S.1 Field campaign overview: sampling, meteo and air masses

Table S1. Table with temporal period (start, end) of the 23 off-line PM$_1$ filters collected at Signy (S) and Halley (H). Underscore highlighted at the 42 days overlap period. Whilst the start and end overlap time at the two station is similar, at times the time overlap of the time resolution filters do not match well, this is due to the man power limitation and the logistic complexity at the two stations. Nevertheless, the time resolution presented is the real one and fits the purpose of the work presented.

Month of the study	Filter number at Signy station	Date & time Start (Signy)	Date & time Stop (Signy)	Filter number at Halley Station	Date & time start (Halley)	Date & time Stop (Halley)
Dec-18	S1	10/12 18	14/12 15			
Dec-18	S2	14/12 15	18/12 20			
Dec-18	S3	18/12 20	21/12 20			
Dec-18	S4	21/12 20	24/12 20			
Dec-18	S5	24/12 20	28/12 19	H1	24/12 12	02/01 12
Dec-18	S6	28/12 19	31/12 18	H2	02/01 12	06/01 10
Dec-18	S7	31/12 18	03/01 17	H3	06/01 10	11/01 18
Jan-19	S8	03/01 17	11/01 15	H4	11/01 19	16/01 21
Jan-19	S9	11/01 15	17/01 20	H5	16/01 21	21/01 09
Jan-19	S10	17/01 21	23/01 20	H6	21/01 14	24/01 13
Jan-19	S11	23/01 20	31/01 21	H7	24/01 17	30/01 11
Feb-19	S12	31/01 21	08/02 18	H8	01/02 09	04/02 09
Feb-19	S13	08/02 18	15/02 21			
Feb-19	S14	15/02 21	02/03 20			

15   **Table S2.** Average meteorological data for the sampling periods at Halley and Signy BAS stations.

Samples number	Meteo variable				
	T (ºC)	RH (%)	P (mbar)	WD (º)	WS (m/s)
Signy					
S1	-0.8±2	90±6	971±8	262±20	5.5±2
S2	0.5±2	88±6	992±9	266±18	4.7±3
S3	0.6±2	86±5	992±5	256±28	4.4±3
S4	-0.2±1	83±6	982±8	259±15	2.7±2
S5	1.6±2	94±	983±8	272±20	2.1±2
S6	-0.2±1	92±6	982±9	267±21	3.5±3
S7	2.2±1	87±6	985±8	282±22	2.9±2
S8	0.9±1	90±4	977±8	269±18	4.4±4
S9	-0.1±2	85±6	985±9	290±12	1.3±1
S10	1.1±1	91±6	983±9	271±22	3.2±2
S11	-0.4±2	90±5	983±8	260±20	2.6±2
S12	1.3±1	93±6	981±9	278±22	3.0±2
S13	0.5±1	94±7	986±8	271±21	3.7±2
S14	0.0±1	92±5	978±8	142±20	0.8±1
Halley					
H1	-4.2±2	81±4	986±8	264±20	0.5±1
H2	-5.2±2	86±6	977±8	91±9	2.8±3
H3	-5.1±2	80±4	986±8	149±11	0.2±2
H4	-5.0±1	83±6	987±8	67±8	0.9±2
H5	-2.7±1	82±7	978±8	92±8	7.1±2
H6	-4.7±1	76±7	982±8	96±8	2.7±2
H7	-5.2±1	83±6	983±8	85±7	1.8±2
H8	-6.0±2	88±6	984±8	91±9	3.3±2

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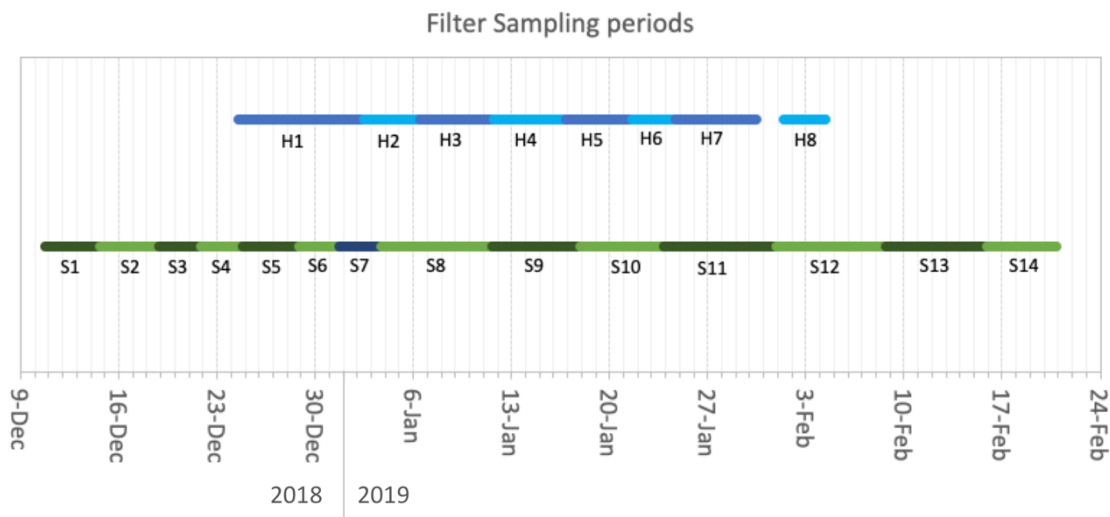
Figure S1. Graphical summary of the measurement periods of the 22 off-line PM$_1$ filters collected at Signy (S, dark-light green bars) and Halley (H, dark-light blue bars) stations.

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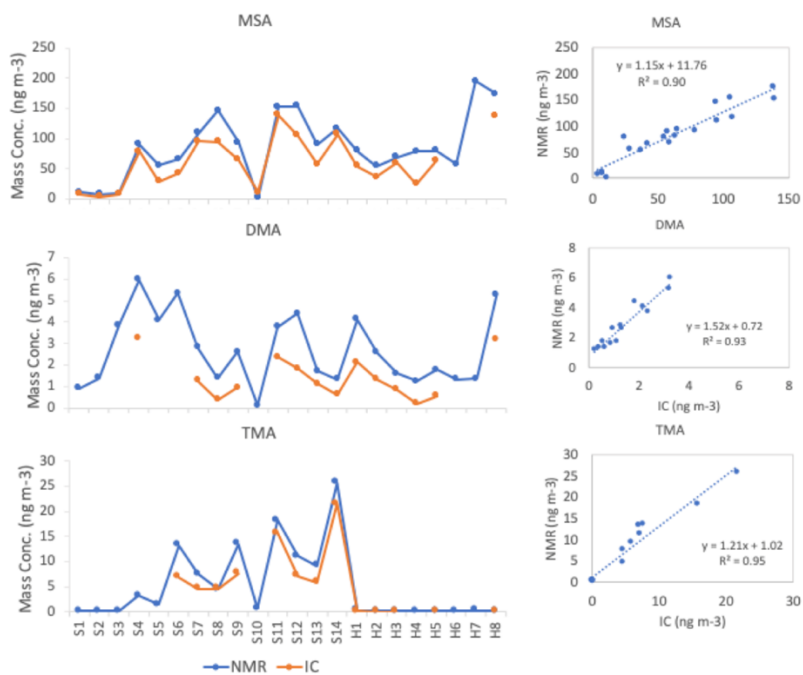
Figure S2. Comparison between mass concentrations of alkylamines and MSA identified and quantified by NMR and IC analyses

S.2 Examination of the Non-negative Factor Analysis of H-NMR Spectra

30   The 22 NMR spectra of the PM$_1$ samples collected at both Signy and Halley were processed using non-negative factor analysis techniques following the method already described in previous publications (Decesari et al., 2011; Finessi et al., 2012; Paglione et al., 2014a). The original NMR spectra were subjected to several preprocessing steps in order to remove spurious sources of variability prior to the application of factor analysis. A polynomial fit was applied to baselines and subtracted from the spectra. Careful horizontal alignment of the spectra was performed using the Tsp-d4 and buffer singlets as reference positions (at

35   0.00ppm and 8.45ppm, respectively). The spectral regions containing only noise or sparse signals of solvent/buffer (H< 0.5 ppm; 4.7 < H< 5.2 ppm; and 8.15< H <8.60 ppm) were omitted. Signals associated to blanks (Ar-H at 8.14-8.10, 7.69-7.62, and 7.38-7.36 ppm; vynil-anomeric at 6.43-6.39, 6.20-6.16, and 5.98-5.96ppm; HC-C=O at 2.38-2.36 ppm) were removed because considered not environmentally relevant. Binning over 0.02 ppm of chemical shift intervals was applied to remove the effects of peak position variability caused by matrix effects. Low-resolution spectra (~400-points) were finally obtained

40   and processed by factor analysis. The factor analysis techniques used in this study include two different algorithms: the "multivariate curve resolution" (MCR), according to the classical alternating least-square approach (Jaumot et al., 2005; Tauler 1995) and the "Positive Matrix Factorization" approach (PMF, Paatero and Tapper, 1994) by applying the Multilinear Engine 2 solver (ME-2, Paatero, 2000) controlled within the Source Finder software (SoFi v4.8, Canonaco et al., 2013; Crippa et al., 2014). Since PMF also requires uncertainties, an uncertainty matrix was derived here from the signal-to-noise ratios of the

45   NMR spectra (as already described in previous publications already mentioned).

Solutions with different number of factors (p= from two up to eight) were explored for the spectral datasets. Eventually, a five-factors solution was chosen because of the best separation of interpretable spectral features and of the best agreement between the two algorithms applied with respect to both spectral profiles and contributions. The 4-factors solution (p=4) was also considered, but rejected in the end because not able to separate the POA enriched of lipo-polisaccharides from the POA-SOA

50   mixed factor (see later description). Going to 6-factors instead, the solutions start to be less robust producing multiple factors for the same constituents and in disagreement between the two methodologies of factor analysis applied.

The interpretation of factor spectral profiles was based on the presence of molecular resonances of tracer compounds, and on the comparison with a library of reference spectra recorded in laboratory or in the field during near-source studies (Decesari et al., 2020; Dall'Osto et al., 2023 *in prep.*).

55   Figure S3 reports profiles and contributions of the H-NMR PMF factors identified. In particular, the Factor 1 is mainly characterized by the presence in the spectral profile of bands at 0.9, 1.3 and 1.6 ppm, corresponding to aliphatic chains with terminal methyl moieties typical of lipids, and at 3.2-3.8 ppm characteristics of sugars and polyols. Lipid and polyols enrichment has already been documented in sea-spray aerosol from bubble-bursting experiments by previous studies reporting NMR compositional data (Facchini et al., 2008; Schmitt-Kopplin et al., 2012; Decesari et al., 2020). It is plausible that glycerol,

60   and other polyols or sugars (i.e., sucrose, glucose) together with some oligomers (such as betaine) identifiable in the NMR spectra, have a chemical bond to lipids, making glycolipids and phospholipids.
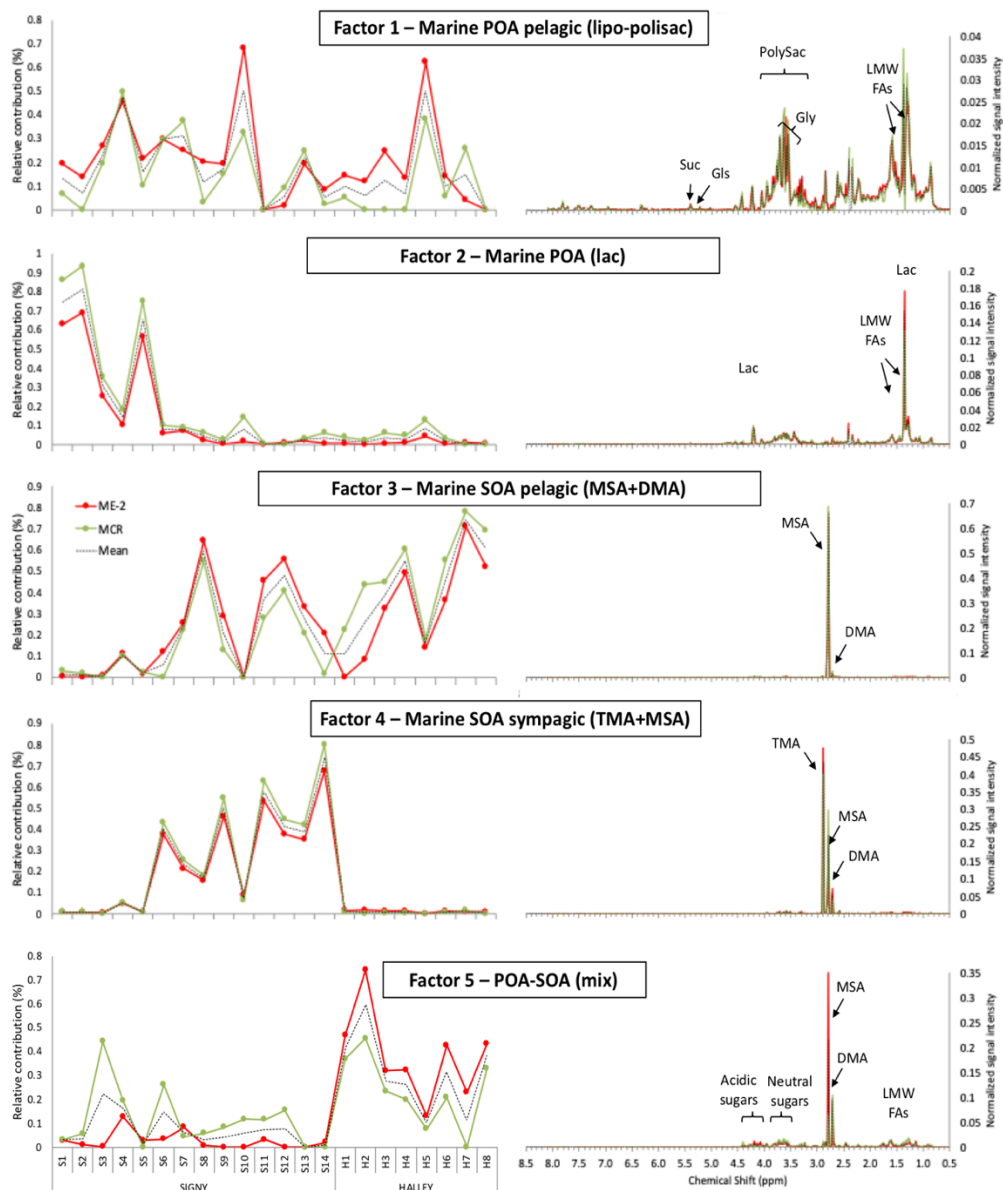
Figure S3: Profiles and contributions of the 5-factors solution from NMR spectra factor analysis. Results from the two different algorithms and the average between them are reported: PMF ME-2 (red line), MCR-ALS (green line), and average value (black dashed line) in each graph. H-NMR peaks of individual compounds (MSA: methane-sulfonate; DMA & TMA: di- and tri- methylamines; Lac: lactic acid; Gly: glycerol; Suc: sucrose; Gls: glucose) are specified in the profiles, along with the band of unresolved mixtures: LMW-FAs (low-molecular weight fatty acids), acidic and neutral sugars and and generic polySac (polysaccharides).

For this reason, Factor 1 is considered as a Marine Primary Organic Aerosol (POA) factor impacting both Signy and Halley
and so representing a background component in the region. Moreover, looking at the CWT maps (Figure 8) this POA
component is more associated with air-masses coming from the pelagic open ocean regions (North-Western from Signy and
Eastern from Halley. For all these reasons Factor 1 is called "Marine POA pelagic (lipopolysaccharides)".

Factor 2 then, representing a significant portion (up to ~70%) of some samples especially in Signy (i.e., S3-S5), shows a
mixture of lipids and polyols, similar to Factor 1 even if in lower proportion. But it shows also important differences, with a
substantial contribution of lactic acid signals (at 1.35 and 4.21ppm). 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., 2023 *in prep.*). For these
reasons, and given that this factor was characterizing especially the first sampling period at Signy dominated by primary
components (both organic and inorganic – sea-salt), Factor 2 is considered as another marine POA component more
characteristic of specific areas around Antarctic Peninsula (as highlighted by CWT maps in Figure 8) and in fact influencing
only few Signy samples (i.e., S1-S5). This factor was so called "Marine POA (lac)"

Factor 3 and Factor 4 profiles are instead dominated by methane-sulfonate (MSA), with its specific singlet at 2.80ppm, and by
low molecular methylamines (especially DMA and TMA), characterized by singlets at 2.71 and 2.89ppm, respectively. The
predominance of these compounds indicates marine biogenic secondary formation processes for these factors (both
representing Marine SOA). But interestingly, Factor 3 is strongly dominated by MSA and retains especially DMA, while
Factor 4 profile shows a higher impact of methylamines, especially TMA. Noticeably, looking at the contributions time series,
whilst Factor 3 is present at both sites showing more or less the same trends of MSA concentrations, Factor 4 is instead
characteristic of Signy only and in particular of the second sampling period, the one characterized by air masses recirculating
over sympagic waters of the Weddell Sea. This confirm our previous findings in the same area pointing out 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 is very characteristic of Halley samples and it is specifically identified by the signals at chemical shift between 4 - 4.5
ppm attributed to acidic sugars (e.g., uronic acids) or sulfonate-esters, as suggested in Section 3.2 of the main text. As already
mentioned alkoxyl groups are usually considered as primarily emitted (confirmed also by the presence of degraded/oxidized
lipids signals in the alkyls region at 0.9, 1.3, and 1.6 ppm) but the factor profile shows contemporary also some secondary
features, such as MSA and DMA signals which makes the source associated with this factor of difficult interpretation. For this
reason, we consider this factor as a mixture of primary and secondary OA specifically characterizing Halley site and worth of
a deeper investigation. Considering that this component seems to be present just in Halley samples, we could speculate that it
is a mixture of primary and secondary components coming partially from a specific local source not influencing Signy and
partially from marine very processed air masses. The fact that the air masses coming to Halley had previously travelled almost

entirely above the PBL (Figure S9b), supports this second possible hypothesis of Factor 5 as influenced by marine emissions transported and re-processed following the katabatic Antarctic circulation.

105 Moreover, in order to check the possible influence of single species or single samples on the factor analysis, a series of sensitivity tests were run (using only the ME-2 algorithm) and the corresponding results were compared between each other in order to find the most robust factorization. Figure S4 shows the comparison of the results on the complete dataset (already discussed) and 2 other runs in which we excluded from the PMF-input matrix: 1- the MSA signal (i.e., singlet at 2.80ppm) and, 2- the sample S3, characterized by very specific spectral features possibly influencing the factorization. Removing MSA

110 signal the PMF best solution became a 5-factor solution, because was not possible to isolate the Factor 2 representing the Marine regional SOA (dominated by MSA signal), but all the other factors looked in good agreement.

These sensitivity analyses showed that removing single samples or variables did not change the main results, confirming the apportionment of the different factors/sources already presented.

Likewise, in order to specifically check the separation between primary and secondary sources, we applied the factor analysis

115 adding to the ambient aerosol spectra also 16 H-NMR spectra of Sea-Spray Aerosol (SSA) generated in bubble bursting tank experiments by local Antarctic sea-waters and melted sea-ice during PI-ICE project, as described by Dall'Osto et al. (2023, *in prep.*).

Figure S4 reports the full comparison in term of both factor profiles and contributions.

The results strongly confirmed the attribution of POA factors identified to primarily emitted particles resembling very well the

120 SSA from bubble bursting experiments. Particularly significant in this regard is the fact that looking at the relative contributions of the different factors (showed in Figure S5) all the SSA samples are entirely (almost) explained by Factor 1 and 6, which are the components interpreted as POA in the solution presented in the main text.

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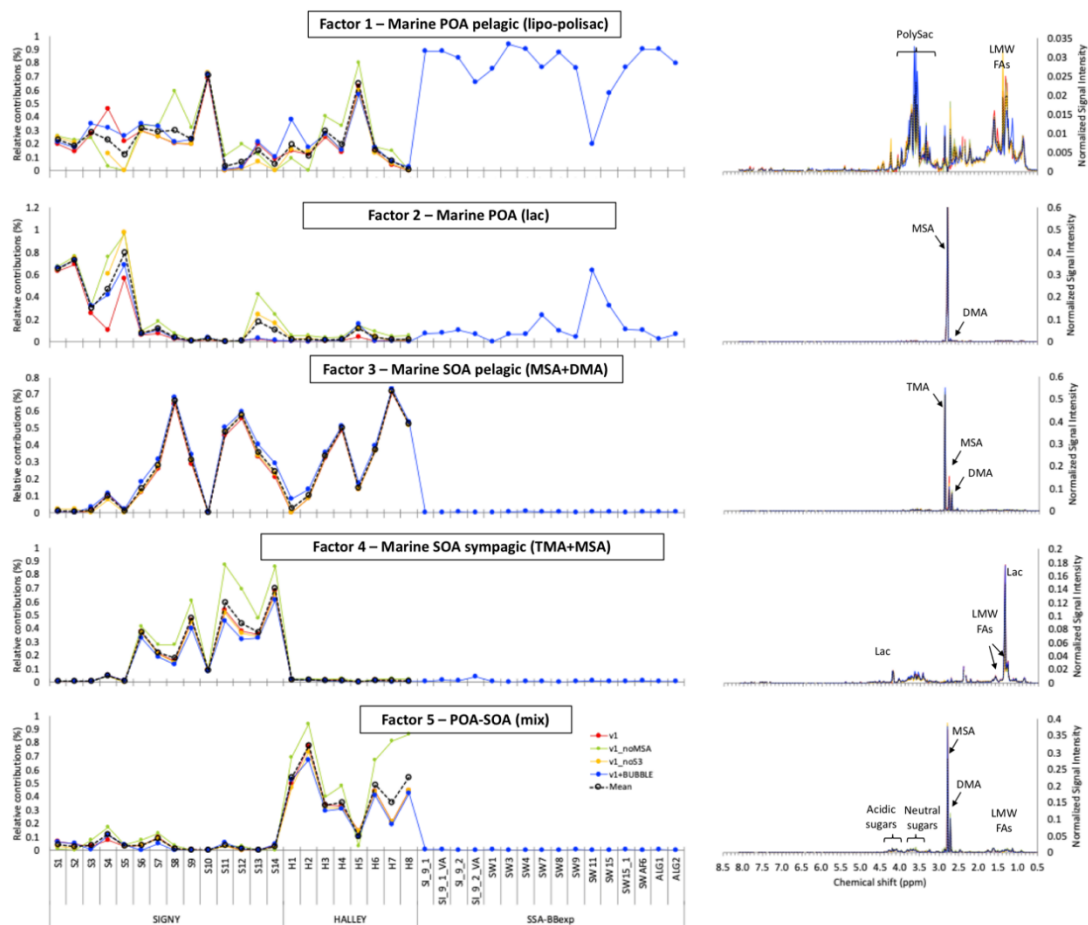
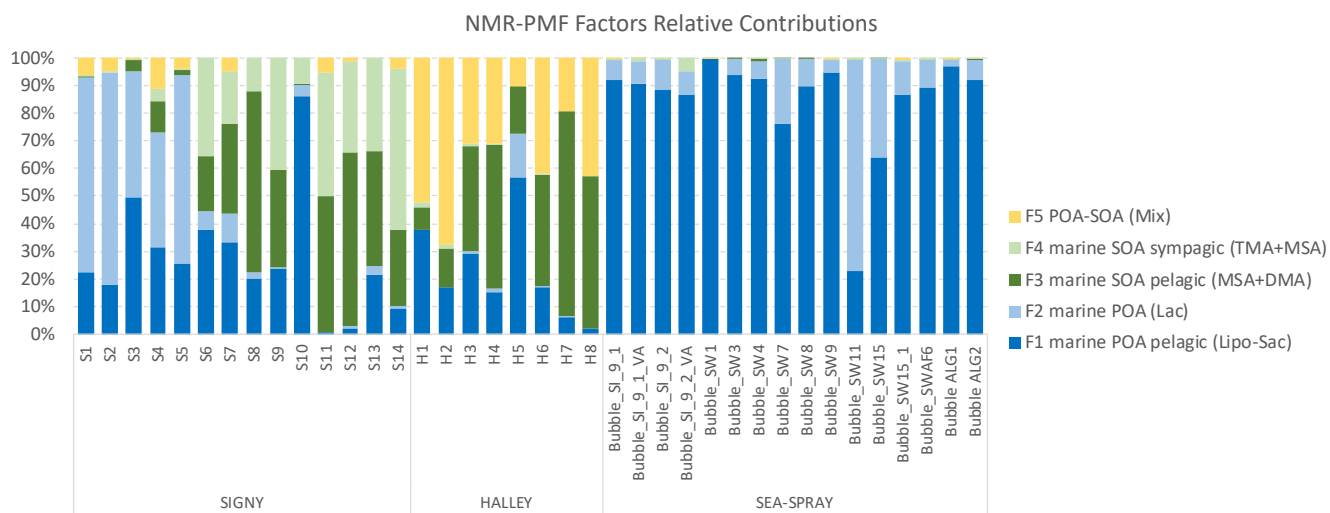


Figure S4: the same as Figure S3 but including results of different runs of ME-2 starting from slightly different input datasets: v1 is the solution already presented in Figure S3 and discussed in the text; v1_noMSA is the p=5 solution using NMR-spectra without the MSA signal (removing 2.79 & 2.81ppm from the input matrix); v1_noS3 is the p=6 solution using a dataset without sample S3; finally, v1+BUBBLE is the p=6 solution starting from the combined dataset of ambient-aerosol samples + sea-spray aerosol samples generated in bubble bursting experiments.

140 **Figure S5**: Factors relative contributions for the 5-factors solution using both ambient PM_1 samples from Signy and Halley and sea-spray samples from PI-ICE Bubble Bursting experiments (labelled as "Bubble_x").

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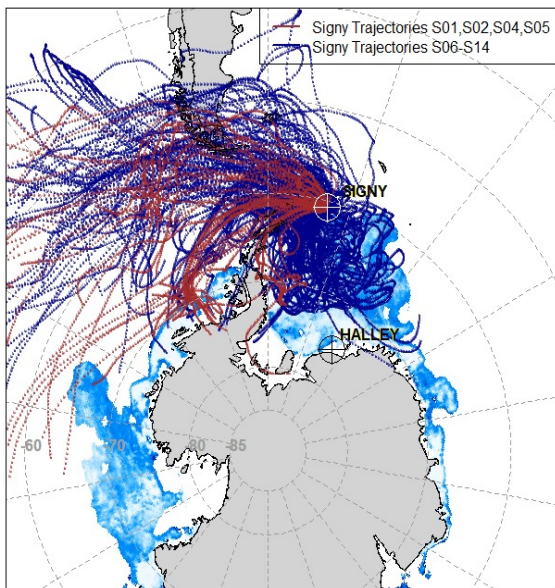
150   **Figure S6.** Air mass back trajectories for the two distinct periods sampled at Signy : first period (n=5, S1-S5) and second period (n=9, S6-S14)
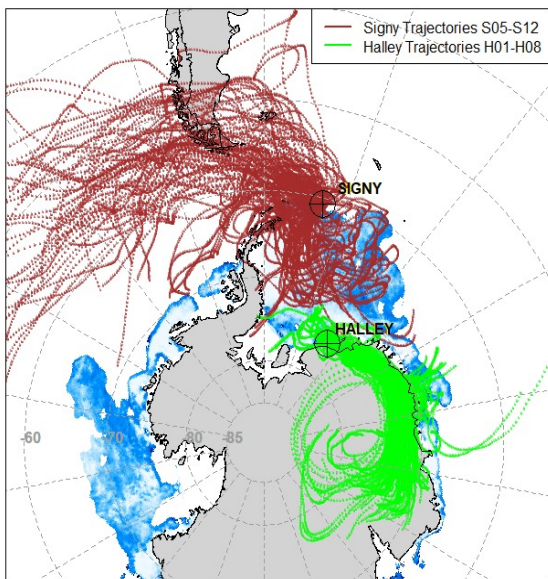
Figure S7. Air mass back trajectories for the overlapped Signy and Halley aerosol samples during approximately the same time period for
155   Signy (n=8, S5-S12) and second period (n=8, H1-H8)
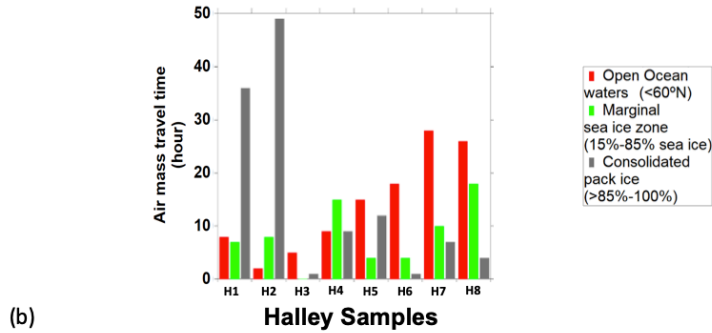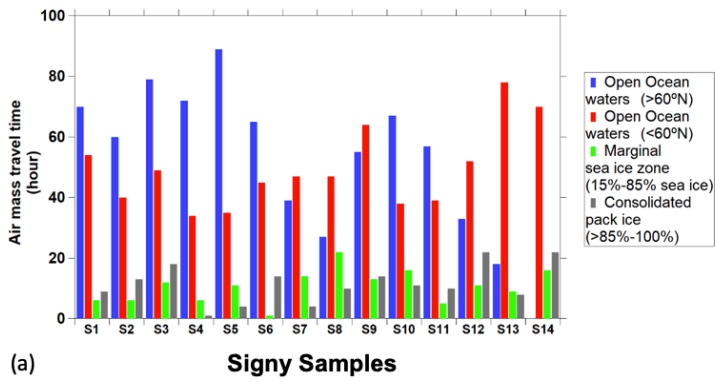
Figure S8 air mass travel time over different surfaces corresponding to (a) Signy and (b) Halley samples

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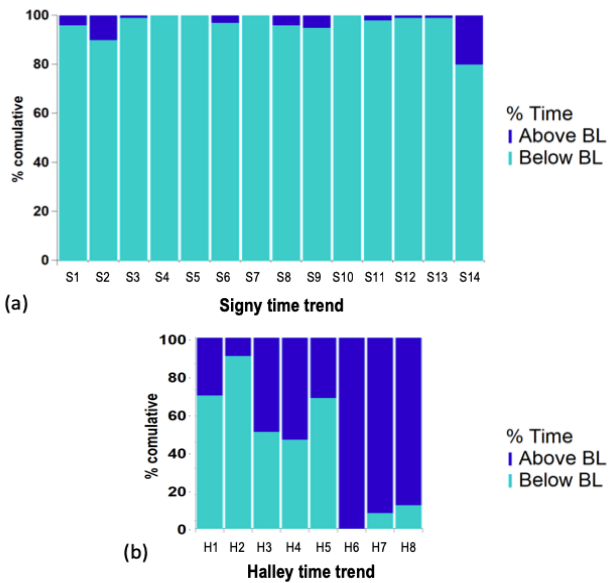
Figure S9. Air mass back trajectories time spent above and below the marine boundary layer for (a) Signy and (b) Halley.
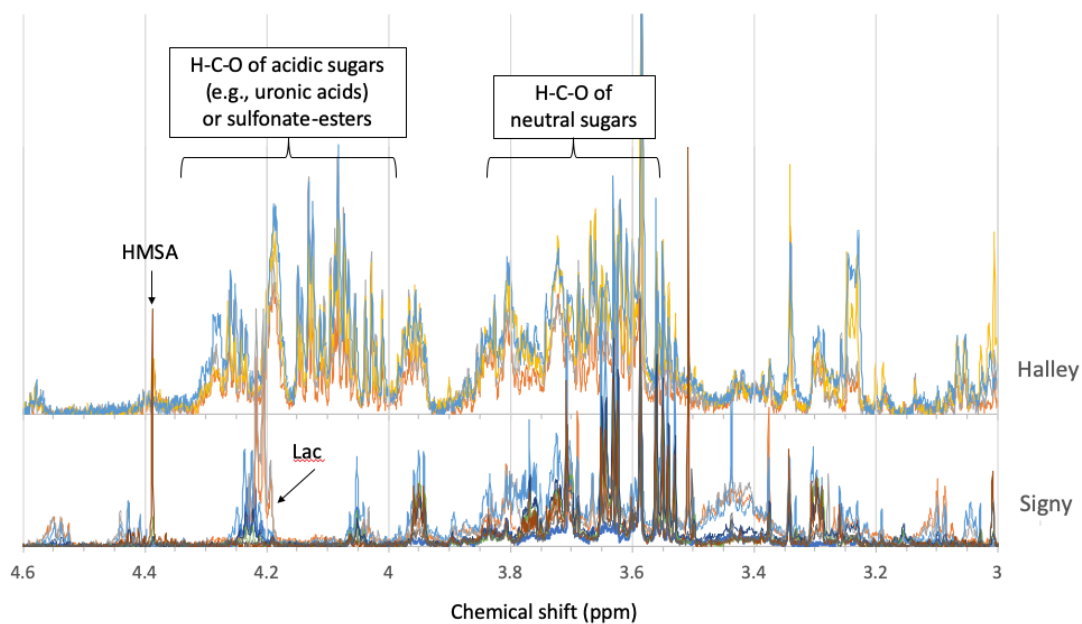
Figure S10. Alcoxy region of the H-NMR spectra of three Halley and eight Signy PM$_1$ samples. Specific NMR resonances were assigned to lactic acid (Lac) and hydroxymethane-sulphonate (HMSA). Highlighted are also the two systems of peaks tentatively linked to neutral sugars (3.5 - 3.9 ppm, such as glycerol) and acidic sugars and/or sulfate-esters (4 - 4.3 ppm).