

# Seasonal and interannual variability on the chemical composition of the Svalbard surface snowpack

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## 31    **Abstract**

32    The Svalbard Archipelago, highly sensitive to rapid environmental changes, offers an ideal physical  
33    laboratory to investigate how environmental drivers can shape the seasonal chemical composition of  
34    snow in a warming climate. From 2018 to 2021, sampling campaigns at the Gruvebadet Snow  
35    Research Site in Ny-Ålesund, in the North-West of the Svalbard Archipelago, captured the  
36    interannual variability in ionic and elemental impurities within surface snow, reflecting seasonal  
37    differences in atmospheric and oceanic conditions. Notably, warmer conditions prevailed in 2018-19  
38    and 2020-21, contrasting with the relatively colder season of 2019-20. Our findings suggest that  
39    impurity concentrations in the 2019-20 colder season are impacted by enhanced sea spray aerosol  
40    production, likely driven by a larger extent of sea ice, and drier, windy conditions. This phenomenon  
41    was particularly evident in March 2020, when extensive sea ice was present in Kongsfjorden and  
42    around Spitsbergen due to an exceptionally strong, cold stratospheric polar vortex and unusual Arctic  
43    Oscillation (AO) index positive phase. This study provides a detailed characterization of how snow  
44    chemistry in this area responds to major environmental conditions, with particular attention to sea-  
45    ice extent, atmospheric circulation, synoptic conditions, and Arctic climate variability.

## 46    **1. Introduction**

47    Chemical analysis of surface Arctic snow can provide valuable comprehension of the composition of  
48    Arctic aerosols, its deposition, and related exchange processes (Lai et al., 2017). In Svalbard, climate-  
49    driven changes in air temperature, precipitation, and sea ice extent over recent decades have strongly  
50    shaped these processes, underscoring the importance of a detailed snow chemical characterisation  
51    (Gjermundsen et al., 2020; Rantanen et al., 2022).

52    The Svalbard region, located at the southern edge of the seasonal Arctic sea-ice zone, is characterised  
53    by a maritime climate with strong temperature variations during winter (Hansen et al., 2014; Barbaro  
54    et al., 2021). In the Arctic winter, the stratospheric polar jet fosters a high-atmospheric vorticity zone.  
55    This winter vortex typically acts as a strong barrier for the long-range transport of pollutants from  
56    mid-latitudes (Lawrence et al., 2020). However, it occasionally allows warm southern air to penetrate  
57    the region (Schoeberl and Newman, 2015). Additionally, Svalbard frequently experiences intense  
58    cyclonic storms in autumn and winter, which bring both heat and moisture from lower latitudes  
59    (Rinke et al., 2017). These intense meteorological variations, generally linked with a weaker polar  
60    vortex (Sobota et al., 2020; Salzano et al., 2023), favour long-range transport of aerosols to the  
61    archipelago, including pollutants from continental sources (Stohl et al., 2006b; Yttri et al., 2014a;  
62    Vecchiato et al., 2024; D'Amico et al., 2024).

Arctic snow captures dry and wet deposition and forms an archive that includes a range of seasonal chemical species such as major ions and trace elements, as well as human-made pollutants emitted into the Arctic atmosphere (Koziol et al., 2021). Ny-Ålesund is a well-monitored area and a natural laboratory for complex system observations, ideal for exploring both long-range contaminants from mid- to high-latitude regions of Eurasia and Canada (Nawrot et al., 2016; Song et al., 2020; Vecchiato et al., 2024; D'Amico et al., 2024), and local inputs from both natural processes and human settlement (Vecchiato et al., 2018). Previous research has extensively investigated the chemistry of Arctic snow and the exchange of inorganic species between the cryosphere and the atmosphere across multiple sites, including Barrow, Summit Greenland, Alert, Sodankylä, and over the Arctic Ocean during the MOSAiC expedition (e.g., Beine et al., 2003; Björkman et al., 2013; Jacobi et al., 2019). Specific studies in Ny-Ålesund and surrounding areas have explored the temporal and compositional aspects of the lower atmosphere (Stohl et al., 2006a; Eleftheriadis et al., 2009; Geng et al., 2010; Zhan et al., 2014; Feltracco et al., 2020, 2021; Turetta et al., 2021), though relatively few have addressed the detailed seasonal dynamics of snow-atmosphere interactions in this region. Building on this existing research, our study aims to enhance the understanding of these interactions, particularly in the context of recent climatic changes.

In this study, we evaluate the surface snow concentration of ionic ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , methane sulphonic acid (MSA),  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ) and elemental impurities (Li, Be, Mg, Al, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Ag, Cd, Sb, Cs, Ba, Tl, Pb, Bi, U) for the snow seasons between 2018-2021, at the Gruvebadet Snow Research Site (GSRS) location, 1 km south of Ny-Ålesund, where clean and undisturbed snow conditions are guaranteed throughout the whole sampling season. The differences in average meteorological and climatological conditions across the studied seasons are analysed to assess how sea ice extent, polar vortex, and Arctic Oscillation (AO) conditions influence the composition of surface snow in connection with the aerosol-producing and deposition processes in Kongsfjorden. Additionally, a Kruskal-Wallis's test, followed by Dunn's post-hoc analysis, has been employed to identify species most affected by inter-annual and seasonal variations, with the goal of uncovering potential correlations between meteorological-climatic conditions and chemical concentrations.

## **2. Methodology**

### *2.1 Sampling and processing*

Three sampling campaigns were conducted in Svalbard between 2018 and 2021, covering the period from October to May according to the onset of the snowpack formation and melting. Sample

95 collection followed the protocol presented in Spolaor et al. (2019), further adopted by Bertò et al.  
96 (2021), where consecutive and adjacent sampling was carried in a 3x3 meters snow sampling area,  
97 within a clean sampling snowfield of 100 m width. Each sample was collected 10 cm apart from the  
98 previous one, along a precise path. This method was designed to minimise the temporal variability  
99 between consecutive samples and reduce the impact of potential spatial variability (within the 5-15%  
100 range, according to Spolaor et al., 2019).

101 During the first sampling campaign, carried out from October 4<sup>th</sup>, 2018 to May 10<sup>th</sup>, 2019, 133 snow  
102 samples were collected at the Gruvebadet Snow Research Site (GSRS), a clean-area located about 1  
103 km south of Ny-Ålesund, nearby the Gruvebadet Atmospheric Laboratory (GAL), dedicated to the  
104 chemical and physical monitoring of the seasonal snowpack (Scoto et al., 2023; Fig. 1).

105 The surface snow was sampled within the upper 3 cm, as this layer is the most directly affected by  
106 atmospheric deposition and snow-atmosphere exchanges (Spolaor et al., 2018, 2021b). Sampling only  
107 the uppermost layer reduces the risk of signal dilution in deeper snow layers, and ensures a simple,  
108 robust protocol suitable for long-term campaigns with minimal disturbance of the snowpack.

109 Throughout the season, the sampling resolution varied based on light conditions. During the polar  
110 night (from October to early March), snow sampling was carried out every 3-5 days. With the  
111 beginning of the polar day, daily sampling was conducted until the end of the snow season.

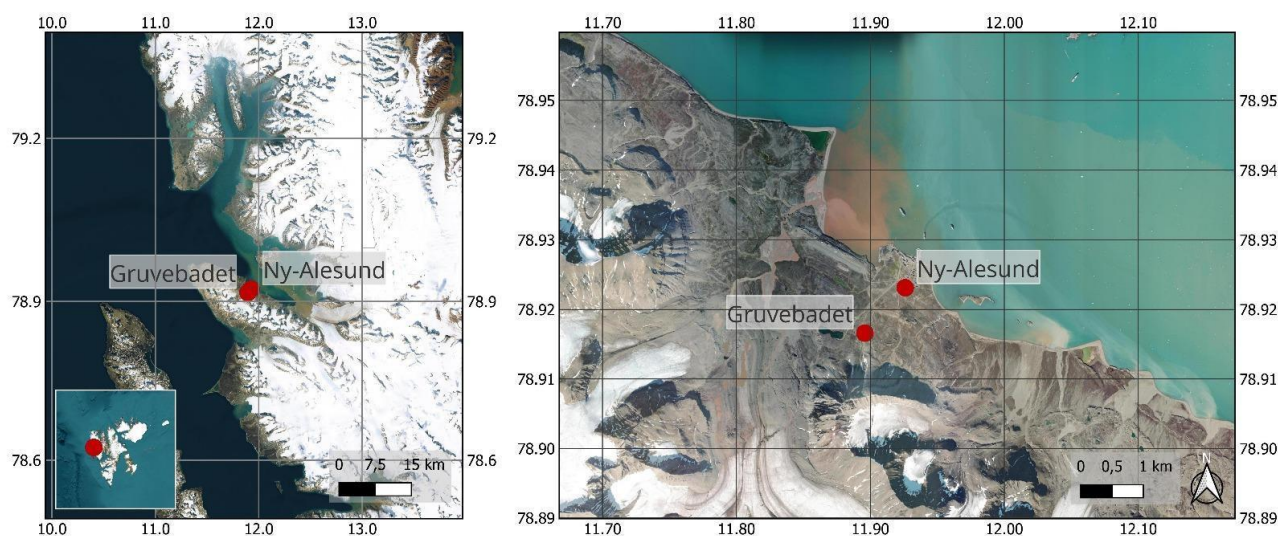
112 The second campaign was carried out from October 26<sup>th</sup>, 2019 to May 25<sup>th</sup>, 2020, with a total of 107  
113 samples collected. Consecutive samples represent the same snow layer in the absence of snowfall or  
114 wind drift/erosion. However, factors such as snow aging, potential element re-emission,  
115 transformation, and dry deposition can introduce variability, making continuous monitoring essential.

116 Finally, during the third snow sampling campaign, lasting from October 27<sup>th</sup>, 2020 to June 15<sup>th</sup>, 2021,  
117 a weekly sampling was conducted at GSRS, with a total of 32 samples collected.

118 During snow sampling, the temperature and density of surface snow were measured, and the density  
119 of snow was calculated based on weighting a 100 cc cylinder. After collection, snow samples were  
120 melted, and two different aliquots were obtained and stored in separate vials. In a 1.5 mL  
121 polypropylene (PP) vial, 1 mL of sample was stored for ionic species, while another aliquot was  
122 stored in a 5 mL LDPE vials for trace elements analysis. PP vials designated to ionic species analysis  
123 were previously sonicated for 30 min in UltraPure Water (UPW) ( $18\text{ M}\Omega\text{ cm}^{-1}$  at 25 °C) for  
124 decontamination. LDPE vial used for trace elements analysis were instead conditioned with HNO<sub>3</sub>  
125 2% and sonicated for 30 min. All sample aliquots were stored at -20°C in dark conditions and  
126 transported to the Venice ISP-CNR laboratories.

127 To assess potential contamination during sampling, handling, and transport, field blanks were  
128 collected during each campaign. Metal-free vials (Avantor, VWR Centrifuge Tubes, CHN) were

129 opened to ambient air at the sampling sites for a few minutes without collecting snow, then sealed  
 130 and transported to the Ny-Ålesund laboratory. There, they were filled with 2% HNO<sub>3</sub> and stored under  
 131 the same conditions as the snow samples. In parallel, analytical blanks were prepared by opening  
 132 vials to air, sealing them, and transporting them directly to Venice, where they were filled with 2%  
 133 HNO<sub>3</sub> and ultrapure water from the laboratory. Both field and analytical blanks were analysed  
 134 alongside the snow samples, confirming that background contamination levels were consistently  
 135 below LODs or one order of magnitude lower than the lowest concentration detected for all analytes.  
 136  
 137 Furthermore, seawater temperatures and salinity at 10 m depth were also monitored in Kongsfjorden  
 138 (Kb3; 78°57.228'N, 11°57.192'E) during 2019-2021 spring seasons, with data collected every 3-6  
 139 days (Assmy et al. 2023). Data was derived from Conductivity Temperature Depth (CTD) casts with  
 140 either a MiniSTD model SD-204 (SAIV A/S, Bergen, Norway) or a XR-620 CTD (RBR Ltd, Ottawa,  
 141 Canada). Combined casts of both instruments conducted in May 2020 and 2021 did not reveal  
 142 differences in temperature or salinity in the reported accuracy (two post comma digits).



**Fig. 1.** Gruvebadet Snow Research Site (GSRS) location with respect to Ny-Ålesund Research Station, in the Brøgger peninsula (Svalbard Islands).

## 2.2 Analysis of ionic species

147 The analysis of anionic species (Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, MSA) was carried out using an ion  
 148 chromatograph (IC, Thermo Scientific Dionex™ ICS-5000, Waltham, MA, USA) coupled with a  
 149 single quadrupole mass spectrometer (MS, MSQ Plus™, Thermo Scientific, Bremen, Germany). The  
 150 separation was performed using an anionic exchange column (Dionex Ion Pac AS 19 2 mm ID × 250  
 151 mm length) equipped with a guard column (Dionex Ion Pac AG19 2 mm ID × 50 mm length). Sodium

hydroxide (NaOH), used as mobile phase, was produced by an eluent generator (Dionex ICS 5000EG, Thermo Scientific). The NaOH gradient with a  $0.25 \text{ mL min}^{-1}$  flow rate was: 0–6 min at 15 mM; 6–15 min gradient from 15 to 45 mM; 15–23 min column cleaning with 45 mM; 23–33 min equilibration at 15 mM. The injection volume was 100  $\mu\text{L}$ . A suppressor (ASRS 500, 2 mm, Thermo Scientific) removed NaOH before entering the MS source. The IC-MS operated with a negative electrospray source (ESI) with a temperature of  $500^\circ\text{C}$  and a needle voltage of 3 kV. The other MS parameters are reported by Barbaro et al. (2017). The same IC system was simultaneously used to determine cationic species ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$ ). However,  $\text{Ca}^{2+}$  was not measured within the samples collected during the second campaign due to instrumental limitations.

The separation occurred with a capillary cation-exchange column (Dionex Ion Pac CS19–4 mm 0.4 mm ID  $\times$  250 mm length), equipped with a guard column (Dionex Ion Pac CG19–4, 0.4 mm ID  $\times$  50 mm length), and the species were determined using a conductivity detector. Analytical blanks of ultrapure water ( $> 18 \text{ M}\Omega \text{ cm}$ ) were included in the analysis, and the Method Detection Limit (MDL) was set to 3 times the standard deviation of the blank values. Checks for accuracy were made using certified multi-element standard solutions for anions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , no. 89886-50ML-F, Sigma Aldrich) and cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , no. 89316-50ML-F, Sigma Aldrich) at a concentration of  $10 \text{ mg L}^{-1} \pm 0.2\%$ . The analytical precision was quantified as the relative standard deviation (RSD) for replicates ( $n > 3$ ) of standard solutions and was always  $< 10\%$  for each ion.

### 2.3 Trace Elements analysis

Twenty-six elements (Li, Be, Mg, Al, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Ag, Cd, Sb, Cs, Ba, Tl, Pb, Bi and U) were analysed on samples previously melted and acidified to 2% v/v with  $\text{HNO}_3$  (UpA grade, Romil, UK) for 24 hours before analysis (Spolaor et al., 2018; Spolaor et al., 2021a).

The analysis was performed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS, iCAP RQ, Thermo Scientific, US). The ICP-MS was equipped with an ASX-560 autosampler (Teledyne Cetac Technologies), PolyPro PFE nebulizer, PFE cyclonic spray chamber thermostated at  $2.7^\circ\text{C}$ , sapphire injector, quartz torch and Ni cones. The acquisition was performed at 1550 W of plasma RF power in Kinetic Energy Discrimination (KED) – high matrix mode, using He as collision gas ( $4.3 \text{ mL min}^{-1}$ ). Instrument parameters were optimised for best sensitivity in the whole mass range, minimum oxides ( $< 1\%$ ) and double charges ( $< 3\%$ ). Quantification was obtained by external calibration with multi-elemental standards prepared in ultrapure water ( $18 \text{ M}\Omega \text{ cm}^{-1}$  at  $25^\circ \text{C}$ ) with 2% v/v ultrapure grade  $\text{HNO}_3$  (UpA grade, Romil, UK), with a combination of certified level multi-elemental solutions IMS-102 and IMS-104 from UltraScientific. Analytical quality control was

185 performed by memory test blank (repeated analysis of ultrapure grade HNO<sub>3</sub> 2% v/v blank solution)  
186 after each sample and calibration verification (repeated analysis of reference standards) every 11  
187 samples. More details are found in Spolaor et al., 2021a.

188

#### 189 *2.4 Transport modelling, sea ice, Kongsfjorden condition, and polar vortex*

190

191 The Lagrangian particle dispersion model HYSPLIT (Draxler, 1998; Stein et al., 2015) was used to  
192 determine the source region of air masses over Ny-Ålesund. This model has previously been shown  
193 to be an effective tool for the prediction of transport pathways into and within the Arctic and Antarctic  
194 regions (Barbaro et al., 2015; Feltracco et al., 2021). The simulations were driven using  
195 meteorological data from the Global Data Assimilation System (GDAS) one-degree archive, set the  
196 top of the model at 10000 m and the height source equal to the GSRS altitude. Back-trajectories were  
197 calculated every 6 h, with a propagation time of 120 h for each sampling period. The choice of a 6-  
198 hour interval for the calculation of back-trajectories allows for the capture of temporal variability in  
199 air mass origins over the day, which is particularly important in polar regions where atmospheric  
200 circulation patterns can change rapidly. This temporal resolution strikes a balance between  
201 computational efficiency and the need for sufficient detail to characterise the variability in source  
202 regions during each sampling period. The propagation time of 120 hours was selected to provide an  
203 adequate temporal window to trace long-range transport pathways that influence air mass  
204 composition at Ny-Ålesund. This configuration is consistent with previous studies on atmospheric  
205 circulation in the same site (Feltracco et al., 2021).

206 This approach was used to ensure an envelope working for all investigated tracers. The resulting  
207 multiple trajectories were based on the screen-plot analyses of total spatial variance.

208 The Ice Service provided by the Norwegian Meteorological Institute (NIS) was employed to analyse  
209 the weather conditions via remotely sensed data and to generate ice charts of Svalbard, ice-edge  
210 information, and sea surface temperatures trends. Sea ice extent variability in Kongsfjorden was  
211 evaluated based on dataset made available by Gerland et al. (2022).

212 Differences between the sampling campaigns were evaluated through the National Centers for  
213 Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) Reanalysis  
214 data from NOAA Physical Sciences Lab's daily composites tool, used to calculate the near-surface  
215 air temperatures across the Northern Hemisphere from October to May.

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## 2.5 Statistical procedures and Enrichment Factors (EFs) Analysis

Results below the limit of detection were assumed to be equal to  $\frac{1}{2}$  of Method Determination Limit (MDL) prior to perform statistical analysis, to approximate their likely level based on the data distribution curve (best approximated as log-normal for most of the studied variables) (George et al., 2021).

Enrichment Factors (EFs) were calculated to explore the mixed sources of the investigated elements (Widepohl, 1995). For this scope, Ba was used as a crustal element of reference (Spolaor et al., 2021a; Ruppel et al., 2023). To complement the EFs analysis, a Hierarchical Cluster Analysis (HCA) was performed using Ward's algorithm and Euclidean distances as clustering criteria, to determine the presence of some clusters and simplify the interpretation of the dataset.

Additionally, to examine the inter-annual and seasonal variations in chemical's concentrations and to identify the species most affected by these changes, a Kruskal-Wallis' test was employed, followed by Dunn's post-hoc test for pairwise comparisons. The Kruskal-Wallis' test, a nonparametric alternative to Anova, which is typically applied when samples do not follow a normal distribution (Van Hecke, 2013), was chosen to assess differences in chemical concentrations across the years of sampling campaigns and multiple seasons. This allowed for an objective evaluation of temporal differences in concentration levels, while Dunn's post-hoc analysis, which uses the same shared rankings and pooled variance assumed under the Kruskal-Wallis null hypothesis, helped identify which specific seasons showed statistically significant differences from each other. The Bonferroni correction was used for the Dunn's test to control for false positives when performing multiple pairwise comparisons (Dunn, 1961).

The ultimate goal of this analysis was to uncover potential correlations between meteorological-climatic conditions and chemical concentrations in surface snow, helping to better understand how environmental factors contribute to contamination trends.

These combined statistical approaches provided a comprehensive framework for analysing the complex dataset.

## 3. Results

### 3.1 Interannual trends of chemical species on the surface snow

Three consecutive snow seasons were evaluated to define the chemical composition of the surface snow in the Arctic site of GSRS. The sea salt ions  $\text{Cl}^-$  (50 %), and  $\text{Na}^+$  (23%) represent the most abundant species, followed by  $\text{SO}_4^{2-}$  (11 %), Mg (7 %), Ca (2%), Fe (1%) and Al (1%). Similar

relative concentration abundances were also found in previous studies on the snow of the Svalbard Archipelago (Beaudon and Moore, 2009; Vega et al., 2015; Barbaro et al., 2021; Spolaor et al., 2021b).

Table 1 reports the average ionic loads of the most abundant (> 1%) species in the surface snow, considering three different seasons: autumn is defined until December 21<sup>st</sup>, winter until March 21<sup>st</sup>, and spring from then to the melt onset, identified by 5-6 consecutive days of negative snow accumulation. The average ionic loads of the less abundant (< 1%) species are reported instead in Table S1. Average loads are presented in place of medians to avoid underrepresentation of the occasional high concentration events, which are critical for understanding the snowpack chemistry dynamics in the Arctic environment.

**Table 1.** Average ionic loads of the most abundant (>1%) ionic and elemental species in the surface snow during each season of the three consecutive sampling campaigns. The standard deviation is shown in brackets, while in the case of nss-SO<sub>4</sub><sup>2-</sup> the brackets represent the percentage of nss-SO<sub>4</sub><sup>2-</sup> compared to the total SO<sub>4</sub><sup>2-</sup>. “n” indicates the number of samples considered for the calculation of the average. Annual averages are reported at the end of each sampling year.

| mg m <sup>-2</sup>    | Total                 | Cl <sup>-</sup>      | Na <sup>+</sup>     | SO <sub>4</sub> <sup>2-</sup> | nss-SO <sub>4</sub> <sup>2-</sup> | Mg                 | Fe               | Ca                 | NO <sub>3</sub> <sup>-</sup> | K <sup>+</sup>     | NH <sub>4</sub> <sup>+</sup> |
|-----------------------|-----------------------|----------------------|---------------------|-------------------------------|-----------------------------------|--------------------|------------------|--------------------|------------------------------|--------------------|------------------------------|
| autumn 2018 (n=22)    | 32<br>(25)            | 15<br>(21)           | 7<br>(11)           | 3<br>(4)                      | 1<br>(36%)                        | 3<br>(3)           | 2<br>(5)         | 0.3<br>(0.3)       | 0.5<br>(0.5)                 | 0.3<br>(0.4)       | 0.04<br>(0.03)               |
| winter 2018-19 (n=41) | 115<br>(80)           | 55<br>(68)           | 31<br>(39)          | 16<br>(16)                    | 8<br>(51%)                        | 8<br>(8)           | 0.4<br>(0.3)     | 0.4<br>(0.3)       | 2<br>(2)                     | 2<br>(2)           | 0.3<br>(0.3)                 |
| spring 2019 (n=51)    | 75<br>(50)            | 36<br>(43)           | 19<br>(24)          | 9<br>(9)                      | 4<br>(48%)                        | 6<br>(5)           | 2<br>(3)         | 0.6<br>(0.4)       | 1<br>(1)                     | 1<br>(1)           | 0.5<br>(0.4)                 |
| <b>Year 2018-19</b>   | <b>222<br/>(25)</b>   | <b>106<br/>(20)</b>  | <b>58<br/>(12)</b>  | <b>28<br/>(7)</b>             | <b>13<br/>(48%)</b>               | <b>17<br/>(3)</b>  | <b>4<br/>(1)</b> | <b>1<br/>(0.1)</b> | <b>4<br/>(0.8)</b>           | <b>3<br/>(0.6)</b> | <b>0.8<br/>(0.2)</b>         |
| autumn 2019 (n=15)    | 212<br>(98)           | 101<br>(71)          | 40<br>(53)          | 26<br>(20)                    | 16<br>(61%)                       | 10<br>(6)          | 1<br>(1)         | 9<br>(12)          | 5<br>(4)                     | 2<br>(3)           | 4<br>(5)                     |
| winter 2019-20 (n=43) | 335<br>(120)          | 159<br>(88)          | 79<br>(73)          | 41<br>(20)                    | 21<br>(52%)                       | 16<br>(8)          | 2<br>(5)         | 9<br>(10)          | 3<br>(2)                     | 3<br>(4)           | 7<br>(8)                     |
| spring 2020 (n=49)    | 264<br>(131)          | 110<br>(91)          | 52<br>(77)          | 28<br>(25)                    | 15<br>(53%)                       | 21<br>(21)         | 6<br>(9)         | 13<br>(16)         | 4<br>(2)                     | 2<br>(4)           | 5<br>(8)                     |
| <b>Year 2019-20</b>   | <b>811<br/>(39)</b>   | <b>370<br/>(31)</b>  | <b>171<br/>(20)</b> | <b>95<br/>(8)</b>             | <b>52<br/>(55%)</b>               | <b>47<br/>(6)</b>  | <b>9<br/>(3)</b> | <b>31<br/>(6)</b>  | <b>12<br/>(1)</b>            | <b>7<br/>(1)</b>   | <b>16<br/>(2)</b>            |
| autumn 2020 (n=6)     | 796<br>(542)          | 435<br>(466)         | 191<br>(205)        | 66<br>(83)                    | 18<br>(27%)                       | 84<br>(165)        | 1<br>(2)         | 2<br>(5)           | 6<br>(11)                    | 9<br>(10)          | 2<br>(2)                     |
| winter 2020-21 (n=13) | 327<br>(203)          | 207<br>(194)         | 64<br>(48)          | 41<br>(36)                    | 24<br>(60%)                       | 6<br>(5)           | 0.2<br>(0.4)     | 0.2<br>(0.1)       | 5<br>(3)                     | 3<br>(2)           | 1<br>(1)                     |
| spring 2021 (n=13)    | 178<br>(92)           | 107<br>(86)          | 36<br>(26)          | 16<br>(12)                    | 7<br>(43%)                        | 9<br>(10)          | 4<br>(7)         | 1<br>(2)           | 3<br>(2)                     | 2<br>(2)           | 1<br>(1)                     |
| <b>Year 2020-21</b>   | <b>1300<br/>(194)</b> | <b>749<br/>(168)</b> | <b>291<br/>(83)</b> | <b>123<br/>(25)</b>           | <b>49<br/>(40%)</b>               | <b>99<br/>(44)</b> | <b>5<br/>(2)</b> | <b>3<br/>(1)</b>   | <b>14<br/>(2)</b>            | <b>14<br/>(4)</b>  | <b>4<br/>(0.5)</b>           |

The average loads of the first sampling year were lower compared to the other campaigns (Fig. S1; Table 1).

High average loads were observed instead for Cl<sup>-</sup> and Na<sup>+</sup> in the top snowpack layer during the 2019-20 and 2020-21 winter seasons. The highest concentrations of sea salt species were found in autumn

272 2020, despite low snow accumulation (17.25 cm) in a period of relatively high precipitation (4.91  
 273 mm) (Fig. 2, Table S3). This apparent contradiction can likely be attributed to the increased wind  
 274 speeds during that time, which may have caused snow redistribution, thereby limiting accumulation  
 275 despite the considerable precipitation.

276 The non-sea-salt sulphate ( $\text{nss-SO}_4^{2-}$ ), calculated using a seawater  $\text{SO}_4^{2-}/\text{Na}^+$  mass ratio of 0.252  
 277 (Millero et al., 2008), was the most abundant fraction of the total sulphate in autumn 2019 and winter  
 278 2020-21, while in autumn 2018 and 2020 sea salt sulphate ( $\text{ss-SO}_4^{2-}$ ) was the dominant fraction. No  
 279 clear predominance between the two fractions was achieved during the other investigated seasons,  
 280 which may reflect a more mixed influence of marine and continental sources (Table 1).

281 The abundance of all chemical species investigated is quite similar for all years (Fig. S1), although  
 282 the sampling campaign 2019-20 showed higher percentage of calcium ranging between 3% and 5%,  
 283 in contrast to the typical concentrations  $< 1\%$  found in the other two campaigns.

284 To further examine differences in species concentrations across seasons and years, a Kruskal-Wallis  
 285 test was performed. The test indicates significant differences ( $\chi^2 > 15.51$ ,  $\text{df} = 8$ ,  $\text{p-value} = 0.05$ ) for  
 286 several species across the nine seasons of the three sampling campaigns. These species include Br  
 287 ( $\chi^2 = 16.9$ ), MSA ( $\chi^2 = 81.3$ ),  $\text{SO}_4^{2-}$  ( $\chi^2 = 21.3$ ),  $\text{nss-SO}_4^{2-}$  ( $\chi^2 = 23.4$ ), Bi ( $\chi^2 = 19.2$ ), Cd ( $\chi^2 = 31.9$ ),  
 288 Cu ( $\chi^2 = 44.5$ ), Fe ( $\chi^2 = 21.9$ ), Pb ( $\chi^2 = 45.1$ ), Ni ( $\chi^2 = 20.6$ ), Ag ( $\chi^2 = 24.5$ ), U ( $\chi^2 = 22.1$ ), V ( $\chi^2 =$   
 289  $40.9$ ), Zn ( $\chi^2 = 29.9$ ). To identify which seasons accounted for these differences, a Dunn's test with  
 290 Bonferroni correction was applied as a post-hoc test, revealing significant seasonal differences for  
 291 multiple elements (Fig. S2), with pronounced differences particularly between autumn and winter,  
 292 and between spring and winter ( $\text{P.adj} < 0.05$ ; Table S5).

293 Finally, correlations between meteo-climatic variables (air temperature, wind speed, wind direction,  
 294 precipitation, AO index) and the concentrations of the selected species were computed to assess  
 295 potential meteorological influences. The results indicated generally weak positive correlations ( $\rho <$   
 296  $0.5$ ,  $\text{p-values} < 0.05$ ) for the variables considered. Notably, MSA showed a correlation with air  
 297 temperature ( $\rho = 0.2$ ,  $\text{p-values} < 0.05$ ), as did Bi ( $\rho = 0.2$ ,  $\text{p-values} < 0.05$ ), Cu ( $\rho = 0.2$ ,  $\text{p-values} <$   
 298  $0.05$ ), Fe ( $\rho = 0.2$ ,  $\text{p-values} < 0.05$ ), Pb ( $\rho = 0.1$ ,  $\text{p-values} < 0.05$ ), Ni, ( $\rho = 0.2$ ,  $\text{p-values} < 0.05$ ), Ag ( $\rho =$   
 299  $0.2$ ,  $\text{p-values} < 0.05$ ), U ( $\rho = 0.3$ ,  $\text{p-values} < 0.05$ ), V ( $\rho = 0.3$ ,  $\text{p-values} < 0.05$ ), and Zn ( $\rho = 0.3$ ,  $\text{p-}$   
 300  $\text{values} < 0.05$ ).

### 301 *3.2 Polar vortex and Arctic Sea ice extent in 2019-20*

302 According to the 2023 survey conducted by the National Snow and Ice Data Center (NSIDC), the  
 303 maximum extent of Arctic sea ice since 2014 has been recorded in March 2020, with 14.73 million  
 304 square kilometres of the Arctic Ocean surface, in a decadal trend characterised by a -2.53% of decline.

305 Considering the Kongsfjorden area, the total sea ice extent varied from 63.94 km<sup>2</sup> in March 2019 to  
306 129.81 km<sup>2</sup> in March 2020, and was with 46.26 km<sup>2</sup> lowest in March 2021 (Gerland et al., 2022).  
307 Specifications on Drift Ice (DI), Fast Ice (FI), and Open Water (OW) extent are reported in Table S2.  
308 The 2020 maximum sea ice extent followed the exceptionally strong and cold stratospheric polar  
309 vortex that took place in the Northern Hemisphere (NH) during the 2019-20 polar winter, together  
310 with low wave activity from the troposphere, which allowed the polar vortex to remain relatively  
311 undisturbed (Lawrence et al., 2020). Notably, the 2020 Arctic Sea ice extent is 16% and 9% higher  
312 than previous (2018-19) and following (2020-21) records (dataset NSIDC, NOAA). Lower surface  
313 mean air temperatures (-14.7°C, compared to the -11.4°C recorded in 2018-19, and the -8.0°C  
314 recorded in the 2020-21), average reduced precipitations (2.1 mm compared to 2.6 mm in 2018-19,  
315 and 3.2 mm in 2020-21), higher maximum mean wind speed (17.7 ms<sup>-1</sup> for 6 days, compared to 15.4  
316 ms<sup>-1</sup> for 3 days in 2018-19, and 13.8 ms<sup>-1</sup> for 5 days in 2020-21), and higher mean snow height (62.63  
317 cm compared to 58.06 cm in 2018-19, and 57.77 cm in 2020-21) were observed during the 2019-20  
318 winter season, attributed to the influence of a strong polar vortex triggered by a net positive Arctic  
319 Oscillation (AO) phase. The 2020 anomalous AO index is displayed in Fig. S3. Seasonal values of  
320 mean air temperatures (°C), mean precipitation (mm), maximum mean wind speed (m sec<sup>-1</sup>) and mean  
321 snow depth (cm) during the three consecutive sampling campaigns are reported in Table S3.  
322 Temperature data were provided by the Norwegian Centre for Climate Services (NCCS), while sea  
323 ice extent data were supplied by National Snow and Ice Data Center (NSIDC). Seawater temperature  
324 data collected at 10 m depth at a mid-fjord station near Ny-Ålesund (Kb3) was found to be colder  
325 during 2020 compared to 2019 and 2021 spring seasons (Table S4). Although these temperatures  
326 were still above the freezing point for the observed salinity levels, they contributed to colder overall  
327 conditions in Kongsfjorden, supporting the formation and prolonged presence of sea ice when  
328 combined with cold atmospheric conditions.

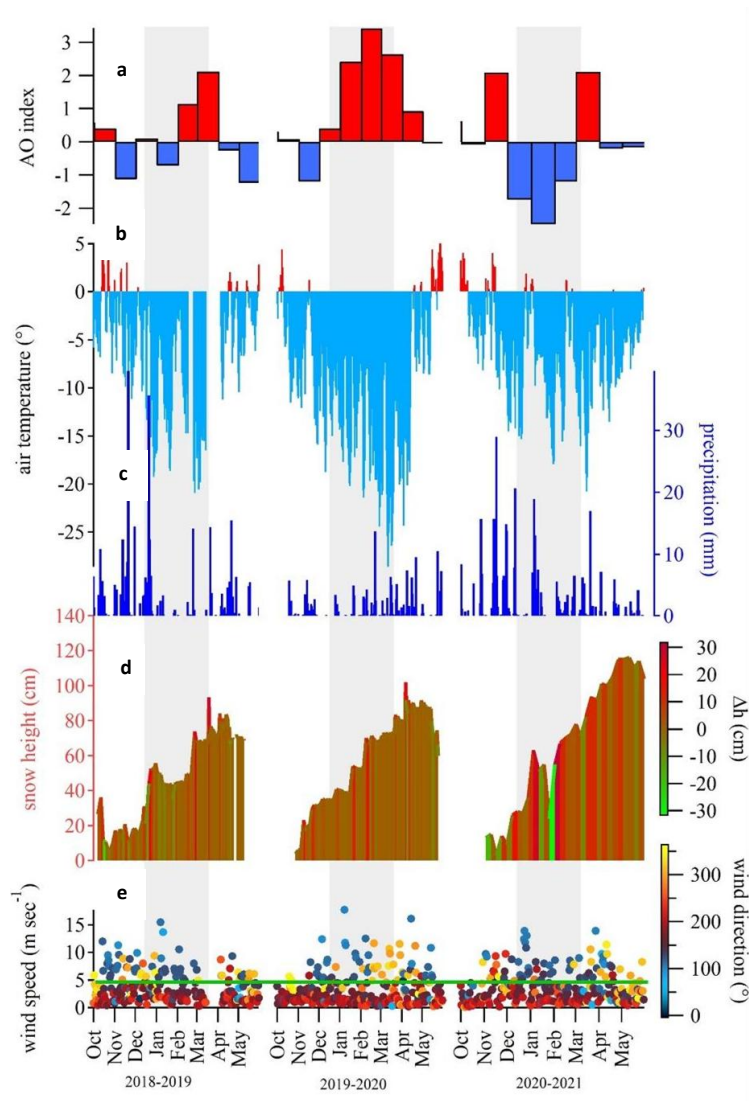
## 329 **4. Discussion**

### 330 *4.1 Ny-Ålesund seasonal and interannual trends variability in surface snow*

331 The three consecutive sampling campaigns conducted from 2018 to 2021 confirmed the dominance  
332 of sea salt input in the surface snow of Svalbard, due to the proximity of the sampling site to the  
333 coastline (Barbaro et al., 2021). The dominant ions are Na<sup>+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>, associated with the  
334 scavenging precipitation of marine aerosol (Hodgkins and Tranter, 1998). The observed mean  
335 seasonal trends (Fig. S1) display the highest concentrations of marine species in autumn 2020,  
336 followed by 2020-21 and 2019-20 winter seasons. However, wintertime concentrations are  
337 presumably linked to weakened (2019-20) or destroyed (2020-21) polar vortex (Fig. 2) and intense

338 cyclonic storms, associated with anomalous warming events capable of transporting both heat and  
339 moisture from lower latitudes to Svalbard (Rinke et al., 2017). In addition to these factors, it is  
340 important to account for snow ablation or erosion by wind. The change in snow height ( $\Delta h$ ) between  
341 consecutive sampling events provides valuable insights into such processes. A decrease in snow  
342 height signals ablation can indeed result from snow melting (under positive temperatures), snow  
343 aging, sublimation, or snow drift. In particular, when wind speeds exceed  $5 \text{ m s}^{-1}$ , the threshold  
344 commonly accepted for initiating snow drift and ablation episodes (Pomeroy, 1989), we can infer the  
345 snow erosion due to wind drift likely occurred (Fig. 2). This effect may explain some of the variability  
346 in snow ion concentrations, especially during intense storms or strong winds.

347 Autumn 2020 represents most likely an outlier, due to scarce precipitations (Fig. 3) that led to more  
348 concentrated impurities in the surface snow. In contrast, late spring 2020 saw a notable increase in  
349 typical marine ions ( $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{MSA}$ ,  $\text{SO}_4^{2-}$ ) and geogenic elements (Al, Ca, Mn, Fe, Sr), compared  
350 to spring 2019 (Fig. 3). This increase may be attributed to the very close drift Arctic Sea ice presence  
351 in Kongsfjorden (Table S2), which reached its maximum extent in March 2020 due to low-  
352 temperature anomalies and intensified atmospherically driven sea ice transport and deformation,  
353 caused by higher than normal winter wind speeds (Fig. S4). These conditions likely enhanced the  
354 production of sea spray aerosols, which, when carried by winds, may have increased the deposition  
355 of marine species onto the snowpack. The increased deposition of geogenic elements might also have  
356 been influenced by low temperature anomalies (as seen with Fe), and/or by stronger wind speeds,  
357 although significant correlations have not emerged in this preliminary statistical analysis.  
358 Additionally, an outstanding positive phase of the Arctic Oscillation (AO) in the troposphere (Fig. 2)  
359 was recorded in January-March 2020 (Lawrence et al., 2020; Dethloff et al., 2022). Although the  
360 entire period was remarkable, January and February featured as clear outliers in the historical  
361 timeseries (1950–2023) reported by the NOAA service, while March 2020 exhibited significantly  
362 elevated values but did not exceed the statistical threshold for outliers (Fig. S3).

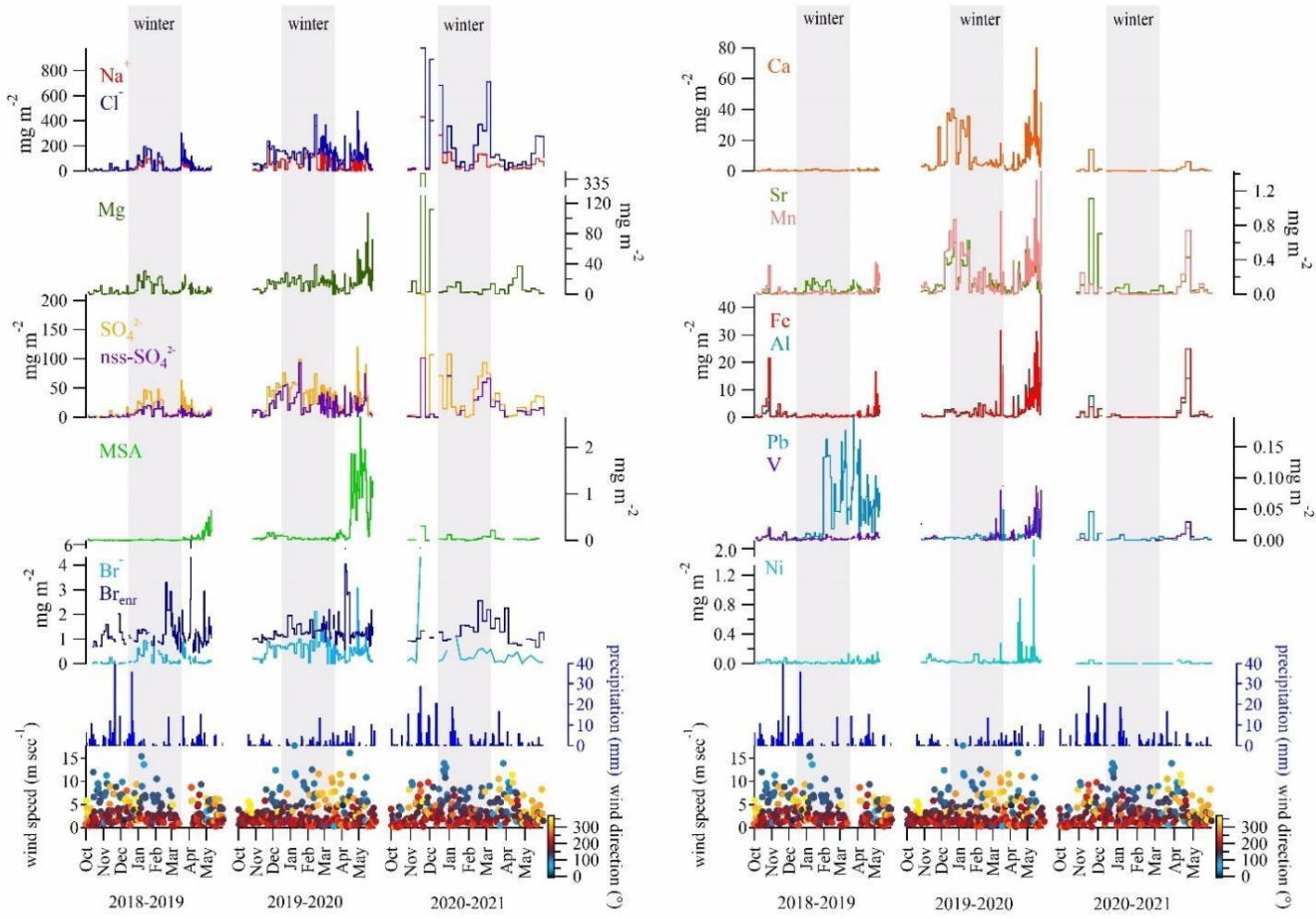


364

365 **Fig. 2.** a) AO Index; b) air temperature (°C); c) precipitation (mm); d) snow height (cm) and  $\Delta h$  snow height (cm); e)  
366 wind speed ( $\text{m sec}^{-1}$ ) and wind direction (°) from the NCEP/NCAR Reanalysis data. The green horizontal line in panel e)  
367 indicates the  $5 \text{ m sec}^{-1}$  threshold, above which wind drift may occur on surface snow layers. The colour of this line refers  
368 to the  $\Delta h$  color scale shown in panel d), where green indicates negative values of  $\Delta h$ . NOAA Physical Sciences Lab's  
369 daily composites tool was used to calculate the near-surface air temperatures across the Northern Hemisphere from  
370 October to May. Grey bands across the panels indicate the winter periods.

371 A 2021 spring peak of marine species was also recorded, although more attenuated than in spring  
372 2020 (Fig. 3, Fig. S1). This variation is likely attributable to different extents of sea ice in the fjord.  
373 Nonetheless, seawater temperatures in 2021, similar to those in 2020 and  $2.3^\circ\text{C}$  colder than in 2019  
374 (Table S4), along with comparable wind speed conditions (Fig. S4), may also have contributed to the  
375 observed trends in marine species concentrations. Similarly, the spring peak of Mg, Sr, Mn, Fe, Al,  
376 and V in 2021 seems to reflect the high wind speed (Fig. 3) and positive AO index (Fig. 2a) recorded

377 from March to April 2021. Positive anomalies for air temperatures (A) and wind speed (W) conditions  
 378 (Fig. 2b and 2e), together with negative anomalies in seawater (O) conditions (Table S4) were  
 379 observed during the 2020-21 campaign, while negative A and O conditions were accompanied to  
 380 positive W during 2019-20. On the contrary, 2018-19 diverges from the other campaigns for positive  
 381 O condition associated to negative W condition anomalies. These contrasting patterns suggest that  
 382 variability in atmospheric circulation and oceanic state exerts a direct control on the timing and  
 383 intensity of aerosol deposition to the snowpack. In particular, stronger winds and warmer air masses  
 384 enhance the transport and deposition of crustal and sea-salt species, whereas negative oceanic  
 385 anomalies appear to modulate their availability as sources. This highlights how combined shifts in  
 386 atmospheric and oceanic conditions drive the observed interannual variability of ionic and elemental  
 387 concentrations in surface snow.



388  
 389 **Fig. 3.** Ionic loads ( $\text{mg m}^{-2}$ ) of  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}$ ,  $\text{SO}_4^{2-}$ ,  $\text{nss-SO}_4^{2-}$ ,  $\text{MSA}$ ,  $\text{Br}^-$ ,  $\text{Br}_{\text{enr}}$ ,  $\text{Ca}$ ,  $\text{Sr}$ ,  $\text{Mn}$ ,  $\text{Fe}$ ,  $\text{Al}$ ,  $\text{Pb}$ ,  $\text{V}$ ,  $\text{Ni}$  in the surface  
 390 snow for the three sampling campaigns: 2018-19, 2019-20, 2020-21. Seasonal trends are here presented for specific  
 391 elements to provide a detailed view of how concentrations vary across distinct sampling periods. Precipitation trends  
 392 ( $\text{mm}$ ), wind speed ( $\text{m sec}^{-1}$ ), and wind direction ( $^\circ$ ) are reported twice for visual clarity.

393

#### 4.2 Enrichment Factors and source attribution

Enrichment Factors (EFs) are a mean of identifying and quantifying human interference with element cycles (Wedepohl, 1995). EFs are calculated from elemental ratios, and are most often used to indicate the impacts of pollution according to Eq. (1):

$$EF = \frac{\frac{[TE]}{[Ba]_{sample}}}{\frac{[TE]}{[Ba]_{UCC}}} \quad (1)$$

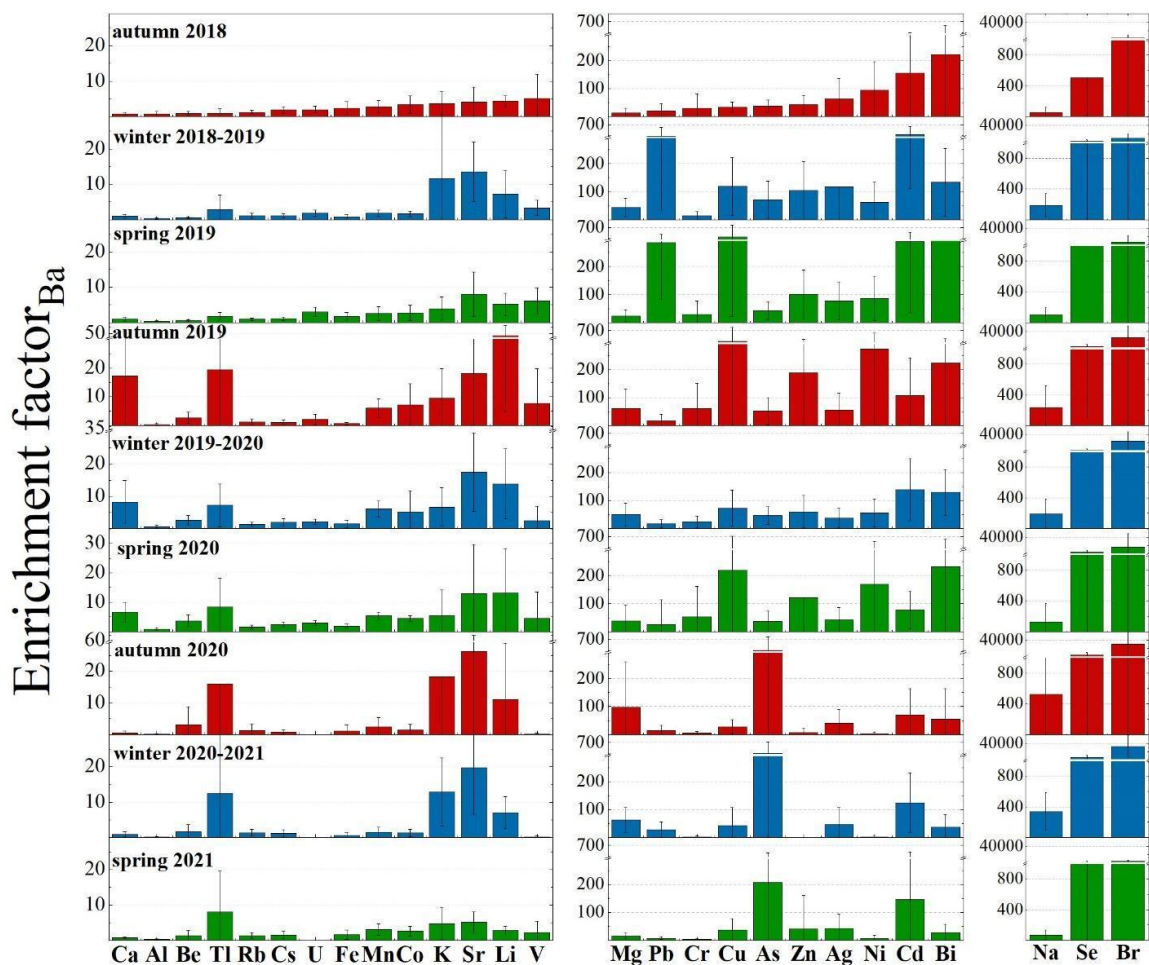
where [TE] is the concentration of the trace element of interest, [Ba] is the concentration of a lithogenic tracer (in this case Ba substitutes Al), and the subscripts ‘sample’ and ‘UCC’ refer to the concentration of the lithogenic tracer within the sample and the UCC (e.g., Taylor and McLennan, 1995).

Evaluation of EF can help to discuss the singular case of Pb, which showed a 12.5-fold increase during winter-spring 2019 period compared to autumn 2018 (Fig. 3), and provide insights into element sources.

##### 4.2.1 Enrichment Factors in seasonal snow of Ny-Ålesund

The calculated EFs (Fig. 4) for Be, Al, V, Mn, Fe, Co, Rb, Cs, and U were consistently below 10, indicating a predominantly crustal (geogenic) origin for these elements (Wedepohl, 1995; Gabrieli et al., 2011). In contrast, Ni, and Sr displayed EFs greater than 10, suggesting contributions from mixed sources. Notably, Ni exhibited exceptionally high EF values – above 100 – during autumn 2019 and spring 2020 (Ni). Mixed sources were also recognised for Li, K, Cr, Cu, Zn, As, Ag, Cd, and Tl with occasional EF values over 100. This suggests significant anthropogenic contributions, especially for Cu (spring and autumn 2019; spring 2020), As (from autumn 2020 to spring 2021), Zn (autumn 2019) and Cd (from autumn 2018 to spring 2019; winter 2019-20).

The EF for Pb during all seasons exceeded 100, indicating a strong anthropogenic contribution. In contrast, the peak observed in 2020 no longer shows such elevated EF values (i.e., EF = 26), suggesting a mixed source (Fig. 4). This implies that the April-May 2020 peak is largely of crustal origin, as the overlap with V (EF < 10) also suggests, possibly due to local dust events driven by strong winds exceeding the 5 m sec<sup>-1</sup> threshold (Fig. 3; Table S3).



420

421 **Fig. 4.** Enrichment Factors (EFs) calculated on all the presented trace elements for the three sampling campaigns: 2018-  
 422 19, 2019-20, 2020-21. Calculating EFs for the full dataset offers a more robust assessment of potential sources and  
 423 enrichment patterns, minimizing the variability inherent in individual seasons and allowing for a clearer distinction  
 424 between crustal and non-crustal contributions.

425 The 2019 springtime Pb concentration maxima are typically consistent with a mixture of eastern and  
 426 western European sources (Sherrell et al., 2000; Bazzano et al., 2015, 2021). In this study, cluster  
 427 mean trajectories obtained for winter 2018-2019 highlighted a 25% of air mass provenance from  
 428 Russian Arctic and a 13% from eastern Siberia (Fig. S5), possibly explaining the higher  
 429 concentrations of Pb revealed in spring 2019, following a reduced precipitation regime that occurred  
 430 in January 2019. A local anthropogenic origin can be excluded though, since no activities (ordinary-  
 431 extraordinary maintenance or particular events) were recorded in the vicinity of the sampling site in  
 432 the 2019 sampling season. However, at present, the long-range transport of Pb remains a hypothesis,  
 433 likely supported by the breakdown of polar vortex (Fig. 2).

434 Backward trajectories (Fig. S5) for Ny-Ålesund area (78.92° N, 11.89° E) appear mostly in line with  
 435 literature findings (Platt et al., 2022; Vecchiato et al., 2024), showing three main seasonal characters:

a prevalent mass movement from ice-covered Central Arctic Ocean, Kara Sea, and Greenland Sea during autumn, a main provenance from Central Arctic Ocean and Kara Sea during winter, and a predominant trajectory from Northern Canada in addition to air masses arriving from Arctic Ocean and Kara seas during spring.

#### 4.2.2 Main ion sources in seasonal snow of Ny-Ålesund

Examining the dominant ions associated with marine aerosol, we found  $\text{Cl}^-/\text{Na}^+$  median ratios ranging from 1.3 to 1.5  $\text{w w}^{-1}$ , slightly lower than the expected value of 1.8  $\text{w w}^{-1}$  in the pure seawater (Zhuang et al., 1999), pointing the occurrence of a minimum  $\text{Cl}^-$  depletion in aerosol, quantified as 14% for the 2018-19 and 2019-20 campaigns, and as just 2% for the 2020-21 campaign. A possible explanation for this phenomenon could be the de-chlorination of sea-spray aerosol during transport. This reaction occurs when sea-salt particles containing NaCl interact with acids such as  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , or organic acids, leading to the release of gaseous HCl (Zhuang et al., 1999, and reference therein). Although less likely, this process could also occur at the snow-atmosphere interface. On the contrary, a possible influence of biomass burning on  $\text{Cl}^-$  depletion process has been excluded by the very low correlation (0.18,  $p\text{-value} < 0.05$ ) found between  $\text{Cl}^-$  depletion values and  $\text{nss-K}^+/\text{K}^+$  ratios, which is a tracer of relative contribution of biomass burning (Song et al., 2018).

Positive correlations between Mg, Ca, and  $\text{K}^+$  with  $\text{Na}^+$  and  $\text{Cl}^-$  (Fig. 5,  $p\text{-value} < 0.05$ ) suggest a common sea-spray source. However, the concentrations of Mg are also positively correlated with  $\text{nss-Ca}$  ( $\rho_{\text{load}} = 0.55$ ,  $p\text{-value} < 0.05$ ), calculated according to Morales et al. (1998), indicating a shared non-marine source. This suggests that in addition to their marine origin, these ions (Mg, Ca) also have contributions from a non-marine, crustal source. Further evidence comes from the Ca/Mg ratios in surface snow samples collected during the three campaigns, which were higher than those found in seawater (0.32, Millero et al., 2008). This excess indicates the likely presence of mineral particles (i.e., calcite and dolomite), potentially originating from local rock or soil dust (e.g., limestone, dolostone, and marble, which are abundant in Svalbard), as previously observed by Barbaro et al. (2021). To further explore the mixed sources of these elements, we calculated the Enrichment Factors (EFs) of Mg and Ca. For Mg, the EF values were consistently above 10 in all the seasons analysed, indicating a significant non-crustal source (e.g., marine). In contrast, Ca displayed EF values greater than 10 only during autumn 2019, suggesting that its non-crustal contribution (likely from sea spray) was more pronounced during that specific season. Based on these findings, we conclude that Mg and Ca effectively share a common sea spray origin, but the sea-salt contribution of Ca was mainly

467 significant in autumn 2019, while the excess of Ca in other seasons likely reflects inputs from crustal  
468 source, such as local mineral dust.

469 Similarly, sulphate ( $\text{SO}_4^{2-}$ ) is highly and significantly correlated (p-values  $< 0.05$ ) with both  $\text{Na}^+$  ( $\rho_{\text{load}} = 0.80$ ) and  $\text{Cl}^-$  ( $\rho_{\text{load}} = 0.91$ ), indicating that sea-spray is its main source. Nonetheless,  $\text{Na}^+/\text{SO}_4^{2-}$  and  
470  $\text{Cl}^-/\text{SO}_4^{2-}$  ratios are significantly lower than typical seawater values (3.97 and 7.13, respectively,  
471 according to Millero et al., 2008) for the former two campaigns (2018-19, 2019-20). The elevated  
472 sulphate concentrations compared to sodium, also in winter snow, suggest the absence of a strong  
473 frost flower signature. Additionally, the lack of significant depletion in  $\text{nss-SO}_4^{2-}$  further supports the  
474 minimal role of frost flowers in contributing to the snow composition. Therefore, while frost flowers  
475 are known to impact snow chemistry in Svalbard (Rankin et al., 2002; Beaudon and Moore, 2009;  
476 Roscoe et al., 2011), our analysis indicates that their contribution to the observed sea salt peaks in  
477 Kongsfjorden during the 2018-19, 2019-20 campaigns was likely limited. This analysis highlights  
478 that, while sea ice extent supports higher sea-salt concentrations in snow, the specific sulphate and  
479 ion ratios observed point to sea spray as the main source, with only a minor role for frost flower-  
480 related inputs.  
481

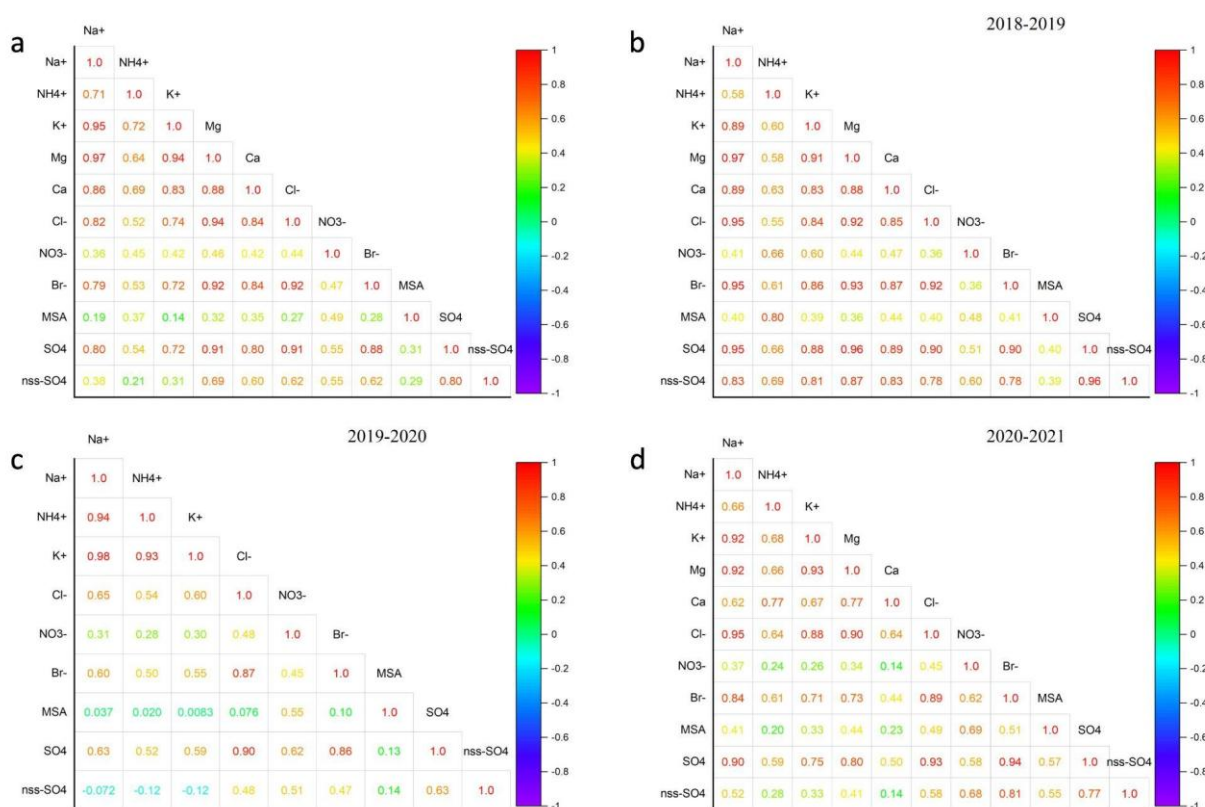
482 Instead, the presence of  $\text{nss-SO}_4^{2-}$  suggests potential inputs from other sources, such as crustal  
483 material, anthropogenic emissions (e.g., fossil fuel combustion), or the oxidation of dimethylsulfide  
484 (DMS) released from marine biological activities.

485 To estimate the crustal fraction of sulphate ( $\text{cr-SO}_4^{2-}$ ), the  $\text{nss-Ca}$  (as crustal marker) content was  
486 multiplied by 0.59 ( $\text{SO}_4^{2-}/\text{Ca}$  w/w ratio in the uppermost Earth crust - Wagenbach et al. 1996),  
487 obtaining variable contributions for the three sampling campaigns, ranging from 2.45% up to 12.94%.  
488 Conversely, the anthropogenic contribution to  $\text{nss-SO}_4^{2-}$  concentrations was investigated by the  
489 application of the [ex-  $\text{SO}_4^{2-}$ ] concentration formula (Schwikowski et al., 1999), considering the  
490 average concentration of [Ca] instead of the average ionic concentration [ $\text{Ca}^{2+}$ ] because  $\text{Ca}^{2+}$   
491 concentrations were not measured in the samples collected during the second campaign due to  
492 instrumental limitations:

$$493 \quad [\text{ex- SO}_4^{2-}] = [\text{SO}_4^{2-}] - (0.12 [\text{Na}^+]) - (0.175 [\text{Ca}^{2+}])$$

494 The coefficient 0.12 is based on the molar ratio of  $\text{SO}_4^{2-}$  to  $\text{Na}^+$ , while the value 0.175 represents the  
495 observed slope corresponding to the pre-industrial  $\text{nss-SO}_4^{2-}/\text{nss-Ca}$  ratio in mineral dust found in  
496 snow (Schwikowski et al., 1999, and reference therein). The obtained results showed a 50 up to 60%  
497 of anthropogenic contribution for the  $\text{nss-SO}_4^{2-}$  input. This finding corroborates previous results from

Amore et al. (2022), who noted that anthropogenic sulphate was the most abundant apportioned component at Gruebadet, accounting for at least 50% all over the year during the 2010-2019 investigated period. The plausible source of the anthropogenic fraction is the atmospheric transport of secondary aerosols containing  $\text{SO}_4^{2-}$ , and ammonium sulphate. This sulphate can be formed by  $\text{SO}_x$  emitted from coal combustion throughout the winter and biomass burning in the spring (Barbaro et al., 2021 and reference therein). The  $\text{nss-SO}_4^{2-}$  does not correlate significantly with other ionic species (except for Mg), thus suggesting a separate origin (Fig. 5).



505

**Fig. 5.** Spearman correlation plots. a) Correlation plot for the three sampling seasons; b) Correlation plot for the 2018-2019 season; c) Correlation plot for the 2019-2020 season; d) Correlation plot for the 2020-2021 season. Higher positive correlations are presented in shades of red, while lower negative correlations are shown in shades of blue.

To quantify the biogenic  $\text{nss-SO}_4^{2-}$  contribution, the methanesulfonic acid (MSA) loads - the final product of DMS oxidation - were multiplied by 3.0 (Udisti et al., 2016), revealing biogenic  $\text{SO}_4^{2-}$  contributions ranging from 0.15% (2018-19, 2020-21) up to 0.38% (2019-20). Furthermore, the MSA/ $\text{nss-SO}_4^{2-}$  ratio was inspected, revealing a mean value of  $0.02 \pm 0.03$  during the first (2018-19) and the third (2020-21) sampling campaigns, and a maximum ratio equal to  $0.06 \pm 0.18$  reached during the second campaign (2019-20), similar to the subarctic western North Pacific ratio found by

515 Jung et al. (2014). However, several factors can influence MSA formation, a univocal marker of  
516 biogenic emissions, including higher biological productivity related to higher nutrient input; the  
517 concentrations of  $\text{NO}_3$  radicals as key oxidants for DMS decomposition (higher  $\text{NO}_3$  gives higher  
518 MSA); and lower air temperatures, which tend to yield higher MSA levels (Andreae et al., 1985;  
519 Udisti et al., 2020).

520 For the 2019-20 campaign, it seems likely that a combination of these three factors, together with the  
521 positive expansion of sea ice and the very close drift ice presence in March 2020, as revealed from  
522 satellite reconstructions (Fig. S6), contributed to the increased release of MSA in aerosol, and its  
523 consistent deposition in surface snow (Fig. 3). Indeed, DMS was likely accumulated under the sea  
524 ice cover in the fjord and surrounding areas, and then being released and oxidised in the atmosphere  
525 when the ice broke off and melted (April-May). Furthermore, lower temperatures ( $-17.3^\circ\text{C}$  in March  
526 2020, compared to  $-16.1^\circ\text{C}$  in March 2019, and  $-9.8^\circ\text{C}$  in March 2021), positive correlation between  
527 MSA and  $\text{NO}_3^-$  ( $\rho_{\text{load}} = 0.49$ ,  $p\text{-value} < 0.05$ ), and high-speed short-range transport (wind directions  
528 between  $0^\circ$ - $60^\circ$  and speeds  $> 5 \text{ m sec}^{-1}$ ) from the source to the near-coast sink site (GSRS) would  
529 have aided elevated concentrations of MSA in atmospheric depositions. However, the dominant south  
530 and southwest winds ( $180^\circ$ - $240^\circ$ ) during the major MSA peak in April 2020 (Fig. 3) likely transported  
531 marine aerosols and DMS from open ocean regions, further facilitating the increased MSA  
532 concentrations observed.

533 Contrarily, in the 2018-19 season, sea ice lasted only until April and was restricted to the inner,  
534 shallower parts of Kongsfjorden (Assmy et al., 2023). This limited duration may not have provided  
535 enough time with adequate sunlight for substantial biological activity to accumulate beneath or within  
536 the ice. This occurred despite the dominance in 2019, unlike the following year, of *Phaeocystis*  
537 *pouchetii*, a phytoplankton species known for its capacity to generate DMS in significant quantities  
538 (Assmy et al., 2023).

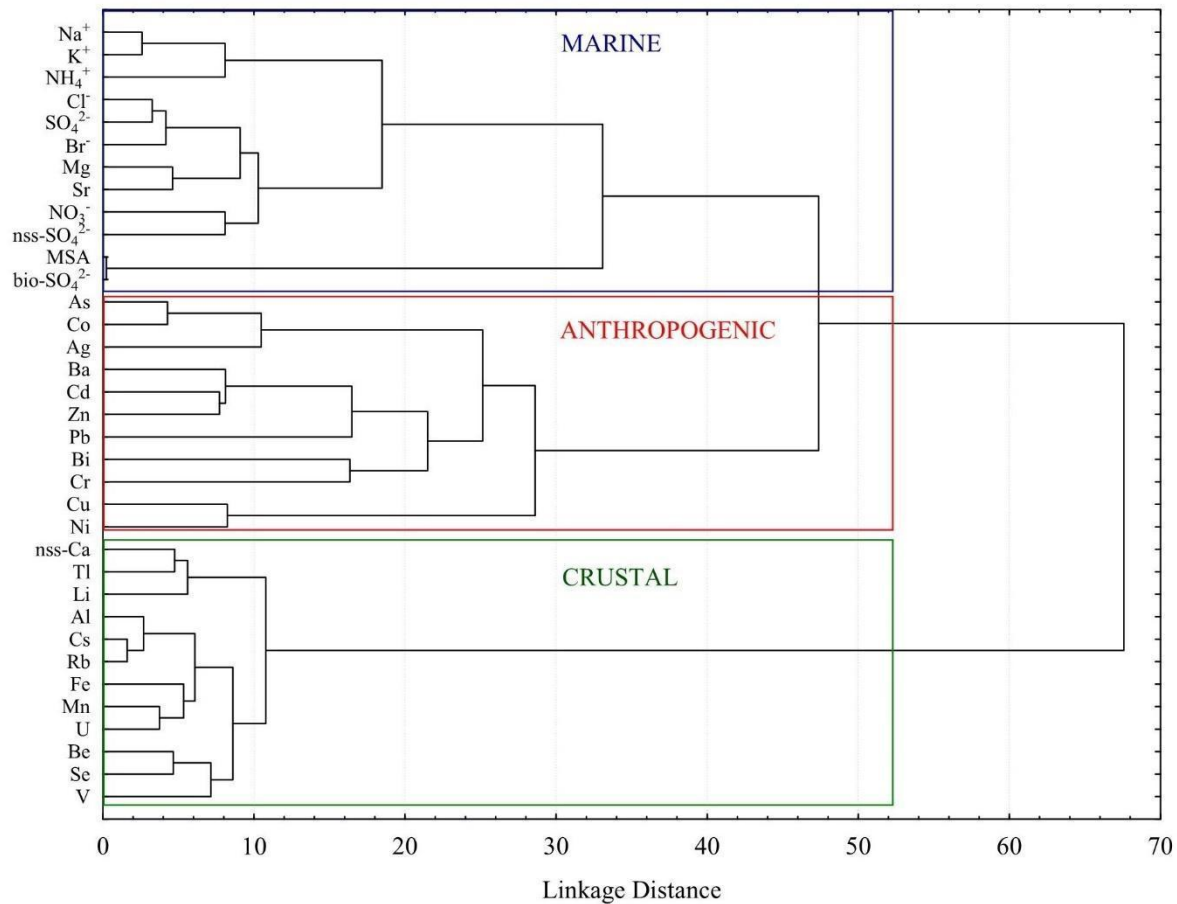
539 Finally, the ammonium ( $\text{NH}_4^+$ ) load showed positive correlations with several ions (Fig. 5). It was  
540 strongly correlated with  $\text{Na}^+$  ( $\rho_{\text{load}} = 0.71$ ,  $p\text{-value} < 0.05$ ),  $\text{Cl}^-$  ( $\rho_{\text{load}} = 0.52$ ,  $p\text{-value} < 0.05$ ) and  $\text{K}^+$   
541 ( $\rho_{\text{load}} = 0.72$ ,  $p\text{-value} < 0.05$ ). Positive correlations were also observed with  $\text{SO}_4^{2-}$  ( $\rho_{\text{load}} = 0.54$ ,  $p\text{-value} < 0.05$ ),  $\text{NO}_3^-$  ( $\rho_{\text{load}} = 0.45$ ,  $p\text{-value} < 0.05$ ), MSA ( $\rho_{\text{load}} = 0.37$ ,  $p\text{-value} < 0.05$ ) and  $\text{Br}^-$  ( $\rho_{\text{load}} =$   
543  $0.53$ ,  $p\text{-value} < 0.05$ ). These results suggest a close link with sea-salt ions and biogenic emissions.  
544 However, some contribution from biomass burning events and potential influence from  
545 anthropogenic activities cannot be excluded.

547 The bromine enrichment factor ( $Br_{\text{enr}}$ ) is well known to reflect specific processes (i.e., sea ice gas  
 548 phase Br emission) that affect the Br concentration and load in the snowpack (Spolaor et al., 2014).  
 549 Therefore, calculating the relative enrichment over the Br/Na ratio in sea water can offer crucial  
 550 insights on sea ice variability for the investigated Arctic areas (Barbaro et al., 2021). As reported in  
 551 previous studies (Maffezzoli et al., 2017; Barbaro et al., 2021), the Br enrichment factor ( $Br_{\text{enr}}$ ) can  
 552 be calculated as  $Br_{\text{enr}} = Br^- / (0.0065 Na^+)$ , where 0.0065 represents the  $Br^-/Na^+$  seawater mass ratio.  
 553 Contrarily to what observed in a former study (Barbaro et al., 2021) for the Hornsund area and north-  
 554 western Spitsbergen, where the  $Br_{\text{enr}}$  mean values were often  $< 1$ , indicating some  $Br^-$  depletion, in  
 555 this study we observed  $Br_{\text{enr}}$  mean values ranging from 1.5 up to 17.7, with the highest value  
 556 associated to the second sampling campaign conducted in 2019-20, which showed the most extensive  
 557 sea ice coverage. These results support the impact of the sea ice expansion and the close drift ice in  
 558 the Kongsfjorden on the snow chemical composition. Indeed, newly formed sea ice releases gas-  
 559 phase Br into the polar atmosphere, thus supplying an extra  $Br^-$  source in addition to sea spray  
 560 (Spolaor et al., 2016).

### 561 4.3 Anthropogenic and natural sources of ions and particulate trace elements

562 To complement the EFs analysis and further distinguish possible anthropogenic contributions from  
 563 natural ones (marine and geogenic) for ions and particulate trace elements, a Hierarchical Cluster  
 564 Analysis (HCA) method was carried out using the whole dataset, which encompasses all three  
 565 sampling campaigns (2018-2021) to capture the full variability in sulphate sources and atmospheric  
 566 processes across different seasons and years. Results of clustering (Fig. 6) clearly disentangle marine  
 567 ( $Na^+$ ,  $Cl^-$ ,  $K^+$ ,  $NH_4^+$ ,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $Br^-$ , Mg, Sr, bio- $SO_4^{2-}$ , MSA), anthropogenic (As, Co, Ag, Ba, Cd,  
 568 Zn, Pb, Bi, Cr, Cu, Ni), and geogenic (nss-Ca, Tl, Li, Al, Cs, Rb, Fe, Mn, U, Be, Se, V) sources of  
 569 ionic and elemental species, considering the whole sampling campaign period (2018-2021).  
 570 Interestingly, nss- $SO_4^{2-}$  is brought together with the marine cluster, suggesting that its presence is  
 571 largely influenced by marine biogenic sources, alongside contributions from secondary sulphate  
 572 formation in the atmosphere. This indicates that nss- $SO_4^{2-}$ , despite having a variety of sources such  
 573 as human contribution or dust, is closely linked to the marine environment. One important reason for  
 574 this is the emission of DMS by phytoplankton. Additionally, secondary sulphate formation may have  
 575 further contributed to the nss- $SO_4^{2-}$ . Cobalt was grouped within the anthropogenic cluster in HCA, in  
 576 contrast with EFs that suggested a crustal origin. This apparent discrepancy may reflect the relatively  
 577 larger uncertainties typically associated with EF calculations, which can inherit errors from the choice

578 of reference element, assumptions about crustal composition, and variability in background  
 579 concentrations, compared to the more integrative approach of HCA (e.g., Reimann and de Caritat,  
 580 2000). Moreover, the trend for Co closely aligns with anthropogenic ones (e.g., As), while distinct  
 581 trends are evident for crustal elements. Therefore, while the HCA results offer a reliable perspective  
 582 on source differentiation and clustering patterns, they are best interpreted as complementary to the  
 583 EF calculations rather than directly integrated with them. Incorporating EFs directly into the HCA  
 584 could introduce significant inaccuracies, as EFs rely on reference element ratios that may vary and  
 585 thus add complexity to the clustering process, potentially skewing the results. Consequently, HCA  
 586 independently provides robust insights in this context, enhancing our understanding without the  
 587 additional uncertainties that EF-based clustering might introduce.



588  
 589 **Fig. 6.** Hierarchical cluster analysis applied to further disentangle the particulate trace element non-crustal sources.  
 590

## 591 **5. Summary and Conclusion**

592 In this study, trace elements and major ions were investigated in surface snow samples collected in  
 593 Ny-Ålesund between October 2018 to June 2021. Seasonal and interannual variations of impurities

were observed, with the highest concentrations of marine species recorded in late spring 2020 (e.g.,  $\text{Cl}^- = 110 \text{ mg m}^{-2}$ ,  $\text{Na}^+ = 52 \text{ mg m}^{-2}$ ,  $\text{SO}_4^{2-} = 28 \text{ mg m}^{-2}$ ). These elevated levels coincided with the most extensive sea ice in Kongsfjorden in March 2020 ( $\text{FI} = 113.28 \text{ km}^2$ ,  $\text{DI} = 16.53 \text{ km}^2$ ), driven by negative temperature anomalies in both the atmosphere ( $-7.47^\circ\text{C}$ ) and ocean ( $-0.55^\circ\text{C}$ ), and likely related to higher air mass recycle within the Arctic. This provides direct evidence that sea ice extent modulates the storage, release, and transport of marine-derived impurities, influencing snow-atmosphere chemical exchange processes under varying climatic conditions. Higher concentrations in spring 2020 for geogenic (e.g.,  $\text{Fe} = 6 \text{ mg m}^{-2}$ ,  $\text{Ca} = 13 \text{ mg m}^{-2}$ ) and anthropogenic (e.g.,  $\text{Co} = 5 \text{ }\mu\text{g m}^{-2}$ ,  $\text{Cr} = 25 \text{ }\mu\text{g m}^{-2}$ ,  $\text{Ni} = 131 \text{ }\mu\text{g m}^{-2}$ ) species are consistent with the combined influence of higher wind speeds ( $16.09 \text{ m s}^{-1}$ ), low temperatures, and generally drier conditions resulting from the exceptional occurrence of a strong and cold stratospheric polar vortex, accompanied by an unprecedentedly positive phase of the Arctic Oscillation in the troposphere during January-March 2020. While correlations between meteorological variables and concentrations were generally weak, the overall meteorological context suggests that these unusual conditions likely contributed to the observed deposition patterns. This is particularly evident especially in the cold year of 2020, when the production of sea spray related aerosol likely derives by a larger extension of sea ice and stronger local Arctic circulation, as also indicated by elevated  $\text{Br}_{\text{enr}}$  mean values (17.7 compared to the usual  $< 1$ ; Barbaro et al., 2021). The identification of geogenic, marine, and anthropogenic sources in the snowpack was allowed by a chemometric approach (HCA), which complemented the enrichment factor analysis. This approach mitigates potential biases for EFs results that may come from reference element selection, assumptions about crustal composition, and background variability (Reimann and de Caritat, 2000). In this work, the use of chemometric techniques (HCA) and back-trajectory analysis enabled a clearer attribution of sources and transport pathways, improving interpretation of snow composition in relation to meteorological drivers. Notably, seasonal air mass patterns revealed dominant Arctic-origin air masses in fall and winter and reduced mid-latitude inputs in spring, highlighting shifts in snow-atmosphere interactions under a warming Arctic. These results demonstrate that recent climatic anomalies, including changes in sea ice extent, shifts in Arctic Oscillation phases, and stronger polar vortices, significantly modulate the chemical composition of the snowpack in Svalbard. Our findings underscore the sensitivity of snow-atmosphere exchanges to both local and large-scale climatic processes, providing valuable context for interpreting trends in snow chemistry in a rapidly changing Arctic environment. Limitations such as weak correlations between meteorological variables and concentrations suggest that further multivariate and long-term analyses are needed to quantify these relationships more robustly. Overall, this study emphasizes that snow chemistry can serve as a sensitive indicator of Arctic atmospheric dynamics and climatic

628 variability, advancing our understanding of the links between cryosphere processes, atmospheric  
629 circulation, and ionic-elemental deposition.

### 630 **Data availability**

631 The data supporting the findings of this study are available within the article and its supplementary  
632 materials. Other data that support the findings of this study are available at  
633 <https://doi.org/10.5281/zenodo.17243936>.

### 634 **Author contribution**

635 AS: Conceptualization, Data curation, Investigation, Writing-original draft, Writing-review and  
636 editing. EB: Conceptualization, Field work, Data curation, Formal Analysis, Writing-original draft,  
637 Writing-review and editing, Funding acquisition. MF: Formal Analysis, Field work, Data curation,  
638 Writing-review and editing. FS: Field work, Formal analysis, Investigation, Writing-review and  
639 editing. MV: Writing-review and editing. MV: Field work, Writing-review and editing. MM:  
640 Investigation. FB: Investigation, Writing-review and editing. FB: Investigation. Field work. CJMH:  
641 Investigation, Data curation, Writing-review and editing. AB: Field work, Data curation, Writing-  
642 review and editing. AG: Resources, Supervision, Validation, Writing-review and editing, Funding  
643 acquisition. CB: Resources, Supervision, Validation, Writing-review and editing, Funding  
644 acquisition. AS: Funding acquisition, Supervision, Validation, Writing-review and editing.

### 645 **Competing interests**

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

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