We thank the Reviewer #1 for the helpful and constructive comments, which have led to significant improvements in the manuscript. We have carefully revised the text. Our point-by-point replies are given below (blue), following the referees' comments (black). Changes to the manuscript are marked with green. In our replies, the line numbers (when reported) refer to the revised manuscript.

Reviewer 1:

Paglione et al. describe the chemical composition of aerosol particles (PM1) collected at two Antarctic stations (Signy and Halley) during a field campaign from December 2018-March 2019. For the chemical analysis of the organic and inorganic compounds they applied several types of offline methods, such as H-NMR and ion chromatography. They observed differences in the chemical composition based on the dominance of either open ocean or sea ice in the air mass history. By applying non-negative matrix factorization, they identified five sources for organic aerosol relevant to this polar marine region.

Ambient aerosol particles contain a plethora of organic molecules, where a majority still eludes chemical characterization and quantification using classical instrumental approaches. The use of H-NMR appears to me unconventional, but promising with the large potential to enhance the knowledge about chemical compounds in aerosol particles. Even though, I am aware that the colleagues from Bologna are skilled and experienced in the use of NMR, I am very impressed, partially sceptic, with which confidence the authors attribute signals to individual compounds in the 'forest' of NMR signals in ambient samples, where potential interferences from other chemical compounds in the NMR spectra are very likely.

I believe that the scientific community could largely benefit from the findings of this study. A revised manuscript should be eventually published in ACP. However, I noticed large gaps in confirmability and thoroughness, which makes it hard to readers without profound knowledge in NMR analysis to understand (and get convinced of) the train of thoughts of the authors from their observations to their scientific conclusions. To enhance accessibility, I encourage the authors to conduct a meticulous revision, addressing these gaps and providing clarity in their reasoning from observations to scientific conclusions.

Response: We thank the Reviewer for the supportive comments and the constructive criticisms.
We recognize the difficulty and the potential skepticism about extracting molecular-level chemical information from the complexity of the NMR spectra of environmental matrices, such as those of atmospheric organic aerosol. Nonetheless, the employ of NMR spectroscopy for characterization of atmospheric organic matrices is not new and actually now exists a quite large literature targeting several specific applications, encompassing functional group analysis, identification of chemical classes and molecular identification, which was recently summarized in a review paper just issued (Decesari et al., 2024). The attributions and quantifications proposed in the present manuscript are indeed based on methodologies developed in 25 years of NMR research.
Anyway, we thank the Reviewer for highlighting the lack of clarity in the presentation of the NMR methodology used in this study. We realized that the nomenclature adopted in the Supplementary material had not been edited carefully and this certainly has caused confusion in attentive readers like the Reviewer. Based on his/her comments and suggestions we have revised the manuscript trying to enhance its accessibility, as detailed below.

General concerns:

The presentation of chemical compounds in this study lacks clarity, resulting in a somewhat chaotic manuscript. Figures 2, 4, and 6 highlight various substances such as WSOM, ammonium, nitrate, 'nSS other ions', nSS sulfate, and sea salt. Figures 3 and 5 introduce amines, MSA, and organic functional groups, including unsubstituted aliphatic groups, polysubstituted aliphatic groups, and anomeric and vinylic groups. Figure S3 identifies lactic acid, low-molecular fatty acids, glucose,

sucrose, ‘generic polysaccharides’ (What is that?), acidic sugars, neutral sugars, glycerol, MSA, TMA, and DMA. Figure S10 includes HMSA and 'acidic sugars (e.g., uronic acids) or sulfonate-esters'. Additionally, the written text discusses 'threitol' (Line 265), ‘oligomers (such as betaine)’ (SI, Line 60), ‘glycolipids and phospholipids’ (SI, Line 61), ‘lipopolysaccharides’ (SI, Line 72), and ‘lipids and polyols’ (SI, Line 74). To enhance the clarity and organization of this information, I suggest incorporating two comprehensive tables into the manuscript. The first table should summarize substances identified through chromatographic analyses, while the second should focus on substances identified through H-NMR analysis. The proposed H-NMR tables could include columns for the ‘name of the substance/functional group’, ‘chemical shifts used for identification’, ‘chemical shifts used for quantification’, ‘examples for molecules’, and ‘references’. This structured approach would greatly improve the accessibility and overall understanding of the diverse chemical compounds identified in this study.

Response: we thank the Reviewer for highlighting this flaw of clarity. Certainly, the nomenclature of chemical classes presented in the Supplementary material was not carefully edited resulting in confused or inconsistent terminology. Following his/her suggestion we carefully revised text, tables and figures trying to give more systematic and homogeneous definitions of chemical substances and categories measured and discussed. We have also agreed to add in the Supplementary two new Tables reporting a list and a description of the main chemical species/categories measured by chromatographic and spectroscopic analyses used in the manuscript (new Table S3 and S4, also reported below). We agree that the reader needs support in understanding the reasoning behind the use of NMR spectroscopy for the identification of individual compounds and chemical classes in organic aerosol samples. We have added more information in Table S4 and S5.

Table S3. Ion Chromatography measured species list

ions name	***ions ID***	***category***	***sea-salt components****	***non sea-salt components***
acetate	ace	organicanions		
formate	for	organic anions		
methan-sulfonate	MSA	organic anions		
chloride	Cl	inorganic anions	SS_Cl	nSS_Cl
nitrate	NO3	inorganic anions		
sulfate	SO4	inorganic anions	SS_SO4	nSS_SO4
oxalate	oxa	organic anions		
sodium	Na	inorganic cations	SS_Na	nSS_Na
ammonium	NH4	inorganic cations		
methyl-amine	MA	organic cations		
ethyl-amine	EA	organic cations		
potassium	K	inorganic cations	SS_K	nSS_K
di-methyl-amine	DMA	organic cations		
di-ethyl-amine	DEA	organic cations		
tri-methyl-amine	TMA	organic cations		
magnesium	Mg	inorganic cations	SS_Mg	nSS_Mg
calcium	Ca	inorganic cations	SS_Ca	nSS_Ca

*the main ions constituting sea-salt are calculated and grouped based on the global average sea-salt composition found in Seinfel&Pandis, 2016. Briefly, Na concentrations are considered to come entirely from sea-salt. Then, starting from Na concentrations the other sea-salt components are calculated by the relative contribution to the total based on the average global composition of sea-salt (Seinfeld and Pandis, 2016). Finally, the total sea-salt is the sum of the different sea-salt components.

**non sea-salt components are calculated for each species subtracting the sea-salt part from the total concentrations

Table S5. H-NMR identified/measured functional groups/chemical species/categories. *Functional groups are in *italic*. **Categories including some of the other species specifically identified are in underlined italic

name of the species/ functional group*/ category of compounds**	ID of the species/ functional group	chemical shifts used for identification & quantification	examples for molecules	possible origin/source	references
aromatic protons	Ar-H	band 6.5-8.5 ppm	phenols, nitro-phenols [...]	biomass burning, [...]	Decesari et al., 2001; Tagliavini 2006; Decesari et al., 2007; Chalbot and Kavouras, 2014
anomeric and/or vinyl protons	O-CH-O	band 6-6.5 ppm	vinylic protons of not completely oxidized isoprene and terpenes derivatives, of products of aromatic-rings opening (e.g., maleic acid), or anomeric protons of sugars derivatives (glucose, sucrose, levoglucosan, glucuronic acid, etc.)	biogenic marine mostly primary	Decesari et al., 2001; Claeys et al. 2004; Schkolnik & Rudich, 2005; Tagliavini 2006; Decesari et al., 2007; Chalbot and Kavouras, 2014
hydroxyl/alkoxy groups	H-C-O	band 3.2-4.5 ppm	aliphatic alcohols, polyhols, saccharides, ethers, and esters	biogenic marine primary	Chalbot and Kavouras, 2014
benzyls and acyls/ amines, sulfonates	H-C-C= / H-C-X (X≠O)	band 1.8-3.2 ppm	protons bound to aliphatic carbon atoms adjacent to unsaturated groups like alkenes (allylic protons), carbonyl or imino groups (heteroallylic protons) or aromatic rings (benzylic protons)	biogenic/anthropogenic mostly secondary	Decesari et al., 2001; Graham et al., 2002; Decesari et al., 2007; Chalbot and Kavouras, 2014
unfunctionalized alkylic protons	H-C	band 0.5-1.8 ppm	methyls (CH3), methylenes (CH2), and methynes (CH) groups of several possible molecules: fatty acids chains, alkylic portion of biogenic terpenes, etc.	biogenic/anthropogenic primary/secondary	Decesari et al., 2001; Graham et al., 2002; Decesari et al., 2007; Chalbot and Kavouras, 2014
hydroxymethansulfopnic acid	HMSA	singlet at 4.39 ppm		anthropogenic secondary	Suzuki et al., 2001; Gilardoni et al., 2016; Brege et al 2018
methane-sufonate	MSA	singlet at 2.80 ppm		biogenic marine secondary	Suzuki et al., 2001; Facchini et al., 2008a; Decesari et al., 2020
di-methylamine	DMA	singlet at 2.72 ppm		biogenic marine secondary	Suzuki et al., 2001; Facchini et al., 2008a
tri-methylamine	TMA	singlet at 2.89 ppm		biogenic marine secondary	Suzuki et al., 2001; Facchini et al., 2008a
N-osmolytes		singlets between 3.1 and 3.3	betaine, choline and other structurally similar N-containing compounds not unequivocally identified (e.g., phosphocholine)	biogenic marine primary	Cleveland et al., 2012; Chalbot et al., 2013; Decesari et al., 2020; Dall'Osto et al., 2022b
betaine	Bet	singlet at 3.25 ppm (not quantified here but possibly quantifiable)		biogenic marine primary	Cleveland et al., 2012; Chalbot et al., 2013; Decesari et al., 2020; Dall'Osto et al., 2022b
choline	Cho	singlet at 3.18 ppm (not quantified here but possibly quantifiable)		biogenic marine primary	Cleveland et al., 2012; Chalbot et al., 2013; Decesari et al., 2020; Dall'Osto et al., 2022b
saccharides	Sac	used synonymously for compounds carrying H-C-O groups in unresolved mixtures but when also anomeric protons (O-CH-O) are present	glucose, sucrose and other sugars structurally similar not unequivocally identified	biogenic marine primary	Graham et al., 2002; Facchini et al., 2008b; Decesari et al., 2011; Decesari et al, 2020; Liu et al., 2018; Dall'osto et al., 2022a
glucose	Gls	anomeric doublet at 5.22 ppm & specific structures between 3.5 and 4.2 ppm (not quantified but possibly quantifiable @5.22 ppm)		biogenic marine primary	Decesari et al., 2020; Dall'Osto et al., 2022b
sucrose	Suc	anomeric doublet at 5.40 ppm & specific structures between 3.5 and 4.2 ppm (not quantified but possibly quantifiable @5.40 ppm)		biogenic marine primary	Decesari et al., 2020; Dall'Osto et al., 2022b
polyols		unresolved mixture not quantified (including glycerol and D-threitol)	glycerol, threitol, erytritol and structurally similar molecules not unequivocally identified		
glycerol	Gly	specific structures at 3.55, 3.66 & 3.77 ppm (not quantified but possibly quantifiable @ 3.55 ppm)		biogenic marine primary	Decesari et al., 2020; Dall'Osto et al., 2022b
D-threitol		specific structures between 3.6 - 3.7 ppm (not quantified)		biogenic marine primary	suggested in this study (to be confirmed)
acidic-sugars / sulfonate esters		band 4-4.3 ppm (not quantified)	uronic acids, sulfonate-derivatives of polyols	biogenic marine primary/secondary	suggested in this study (to be confirmed)
neutralsugars (saccharides) and polyols		band 3.5-3.9 ppm (not quantified)	glucose, sucrose and other sugars structurally similar not unequivocally identified	biogenic marine primary	Graham et al., 2002; Facchini et al., 2008b; Decesari et al., 2011; Decesari et al, 2020; Liu et al., 2018; Dall'osto et al., 2022a
low-molecular weight fatty acids or "lipids"	LMW-FA	unresolved complex resonances at 0.9, 1.3, and 1.6 ppm in the H-C spectral region	fatty acids (free or bound) from degraded/oxidized lipids (e.g. caproate, caprylate, suberate, sebacate, etc.) and similar compounds owning a chemical structures of alkanoic acids.	biogenic marine primary	Graham et al., 2002; Facchini et al., 2008b; Decesari et al., 2011; Decesari et al, 2020; Liu et al., 2018
lactic acid	Lac	doublet 1.37-1.36 ppm & quadruplet at 4.23 ppm (not quantified but possibly quantifiable @1.37-1.36 ppm)		biogenic marine primary	Suzuki et al., 2001; Decesari et al., 2020; Dall'Osto et al., 2022a

To reply point-by-point to the raised unclear definitions/explanations:
-regarding the species showed in Figure 2, 4 and 6, following also the suggestion of Referee#2, we changed the text about ion chromatography and TOC measurements in section 2.3 as follow:

"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 (IC) for the quantification of water-soluble inorganic ions (sodium, Na+; chloride, Cl-; nitrate, NO3-; sulfate, SO42-; ammonium, NH4+; potassium, K+; magnesium, Mg2+; calcium, Ca2+), organic acids (acetate, ace; formate, for; methanesulfonate, MSA; oxalate, oxa) (Sandrini et al., 2016) and low molecular weight alkyl-amines (methyl-, ethyl-, dimethyl-, diethyl- and trimethyl-amine, MA, EA, DMA, DEA and TMA, respectively) (Facchini et al., 2008a). An IonPac CS16 3 × 250 mm Dionex separation column with gradient MSA elution and an IonPac AS11 2 × 250 mm Dionex separation column with gradient KOH elution were deployed for cations and anions, respectively. The sea-salt and non-sea-salt fractions of the main aerosol components measured by IC (SS-x and nSS-x, respectively) were derived based on the global average sea-salt composition found in Seinfeld and Pandis (2016) using Na+ as the sea-salt tracer. A complete list of the species quantified by IC and used in the subsequent discussion is reported in Table S3. The data are also available at Zenodo Data public repository (doi:10.5281/zenodo.10663787).

The water-soluble organic carbon (WSOC) content was quantified using a TOC thermal combustion analyzer (Shimadzu TOC-5000A). Given MSA high relative contribution to the total organic mass, it is separated by subtracting its carbon contribution (in μgC m-3) from total WSOC, obtaining the non-MSA WSOC. A carbon-to-mass conversion factor of 2 was used to estimate the non-MSA water-soluble organic matter (non-MSA WSOM) from non-MSA WSOC measurements, following the values suggested for marine organic aerosols by Jung al. (2020). The total WSOM was then calculated as the sum of MSA and the non-MSA WSOM mass concentrations."

-regarding the functional groups and the tracers identified and quantified by H-NMR and presented/discussed in several figures and parts of the text, beyond the addition of Table S5, we also integrated with more info the text in section 2.3 as follow:
"The main functional groups identified include unfunctionalized alkyls (H-C), i.e. methyls (CH3), methylenes (CH2), and methynes (CH) groups of unsubstituted aliphatic chains (i.e., also named later "Aliphatic chains"); aliphatic protons adjacent to unsaturated groups (benzyls and acyls: H-C-C=) and/or heteroatoms (amines, sulfonates: H-C-X, with X≠O), like alkenes (allylic protons), carbonyl or imino groups (heteroallylic protons) or aromatic rings (benzylic protons) (i.e., also named later "Polysubstituted aliphatic chains"); aliphatic hydroxyl/alcoxy groups (H-C-O), typical of a variety of possible compounds, like aliphatic alcohols, polyhols, saccharides, ethers, and esters (i.e., also abbreviated later as "Sug-Alc-Eth-Est"); anomeric and vynilic groups (O-CH-O), from not completely oxidized isoprene and terpenes derivatives, from products of aromatic-rings opening (e.g., maleic acid), or from sugars/anhydrosugars derivatives (glucose, sucrose, levoglucosan, glucuronic acid, etc.); and finally aromatic functionalities (Ar-H, also abbreviated later as "Arom"). 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): briefly, the choice of specific H/C molar ratios is based on the expected stoichiometry and structural features of the molecules that every region of the H-NMR spectra can actually represents in atmospheric aerosol samples on average. The H/C ratios used in this study are showed in Supplementary Table S4. Although the sum of NMR functional group 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 NMR tube.
Organic tracers were identified in the H-NMR spectra on the basis of their characteristic patterns of resonances and chemical shifts: we used for this scope libraries of reference spectra from the literature (of standard single compounds and/or mixtures from laboratory/chamber experiments and/or from ambient field studies at near-source stations). We also validated our interpretations using extensive libraries of biogenic compounds and theoretical simulations of H-NMR spectra of atmospheric relevant molecules offered by specific elaboration tools/software such as Chenomx NMR suite (Chenomx inc., evaluation version 9.0) and ACD/Labs (Advanced Chemistry Developments inc., version 12.01), some examples of which are reported in Supplementary (Figures S2 and S3). Among the tracers identified, MSA and two low-molecular-weight alkyl-amines (di- and tri- methyl amines, DMA and TMA respectively) were quantified in mass concentrations. Speciation and quantification of these tracers by H-NMR were validated by comparison with the IC measurements of the same species showing excellent agreements between the two techniques (Figure S2). Other molecular tracers (such as lactic acid - Lac, betaine - Bet, choline - Cho, glycerol - Gly, glucose - Gls, sucrose - Suc, hydroxymethanesulfonic acid - HMSA) were unequivocally identified but not quantified in this study, where they are used mainly for source identification. In the present study we also refer to broadly defined chemical classes sometimes synonymously to the classes of compounds carrying specific functional groups or combinations of them, like "polyols" (i.e. compounds with NMR bands in the H-C-O region) or "saccharides" (similarly to polyols but with the concomitant presence of NMR signals in the anomeric region O-CH-O). Intense NMR bands in the H-C (unfunctionalized alkyls) region with prominent peaks characteristic of aliphatic chains (terminaly methyls at 0.9 ppm, methylenic chains at 1.2 ppm and methines or methylenes in beta position to a C=O group or an oxygen atom at 1.5 ppm) were attributed to compounds from the degradation of lipids (sometimes defined concisely as "lipids") including low-molecular weight fatty acids (LMW-FA) and mixtures of other alkanoic acids. A comprehensive list and a description of the functional groups, molecular species and categories of compounds identified in this study by H-NMR spectra analysis is reported in Table S5."

In general, in modern high-field NMR spectroscopy, even 1 D techniques can be accurate for molecular-level identification in complex matrices when well-resolved individual resonances match the spectra of standard compounds. The employ of a pH buffer can overcome the chemical shift variability of the resonances of weak acids and bases. When the overlap with background signals is such that the resolution of specific resonance is imperfect, then the match with the spectra in the libraries can be obtained only tentatively, and we have stated this clearly in the text (as in the case of threitol). In other parts of the discussion, the spectra of standard compounds were used only to characterize spectral bands in the samples in certain ranges of chemical shifts without attempting any attribution to individual compounds or families of homologous compounds: for instance, the spectra of uronic acids and sulfonate-esters were used to formulate hypotheses about the origin of the system of peaks between 4.0 and 4.3 ppm in the spectra of the Halley samples, and we concluded that the attribution of such resonances in the spectra of the samples to acidic sugars (broadly defined) and/or sulfonate esters of sugars is possible but remains uncertain. Finally, the identification of broad spectral bands to functionalities and chemical classes is largely based on the comparison with the available spectra for mixtures of POA and SOA obtained in laboratory conditions (reaction chambers, bubble-bursting tanks etc.) (Decesari et al., 2024). Such identification is not free from interference and is context-specific. For instance, the attribution of alkylic groups in the samples showing broad peaks at 0.9 ppm (terminal methyls), 1.2 ppm (methylenic chains) and 1.5 ppm (methynes in branched

structures, or methylenes in beta position to C=O groups) to the linear aliphatic chains of mixtures of alkanoic acids like low-molecular weight fatty acids and other products originating from the hydrolysis or degradation of lipids is based on the characteristic spectral features obtained for bubble-bursting aerosols (Facchini et al. 2008; Decesari et al 2020). In principle, such attribution cannot be considered free of interference, as linear aliphatic structures can originate also from pollution sources, but it becomes plausible given the environmental conditions in which the samples have been collected which are characterized by very scarce anthropogenic influence. As a general statement, the interpretation of the broad, unresolved NMR spectral features in the spectra of ambient organic aerosols remains challenging. It is a matter of fact that even in the organic aerosol analysis with very high-resolution analytical techniques like Orbitrap MS, the identification of chemical classes is prevalently based on given ranges of variability in the composition space (Van Krevelen plots) considered characteristic for some broad chemical classes (Jang et al., 2023). Even in the case of techniques like high-resolution MS capable to obtain thousands of chemical formulas, the number of isobaric isomers can be large and the chemical structures involved the most diverse ones. With respect to such techniques, NMR spectroscopy, in spite of the lower resolution, allows to confine the range of the major functionalities to given intervals of chemical shift. To illustrate the potential of NMR spectroscopy for molecular-level identification of organic tracers in the Antarctic aerosol samples, some examples of on the application of the Chenomx tool (Chenomx inc., evaluation version 9.0) are shown in the new Supplementary Figure S2 and S3

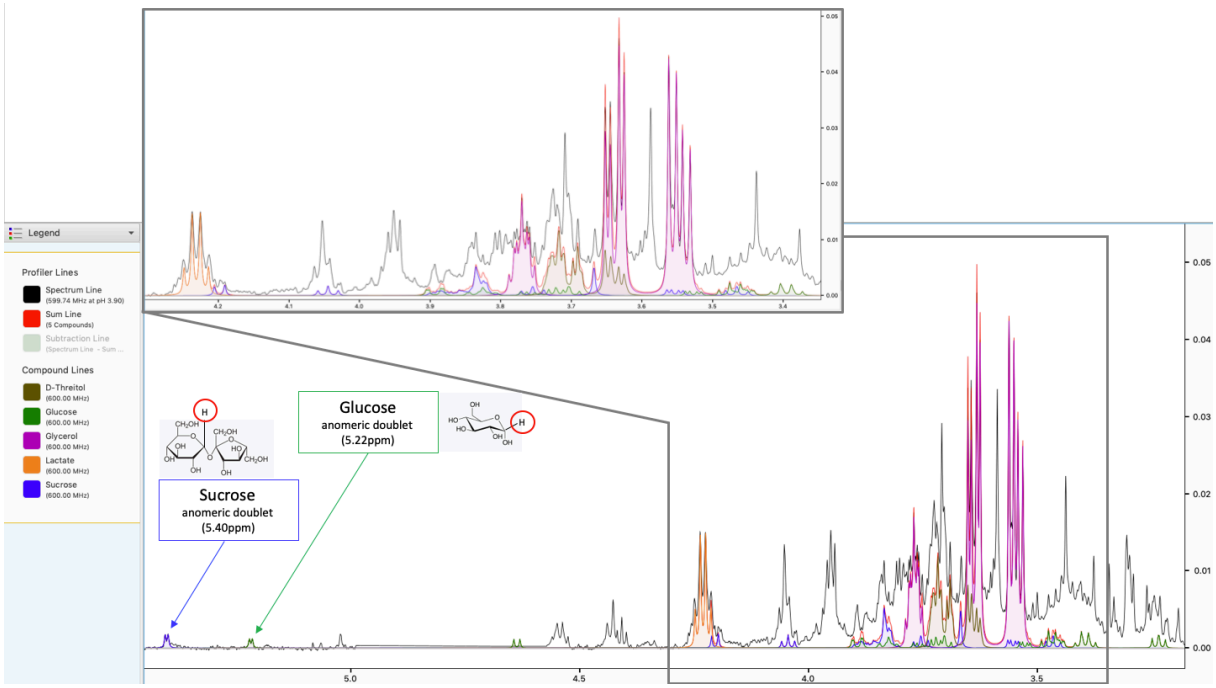

Figure S2. Example of identification of possible tracers using the extensive libraries of compounds offered by Chenomx NMR suite (Chenomx inc., evaluation version 9.0). In this figure are shown the expected NMR spectral patterns of some sugars and polyols, specifically sucrose (blue line), glucose (green line), glycerol (magenta line), D-threitol (brownish line) and lactate (orange line), against the NMR spectrum of PM1 sample S4 (black line). Sucrose and glucose molecular structures are also drawn in the figure, highlighting (with the red circles) the anomeric hydrogen used for their identification.

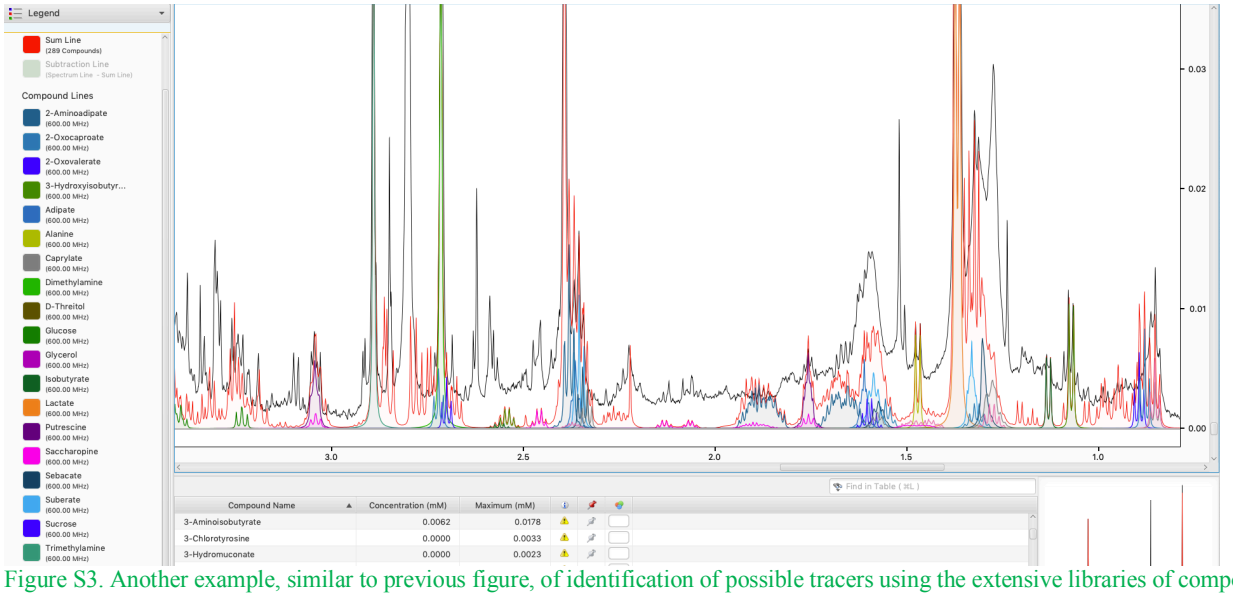

Figure S3. Another example, similar to previous figure, of identification of possible tracers using the extensive libraries of compounds offered by Chenomx NMR suite (Chenomx inc., evaluation version 9.0). Here it is reported an attempt of fitting the ambient PM1 spectrum of sample S4 with the signals expected for the molecules available in the database. Legend reports a list of compounds identified in this spectrum. Especially noteworthy are the signals of some fatty acids esters such as caproate, caprylate, suberate, sebacate, etc.

Connected to the previous comment, the authors should elaborate how they conclude from certain signals of groups (e.g. unsubstituted aliphatic groups, polysubstituted aliphatic groups, and anomeric and vinylic groups) to specific substances, such as lipopolysaccharide, low-molecular fatty acids or polyols.

Response: as already mentioned in the response to the previous comment (and now elaborated in the revised text and supplementary), we interpreted the spectra based on their characteristic patterns of resonances and chemical shifts, using for this scope libraries of reference spectra from the literature (of standard single compounds and/or mixtures from laboratory/chamber studies and or from ambient, in the field, at near-source stations). We also validated our interpretations using theoretical simulations of H-NMR spectra of atmospheric relevant molecules and extensive libraries of biogenic compounds offered by specific elaboration tools/software such as Chenomx NMR suite (Chenomx inc., evaluation version 9.0) and ACD/Labs (Advanced Chemistry Developments inc., version 12.01). More specifically, we discuss about "polysaccharides" or "sugars" because of the presence (unequivocally identified) of some molecular tracers such as glucose and sucrose, but also because of the concomitant presence of unidentified signal in alcoxy and anomeric region of the spectra (bands between 3.2-4.3ppm + peaks in the range 5-6ppm, typical of sugars); or "low-molecular weight fatty acids" because of the characteristic shape of bands at 0.9, 1.3, and 1.6 ppm (resembling a series of possible aliphatic chains of fatty acid esters such as caproate, caprylate, azelate, suberate, sebacate etc., even if it is not possible to identify all of them). And on the same criterium we made the hypothesis of the possible interrelationship between these polysaccharides and the fatty acids chains as coming from common lipo-polysaccharides precursors emitted/released by the marine biota.

Please revise the use of the abbreviations throughout the manuscript: (I) The authors introduce many abbreviations and are partially not needed, since they don't appear another time: e.g. 'open ocean (OO)' (Line 77). (II) The authors introduce other abbreviations repeatedly throughout the manuscript: (e.g. 'methanesulfonic acid (MSA)' (Line 46), 'methane-sulfonic Acid (MSA)' (Line 152), 'methanesulphonic acid (MSA)' (Line 290)). (III) The authors introduce abbreviations and do not use them consequently (E.g. Line 129: 'factor of 2 was used to estimate the WSOM from organic carbon…', 'organic carbon'=WSOC?, or DMA, TMA versus dimethyl amine, trimethyl amine)

Response: we thank the Reviewer for noticing these discrepancies. We revised the use of abbreviations along the whole manuscript.

It is not clear to me, which data (from chromatographic and H-NMR analysis) eventually were included in the factor analysis. Which signals were used to receive these five Factors?
Response: as mentioned both in section 2.4 of the main text and even more in details in the supplementary section 2, we applied non-negative factor analysis directly on the H-NMR spectra. The input variables are the spectral signals at the different chemical shift (binned every 0.02ppm) integrated and normalized in order to be proportional to the WSOC concentrations of each sample (always as reconstructed by H-NMR spectra following the approach based on functional groups distribution described in section 2.2).
In any case, in order to enhance clarity of the study we added a sentence to Section 2.4 of the main text:
The factor analysis was applied directly on the collection of spectra, using as input variable the spectral signals at the different chemical shifts (after several preprocessing steps described more in details in Supplementary Section S2).

Given the significance of the 'sympagic' versus 'pelagic' environment, particularly emphasized in the Results and Discussion sections, providing a summary of the current understanding of their influence on chemical composition from latest literatures in the introduction would greatly enhance the comprehensibility of the manuscript.
Response: we thank the Reviewer for appreciating the significance of the new concept proposed. The current paper greatly supports previous studies, showing the importance of different marine bioregions. We addressed the comment adding/editing the following paragraph in the Introduction:
"We previously showed that the microbiota of sea ice and the sea ice-influenced ocean (sympagic environment) can be a stronger source of atmospheric primary and secondary organic nitrogen (ON), specifically low molecular weight alkylamines (Dall'Osto et al., 2017; 2019) relative to open ocean areas not influenced by sea ice (pelagic ocean). Rinaldi et al. (2020) reported that non-methanesulfonic acid Water-Soluble Organic Matter (non-MSA WSOM) represents 6−8% and 11−22% of the aerosol PM1 mass originated in open ocean and sea ice regions, respectively. This study showed that the Weddell sea areas covered by open or consolidated packed sea ice (sympagic environment) 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 the known role played by sulfur aerosols (Brean et al., 2021). By means of chamber experiments simulating primary aerosol formation on site in the same area around Antarctic peninsula and Weddell sea, Decesari et al. (2020) has previously reported that the process of aerosolization enriches submicron primary marine particles with lipids and sugars while depleting them of amino acids (Decesari et al., 2020). From these experiments emerged that the potential impact of the sea ice (sympagic) planktonic ecosystem on aerosol composition were overlooked in past studies, and that multiple eco-regions (sympagic environments, pelagic waters, coastal/terrestrial ecosystems) act as distinct aerosol sources around Antarctica (Decesari et al., 2020; Rinaldi et al., 2020). In particular, Decesari et al. (2020) found at least three main bioregions sources 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."

Data availability: Atmospheric data from the Antarctic and Southern Ocean are sparse and hence precious to the scientific community. The authors have not published any raw data of atmospheric concentrations in the current version of the main manuscript or supplement, which makes it impossible to reproduce, reuse or compare their results. For a more transparent research and a

reusability of field data for future projects, the authors are strongly encouraged to publish their atmospheric concentrations on a public repository, such as PANGAEA. The comment 'Data are available from the authors on request' (Lines 456-457) should not be accepted by scientific journals anymore.
Response: we agree with the Reviewer and we decided to publish an asset of the data reported in this manuscript on Zenodo Data public repository (doi:10.5281/zenodo.10663787).
The dataset includes:
- concentrations of Water Soluble Organic Carbon and main other ions as measured by TOC-Analyzer (Shimadzu TOC-5000A) and Ion-Chromatography (IC, Dionex);
-H-NMR data in term of: the functional groups distribution; the concentrations of some molecular tracers (namely MSA, DMA and TMA); the contributions of the factors resulting from the Factor analyses of H-NMR spectral dataset;
-H-NMR ambient spectra at full resolution and after the binning (input matrix for the non-negative factor analysis) as well as the resulting spectral profiles of the sources identified by the statistical analysis

Specific comments:
Line 21: You mention the 'non-negative factor analysis' in the abstract. However, this term does not appear anywhere in the manuscript anymore.
Response: we thank the Reviewer for highlighting this discrepancy. We removed the "non-negative" from the abstract. On the contrary, because we believe it is important to specify that the factor analysis used in the study is based on non-negative algorithms, we added "non-negative" when we mention the methods the first time in Section 2.4.

Line 81: Who is 'we'? please add citation of reference.
Response: we changed the sentence to clarify:
"it has been previously reported that the process of aerosolization enriches submicron primary marine particles with lipids and sugars while depleting them of amino acids (Decesari et al., 2020)."

Line 93: '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 scientific cooperation (Dall´Osto et al., 2019; Schmale et al., 2021).' In general, I agree with the authors that international collaborations are essential for advancing in science. However, I don't believe this sentence is suitable for finishing an introduction of a scientific paper. Instead, I recommend to replace this sentence with one that is related to your scientific findings or atmospheric implications.
Response: we removed the sentence and we replaced it with a new one on the relevance of our study:
"Our findings highlight the heterogeneity of the Antarctic ecosystems and how this heterogeneity impacts also on the organic aerosol sources allowing also - for the first time - to report some unique insights on their space and time variability in this region of the world."

Line 105: '[...] with mean annual air temperature of 3.5 C and annual precipitation ranging from 350 to 700 mm, primarily as summer rain.' First, the authors should give this meteorological information for both stations (not only Signy). Second, it would be more interesting to give a meteorological overview just for the period relevant for the campaign, not for the entire year.
Response: following the reviewer suggestion, we added some meteorological information also about Halley station, focusing more on summer period (relevant for our campaign). Moreover, in the supplementary Table S2 are already summarized some other meteo data more specific of the sampling periods.

"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. Temperatures at Halley rarely rise above 0°C although temperatures around -10°C are common on sunny summer days. Winds are predominantly from the east. Strong winds sometimes pick up the surface snow, reducing visibility to a few metres. 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, extremely windy, with mean annual air temperature of 3.5 C and annual precipitation ranging from 350 to 700 mm, primarily as summer rain. Summer air temperatures are generally positive (record maximum 19.8°C), although sudden falls in temperature can occur throughout the summer (-7°C has been recorded in January). Signy is also extremely windy, with prevailing westerly winds."

Line 107: How did you prewash and prebake the quartz fiber filters? Solvent? Temperature?
Response: filters are pre-washed with ultrapure water (in order to reduce the ions concentrations in the blanks) and prebaked at 800° for 1h (for volatilize possible organic contaminants). We added this information in the revised text.

Line 119: 'Aerosol offline measurements and H-NMR analysis'- Isn't H-NMR one of the 'offline measurements'?
Response: true, we wanted to highlight the NMR but can be misleading. For this reason, we removed "and H-NMR analysis" from the title of the subsection.

Line 122-123: The authors measured organic acids, such as acetate, formate, oxalate. Where they all below limit of detection? Or why do they not appear as part of your WSOM discussion?
Response: we introduced the chromatographic measurements of organic acids because they are routinely measured with the procedure used in our lab and in this study as well. However, eventually we do not consider them in the discussion for several reasons: first of all, we wanted to focus on the H-NMR description of WSOM (that is more comprehensive than a discussion on few single organic acids molecules); second, the concentrations of these organic acids were often below the limit of detection (LOD) or too low to be interpreted. At Signy acetate concentrations are above the LOD only in 3 samples, in Halley in 6 out of 8 but with very low values (representing in any case less than 3% of WSOM); formate is always above LOD in Signy but represents less than 1% of WSOM, oxalate is not detectable at all in Halley samples and in Signy is above the LOD only in 3 samples (representing in any case less than 1% of WSOM). The same applies for organic cations others than di- and tri-methyl amines: methyl-, ethyl- and di-ethyl- amines even if detectable in some samples are not discussed in this paper intended to be more focused on H-NMR. We have so chosen to show the total water-soluble PM1 mass using directly the more straightforward total WSOM mass as measured by TOC-analyzer, that includes of course also these acids and amines. Nevertheless, we have now reported the concentrations of also these compounds in the dataset published on the Mendley public repository.

Lines 124-127: The authors give here information on the chromatographic analysis of inorganic ions. However, on which column and how did you analyze amines?
Response: the column and system used are the same for inorganic and/or organic cations (essentially amines). That was already specified in the section 2.3 of the original version ("An IonPac CS16 3 × 250 mm Dionex separation column with gradient MSA elution"). The procedure to separate and quantify amines is described in previous publications (e.g. Sandrini et al., 2016, already cited in the original manuscript)

Line 209: 'The meteorological conditions are not statistically different […]' How did you test the statistical difference?
Response: we applied both a parametric test (t-test) and a non-parametric one (Mann-Whitney test), on the mean values corresponding to each sample sampling-time. Both of them agree that no statistically significant difference can be found between the two periods at Signy, with a confidence interval of 95%.

Line 265: Why do you mention 'threitol' as a possibility here? Is glycerol not so sure? Threitol is not discussed anywhere else within the manuscript, so you should elaborate it a bit. When glycerol and threitol are possible polyols, then why not arabitol or mannitol (tracers for fungi in aerosol particles)?
Response: Glycerol is very evident in most of the spectra (as showed in the example below, Figure R1, and in the new supplementary Figure S2). D-threitol (as well as its diastereomer erythritol) exhibits a pattern of resonances overlapping with complex systems of NMR signals within the broader H-C-O region but distinct with respect to the peaks of glycerol. The signals at 3.7 ppm of chemical shift in the spectra of the samples are therefore "tentatively attributed" to D-threitol (as specified in the text). Mannitol and arabitol exhibit distinct patterns of resonances which cannot be confused with those of glycerol and D-threitol in NMR spectroscopy at 600 MHz.

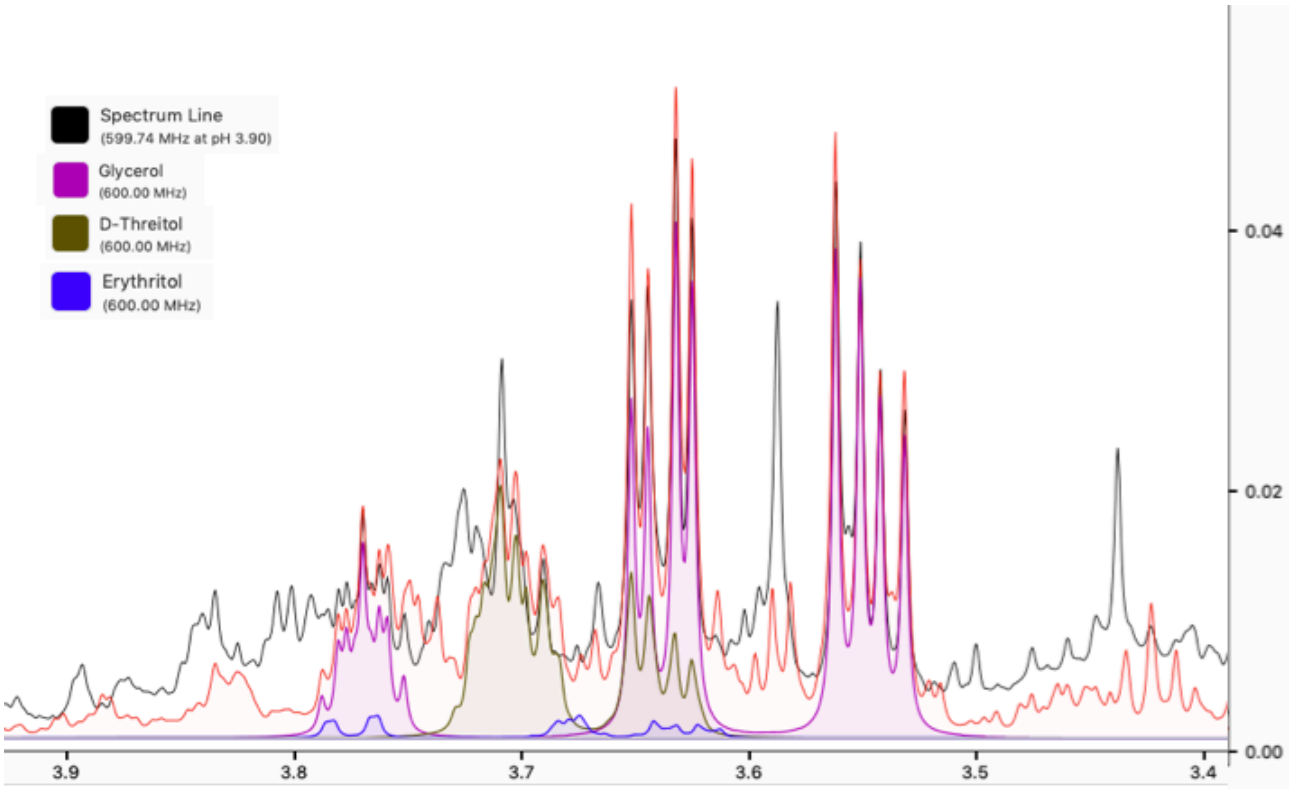

Figure R1: fitting between the expected signals for glycerol (magenta line), D-threitol (brownish line), erythritol (blue line) and the H-NMR spectrum of sample S4 using the Chenomx NMR suite (Chenomx inc., evaluation version 9.0). Red line is the fitting line using the sum of the possible molecules available in the database.

Line 266: Do you equate 'low-molecular-weight fatty acids' with 'lipids'? I think this is deceptive and misleading for the readers to expand from a small subgroup to a big diverse class of molecules. Instead, I recommend to stick to the most correct terms possible.
Response: we thank the Reviewer for his/her suggestion. We removed the sentence as it can be misleading. The NMR analysis of WSOC cannot be accurate in detecting fatty acids with respect to other lipids. As explained above, the chemical classes identified on the basis of patterns in the unresolved NMR resonances are mainly based on the comparison between the spectroscopic properties of the ambient samples with those of aerosol source types, like the bubble bursting aerosols produced during tank experiments. In such samples, the most characteristic fingerprint for materials

originating from lipids is the pattern of complex resonances at 0.9, 1.2 and 1.5 ppm of chemical shift which is characteristic of aliphatic compounds with a linear structure. Such chemical structure cannot form from the oxidation of other biogenic compounds like isoprene and monoterpenes and, in this environment, must be linked to the atmospheric cycling of fatty acids. We refer here to "low-molecular weight fatty acids" (LMW-FA) because the methylenic chains are short (probably up to C8 – C10 at most) as C16 - C18 fatty acids are not recovered in WSOC. We sometimes refer to "lipids" to acknowledge that the LMW-FA can be part of a broader family of compounds although our method allows to fingerprint mainly the alkanoic acids (identified as LMW-FA).

Line 275: Based on which observation do you assume that this POA is 'apparently being transported for thousands of kilometers and across the Antarctic continent.'?
Response: One of the most striking result of the sampling campaign is that we found the same OA component (with its specific primary chemical features linked to sea-spray aerosol) at both sites, i.e. at locations 2000 km away from each other (with Halley distant from the ocean at least 200 kilometers). The remoteness of Halley from the sea excludes that marine POA are formed locally and must be advected from lower latitudes i.e. from the SO. In Figure 7, we show that during January, when the SOA component progressively takes over the SOA fraction of the organic aerosol, but around the 18th Jan an event of transport of POA have impacted both stations. This suggests that the POA concentrations are largely influenced by the synoptic-scale weather systems rather than by local production. We have modified the sentence to acknowledge that we report a first evidence for this phenomenon which deserves more investigation:
"In summary, this POA seems to be a common component of the sea-spray OA associated to open ocean areas across a wide range of longitudes and can be transported for thousands of kilometers."

Lines 461-465/ Author contributions: The abbreviation 'M.R.' could stand for both coauthors 'Mara Russo' and 'Matteo Rinaldi'. Rethink your abbreviation system. Who is 'D.S.C.B.'? (In the author list there is only a 'David C.S. Beddows'. What were the contributions of the coauthors 'Roy M. Harrison' and 'Thomas Lachlan-Cope'? They were not mentioned in this section.
Response: we thank the Reviewer for arising these mistakes/lacks. We have corrected the discrepancies in the revised version.

Figure 1b: I guess the bluish colors represent sea ice. If so, please add a legend to the plots.
Response: yes, the bluish areas represent the sea-ice cover extension. We added the info to the caption. We have also added a legend for the sea-ice percentages.

Furthermore, I was wondering what about the role of shelf ice. Was this considered in the air mass history analysis and discussion in your study? In Figure 1b the Antarctic shelf ice regions are currently presented with the same coloring like open ocean, which might be misleading.
Response: We have shaded the sea ice around the land mass of Antarctica marked on the map to help avoid any misleading

Figures 3 and 5 and 6b: Clarify the abbreviations denoting functional groups in the figure caption and ensure the usage adheres to proper English conventions for chemical terms (e.g., 'alif.' versus 'aliphatic').
Response: We thank the Reviewer for his/her suggestion. We changed the abbreviations accordingly to the CAS Standard Abbreviations & Acronyms lists (https://www.cas.org/support/documentation/references/cas-standard-abbreviations). What is not common abbreviation was explicitly reported in the text describing the H-NMR functional groups and identified tracers (paragraph 2.3).

Figure 6a: Use the same sequence for the substances in the plot as you did in Figures 2 and 4.
Response: We thank the Reviewer for his/her suggestion. We changed the sequence in the figure.

Table S1: Remove the last two sentences ('Whilst the start and end […] fits the purpose of the work presented') from the table caption. The column 'Month of the study' is redundant in regard of column 3,4,6 and 7. I recommend to remove column "Month of the study'. Instead applying a proper date-time format to the remaining columns (e.g. dd/mm/yyyy hh:min)
Response: We accepted the suggestions and revised the Table accordingly

Table S2: Add Std to (S5;RH(%)). Should wind directions (WD) be averaged over sampling time considering that it is an angular dimension? I instead recommend to define four sectors (e.g. North: 315°-45°; East:45°-135°, South:135°-225°, West:225°-315°) to give in this table the percentage of time where wind came from which sector.
Response: The missing Std of RH has been added. Furthermore, about the wind direction we want to specify that the values reported in the original Table S2 are vector averages, i.e., considering already the angular dimension of wind direction. Anyway, we now calculated as suggested the percentage times where the wind came from each sector, whether N, E, S or W. These indeed corroborate our original vector average of wind direction and speed but are probably more straightforward for the reader (as suggested by the Referee) and so we replaced our vector average values with these time percentages in the revised Table S2

SI, Lines 60: How is betaine related to an oligomer?
Response: we thank the Reviewer for arising this oversight. We intended to use the term "osmolytes" and we changed it in the text

Si, Line 77 and in other parts of the manuscript: 'Dall'Osto et al. 2023, in prep.'. I would recommend to remove the year. When this manuscript is still in preparation and not submitted at least, it certainly won't be citable for 2023 anymore.
Response: we thank the Reviewer for arising this oversight. Based on the journal rules we actually have to remove all the *in prep.* references. We replaced that reference with another one already published (Dall'Osto et al., 2022a)

Figure S3: You identify glucose and sucrose in Factor 1, which are known to be neutral sugars. In Factor 5 you attribute a complete different chemical shift to 'neutral sugars', which seem to be identical to 'polysaccharides' and 'glycerol' in Factor 1. It appears inconsistent. Is it possible that the signals currently assigned to glucose and sucrose could also be other monosaccharides, disaccharides or derivatives, such as fructose, arabinose, trehalose or levoglucosan? How does your assignment of substances (e.g. sugars) match with the findings of other groups? Are there publications on glucose, saccharose, 'generic polysaccharides' in the atmosphere of the Antarctic or Southern Ocean (maybe using other analytical tools)?
Response: we thank the Reviewer for his/her attention and suggestions. We have already partially responded to this comment in the previous ones about the interpretation of spectral signals in H-NMR, but we complete the response answering to the specific questions raised here. The questions here involve two main aspects: 1. The different definitions of categories of compounds and 2. The unequivocal identification of single molecular compounds. About the first point, we sometimes used different definitions in different parts of the discussion mainly to highlight different aspects of the analyzed OA chemical composition. We used "neutral sugars" in opposition to "acidic sugars" (when we describe the main features of Halley samples) because these two categories have different prevalent signals in the H-NMR spectra: the former, characterizing more the range 3.2-4ppm, while the latter showing chemical shifts above 4ppm. The term "neutral sugars" is used in this part of the discussion just in contrast with the "acidic sugars", but as a matter of fact "neutral sugars" encompass

both saccharides than polyols like glycerol: this is now clarified in Table S5. While the signals above 4ppm (characteristic of Halley samples) can not be considered of the same category. So, we speculate on which other possible molecules they can represent (new supplementary figure S10 and S17 and related text).
About the second aspect, as already mentioned in previous replies, there are some signals that are clearly and unequivocally attributable to specific molecules: two of these are for instance the Sucrose and the Glucose anomeric doublets at 5.40 and 5.22ppm. These are clearly reported also in previous literature about Antarctic aerosol, sea-water and ice samples (Pautler et al., 2012; Dall'Osto et al., 2022b; Decesari et al., 2020). At the same time there are some molecules that can be excluded because should have specific signals in the spectra that are missing: this is the case of levoglucosan (characterized by a singlet at 5.45ppm, Paglione et al., 2014b) or arabinose (with a characteristic doublet at 4.5ppm and others around 3.9-4ppm, all missing) or trehalose (with its characteristic doublet at 5.18ppm). Instead fructose as well as other possible saccharides or polyols already cited (e.g., arabitol, mannitol, glycerol, etc.) can not be excluded and indeed they could be among those that make up the signal bands between 3.4 and 4ppm. We report here below an elaboration of the spectra using Chenomx evaluation tool to show the expected signals for some of these molecules. However, we cannot identify unequivocally them because if present they have very low concentrations and their specific peaks are all mixed together (scarce sensibility of the NMR for isolation of these compounds). And for this reason we just talk of generic "saccharides" or "neutral sugars".

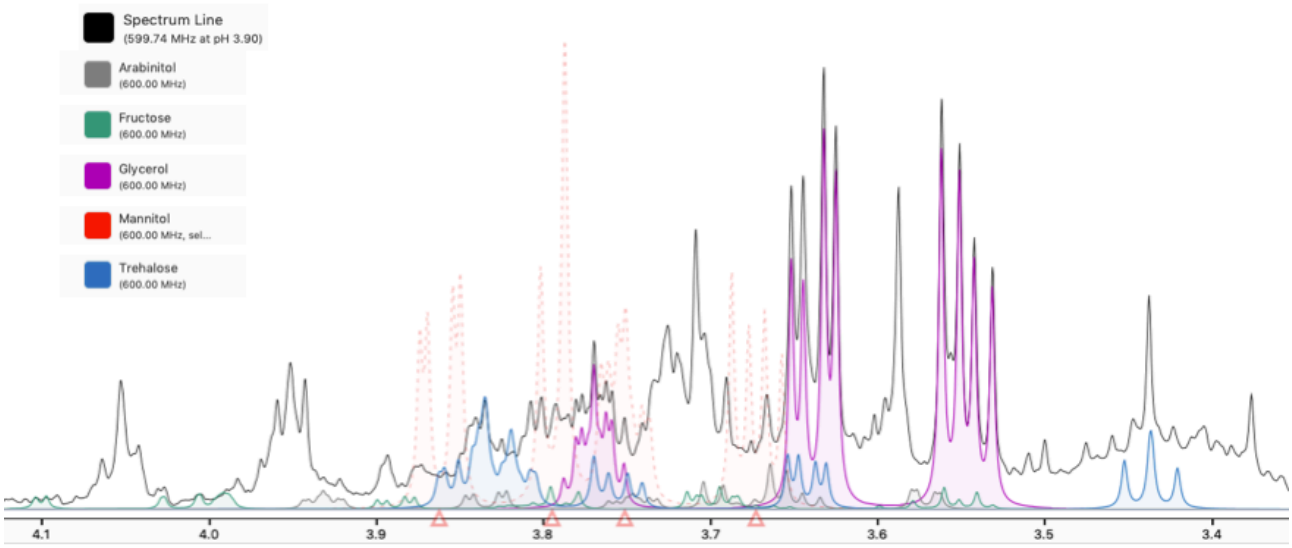

Figure R2: fitting between the expected signals for some sugars relevant for atmospheric aerosol and the H-NMR spectrum of sample S4 using the Chenomx NMR suite (Chenomx inc., evaluation version 9.0). Expected signals in the alcoxy region (3.2-4.2ppm) of the spectrum are reported for: glycerol (magenta line), arabitol (or arabinitol, grey line), fructose (green line), threalose (blue line) and Manitol (red dashed line, because not fitting well).

Figure S8: Why do you differentiate between 'open ocean (<60°N)' and 'open ocean (>60°N)'. How would it impact the results of the measurements? Shouldn't it be '°S' instead of '°N'?
Response: we thank the Reviewer for arising this oversight. Of course, it is "°S" and not "°N", and the symbols for greater or smaller values are inverted. We modified the previous Figure S8 in the new S15, adding some more info in the caption. The distinction between latitudes higher or lower than 60°S is a proxy of the sea ice influence: all the latitudes greater than 60° are considered influenced by sea ice in a not negligible amount even if lower than sea ice marginal zone (that is for definition 15-85% covered by ice). To highlight the importance of the sea ice influence in the definition of this category we modified also its name in "Sympagic waters".

Figure S10: Eliminate the red underlining beneath 'Lac' (It appears the figure may have been copied from PowerPoint or Word).
Response: done.

Additional references:

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