}.
Due to the necessity of collecting sufficient aerosol loading for detailed chemical analyses on the filters, the sampling time
was of the order of about 50 h for each sample. A total of 8 and 14 PM_1 samples were collected during the field study at Halley
110 and Signy stations, respectively. The samples were stored at about -20° C until extraction and chemical analyses.
Temporal periods are reported in the Supplementary Table S1 and Figure S1 while Figure 1 shows a map of the study area.

2.2 Air mass back trajectories analysis and source regions classification

Five-days back-trajectories arriving at a height of 30 m every 6 hours were calculated using HYSPLIT - (Hybrid Single-
115 Particle Lagrangian Integrated Trajectory v4, Draxler et al., 1998; Draxler et al., 2008) and monthly Global NOAA-
NCEP/NCAR pressure level reanalysis data archives. Using these, trajectory level plots were also calculated using the Openair
package (Carslaw and Ropkins 2012) exploiting the Concentration Weighted Trajectory (CWT) method.

2.3 Aerosol offline measurements and H-NMR analysis

120 The aerosol samples from both the sites were extracted with deionized ultrapure water (Milli-Q) in a mechanical shaker for 1
h and the water extracts were filtered on PTFE membranes (pore size: 0.45 μm) in order to remove suspended materials.
Extracts were analyzed by ion chromatography for the quantification of water-soluble inorganic ions, organic acids (acetate,
formate, methanesulphonate, oxalate) (Sandrini et al., 2016) and low molecular weight alkyl-amines (methyl-, ethyl-, dimethyl-
, diethyl- and trimethylamine) (Facchini et al., 2008a). An IonPac CS16 3 × 250 mm Dionex separation column with gradient
125 MSA elution and an IonPac AS11 2 × 250 mm Dionex separation column with gradient KOH elution were deployed for cations
and anions, respectively. The water-soluble organic carbon (WSOC) content was quantified using a TOC thermal combustion
analyzer (Shimadzu TOC-5000A).

Field blanks were collected at both sites and all the sample concentrations were corrected for the blanks, which resulted in negligible values. A carbon-to-mass conversion factor of 2 was used to estimate the WSOM from organic carbon
130   measurements, in the range of the values suggested for marine organic aerosols by Jung al. (2020).

Aliquots of the aerosol extracts were dried under vacuum and re-dissolved in deuterium oxide (D_2O) for organic functional group characterization by H-NMR spectroscopy (hereinafter also referred as NMR), as described in Decesari et al. (2000). The H-NMR spectra were acquired at 600MHz in a 5mm probe using a Varian Unity INOVA spectrometer, at the NMR facility of the Department of Industrial Chemistry (University of Bologna). Sodium 3-trimethylsilyl- (2,2,3,3-d4) propionate (TSP-d4)
135   was used as an internal standard by adding 50 μL of a 0.05% TSP-d4 (by weight) in D2O to the standard in the probe. To avoid the shifting of pH-sensitive signals, the extracts were buffered to pH~3 using a deuterated-formate/formic-acid ($DCOO^-$ =HCOOH) buffer prior to the analysis. The speciation of hydrogen atoms bound to carbon atoms can be provided by H-NMR spectroscopy in protic solvents. On the basis of the range of frequency shifts, the signals can be attributed to H-C containing specific functionalities (Decesari et al., 2000, 2007). The main functional groups identified include alkyls (H-C), i.e.
140   unsubstituted aliphatic groups/chains; aliphatic groups substituted with carbonyls or carboxyls (HC-C=O); aliphatic hydroxyls (HC-O), typical of a variety of possible compounds, like sugars, alcohols, ethers and esters; anomeric and vynilic groups (O-CH-O), and finally aromatic functionalities (H-Ar). Organic hydrogen concentrations directly measured by H-NMR were converted to organic carbon. Stoichiometric H/C ratios were specifically assigned to functional groups using the same rationale described in previous works (Decesari et al., 2007; Tagliavini et al., 2006). Although the sum of NMR functional group
145   concentrations approached total WSOC in many samples, the uncharacterized fraction was significant (on average 30 %). Possible reasons for the "unresolved carbon" are (1) the presence of carbon atoms not attached to protons, thus not-detectable to H-NMR, such as oxalates and compounds containing substituted quaternary carbon atoms or fully substituted aryls (Moretti et al., 2008), (2) the uncorrected estimations of stoichiometric H/C ratios used for the conversion of directed measured organic hydrogens into organic carbon, and (3) evaporative losses during the evaporation of the extract prior to the preparation of the
150   NMR tube.

Organic tracers were identified in the H-NMR spectra on the basis of their characteristic patterns of resonances and chemical shifts. Among such tracers, methane-sulfonic Acid (MSA) and the low-molecular-weight alkyl amines (Di- and Tri- Methyl Amines, DMA and TMA) were quantified. Speciation and quantification of these tracers by H-NMR were validated by comparison with the IC measurements showing excellent agreements between the two techniques (Figure S2).

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2.4 Factor analysis of H-NMR Spectra

The H-NMR spectra collected at both sites were analyzed by factor analysis techniques, following the method already described in previous publications (Decesari et al., 2011; Finessi et al., 2012; Paglione et al., 2014a, 2014b), to apportion major components of WSOC and attribute them to specific sources. The factor analysis methods used in this study include two
160   different algorithms: the "Positive matrix factorization" (PMF, Paatero et al, 1994), using the ME-2 solver (Paatero et al.,

1999), and the "multivariate curve resolution" (MCR), according to the classical alternating least-square approach (Jaumot et al., 2005; Tauler 1995). The factor analysis was applied to Signy and Halley spectral datasets merged together with two main purposes: i) to increase the number of samples (14+8=22) in order to improve the statistics; ii) to find and compare relative contributions of possible common components/sources of the aerosol between the two sites.

165 The solutions with up to eight factors were explored. A full examination of the outcomes of the NMR factor analysis is reported in the Supplementary (Section S2, Figure S3-S5), while in section 3.3 we focus on the five-factors solution, which is the most interpretable and shows a substantial agreement between the two algorithms. Interpretation of factors and their attribution to specific sources is based on an integrated approach including: the comparison between spectral profiles and a unique library of reference spectra (recorded during laboratory studies or in the field at near-source stations, Decesari et al., 2020); the

170 correlation of factors contributions with available chemical tracers (i.e., sea salt and other inorganic ions, MSA and amines); and the examination of backtrajectories and of the concentration-weighted trajectories (CWT) maps of each factor indicating their potential source areas.

Moreover, in order to specifically check the separation between primary and secondary aerosol sources, we applied the factor analysis adding to the ambient aerosol spectra also 16 H-NMR spectra of Sea-Spray Aerosol (SSA) generated in bubble

175 bursting tank experiments by local Antarctic sea-waters and melted sea-ice during the PI-ICE project, as described by Dall'Osto al. (2022). The results of this additional factor analysis (summarized as well in Supplementary Section S2) helped interpreting factors identified by ambient samples and attributing some of them to primary sources (POA) (Figure S4 and S5).

3 Results

180 The result section is divided in three main parts as following: in section 3.1 we discuss the bulk aerosol composition at Signy and the drivers of its variability; in section 3.2 we provide the same analysis for the data collected at Halley station and we discuss the differences between the two stations for the period of sampling overlap (42 days). Finally, in section 3.3 we discuss the WSOC source apportionment results based on the H-NMR spectra factor analysis. Samples collected at Signy are labelled as "S_x", whereas samples coming from Halley are labelled as "H_x".

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3.1 Main aerosol chemical components at Signy

The chemical composition of the fourteen PM_1 aerosol samples collected at Signy station is reported in Figure 2. On average, the concentrations of the PM_1 aerosol water-soluble fraction are small (1.55 ± 1.45 µg m^{-3} average ± standard deviation, n=14) but show a noticeable variability between samples (min=0.28 µg m^{-3} for S10, max=5.52 µg m^{-3} for S5). The major chemical

190 class contributing to the water-soluble PM_1 is sea salt (representing 55% of the total on average of the whole sampling period)

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followed by WSOM (27%) and non-sea salt sulfate (nss-SO4, 10%), leaving the rest to minor contributions of ammonium (3%), nitrate (2%) and other non-sea salt ions (i.e., nss-K, nss-Mg and nss-Ca, amounting to 3% in total).

The sampling period can be divided into two different sub-periods: the first part (samples S1-S5, corresponding to the period 10-28 Dec. 2018), is characterized by relatively high PM_1 concentrations (2.73 ± 1.95 µg m^{-3}), while the second (samples S6-

195 S14, spanning 28 Dec. 2018-15 Feb. 2019) shows lower concentrations on average (0.89 ± 0.37 µg m^{-3}). In regards to composition, the first period is characterized by a higher contribution of sea salt (contributing 64% to total water-soluble PM_1) with respect to the second period which exhibits a smaller sea salt content (43%) and an increased fraction of non-sea salt sulfate (21%). The contribution of WSOM shows lower variability between the two periods (30% and 25% of water-soluble PM_1 in the first and second part, respectively). Nevertheless, the inter-samples variability of the WSOM concentrations is large

200 (0.89 ± 0.37 µg m^{-3} on average, min=0.11 µg m^{-3} for S10, max=1.23 µg m^{-3} for S5). The main difference in WSOM at Signy between the two subperiods stands in the functional group composition, as characterized by H-NMR analyses (Figure 3). Specifically, the first sub-period (S1-S5) is enriched in alcoxy groups (H-C-O) (43±4% relative to 23±8% of total WSOC) and unsubstituted aliphatic chains (H-C) (30±5% relative to 16±5%) respect to the second subperiod (S6-S14). These H-NMR features have been previously associated - by comparing the analysis of tank-generated sea-spray particles - to sugars, polyols

205 (e.g., glucose, sucrose, glycerol, etc.) and lipids of primary biogenic origin (sea and sea-ice microbiota) (Facchini et al., 2008b; Decesari et al., 2011; Decesari et al, 2020; Liu et al., 2018; Dall'osto et al., 2022). By contrast, the second period is enriched of MSA (24±13% relative to 3±3% in the first period) and alkyl-amines (15±8% relative to 2±1%) which are considered mostly secondary in nature (Dall'Osto et al., 2019).

The meteorological conditions are not statistically different between the two periods (Table S2). The analysis of the air masses

210 origin (Figure S6) on the contrary reveals different back-trajectories between the first five samples (S1-S5) and the last nine ones (S6-S14) suggesting that the observed changes in the chemical composition are linked to a different origin of the air masses reaching the sampling site, as we further discuss in the next sections.

3.2 Main aerosol chemical components at Halley and comparison with Signy

215 The chemical composition of the eight PM_1 aerosol samples collected at the Halley station (reported in Figure 4) shows remarkable differences with respect to Signy. Overall, water-soluble PM_1 mass concentrations are substantially lower (0.76 ± 0.57 µg m^{-3} average ± standard deviation, n=8) and shows a smaller variability between samples (min=0.23 µg m^{-3} for H4, max=2.02 µg m^{-3} for H7). Most noticeably, a much lower contribution of sea salt to PM_1 is measured in these samples, representing on average only 8% in striking contrast with Signy. Only one sample (H5) shows a relatively high influence of

220 sea salt (24% of total PM_1). In contrast to Signy, the PM_1 chemical composition at Halley is constantly dominated by non-sea salt sulfate and WSOM, representing on average 62% and 19% respectively. In the samples collected at the end of January, nss-sulfate represents a major component of PM_1 at both Halley and Signy but its concentrations at the former site are greater, peaking above 1 µg m^{-3}.In summary, based on the analysis of the submicron aerosol bulk composition, a first sharp difference

between the two sites can be underlined, with Signy being much more impacted by primary sources (sea-spray) while Halley
by secondary ones (nss-SO4).

The organic composition expressed in terms of H-NMR functional groups and molecular tracers shows a limited variability
between samples at Halley, with a dominant contribution of alcoxyl groups (HC-O), MSA and alkyls (H-C) representing on
average 33, 28 and 18%, respectively (Figure 5). The significant contribution from MSA is in line with the high nss-sulfate
shared in the water-soluble PM$_1$ mass, while the high contributions from HC-O and H-C groups indicate a contribution from
primary sources which does not show up from the inorganic composition data alone.

The contribution of MSA at Halley, representing the 28% of total WSOC on average, is along the whole sampling period a
significant aerosol mass contribution regardless Halley is quite distant from open ocean regions. Alkyl-amines instead
represent only a minor portion of WSOC in Halley samples (3% on average) contrary to Signy. A direct comparison of the
average water-soluble PM$_1$ and WSOC concentrations and composition at Signy and Halley, based on the samples collected
in parallel during 42 days of campaign, is reported in Figure 6 (only the samples of the second sub-period of Signy are
considered here, hence excluding S5). Although the total concentration of water-soluble PM$_1$ in the parallel samples is
comparable between the two sites, the average values reported in Figure 6a highlight once more the much higher contribution
of sea salt at Signy (contributing 0.40±0.29 µg m^{-3}, representing on average 46% of total WS PM$_1$ during the overlapping
period) with respect to Halley, which on the contrary was dominated by nss-SO4 (62% of total WS PM$_1$). WSOM represented
in any case the second major component of PM$_1$, with similar proportions between the two sites but also with remarkable
differences in the functional groups' distribution and tracers' concentrations (Figure 6b). A lower contribution of alcoxyl
groups (HC-O) and higher concentrations of alkyl-amines is observed at Signy with respect to Halley. All these differences
strongly suggest different sources and origin areas for the aerosol collected at the two sites, which is also confirmed by the
analysis of the air masses showed in Figure S7. The analysis of the back-trajectories highlights a much stronger influence of
marine air masses in Signy, in agreement with the substantially higher contribution of sea salt in PM1 and the reduced
secondary organic nitrogen compounds (alkylamines) in Halley. At the same time, however, the MSA concentrations are
similar between the two sites in spite of the remoteness of Halley from the sea, and the nss-SO4 concentrations – which are
known to be impacted by the DMS sources in the ocean – are greater in Halley than in Signy. Finally, the organic composition
in Halley rich of HC-O and H-C groups points to a primary organic contribution which again conflicts with the prevalently
continental back-trajectories reaching the Halley station. Some clues for resolving such discrepancies are provided by the
organic factor analysis discussed in the next section.

3.3 WSOA Source Apportionment: POA & SOA types and their contributions

The large inter-sample variability in the H-NMR spectra characterizing the two sample sets of Signy and Halley makes factor
analysis a potentially powerful tool for source identification and source apportionment in spite of the small numerosity of
samples. A full examination of the outcomes of NMR factor analysis is reported in the Supplementary (Section S.2, Figure

S3-S5). Here we report a description of the 5-factors solution which was identified as the most robust and informative one (Figure 7). The associated concentration-weighted trajectories (CWT) maps for each factor, indicating their potential source areas, are reported in Figure 8. Our factor analysis was able to identify two Primary Organic Aerosol (POA), two Secondary
260   OA (SOA) and another factor prevalently found at Halley and of unknown origin. Specifically, the WSOM factors are:

- Factor 1 - "marine POA pelagic (lipids, polyols and saccharides)", characterizing most of the samples both at Signy and Halley and found in comparable concentrations and relative contributions among the parallel samples at the two sites. Interestingly this factor is characterized by an NMR spectral profile dominated by polyols (glycerol and possibly
265   threitol) and saccharides, (found in some samples as glucose and sucrose) together with aliphatic compounds bearing alkyl chains (such as in low-molecular-weight fatty acids) that we here refer to as "lipids" (in broad sense). All these features are typical of primarily emitted submicron sea-spray particles generated by bubble bursting experiments of biologically-productive sea-waters, as already documented in previous studies conducted in similar Southern Ocean areas (Decesari et al., 2020; Dall'Osto et al., 2022) but also in North Atlantic Ocean (Facchini et al., 2008b). This
270   POA component was present in almost all the samples (especially at Signy) and were prevalently associated with air masses coming from open ocean regions, including large sectors of the SO north-western of Signy and eastern of Halley (see the CWT maps in Figure 8). The CWT maps for Factor 1 in Halley, although showing large overpasses over continental Antarctica clearly show a maximum when being influenced by a northern origin in the SO. In summary, this POA seems to be a common component of the sea-spray OA aerosol associated to open ocean areas
275   across a wide range of longitudes and/or apparently being transported for thousands of kilometers and across the Antarctic continent.

- Factor 2 - "marine POA (lac)", representing a significant portion (up to 70%) of WSOC in specific samples especially at Signy (i.e., S3-S5). It shows a mixture of lipids and polyols, similar to Factor 1, but with an important contribution
280   from lactic acid (peaks at 1.35 and 4.21 ppm in the H-NMR spectra). Lactic acid – a major product of sugars fermentation common to many microorganisms (Miyazaki et al., 2014) – was already identified in sea-water and sea-spray aerosol samples of the region and considered of primary biogenic origin (Decesari et al., 2020; Dall'Osto et al., 2022). In particular, these features are characteristics of specific sea-spray aerosol samples coming from sea-water bubble bursting experiments conducted in coastal areas around Adelaide Island, Davis Coast and Livingston Island
285   (SW3, SW4, SW8, and especially SW11, SW15 in Figure S4 and S5). This factor is found only in the first subperiod of Signy (samples S1-S5) and the associated back-trajectories are similar but somewhat shorter with respect to Factor 1. For this reason, we consider it as a second marine POA factor influenced by aerosol sources in coastal/sympagic areas around the Antarctic Peninsula.

290   • Factor 3 - "marine SOA pelagic (MSA+DMA)", dominated by methanesulphonic acid (MSA) and dimethyl-amine (DMA) (identified by the H-NMR singlets at 2.80 ppm and 2.71 ppm, respectively). The predominance of these compounds indicates a marine biogenic secondary formation for this factor. The contributions time series of Factor 3 shows a good correlation with the concentrations of MSA at both sites (R^2=0.91, n=22, p<0.005) and $nssSO_4$ in

295   particular at Halley (R^2=0.57, n=8, p<0.1). The CWT maps associated with Factor 3 (Figure 8) at Signy shows the predominance of air masses coming from the open Southern Ocean and spending most of the time on pelagic waters (Figure S8). At Halley instead this component shows maxima in air-masses originating in open-ocean areas at North-East but travelling above the PBL (Figure S9) and possibly reaching the station through katabatic circulation. In summary, this component can be considered as a background/regional marine SOA source associated with emissions in pelagic waters of the SO.

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   • Factor 4 - "marine SOA sympagic (TMA+MSA)", characterized by high loadings of trimethyl-amines (TMA), even higher than MSA. This component was very characteristic of Signy (absent in Halley) and especially of the second sampling period at that site (S6-S14). The corresponding CWT maps clearly assign Factor 4 to a source footprint stretching over the sympagic waters of the Weddell Sea. This observation agrees with our previous findings in the

305   same area pointing to sympagic Weddell sea region as a source of biogenic organic nitrogen and in particular amines in ambient aerosols (Dall'Osto et al., 2017; Dall'Osto et al., 2019; Decesari et al., 2020; Brean et al., 2021).

   • Factor 5 - A final factor was found to characterize the organic composition in Halley. It accounts for a substantial fraction of the HC-O and H-C groups at Halley, corresponding as sum to the contribution from the pelagic POA

310   (Factor 1) but with distinct groups of H-NMR resonances. In particular, a complex pattern of H-NMR signals is found at chemical shift between 4 - 4.5 ppm (in the range of the HC-O groups) (Figure S10). These signals have been never observed before in ambient aerosol samples and are largely missing in the Signy samples. They can be tentatively attributed to acidic sugars (e.g., uronic acids) or organic sulfate (sulfate-esters). Considering the high abundance of nss-SO4 and the corresponding acidic nature of the aerosol in Halley, an hypothesis for the formation of these

315   compounds can be the esterification of common polyols (such as glycerol) to organic sulfates. As already mentioned, alkoxyl groups are usually considered primarily emitted (confirmed also by the presence of degraded/oxidized lipids signals at 0.9, 1.3, and 1.6 ppm in the alkyls region of the Factor 5 spectral profile) but the hypothesized substitution of hydroxyls with sulfonate groups can be considered of secondary nature (ageing of primary alcohols/sugars). Moreover, the factor profile shows contemporary some other secondary features, such as MSA and DMA signals

320   which makes this factor of difficult identification. For this reason, we consider it as a mixture of primary and secondary OA ("POA-SOA mix") characterizing Halley site. A clearer interpretation of the nature of this organic fraction could not be achieved at the moment. The CWT maps for Factor 5 do not elucidate any specific source areas.

It is speculated that it could be a mixture of primary and secondary components and partially potentially coming from continental/terrestrial environments (Kyrö et al. 2013).

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Figure 7 reports the average contributions of the five factors at the two sites. It is worth noting how the WSOA factor analysis confirmed the importance of primary sources (POA) in the first sampling period at Signy already evidenced by the bulk chemical analyses: the sum of POA factors in fact represents 89% of the total WSOA on average of the first 5 samples (S1-S5). Much more relevant are the contributions of secondary components (SOA) in the second sampling period at Signy (71% of total WSOA on average of samples S6-S14) and at Halley (35% of WSOA on average). The dominant component at Halley remained in any case the so called "POA-SOA (mix)" factor accounting for the 44% of WSOA at the site. Excluding Factor 5, the trend of the contribution of POA vs SOA is clear: the SOA fraction of OA increases while the austral summer progresses, as a possible consequence of the increasing emissions of reactive vapors from the ocean together with enhanced photochemistry. Nevertheless, one clear episode of high POA concentration is observed in the middle of January at both stations, indicating that synoptic circulation can augment the transport of POA from the Southern Ocean over the entire Weddell Sea region and into the Antarctic continent across a 2,000 km -wide area even in the middle of the Austral summer.

4 Discussion

The variability of the aerosol populations in the polar southern latitudes is affected by strong latitudinal changes in both aerosol sources and atmospheric circulation. Humphries et al. (2021) evidenced, in the area of East-Antarctica, latitudinal gradients in atmospheric aerosol loading and composition driven by the changing position of the atmospheric polar front. Our results extend such observations to the West Antarctica region of Peninsula and Weddell sea, while adding new insights on the nature of aerosol sources and the drivers of aerosol chemistry.

The air mass back trajectories travelling to Signy and Halley, reported in Figure S7, as well as CWT maps in Figure 8, clearly show how the two sites are mostly influenced by different air mass origin and history. In particular, Signy (60°S, in the maritime Antarctica) is impacted by two types of air masses: one (being prominent in the first part of the campaign, samples S1-S5) associated with the Westerlies, and spending most of the time on pelagic waters of the SO; the other (influencing the second period, samples S6-S14) recirculating over the Weddell sea and spending more time over sympagic waters and sea-ice marginal zones (Figure S7-S9). By contrast, Halley (75°S, over the ice shelf) is mainly affected by an anticyclonic flow (from E or SE) over the Antarctic continent (60% of the air mass linked to katabatic winds), involving air masses having travelled over consolidated packed ice with a minor influence from the pelagic environments in the SO (Figure S8 and S9). Whilst the Signy samples were representative of air masses that had previously travelled almost entirely within the PBL, different conditions were observed at Halley, where only 59±24% travelled within the PBL (Figure S9a,b). Since the specific eco-regions (sympagic, pelagic) supply aerosol populations with distinct physical and chemical characteristics (Dall'Osto et al.,

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2017; Dall'Osto et al., 2019; Decesari et al., 2020; Rinaldi et al., 2020; Brean et al., 2021), we show here that the latitudinal change between 60°S and 75°S in the prevalent atmospheric circulation tends to maintain a segregation between the specific aerosol populations produced in the different environments. This explains why primary sea salt particles are found in much greater amounts in Signy and aged nss-SO4 particles affect Halley to a greater extent. However, the results of the organic factor analysis highlight a more complicated picture. Summarizing our findings on the inorganic and organic characterization at the two stations, we can distinguish three atmospheric regimes at least:

(a) During the subperiod in Signy (Dec), PM_1 particles transported by the Westerlies and coming from pelagic waters of the open Southern Ocean (organic Factor 1) with some possibly affected by marine ecosystems in the coastal Antarctica (organic Factor 2) increased the water-soluble PM1 concentrations above 1 (up to 5) µg m^{-3} and were mostly contributed by primary constituents (sea salt and marine POA components);

(b) During the second subperiod in Signy (Jan – Feb), the aerosol originated prevalently from sympagic areas of the Weddell sea region and was characterized by lower concentrations (1 µg m^{-3} or lower) and by a higher contribution of secondary components (nssSO4 and SOA, especially enriched in biogenic organic nitrogen and in particular TMA);

(c) In Halley (Jan), water-soluble PM1 occurred at very low concentrations (only occasionally reaching 1 µg m^{-3}) and were dominated again by secondary components, especially nssSO4, MSA and DMA, but also by OA classes specifically found at this site and of unclear origin.

The relatively high concentrations on nss-SO4 in the sinking anticyclonic air masses arriving to Halley point to processes of atmospheric ageing for this site. However, nss-SO4 is associated to MSA and DMA, i.e. organic components overlapping to the "pelagic SOA" of Signy (and classified accordingly in Factor 1) meaning that the products of oceanic emissions find their way into the free troposphere and lead to aerosol formation in the Antarctic continental atmosphere. This study highlights again the importance of amines and organic nitrogen in SOA formation in southern polar areas, as already evidenced by our previous studies in the same area (Dall'Osto et al., 2017 and 2019). We identify here two factors of organic nitrogen. One – rich of TMA - is associated with sources in the sympagic waters of the Weddell Sea (Factor 4). A second one (characterized by DMA and MSA) is associated with air masses from pelagic open SO waters (Factor 3). Factor 3, in particular, appears to be a background component of the Antarctic atmosphere in the middle of the austral summer (Jan) across latitudes (as it affects both Signy and Halley) and it is linked to long-range transport and to marine emissions in a wide source area (Figure 8). Factor 4, instead, tracing SOA formation from emissions in the Weddell Sea, mainly affects the maritime western Antarctica, not Halley in spite of the proximity of the site to the source regions. This can be explained by the fact that Halley does not receive direct flows from the Weddell Sea itself but rather from coastal Antarctic areas in eastern longitudes where sea ice is much less developed in summer (Figure S8).

The occurrence of specific organic factors at one site and not in the other (Factors 2 and 4 uniquely in Signy, and Factor 5 uniquely in Halley) is in line with the idea that atmospheric circulation maintains chemical gradients in the Antarctic aerosol populations. Nevertheless, we show that the secondary components associated with Factor 3 (MSA and DMA) can break such

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barriers and distributed across latitudes. Figure 9 shows the average concentrations of the WSOA components identified by
390   NMR factor analysis on average at Signy (both as average of the whole sampling period and of the parallel samples) and Halley
stations. Factors 1 and 3 share a common time trend of contribution to WSOA at the two sites, suggesting that they represent
background aerosol spread around a wide area of thousands of kilometers. Such common background components are of
secondary and, more surprisingly, primary marine origin. The factor "marine SOA pelagic (MSA and DMA)" has very similar
concentrations at Signy and Halley (3.21 ± 2.15 and 2.45 ± 2.21 nmolH m^{-3} respectively, on average for the parallel sampling
395   period) (Figure 9). Most noticeably, the same is true for the "marine POA pelagic" factor (1.60 ± 1.20 and 1.84 ± 3.11 nmolH m^{-3} at Signy and Halley, respectively). At Halley, "marine SOA pelagic" is associated to air masses travelling above the PBL
(Figure S9b) and its concentration correlates with those of nssSO$_4$, supporting the hypothesis of a long-range transport
associated to a katabatic flow over the Antarctic dome. By contrast, the "marine POA pelagic" factor did not correlate with
nssSO$_4$ and is associated to strong winds and to air masses coming directly from NE, especially during the episode of mid-
400   January. Therefore, the "marine POA pelagic" factor is not associated to the katabatic circulation and rather reached the station
through transport in the PBL from the Southern Ocean sectors located in the NE to the site (Figure 8). Contrary to Halley, the
Signy site is sometimes dominated by other POA types which looked to have more local origin and an influence from the
sympagic and/or coastal environments, such as the "marine POA (lac)" and the "marine SOA sympagic (TMA+MSA)" factors.
When considering the primary aerosol components, their concentrations normalized by sea salt can be further informative on
405   their origin/importance. It can be observed that the background "marine POA pelagic" enrichment in sea-spray particles is
constant through all the dataset at Signy (0.05 in the first period vs 0.04 in the second). This supports the hypothesis of a
constant contribution of the background POA pelagic component in sea-spray to which other primary components can be
added from local biologically productive waters, as shown by samples S1-S5. In such samples, indeed, the background "marine
POA pelagic" fraction contributes less than 40% to the total POA, mostly represented by the other primary component "marine
410   POA (lac)" (Figure 7). In these samples the total POA/sea salt ratio reached up to 0.14 (averagely). Conversely, the background
POA-pelagic was more enriched with respect to sea salt at Halley (average value of 0.19), where it is also the dominant POA
component. This may depend on different sea-spray production conditions (e.g., reduced salinity close to the shelf or in
polynias) or to some ageing process during transport to the station which removes preferentially the more soluble inorganic
fraction of sea-spray. These hypothetical mechanisms remain just speculative at this stage and needs further investigations,
415   but in any case, it is worth noting that marine POA may influence a much wider geographical area than the simple sea salt
concentrations would suggest.

5 Conclusions

The Antarctic ecosystems are characterized by a substantial spatial heterogeneity across marine (pelagic and sympagic) and
420   terrestrial biomes, with productivity and biodiversity patchiness superimposed to strong environmental gradients (Convey et

al., 2014). This study represents the first chemical characterization and source apportionment of organic aerosol conducted in parallel at the two British Antarctic stations of Signy and Halley, representing two different Antarctic environments separated by 2000 km exposed to different but partly overlapping biogenic sources. In contrast to the paradigm of reducing the aerosol composition in background Antarctic regions to sea spray (primary, mostly composed of sea salt) and non sea salt sulfate

425 (nssSO$_4^{2-}$; secondary), we find that Water Soluble Organic Matter (WSOM) is the second most abundant submicron aerosol component in this area of the world, accounting for a substantial fraction of the total water-soluble PM$_1$ mass, both at Signy (33%, min-max 14-71%, after sea salt 47%) and Halley (25%, min-max 7-40%, after non sea salt sulphate 57%). Our results starkly highlight how the heterogeneity of the Antarctic ecosystems impact also on the organic aerosol sources allowing - for the first time - to report some unique insights on their space and time variability in that region of the world.

430 In particular, significant differences are found between pelagic (characterized by higher PM$_1$ concentrations and more primary components) and sympagic (dominated by secondary components and in particular amines) periods at Signy and at Halley. The sympagic area of the Weddell Sea appear to be a strong source of Organic Nitrogen compounds in the maritime Antarctica (Signy) and in particular of low-molecular weight amines, confirming the results of previous studies in the same area (Dall'Osto et al., 2017; Dall'Osto et al., 2019; Decesari et al., 2020; Rinaldi et al., 2020; Brean et al, 2021). The amines

435 speciation among samples from the different sites and over a longer period highlight that trimethylamine (TMA) is dominant over Weddell-sympagic waters (specifically characterizing Signy during the second part of the measurement period) while DMA is spread on a larger scale, reaching Halley (regional background footprint, similarly to MSA and non-sea salt sulfate). Enclosed between the Antarctic continent and the pack sea-ice of the Weddell sea, Halley station shows a distinct chemical composition, much depleted of sea salt and enriched in nss-SO$_4$ with respect to Signy, likely due to long-range transport and

440 ageing in the free troposphere. The "chemical segregation" of Halley prevents inputs of certain OA types found in Signy including SOA produced by emissions in the Weddell Sea, but also allows specific aerosol organic compounds (possibly associated with organic sulfate) to develop in Halley and not in Signy.

A part from such differences between the two environments, our study highlights the existence of background biogenic marine sources, which influence the aerosol composition on a larger scale (regional or even supra-regional): among these in particular

445 there is a secondary marine component of pelagic origin ("Marine SOA pelagic (MSA+DMA)"), but also noteworthy a marine primary source ("marine POA pelagic (lipids, polyols and saccharides"), which seems to travel for long distances across latitudes. In particular, the sinking FT air masses arriving in Halley are shown to transport SOA originating from marine emissions of DMS and DMA in distant oceanic regions, and that the prevalent atmospheric flow in Halley is occasionally interrupted by the direct transport of POA (from emissions in the SO) in the PBL.

450 In conclusion, our study contributes to highlight the striking complexity of the aerosol sources in a natural/pristine environment such as the Antarctic ecosystems. Ongoing climate change is predictable to change the Antarctic environment (Rintoul et al., 2018), which in turn will feedback to biosphere and cryosphere exchanges with the atmosphere, changing the atmospheric concentrations of aerosols and cloud condensation nuclei (CCN) with a yet unknown further climate feedback. Future

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

Data availability

Data are available from the authors upon request.

Competing interests

460   The authors declare that they have no conflict of interest.

Author contributions

M.D., A.J and M.R. designed the research; M.D., A.J., and M.R. organized the field campaigns; M.D., and A.J. collected the
aerosol samples; M.P., F.M., and M.R. performed the chemical analyses; M.P. performed the factor analysis; S.D., A.M., E.T,
contributed to the factor analysis discussion and correction; D.S.C.B, and K.M elaborated back-trajectories and maps. M.P.,
465   M.D., M.R., and S.D. wrote the paper. All the authors contributed the scientific discussion and paper revision.

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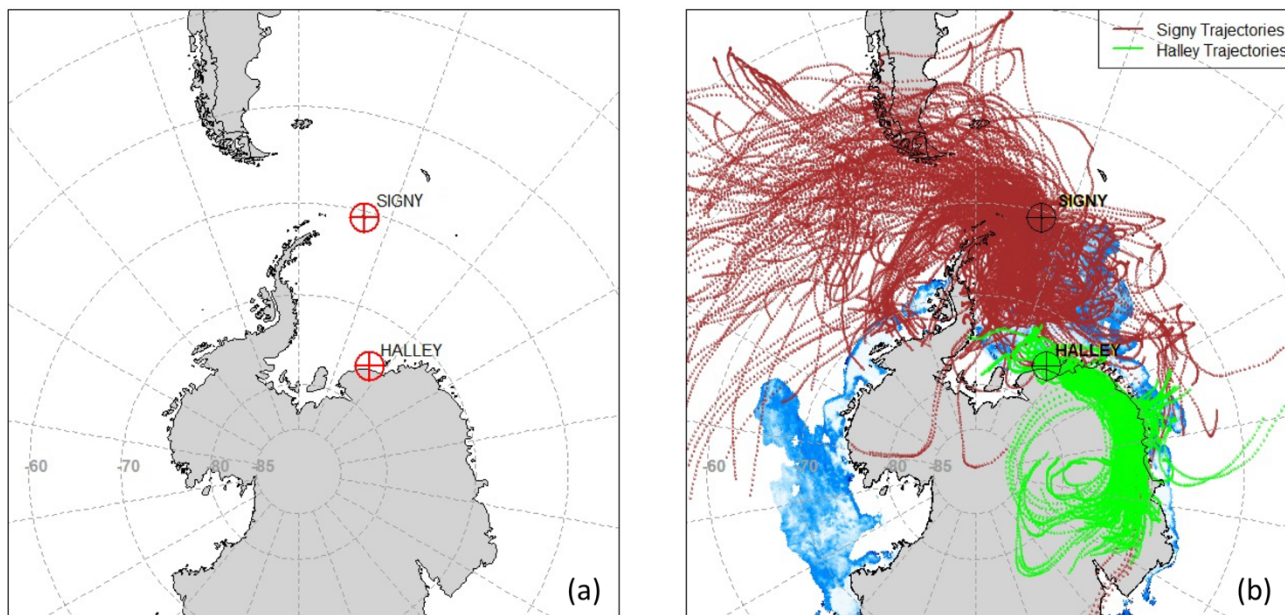
Figure 1. (a) Maps of the study area with BAS Signy and Halley stations and (b) air mass back trajectories for the all the sampling periods at both stations.
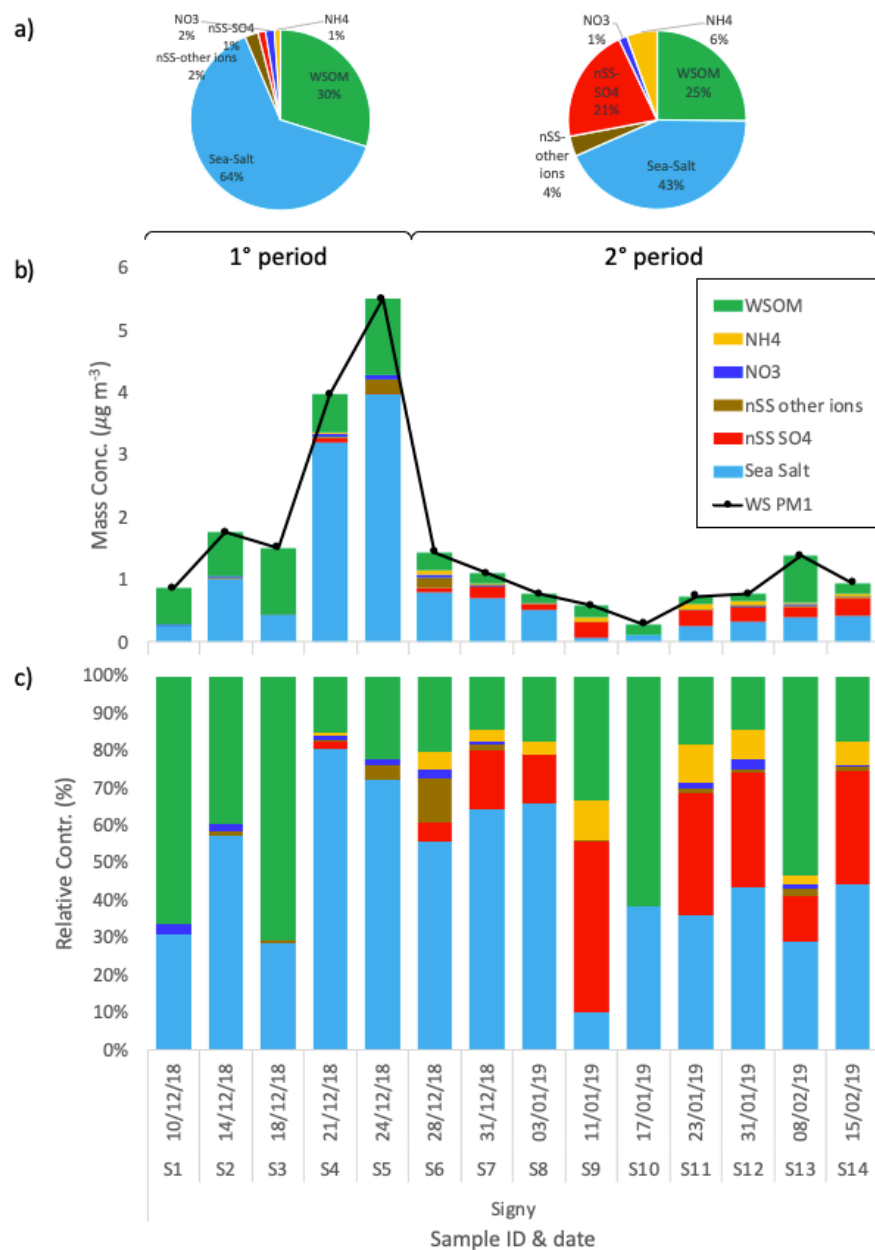
Figure 2. Water-soluble PM$_1$ loadings and chemical composition at Signy during the whole period. Pie charts in panel a) report the average relative contributions for two different periods of the campaign: 1° period (samples S1-S5) and 2° period (samples S6-S14). Panel b) and panel c) show respectively the mass concentrations and the relative contributions of the different chemical species measured in each sample.
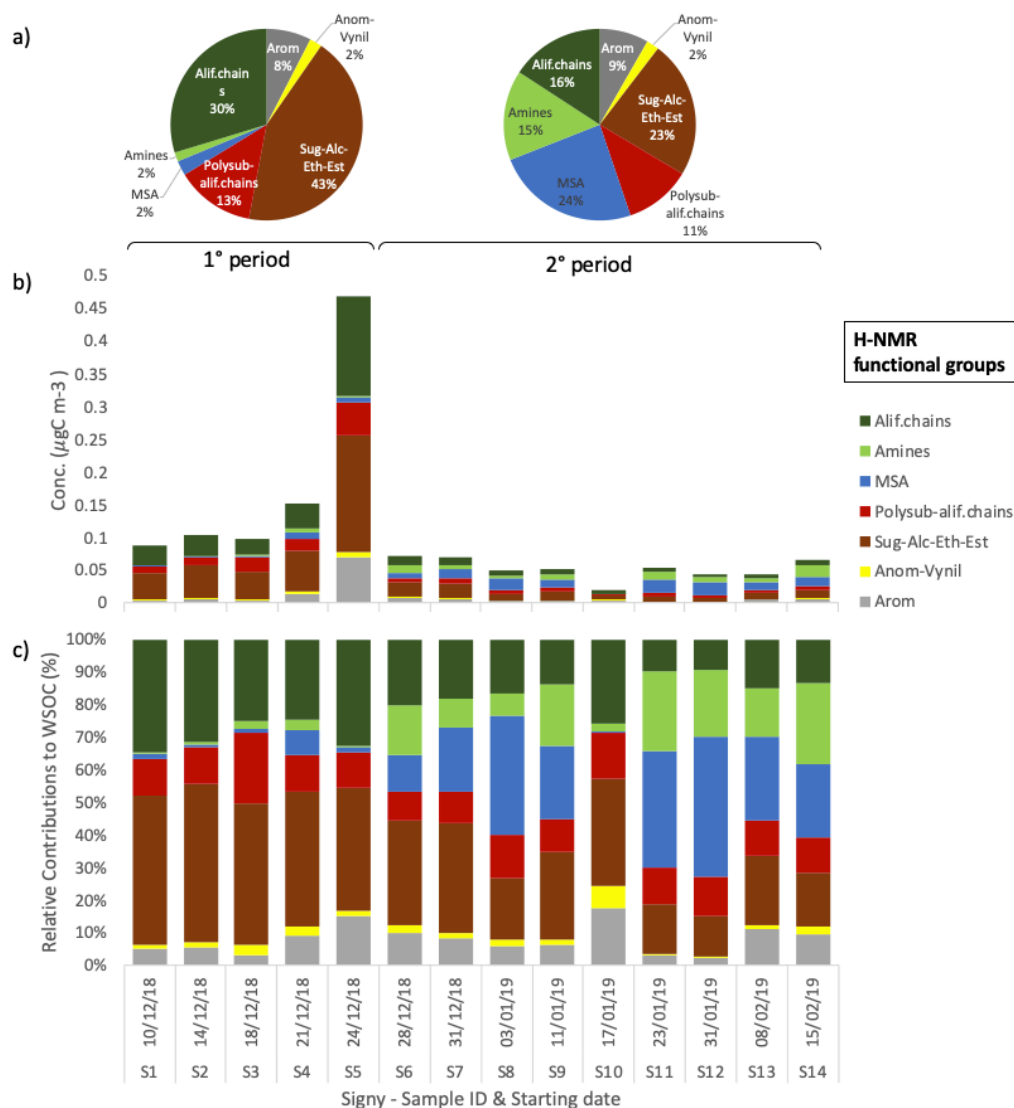
Figure 3. Water-soluble OC concentrations and composition in term of H-NMR functional groups at Signy. (a) average relative contributions of two different periods of the campaign: 1° period (samples S1-S5) and 2° period (samples S6-S14). Panel b) and panel c) show respectively the mass concentrations and the relative contributions of the different functional groups identified and quantified by H-NMR in each sample (expressed in μgC m⁻³).
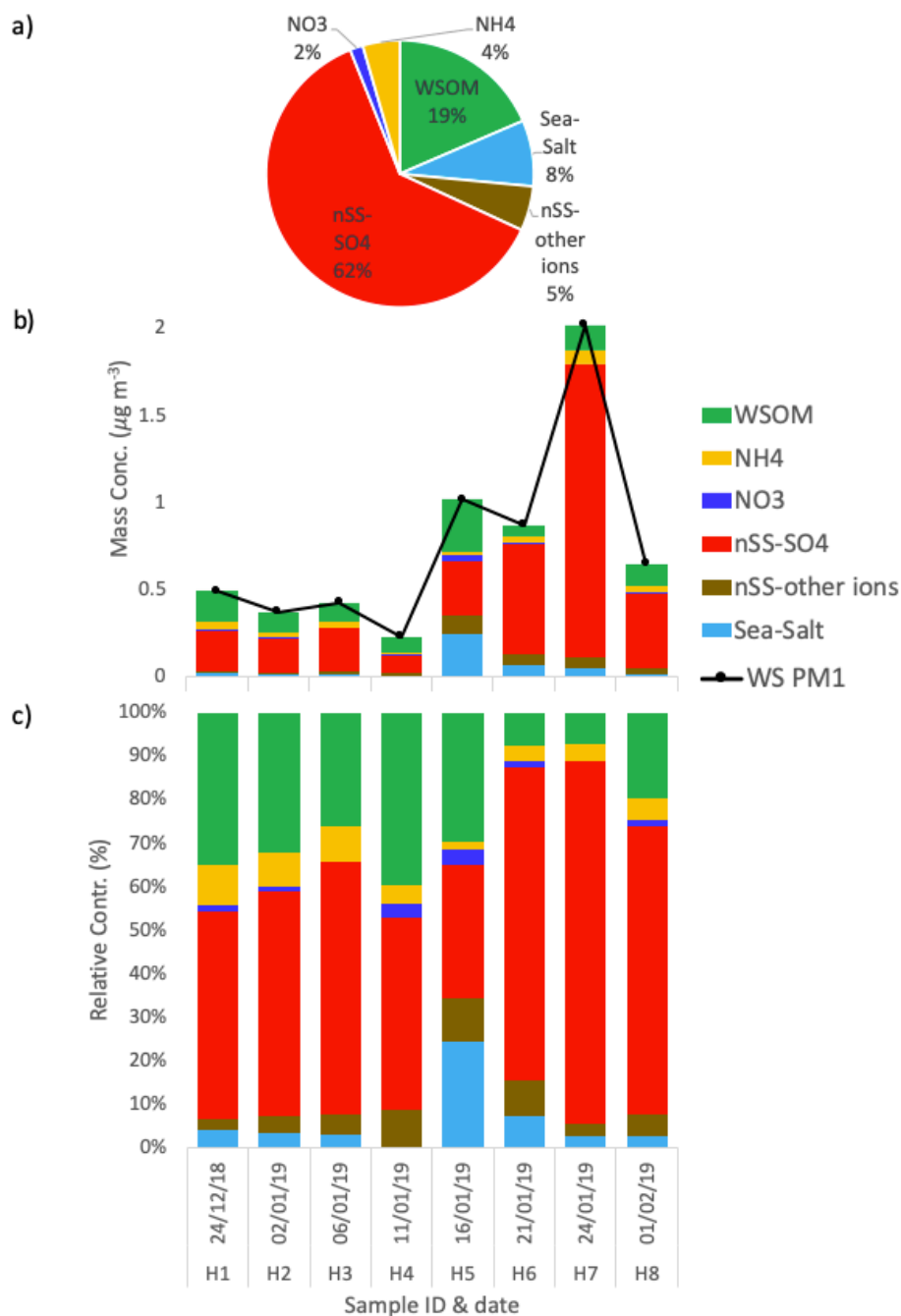
Figure 4. Water-soluble PM₁ loadings and chemical composition at Halley. Pie charts in panel a) represent the average relative contributions of the whole sampling period, while panel b) and c) respectively the mass concentrations and the relative contributions of the different chemical species measured in each sample.
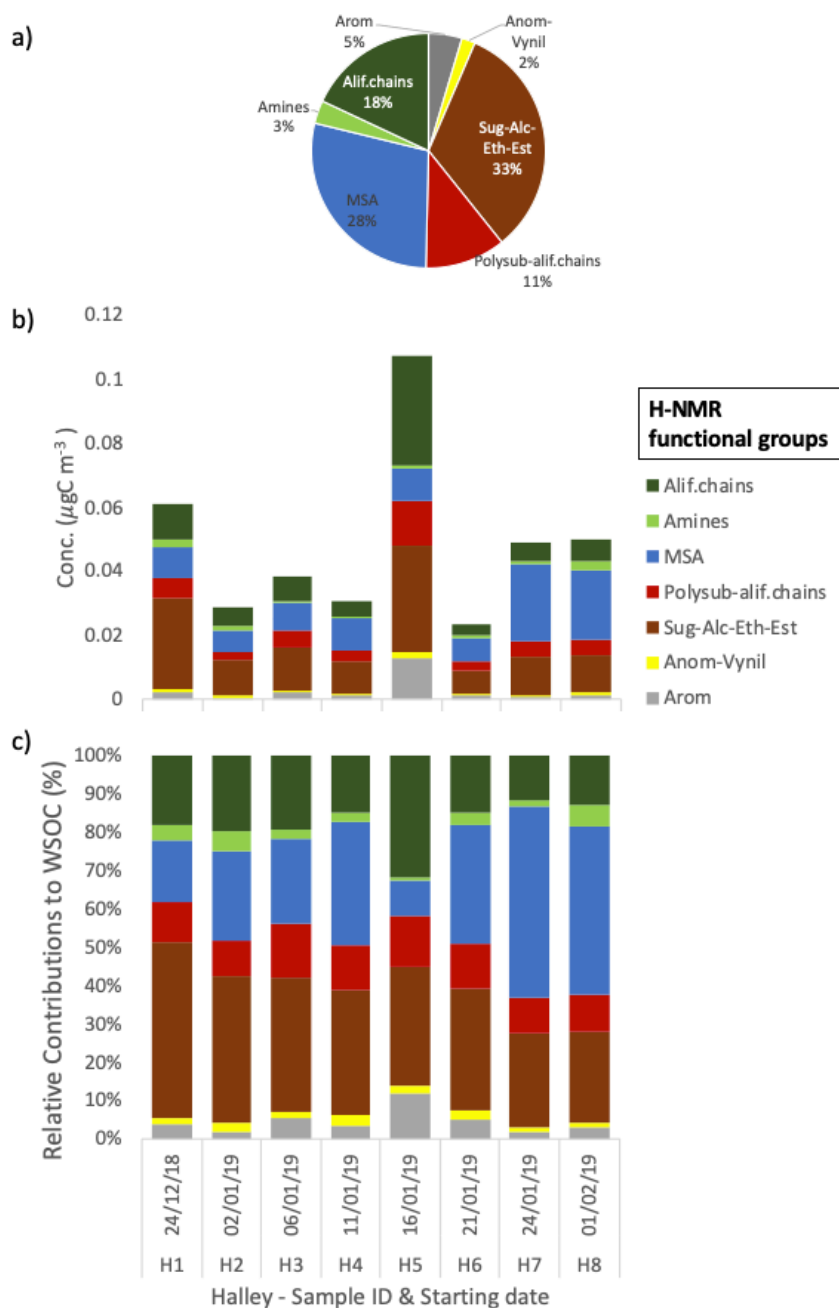
Figure 5. Water-soluble OC concentrations and composition in term of H-NMR functional groups at Halley. (a) average relative contributions; (b) and c) show respectively the mass concentrations and the relative contributions of the different functional groups identified and quantified by H-NMR in each sample (expressed in µgC m⁻³).

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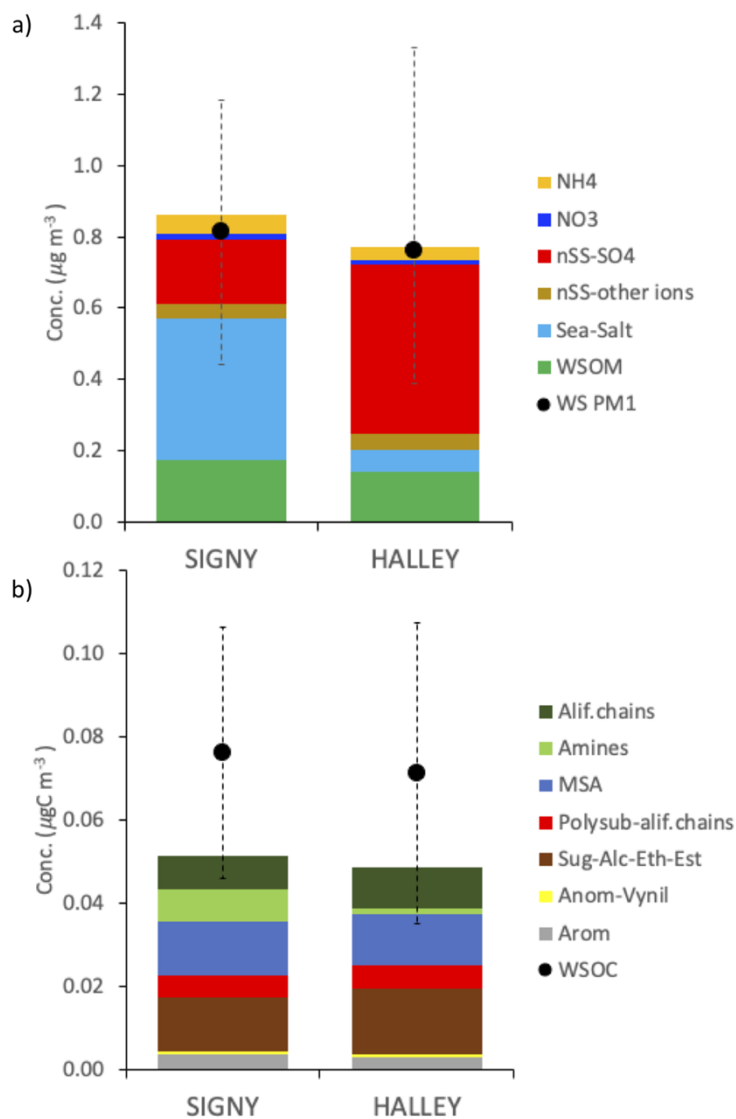
Figure 6. Average concentrations at Signy and Halley for the overlap period (S6-S12 and H1-H8). (a) average concentrations of water-soluble PM$_1$ and its main components; (b) Average concentrations of WSOC measured by TOC and H-NMR functional groups concentrations
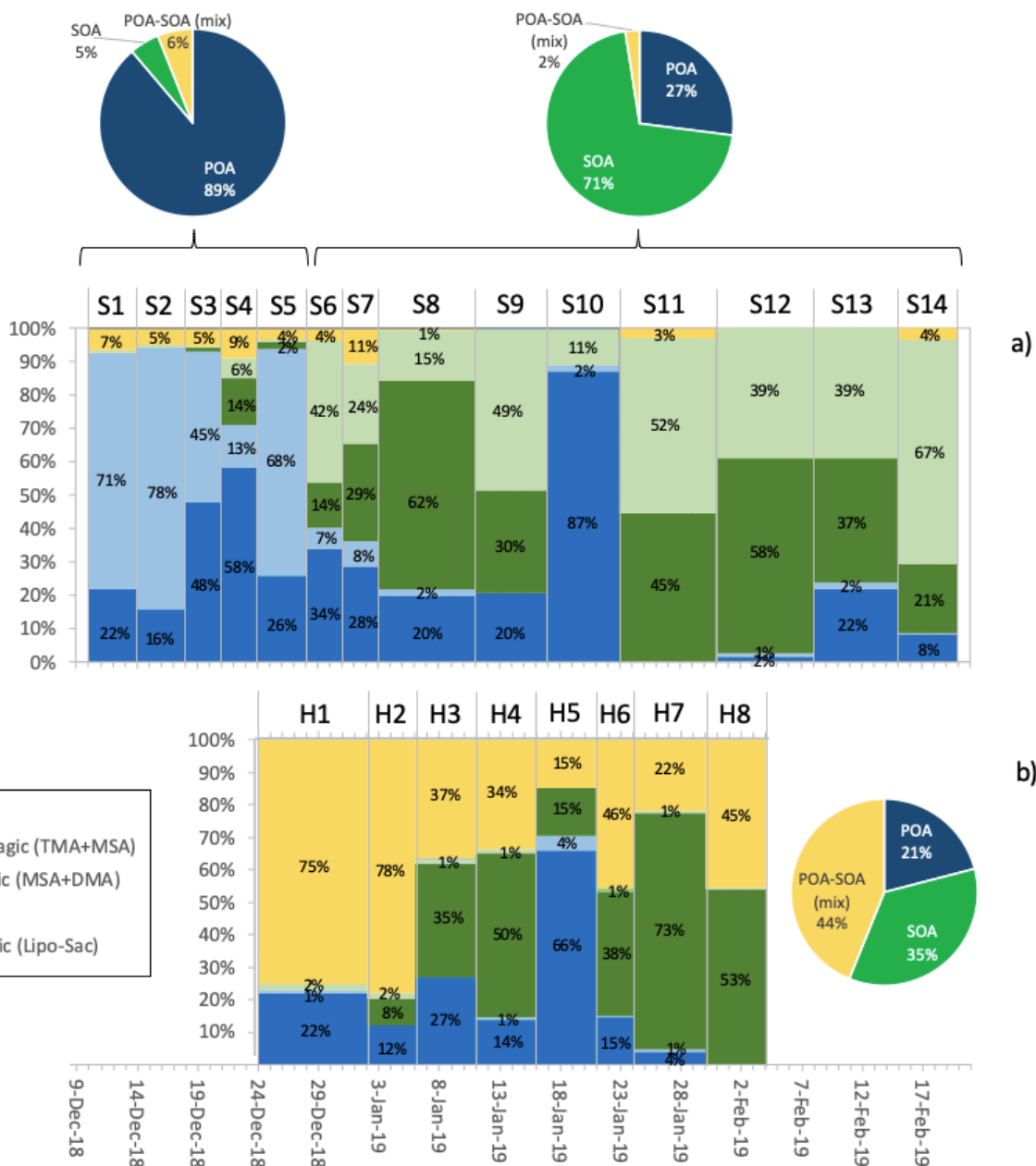
Figure 7. Relative contributions of the WSOA factors identified by H-NMR factor analysis at Signy (panel a) and Halley (panel b).
Histograms show the relative contributions (%) of each factor in each sample: blueish colours refer to POAs component, while
greenish colours to SOA components; in yellow the POA-SOA (mix) factor. Pie charts report the average values of the sum of factors
classified as POA (dark-blue), SOA (green) and POA-SOA mix (yellow) at the two sites and in different periods.
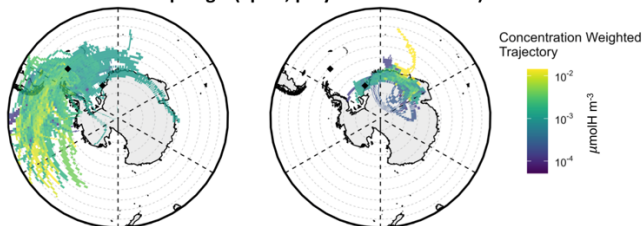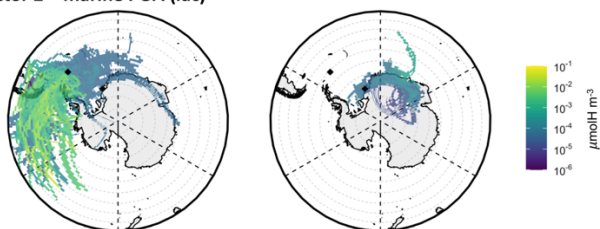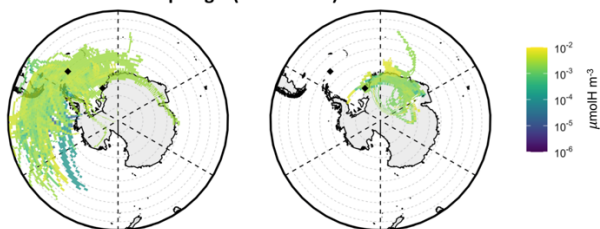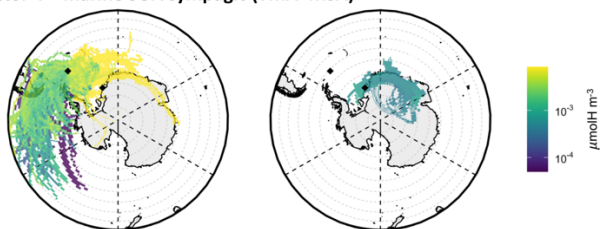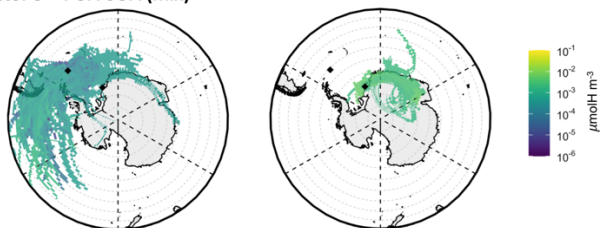
Figure 8. CWT maps of the WSOA factors identified by the statistical analysis of NMR-spectra at Signy (left-side) and Halley (right-side)
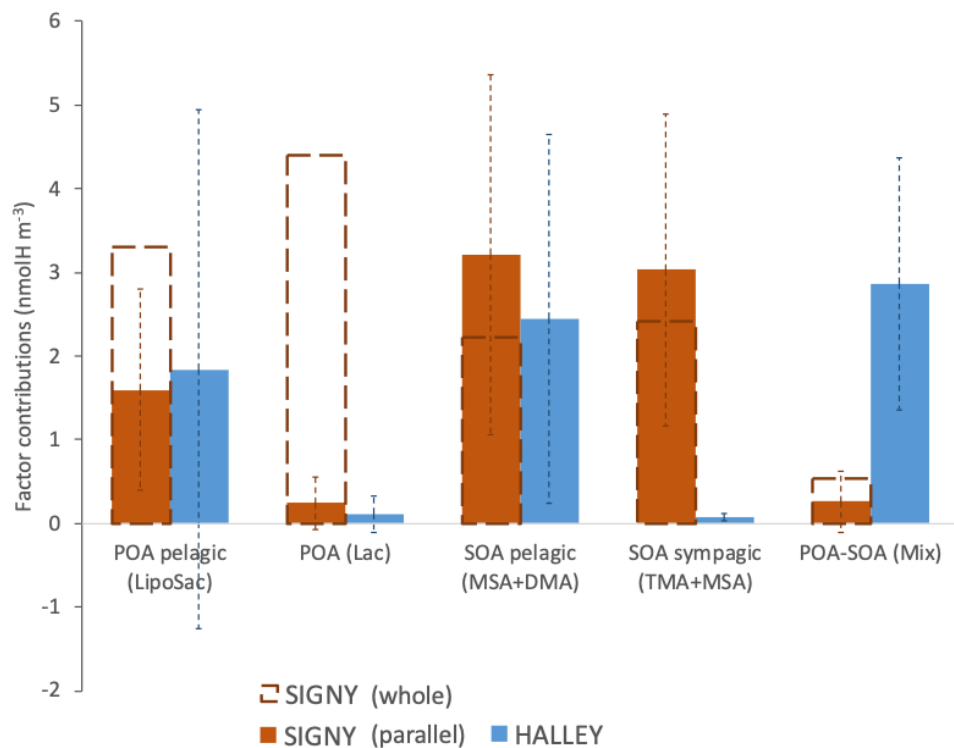
Figure 9. Average contributions of WSOA components identified in the overlapping period at the two Antarctic Stations.