Answers to the Referees' comments regarding the manuscript:

Marine Carbohydrates and Other Sea Spray Aerosol Constituents Across Altitudes in the Lower Arctic Troposphere

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We thank the reviewers for the evaluation of our manuscript. In this document, all of their constructive comments have been answered thoroughly. The referees' comments are marked blue, our replies black, and changed text in the manuscript green. The given line numbers of changed sentences are referring to the new lines in the revised manuscript. Please note that, following reviewer 1's request to move a figure from the supplement to the main manuscript and add another one, the figure numbering has been adjusted.

Reviewer 1:

General comments:

The data set, focusing on carbohydrates in arctic aerosols at different altitudes in the atmosphere and samples of relevant depths from seawater, represents a valuable contribution, which is novel in its detail. Explicitly the high data coverage including autumn to spring months and the three showcases dissecting different meteorological and stratification scenarios are interesting. The manuscript makes a comprehensive contribution to disentangling the sources and role of carbohydrates present in primary marine aerosols, provided that the results and discussion are still appropriately revised. While the methods seem robust and are clearly outlined (however, I am not an expert in sampling aerosols nor in executing meteorological or trajectory calculations), I am not convinced by certain assumptions and interpretations, which are in particular drawn from case III. I would recommend to further include comparative figures and literature to evaluate concentration ranges and composition of CCHO. Overall, the manuscript is well structured and the language is appropriate.

Authors: We thank the reviewer for the positive assessment of the dataset, its coverage, and the detailed analysis of carbohydrates across different altitudes and seawater depths. We also appreciate the constructive suggestions regarding Case III, the interpretation of elevated CCHO and oxalate concentrations, and the value of comparative figures and literature to contextualize our findings.

We carefully considered the reviewer's concerns. In the revised manuscript, we have:

- Reassessed the interpretation of Case III to highlight the role of marine sources, including cloud-enriched TEPs, while reducing emphasis on secondary atmospheric formation.
- Integrated relevant literature to support our interpretations (e.g., Furukawa and Takahashi, 2011, van Pinxteren et al., 2022).
- Clarified limitations in comparing relative CCHO composition across altitudes due to low aerosol mass at balloon and winch sampling points, as discussed in the Methods and Results sections.

We believe that these revisions address the reviewer's concerns and provide a more balanced and transparent discussion of sources and transformations of carbohydrates in Arctic aerosols. Detailed responses to specific comments, including Case III interpretations, relative composition, and comparative context, are provided in the corresponding sections below.

With regards to the conclusions drawn from case III (high CCHO, calcium and magnesium concentrations versus lower sodium concentrations, samples influenced by cloud droplets) and the correlation between oxalate and xylose as discussed in chapter 3.3, I would suggest that the authors consider the following scenario. Elevated oxalate concentrations have been identified to correspond to the biological productive seasons above remote oceanic regions (Rinaldi et al., 2011), while xylose concentrations increase after certain phytoplankton blooms (Sperling et al., 2017). Marine aggregates, such as TEP composed of carbohydrates, also increase during blooms and are further relying on divalent cations such as Ca. Oxalate on the other hand, forms complexes with divalent cations including Ca (Furukawa and Takahashi, 2011), while oxalic acid increases hygroscopicity. In case III, aerosol particles were sampled within cloud water. Cloud water has been previously shown to exhibit a high number of TEP (van Pinxteren et al., 2022). As the authors stated, lower Na concentrations could be explained by previous wet precipitation (L528), while higher Ca and Mg concentration could result from the CCHO matrices

excluding Na. I am thus not sure if the suggested secondary production pathway within the atmosphere is the most obvious/reasonable potential pathway explaining the data sets presented here.

Authors: Our original text in case III stated: 'While $CCHO_{aer}$ and $oxalate_{aer}$ might originate through secondary in-situ atmospheric chemical or microbial processes, particularly in the aqueous phase (as discussed in more detail in the following section), this does not explain elevated inorganic Ca^{2+}_{aer} and Mg^{2+}_{aer} . These ions likely derive from preexisting organic structures in SSA, becoming soluble and detectable after chemical aging. OM-bound Ca^{2+}, as already found in Antarctic SSA (Su et al., 2023), may originate from SML-derived polysaccharide gels and airborne algal cells or fragments, which can release Ca^{2+} and Mg^{2+} through gel dispersion or cell dissolution under the acidic conditions of chemically aged SSA aerosol particles (Aller et al., 2017; Angle et al., 2021; Orellana and Leck, 2015; van Pinxteren et al., 2022; Trainic et al., 2018; Zhu et al., 2014).'

We believe that our original argument regarding the elevated Ca^{2+} and Mg^{2+} levels at high altitudes is consistent with the reviewer's suggestion that these ions are associated with marine aggregates. The reviewer additionally points out that this mechanism could also explain the elevated CCHO and oxalate concentrations observed in cloud-influenced samples. We fully agree that marine carbohydrates, including TEP, are enriched in clouds. Accordingly, we have integrated this point into our discussion and slightly revised the paragraph structure to place less emphasis on secondary formation in the atmosphere. The changed text now reads: "These elevated concentrations cannot be explained by direct local sea spray emissions or remote source contributions alone, suggesting the involvement of cloud-related enrichment and transformation processes.

Soluble Ca^{2+}_{aer} and Mg^{2+}_{aer} possibly derived from preexisting organic structures in SSA, becoming soluble and detectable after chemical aging. OM-bound Ca^{2+}, as already found in Antarctic SSA (Su et al., 2023), may originate from SML-derived polysaccharide gels such as TEPs, and airborne algal cells or fragments, which can release Ca^{2+} and Mg^{2+} through gel dispersion or cell dissolution under the acidic conditions of chemically aged SSA aerosol particles (Aller et al., 2017; Angle et al., 2021; Orellana and Leck, 2015; van Pinxteren et al., 2022; Trainic et al., 2018; Zhu et al., 2014). Since these particles were sampled in cloud water, which contains abundant TEP (van Pinxteren et al., 2022), this mechanism may also explain the elevated CCHO concentrations. Ca^{2+}_{aer} can form complexes with $oxalate_{aer}$ (Furukawa and Takahashi, 2011), and oxalic acid increases hygroscopicity, potentially accounting for the high values observed at the balloon in Case III. In addition, secondary in-situ atmospheric or microbial origins, particularly in the aqueous phase, may contribute to $CCHO_{aer}$ and $oxalate_{aer}$ and is discussed in the following section." (Lines 646-662)

Specific comments:

L68 The critical information here is that carbohydrates are a major product of photoautotrophic organisms, which represent the base of the food web. Carbohydrates can be rapidly consumed by heterotrophic organisms, however, in dependence of their structure and composition.

Authors: We added the information on the formation of marine carbohydrates by photoautotrophs and their degradation by heterotrophic organisms. In addition, we highlight that heterotrophs themselves also can 'produce' carbohydrates by transforming existing substrates into exopolymeric substances (EPS) consisting of polysaccharides. In the revised and more detailed version, we now state it explicitly. The updated text reads: "In seawater, carbohydrates are produced by photoautotrophic organisms, predominantly as linear or branched oligo- and polysaccharides (Aluwihare et al., 1997; Borch and Kirchman, 1997; Engel and Händel, 2011; Khadem, 2012), collectively referred to as combined carbohydrates (CCHO). They also exist as monosaccharides, known as dissolved free carbohydrates (DFCHO). Both DFCHO and CCHO are consumed or transformed by heterotrophic organisms, with turnover

rates largely determined by the molecular structure and composition of the carbohydrates (Arnosti et al., 2021; Engel and Händel, 2011; Ittekkot et al., 1981; Kirchman et al., 2001)." (Lines 67-74)

L362 I would recommend to group winch/pier and balloon samples into the corresponding categories: a) identical, b) lower at the ground, c) higher at the balloon and represent the categorized data in a corresponding plot (e.g. boxplots). It is complicated to track every single date and sodium concentration listed back to the timeseries (Figure 2) and then compare it to the corresponding CCHO concentration (and potentially composition) in aerosol particles (L485-498). Especially, because the authors later state that sodium and CCHO concentrations covaried (L495).

Authors: We agree with the reviewer that the original presentation made it difficult to track relationships between winch, and balloon samples, as well as the covariation of sodium and CCHO concentrations. While boxplots were one possible option, we implemented an alternative visualization approach. We now present the data in a simple scatter plot (Figure 3 in the new version), with samples categorized and visually distinguished into the three groups: (a) identical, (b) higher at the ground, and (c) higher at the balloon. This representation allows direct comparison between sodium and CCHO concentrations across sampling platforms and improves accessibility and interpretability for the reader. We believe this format more clearly illustrates the covariation patterns discussed in the text.

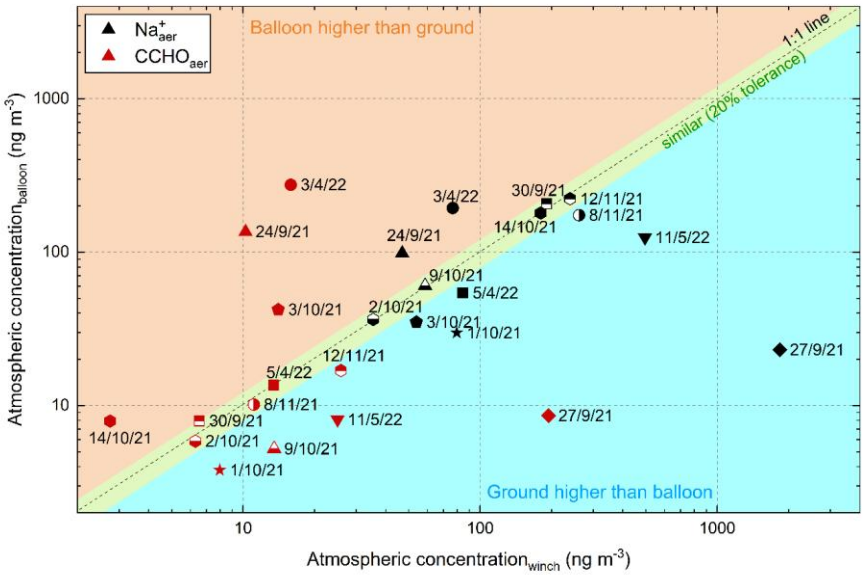

Figure 3. Scatter plot showing Na^{+}_{aer} (black symbols) and $CCHO_{aer}$ (red symbols) concentrations in TSP measured at the winch, and balloon levels. Data points are categorized to indicate whether values were similar, higher at the balloon, or higher at the ground.

L443 As the results from the seawater analysis seem to be an integral part of your results and also the discussion would profit, I would include at least one comprehensive figure on seawater composition in the main manuscript and not only supplement.

Authors: We have moved the former Figure S3 from the supplement into the main manuscript, where it is now presented as Figure 4. This figure best illustrates the trends in seawater carbohydrates. The numbering of the remaining figures in both the supplement and the SI has been adjusted accordingly.

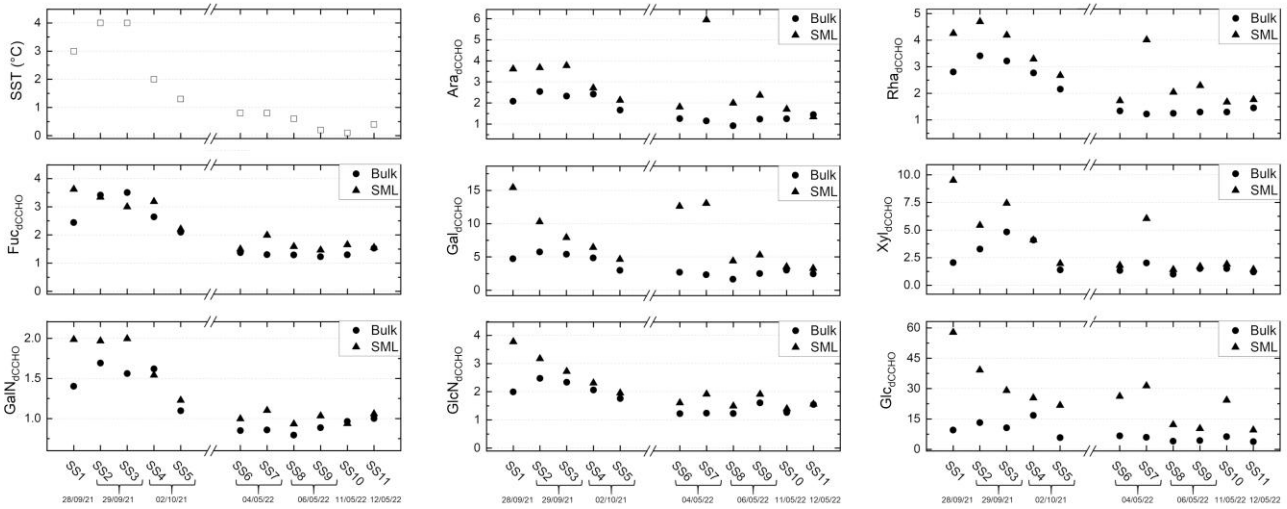

Figure 4. Concentration of measured monosaccharide units in dCCHO from bulk and SML samples collected in Kongsfjorden during autumn 2021 and spring 2022, along with SST measurements taken from bulk samples at the time of sampling.

In general, it would be very interesting to see a comparative figure of the (relative) carbohydrate composition from the seawater, over the pier and winch to higher altitudes (balloon). This would also enable the authors to better judge on the state of transformation (e.g. bacterial degradation) as comparative literature exists at least for oceanic profiles and mesocosm bloom studies (e.g. Goldberg et al., 2009; Engel, Harlay et al., 2012; Sperling et al., 2017; Hasenecz et al., 2020). Potentially further information could be revealed, which may assist with the interpretation of the three case studies.

Authors: We fully agree with the reviewer that a comparative figure of the relative combined carbohydrate (CCHO) composition from seawater and aerosol particles collected at the Old Pier, the winch, and balloon altitudes would be highly informative. Such an approach has proven valuable in previous studies. For example, Zeppenfeld et al. (2021) in the Southern Ocean and Zeppenfeld et al. (2023) in the Arctic compared relative CCHO composition in bulk seawater, the sea surface microlayer, and ambient aerosol particles, revealing substantial compositional differences indicative of atmospheric processing, including potential microbial transformation.

We intended to apply the same framework in the present study. However, we encountered methodological constraints: the aerosol mass collected on balloon and winch filter samples was extremely low. This allowed measurement of major monosaccharides (Glc, Xyl, Gal, and in some cases Ara), whereas minor monosaccharides fell below detection limits in the balloon and winch samples. Using detection limits (or half the detection limit) to construct relative patterns was deemed unsuitable, as differences in detection limits among monosaccharides, especially uronic acids, could introduce misleading artifacts. In contrast, the aerosol mass was sufficient for reliable quantification of the total CCHO pattern only at the Old Pier (and the seawater samples).

Consequently, while we fully appreciate the reviewer's suggestion, the current dataset does not allow a scientifically meaningful comparison of relative CCHO composition for winch and balloon samples. To avoid potentially misleading interpretations, we prefer not to include such a comparative figure in this manuscript.

However, we now addressed this aspect better in both the Experimental and Results & Discussion sections. The added text now reads: "For the winch and balloon samples, the limited air volume and resulting low aerosol mass collected on the filters permitted quantification only of the major monosaccharides (typically Glc, Xyl, Gal, Ara), while minor monosaccharides remained largely below the instrumental detection limits. In contrast, samples from the Old Pier and surface seawater provided sufficient analyte mass to quantify the full suite of the CCHO monosaccharides." (lines 260-265) and "However, because only the major monosaccharides (typically Glc, Xyl, Gal, Ara) could be quantified reliably in the winch and balloon samples, relative CCHO compositions were not assessed across the entire vertical sample set. Therefore, they were not used to further substantiate this conclusion, as it has been done in Zeppenfeld et al. (2021, 2023)." (lines 502-506)

L546 Again, the relative CCHO composition is not represented and would add a valuable contribution to the manuscript (see comment above).

Authors: As addressed above, we chose not to include the relative CCHO composition due to analytical constraints and to avoid potentially misleading conclusions. We have added text in the manuscript to clarify this aspect. The new text now reads: "However, because only the major monosaccharides (typically Glc, Xyl, Gal, Ara) could be quantified reliably in the winch and balloon samples, relative CCHO compositions were not assessed across the entire vertical sample set. Therefore, they were not used to further substantiate this conclusion, as it has been done in Zeppenfeld et al. (2021, 2023)." (lines 502-506)

L697 Sodium was markedly higher at the ground.

Authors: We agree with the reviewer. We have revised the sentence to compare the values more accurately. The changed line now reads: "Furthermore, major inorganic ions (**Figure 5c**) were generally similar at the ground and balloon (Cl^-_{aer}: 289 & 252 ng m^{-3}; $SO^{2-}_{4\,aer}$: 66 & 59 ng m^{-3}; K^+_{aer}: 23 & 20 ng m^{-3}), with Na^+_{aer} (53 & 35 ng m^{-3}) somewhat higher at the ground." (Lines 633-636)

L711 This assumption sounds a little biased, see comments provided above and below with regards to the interpretation of results.

Authors: We have carefully considered the reviewer's major criticism regarding secondary production of $CCHO_{aer}$ and $oxalate_{aer}$, as well as the potential enrichment of these compounds within clouds, which may provide an alternative explanation for the elevated values observed in Case III. As described above, we have revised this section , included the suggested enrichment mechanism and placed less emphasis on secondary atmospheric production. The updated text now reads: "These elevated concentrations cannot be explained by direct local sea spray emissions or remote source contributions alone, suggesting the involvement of cloud-related enrichment and transformation processes.

Soluble Ca^{2+}_{aer} and Mg^{2+}_{aer} possibly derived from preexisting organic structures in SSA, becoming soluble and detectable after chemical aging. OM-bound Ca^{2+}, as already found in Antarctic SSA (Su et al., 2023), may originate from SML-derived polysaccharide gels such as TEPs, and airborne algal cells or fragments, which can release Ca^{2+} and Mg^{2+} through gel dispersion or cell dissolution under the acidic conditions of chemically aged SSA aerosol particles (Aller et al., 2017; Angle et al., 2021; Orellana and Leck, 2015; van Pinxteren et al., 2022; Trainic et al., 2018; Zhu et al., 2014). Since these particles were sampled in cloud water, which contains abundant TEP (van Pinxteren et al., 2022), this mechanism may also explain the elevated CCHO concentrations. Ca^{2+}_{aer} can form complexes with $oxalate_{aer}$ (Furukawa and Takahashi, 2011), and oxalic acid increases hygroscopicity, potentially accounting for the high values observed at the balloon

in Case III. In addition, secondary in-situ atmospheric or microbial origins, particularly in the aqueous phase, may contribute to $CCHO_{aer}$ and $oxalate_{aer}$ and is discussed in the following section." (Lines 646-662)

L721 I am not sure if atmospheric aging has been proven at this point. Potentially refer to 'atmospheric processing'. Differences in aging/ the residence time would also imply differences in source locations.

Authors: We agree with the reviewer that the more general term "atmospheric processing" is more accurate based on the available observations. Accordingly, we have replaced "atmospheric aging" with "atmospheric processing" in this sentence and at other positions throughout the manuscript where this claim had been made.

L771 As the model does not resolve the SML, which is frequently enriched as also stated by the authors, not crossing the marginal-ice zone does not necessarily imply no major oceanic contributions.

Authors: We agree. Here, we actually intended to refer to all productive marine regions that could be considered either from model output (which does not resolve the SML) or from field observations in the SML, not only the marginal ice zone. We have rephrased the paragraph to make this point clearer. The revised text now reads: "However, in cases of high $CCHO_{aer}$ at higher altitudes in this study, air mass trajectories did not pass over any of these productive marine regions within 48 hours before reaching Svalbard (**Figure S7**). These findings suggest that long-range transport of SSA from more productive remote marine sources is unlikely to explain the elevated $CCHO_{aer}$ concentrations at elevated altitudes within the lower troposphere in Ny-Ålesund, further supporting a predominantly local source or atmospheric in-situ formation." (Lines 711-716)

L788 'aerosolized taxa' refers to bacteria, which are commonly found in oceanic or terrestrial surfaces? Clarify.

Authors: We have reworded this sentence to clarify that largely marine bacteria were aerosolized, including taxa previously found in both Kongsfjorden atmosphere and seawater, supporting the relevance of our observations. The changed text now reads: "Our complementary microbiological sampling during our campaign supported such dynamics by detecting diverse marine bacteria in aerosol particles (Wietz et al., 2025). Some aerosolized taxa, for instance *Polaribacter*, encode multiple genes for CCHO metabolism (Avcı et al., 2020) and consistently occur in both Kongsfjorden seawater and atmosphere during the spring bloom (Feltracco et al., 2021)." (Lines 726-730)

L789 Many heterotrophic bacteria metabolize carbohydrates. Especially in the surface ocean, they rely heavily on primary products, including major fractions of carbohydrates, with phytoplankton production at the base of the food chain. I.e. if it is assumed that these bacteria were transferred from the ocean surface into aerosol particles, such metabolic characteristics are ordinary.

Authors: We agree that carbohydrate metabolism is common among heterotrophic bacteria. However, Polaribacter is a well-established specialist for algal-derived carbohydrate degradation and is closely linked to phytoplankton blooms. Its consistent occurrence in both seawater and aerosols during the spring bloom therefore carries specific ecological and biogeochemical relevance. We therefore propose to keep the sentence as it is.

L864-865 This is only one side of the possible interpretation: Maybe xylose was only present in the CCHO of aerosol particles and not at all processed and/or released into the free fraction?

Authors: This is a valid point. We have incorporated this consideration into the main text. The revised passage now reads: "With one exception, free xylose was never detected in any aerosol sample of this study. This suggests two possible explanations. First, xylose may have remained bound within the $CCHO_{aer}$ fraction and was not released into its free form. In this case, it would indicate co-emission without a chemical pathway leading to oxalate. Second, free xylose may have been rapidly processed in the atmosphere via reactions described below." (Lines 804-808)

Technical corrections:

L72-73 Rephrase sentence as incomplete.

Authors: We have added a few words to complete the sentence. The revised sentence now reads: "They also exist as monosaccharides, known as dissolved free carbohydrates (DFCHO). Both DFCHO and CCHO are consumed or transformed by heterotrophic organisms, with turnover rates largely determined by the molecular structure and composition of the carbohydrates (Arnosti et al., 2021; Engel and Händel, 2011; Ittekkot et al., 1981; Kirchman et al., 2001)." (Lines 70-74)

L721 If em-dashes are used instead of comma or brackets, please use a concise size etc. Their usage is rather unusual in a scientific context, and I would recommend to reduce them throughout the whole manuscript.

Authors: We have substantially reduced the use of em-dashes throughout the manuscript and rephrased the affected sentences accordingly.

L402 Balloon (III) is two times mentioned in figure 2a and varies with altitude. Please clarify and include a statement in the figures caption.

Authors: We added this clarification to the caption of Figure 2, which now reads: "In panel (a), the label "Balloon (III)" appears twice because balloon sampling for sodium measurements occurred both below and above the fixed altitude of the Zeppelin Observatory." (Line 401)

L599 'both HALFBACs' As the sentence is very long, it is not clear until L604 if the comparisons are related to the balloon (III) and zeppelin (IV) observations in figure 3a or rather to ground and altitude samples, as specified only at the end. Clarify.

Authors: We moved the information on "ground versus balloon" to the beginning of the sentence to improve clarity. The revised sentence now reads: "HALFBAC samples from ground and balloon showed similar concentrations of inorganic ions (Na^+_{aer}: 240 & 223, Cl^-_{aer}: 586 & 543, $SO^{2-}_{4\,aer}$: 336 & 330, Ca^{2+}_{aer}: 87 & 92, Mg^{2+}_{aer}: 9.5 & 7.8, K^+_{aer}: 34 & 30 ng m^{-3}), $oxalate_{aer}$ (34 & 37 ng m^{-3}), and major CCHO-bound monosaccharides ($Glc_{CCHO,aer}$: 17 & 9.1, $Xyl_{CCHO,aer}$: 5.0 & 4.7, $Ara_{CCHO,aer}$: 1.2 & 0.9 ng m^{-3}), supporting a well-mixed layer." (Lines 562-566)