

Measurement report: Spatial variations in snowpack ionic chemistry and water stable isotopes across Svalbard

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▶ To cite this version:

Elena Barbaro, Krystyna Koziol, Mats P Björkman, Carmen P Vega, Christian Zdanowicz, et al.. Measurement report: Spatial variations in snowpack ionic chemistry and water stable isotopes across Svalbard. Atmospheric Chemistry and Physics, 2021, 10.5194/acp-2020-740. hal-03365920

HAL Id: hal-03365920 https://hal.science/hal-03365920

Submitted on 5 Oct 2021

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1 Measurement report: Spatial variations in snowpack ionic chemistry and water stable

- 2 isotopes across Svalbard
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- 30 Keywords
- 31 Snow, Svalbard, Arctic, inorganic ions, water isotopes
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36 Abstract

The Svalbard archipelago, between 74° and 81° N, is ~60% covered by glaciers and located at the Arctic 37 sea ice edge. The region experiences rapid variations in atmospheric flow during the snow season (from 38 late September to May) and can be affected by air advected both from lower and higher latitudes, which 39 likely impact the chemical composition of snowfall. While long-term changes in Svalbard snow 40 chemistry have been documented in ice cores drilled from two high-elevation glaciers, the spatial 41 variability of the snowpack composition across Svalbard is comparatively poorly understood. Here, we 42 report the results of the most comprehensive seasonal snow chemistry survey to date, carried out in April 43 2016 across 22 sites on 7 glaciers across the archipelago. At each glacier, three snow pits were sampled 44 along altitudinal profiles and the collected samples were analysed for major ions (Ca²⁺, K⁺, Na⁺, Mg²⁺, 45 NH_4^+ , SO_4^{2-} , Br⁻, Cl⁻ and NO_3^{-}) and stable water isotopes ($\delta^{18}O$, $\delta^{2}H$). The main aims were to investigate 46 the natural and anthropogenic processes influencing the snowpack and to better understand the influence 47 48 of atmospheric aerosol transport and deposition patterns on the snow chemical composition. The snow deposited in the southern region of Svalbard was characterized by the highest total ionic loads, mainly 49 attributed to sea salt particles. Both NO_3^- and NH_4^+ in the seasonal snowpack reflected secondary aerosol 50 formation and post-depositional changes, resulting in very different spatial deposition patterns: NO3 had 51 52 its highest loading in northwestern Spitsbergen, and NH₄⁺ in the southwest. The Br enrichment in snow 53 was highest in northeastern glacier sites closest to areas of extensive sea ice coverage. Spatial correlation patterns between Na⁺ and δ^{18} O suggest that the influence of long-range transport of aerosols on snow 54 55 chemistry is proportionally greater above 600-700 m a.s.l.

56

57 1. Introduction

58 Svalbard is a region of the Arctic experiencing rapid climate change, with a mean warming rate of ± 1.35 59 K per decade, much faster than the global average (Isaksen et al., 2016; Maturilli et al., 2013; Nordli et al., 2014). This archipelago is located at the southern edge of the perennial Arctic sea ice, in the North 60 Atlantic Ocean, and is characterized by a maritime climate with large, rapid temperature variations 61 62 during winter (Brage et al., 2014). South-westerly inflow of mild oceanic air, associated with a lowpressure system east of Iceland, often brings relatively warm and moist air in winter months, while Arctic 63 64 air intrusions from the north-east, driven by a high-pressure system over Greenland, result in much 65 colder temperatures (Rinke et al., 2017). In addition to these synoptic fluctuations, intense autumn or 66 winter cyclonic storms associated with anomalous warming events sometimes occur, transporting both 67 heat and moisture from lower latitudes to Svalbard (Rinke et al., 2017).

68

69 The aforementioned meteorological conditions also favor long-range transport of aerosols to the 70 archipelago, including pollutants from continental sources. Depending on the predominant air flow 71 pattern at the time of snowfall, the archipelago may experience regionally different amounts of both 72 snow accumulation (Eneroth et al., 2003; Forland et al., 2011) and chemical loads, the latter reflecting





73 contrasting mixtures of aerosol, varying by source area (Aas et al., 2016; Forsström et al., 2009; Möller 74 and Kohler, 2018). These regional differences are also associated with contrasts in sea ice cover. While 75 all Svalbard coasts are usually ice-free in summer, sea ice can form and cover large parts of the ocean surface in the eastern and northern parts of the archipelago, while the southern and western parts often 76 77 remain ice-free (Dahlke et al., 2020), and therefore tend to experience greater snowfall owing to the 78 proximity of open water. In addition, the West Spitsbergen Current, a branch of the Atlantic Meridional Overturning Circulation (AMOC) that flows to the west of the archipelago, causes markedly different 79 regional climatic conditions between its eastern and western parts (van Pelt et al., 2019): the west 80 81 exhibits higher temperatures and precipitation, while the east is less humid and cooler, and has also 82 experienced a stronger warming trend since 1957.

83

The seasonal snowpack contains a complex mixture of impurities that are either scavenged from the 84 85 atmosphere during snowfall or directly received through dry deposition (Kuhn, 2001). On land, the majority of impurities found in seasonal snow are usually eluted during summer melting, influencing 86 terrestrial and aquatic systems (Björkman et al., 2014; Brimblecombe et al., 1987). However, in the 87 accumulation area of Arctic glaciers and ice caps, impurities can be retained within or below the seasonal 88 89 snow layer (Björkman et al., 2014; Pohjola et al., 2002; Vega et al., 2015b). For this reason, chemical impurities such as major ions (Ca²⁺, K⁺, Na²⁺, Mg²⁺, NH₄⁺, SO4²⁻, Br⁻, Cl⁻ and NO₃⁻) in ice cores have 90 91 been widely used to study past trends of atmospheric and climatic conditions (Barbante et al., 2017; 92 Isaksson et al., 2003; Thompson et al., 2002; Wolff et al., 2010). Previous studies in Svalbard (Goto-93 Azuma et al., 1994; Nawrot et al., 2016; Semb et al., 1984; Winther et al., 2003) have shown that the chemistry of the seasonal snowpack is dominated by sea salt ions (Hodgkins and Tranter, 2017). 94 95 However, the region is also a sink for atmospheric contaminants brought in by long-range transport 96 (Vecchiato et al., 2018). Investigations of precipitation and snow cover chemistry have predominantly focused on the central and western parts of the archipelago (Kühnel et al., 2011; Nawrot et al., 2016; 97 98 Vega et al., 2015a; Virkkunen et al., 2007), due to the accessibility of research facilities in these sectors.

99

In the present study, the concentration, mass loading, spatial and altitudinal distribution of major ion 100 species (Ca²⁺, K⁺, Na²⁺, Mg²⁺, NH₄⁺, SO₄²⁻, Br⁻, Cl⁻ and NO₃⁻) in snow, together with its stable oxygen 101 and hydrogen isotope composition (δ^{18} O and δ^{2} H), were evaluated in the late winter snowpack at 22 102 103 glacier sites across Svalbard. This study was part of the larger Community Coordinated Snow Study in 104 Svalbard (C2S3) project and the most comprehensive survey of seasonal snow chemistry in Svalbard to date. The snowpack survey, which was carried out by coordinated teams using a standardized sampling 105 106 protocol (Gallet et al., 2018) aimed to map and characterize regional differences in the chemical composition and impurity load of the winter snow pack, and interpret the observed differences in relation 107 to meteorological and other environmental factors. In this way, we aim to identify the conditions 108





109 controlling the chemistry of Svalbard snow that are susceptible to be influenced by future climate

- 110 warming across the region.
- 111

112 2. Methods

113 2.1 Sampling location and strategy

114 During April 2016, the seasonal snowpack was sampled at 22 sites on seven glaciers across Svalbard: Austfonna (AF) on Nordaustlandet, Lomonosovfonna (LF) on central Spitsbergen, Hansbreen (HB) and 115 Werenskiöldbreen (WB) in the Hornsund area of southern Spitsbergen, and Austre Lovénbreen (ALB), 116 117 Kongsvegen (KVG) and Holtedahlfonna (HDF) in the vicinity of Ny-Ålesund on northwestern 118 Spitsbergen (Table 1 and Figure 1). The glaciers are of different sizes and hypsometries. Each glacier 119 was sampled in the ablation zone, close to the equilibrium line altitude (ELA), and in the accumulation 120 zone (Table 1). The ELA is the elevation at which the surface mass balance is zero, i.e., where the 121 accumulation of snow is exactly balanced by ablation over a period of a year (Cogley et al., 2011). Although the exact elevation range of these zones differ for each glacier, they share enough glaciological 122 123 similarities to support inter-site comparisons. Snowpit sampling was performed using a standardized common protocol (Gallet et al., 2018) with pre-cleaned equipment (i.e., tubes, plastic scrapers and plastic 124 125 shovels cleaned with ultrapure water) and protective clothing (powder-free plastic gloves, clean suits and 126 face masks). Samples for ionic chemistry were taken in each discrete snow pit layer, according to the 127 visible stratigraphy, and directly into pre-cleaned, 50 mL polypropylene "Falcon" centrifuge tubes. 128 Samples for the isotopic composition of water were collected at a 5-cm resolution for sites in the Ny-129 Ålesund area and at a 10-cm or stratigraphic layer resolution for other sites. All sampling was conducted 130 in a safe distance and upwind from potential local pollution sources, such as the snowmobiles used as 131 transport by the sampling team.

132

133 2.2 Major ion analyses

134 Samples from glaciers in the Hornsund region (HB, WB) were analysed at the Polish Polar Station 135 Hornsund (Institute of Geophysics, Polish Academy of Sciences), while samples from glaciers near Ny-Ålesund (KVG, ALB, HDF) were shipped frozen to the Institute of Polar Sciences (ISP-CNR) in Venice 136 (Italy). Snow sampled in central Spitsbergen (AF, LF) was shipped frozen to the Department of Earth 137 138 Sciences at Uppsala University (Sweden). Due to a temporary equipment malfunction in Uppsala, only 139 cations could be analysed there, and the refrozen samples were forwarded to ISP-CNR for anion analysis. 140 All samples and standards were handled and prepared under clean room conditions, wearing powder-free gloves. In all labs except at the Polish Polar Station Hornsund, laminar flow hoods (class 100) were used. 141 142 Samples were melted immediately before analysis. 143

^{144 2.2.1.} Hornsund





Samples were filtered through 0.45 µm mixed cellulose esters membranes (Merck Millipore S-pak®) 145 prior to analysis. Ion concentrations were determined on a Metrohm 761 Compact IC ion chromatograph 146 equipped with an autosampler (Metrohm, Herisau, Switzerland), with isocratic flow, and chemical 147 suppression for anions (column Metrosep A Supp S + Metrosep A Supp 4/5 Guard 4.0, eluent: NaHCO₃ 148 1.0 mmol L^{-1} + Na₂CO₃ 3.2 mmol L^{-1}). Cations were determined without suppression (column Metrosep 149 C4 + Metrosep C4 Guard; eluent: HNO₃ 1.7 mmol L⁻¹ + 2,6-pyridinecarboxylic acid [dipicolinic acid, or 150 DPA] 0.7 mmol L⁻¹). Cation samples were acidified with 2 μ L of 2mM HNO₃ per 10 mL sample prior to 151 152 analysis, as recommended for this device and column. The injection volume was 20 μ L in the anion 153 system and 100 μ L in the cation system. Nitric acid solutions were prepared from POCH S.A. (Poland) 154 concentrated weighed amounts, while sodium carbonate and hydrogen carbonate, as well as DPA, were 155 dissolved from solid phase (Merck Millipore).

156

157 2.2.2 Uppsala

158 Samples were filtered using 0.22 µm polyethersulfone membranes (Minisart®, Sartorius) and anion determinations were performed using a Metrohm ProfIC850 ion chromatograph (Metrohm, Herisau, 159 Switzerland), equipped with an autosampler and a Metrosep C4 column. The mobile phase of 0.02 M 160 161 DPA and 0.1 M HNO₃ was run in isocratic flow of 0.7 mL min⁻¹. Very low detection limits (≤ 0.006 mg⁻¹ 162 ¹L) were achieved thanks to the sample injection volume of 500 μ L.

163

164 2.2.3. Venice

Anion determination was performed using a DionexTM ICS-5000 ion chromatograph 165 (ThermoScientificTM, Waltham, US) equipped with an anionic exchange column (Dionex IonPac AS 11, 166 167 2×250 mm) and a guard column (Dionex IonPac AG11 2×50 mm). Sodium hydroxide (NaOH), used 168 as a mobile phase, was produced by an eluent generator (Dionex ICS 5000EG, Thermo Scientific). The injection volume was 100 µL. The IC was coupled to a single quadrupole mass spectrometer (MSQ 169 170 PlusTM, Thermo Scientific TM) with an electrospray source (ESI) that operated in negative mode. To 171 determine cations, a capillary ion chromatograph (Thermo Scientific Dionex ICS-5000), equipped with a capillary cation exchange column (DionexIonPac CS19-4 μ m, 0.4 \times 250 mm) and a guard column 172 (Dionex IonPac CG19-4 μ m, 0.4 × 50 mm), was used, coupled to a conductivity detector. The injection 173 volume was 0.4 µL. All details about the anion and cation methods are reported by (Barbaro et al., 2017). 174 175

176 2.2.4. Instrumental performance of each laboratory

For all laboratories, calibration for ions were evaluated using analytical standards (Merck/Sigma 177 178 Aldrich). The calibrations in each lab gave different linear ranges for each ion due to the different methods used (Table S1). Good linearity was demonstrated in each lab and all calibration curves had 179 180 R^{2} 0.99. Samples that had ion concentrations beyond the calibration range were diluted with ultrapure water before re-analysis. Analytical blanks of ultrapure water (>18 M Ω ·cm) were included in the 181





analysis at all three labs. The method detection limit (MDL) was set to three times the standard deviation of the blank values (Table S1). For Na⁺, Mg²⁺, Cl⁻ and SO₄²⁻, values <MDL occurred in less than 10% of cases, and for Ca²⁺ and NO₃⁻ the <MDL concentrations were noted in 12% and 17% of cases, respectively. However, K⁺ and Br⁻ were detected only in 53% and 46% of all samples, respectively, while NH₄⁺ concentration exceeded the MDL only in 36% of all measurements. For the calculation of bulk ionic loading in snow pits, values <MDL were assumed to be equal to half the MDL.

188

189 Accuracy and precision are important parameters to evaluate during method validation. Checks for accuracy were made using certified multi-element standard solutions for anions (F, Cl, Br, NO₃, SO₄²⁻, 190 n° 89886-50ML-F, Sigma Aldrich) and cations (Na⁺, K⁺, Mg²⁺, Ca²⁺, n° 89316-50ML-F, Sigma Aldrich), 191 192 at the concentration of 10 mg $L^{-1} \pm 0.2\%$. Accuracy is expressed as a relative error calculated as 193 $(Q-T)/T \times 100$, where Q is the determined value and T is the "true" value. The accuracy for each ion in all labs was always $\leq \pm 10\%$, except for Mg²⁺ measurements at the Hornsund laboratory. The analytical 194 precision was quantified as the relative standard deviation (RSD) for replicates (n>3) of standard 195 196 solutions and was always <10% for each ion (Table S1).

197

198 2.3. Stable water isotopes

199 The determination of stable isotope ratios of O and H was performed at Tallinn University of Technology 200 using a Picarro L2120-i water isotope analyser with a high-precision AO211 vaporizer. Results are 201 reported in the standard delta notation as δ^{18} O and δ^{2} H relative to VSMOW. Reproducibility was ±0.1‰ 202 for δ^{18} O and ±1‰ for δ^{2} H, respectively.





204 3. Results

205 3.1 Spatial distribution of ionic species

206 To investigate differences in snowpack composition across all glaciers, we compared the total mass of ions that accumulated in snow at the different sampling sites. On average, the snow cover season on 207 208 Svalbard lasts from early September to early May, but snow may also fall in summer months at high 209 elevations. The snow pits in this study were sampled in early to late April 2016 and might therefore not contain the full annual ionic burden, since deposition might occur also in other months. Therefore, we 210 report these data as ionic loads (mg m⁻²) rather than annual fluxes. In each snow pit, the ionic load was 211 212 calculated as the cumulative sum of the ionic concentrations multiplied by the snow water equivalent in 213 each discrete layer. The snowpack chemical characteristics were then compared between glacier zones (ablation zone, ELA, and accumulation zone; Table 2, Figure 1). 214

215

Snow pits samples collected in the Hornsund area (southern Spitsbergen) showed a markedly higher total load for all major ions (Figures 1 and 2) than at all other sites. The samples collected in the accumulation zones of WB and HB had total ionic loads of 8161 and 8023 mg m⁻², respectively, four times higher than those collected in the same zone at KVG (2861 mg m⁻²), AF (2607 mg m⁻²) and ALB (1934 mg m⁻²) and 16 times higher than those sampled at LF (639 mg m⁻²) and HDF (583 mg m⁻²). Similar differences were observed for the snow pits collected at lower altitudes (Figure 2).

222

In the accumulation zone of all glaciers (Figure S1), Na⁺ and Cl⁻ were generally the most abundant ionic 223 224 species, with percentages ranging from 29% (HDF) to 36% (AF) for Na⁺, and from 34% (LF) to 48% 225 (HB and WB) for Cl⁻, respectively. The snowpack on Hornsund glaciers (HB, WB) had higher Cl⁻ percentages (48-49%) compared to that of other glaciers (34-39%), while conversely the SO_4^{2-} percentage 226 was lower there (9%) than on other glaciers (11-23%). The ionic loads were generally highest in the 227 228 accumulation zone of glaciers, and lowest in the ablation zone (Figure 2), mostly due to the lower snow accumulation and greater wind deflation at lower elevations. This pattern held true for Na⁺, Cl⁻, NH₄⁺, 229 K⁺, Ca²⁺, and Mg²⁺ at most glacier sites, except in the Hornsund region. The load of Br⁻ was similar on 230 231 glaciers of the Ny-Ålesund sector (ALB, HDF, KVG) and on LF, but was higher in AF and Hornsund glaciers (HB, WB; Figure 2). The load of NO3⁻ was similar for all glaciers, except for LF, where very low 232 loads were found. Unlike total $SO_4^{2^2}$, the non-sea-salt fraction of sulphate (nss- $SO_4^{2^2}$), calculated using a 233 seawater SO₄²:Na⁺mass ratio of 0.252, (Millero et al., 2008) showed lower loads on Hornsund glaciers 234 (15-107 mg m⁻²) when compared to glaciers in other parts of the archipelago (Figure 1, Table 2). The 235 nss-SO₄²⁻ loads varied between 22-131 mg m⁻² at HDF and LF, 75-266 mg m⁻² at KVG and ALB, and 236 153-206 mg m⁻² at AF. 237

238

239 3.2 Stable water isotopes ($\delta^{18}O$ and $\delta^{2}H$)





Our results provide the first picture of spatial variations in the mean stable water isotope composition of 240 the seasonal snowpack across Svalbard (Table 2, Figure S2). The snow water equivalent (SWE)-241 weighted mean δ^{18} O and δ^{2} H decreased significantly from south to north (Spearman rank correlation ρ 242 with latitude was -0.69 and -0.65 for δ^{18} O and δ^{2} H, with p<0.001 and p<0.01, respectively). The 243 isotopically heaviest snow (least negative δ values) occurred on glaciers of the Hornsund region (δ^{18} O: -244 11.25 to -9.54 ‰; δ^2 H: -77.62 to -63.64 ‰), and the isotopically lightest (most negative δ values) in AF 245 $(\delta^{18}O: -16.00 \text{ to } -13.89 \text{ }\%; \delta^2H: -111.15 \text{ to } -96.89 \text{ }\%)$. Glacier sites in NW Spitsbergen and on LF had 246 mean δ^{18} O and δ^{2} H values that fell within these ranges. On KVG, ALB, HDF and LF, the δ^{18} O and δ^{2} H 247 248 in snow decreased monotonically (becoming gradually more negative) with increasing elevation. 249 However, on other glaciers this pattern did not hold: on AF, we found an increase from AF1 to AF2, but 250 a decrease from AF2 to AF3; on WB the δ^{18} O and δ^{2} H were similar at WB1 and WB2, but less negative 251 at WB3. On HB there was no statistical difference between the mean δ^{18} O and δ^{2} H value in all snow pits. A general, significant anticorrelation with altitude was found for SWE-weighted mean $\delta^2 H$ (ρ = -0.63, 252 p < 0.01), and $\delta^{18}O$ ($\rho = -0.65$, p < 0.01). 253

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256

255 4. Discussion

257 There have been few published studies on recent seasonal snow or firn chemistry in Svalbard, hence 258 comparisons of our data with these earlier results are limited to a few sites. (Virkkunen et al., 2007) and (Vega et al., 2015a) and unpublished data) quantified the annual chemical loads of Na^+ , Ca^{2+} , NO_3^- and 259 nss-SO₄²⁻ at Lomonosovfonna summit (LF3) from 2002 to 2011 using snow and firn cores, and our study 260 extends these data to 2016. The range of annual ionic loads at LF3 over the 15-year period is remarkably 261 wide, but no clear temporal trend can be identified (Table 3). At Holtedahlfonna summit (HDF3), firn 262 core measurements by (Spolaor et al., 2013) found a mean Na^+ concentration of 110 ±73 ng g⁻¹ over the 263 period 2003-2012, while the mean concentration in the April 2016 snowpack (this study) was 191 ng g⁻¹, 264 hence within the range reported in earlier years. 265

266

267 4.1 The main ion sources in the Svalbard seasonal snow

The composition of the Svalbard seasonal snowpack sampled during the C2S3 project clearly indicates 268 that the ocean is the main source of ions in snow, as was shown by Hodgkins and Tranter (2017). At all 269 sites, the dominant ions are Na^+ , Cl^- , and SO_4^{2-} , with comparatively minor amounts of K^+ , Ca^{2+} and Mg^{2+} 270 (Figure S1). To help clarify the possible sources and modes of deposition of ions in snow, we computed 271 Spearman rank correlations between total ionic loads (ρ_{load}), as well as between volume-weighted mean 272 273 ionic concentrations (ρ_{conc}), across all snow pits (n = 22; Table 4). The chemical species that are 274 predominantly wet-deposited and sharing common sources and not undergoing significant composition changes in transport should exhibit similar concentration patterns (high ρ_{conc}) (Schüpbach et al., 2018). 275 The concentrations of Mg^{2+} , K^+ and Ca^{2+} were all positively correlated with those of Na^+ and Cl^- , 276





277 indicating a common sea spray source. The ρ_{load} correlations are very similar for these ionic species, 278 which points to both wet and dry deposition being a significant mechanism in their accumulation in 279 snowpack.

280

The concentrations of Mg²⁺ were positively and significantly correlated with both Ca²⁺ and nss-Ca²⁺ (ρ_{conc} 281 = 0.70 and 0.47, respectively; the latter coefficient was higher for loads at 0.56; Table 4), suggesting they 282 share some non-marine source(s). Furthermore, all glaciers had greater Ca²⁺:Mg²⁺ ratios than seawater 283 (0.32; (Millero et al., 2008) (Figure 3). It is likely that the excess Ca^{2+} and Mg^{2+} came from mineral 284 particles, i.e. CaCO₃ (calcite), and local rock (or soil) dust (Kekonen et al., 2005) derived from calcareous 285 rocks, especially limestone, dolostone and marble, which are abundant in (Dallmann, 1999) The presence 286 of carbonate ions in the collected snow samples would explain the missing negative charge in the ionic 287 288 balance (anion X⁻; Figure S3).

289

Sulphate (SO₄²⁻) was highly and significantly (*p*-value <0.05) correlated with both Na⁺ ($\rho_{load} = 0.92$; ρ_{conc} 290 = 0.80) and Cl⁻ (ρ_{load} =0.93; ρ_{conc} = 0.75), indicating that sea spray is its main source. However Na⁺/SO₄²⁻ 291 and CI⁻:SO₄²⁻ ratios were well below seawater values (Millero et al., 2008) on most glaciers except those 292 near Hornsund (WB and HB), suggesting inputs of nss-SO₄²⁻ (Figure 3). Biogenic nss-SO₄²⁻ can be 293 deposited in the snow as an oxidized by-product of dimethyl sulphide (DMS) emitted by marine algal 294 295 blooms (Gondwe et al., 2003), typically initiated in April but sometimes later (Ardyna et al., 2013). 296 Another plausible source of nss-SO₄²⁻ deposition in Svalbard is long-range transport of SO₄²⁻ aerosols 297 from biomass burning in the spring, or from fossil fuel combustion throughout the winter (Barrie, 1986; Law and Stohl, 2007; Nawrot et al., 2016). The $nss-SO_4^{2-}$ did not correlate significantly with other ionic 298 species, suggesting a separate origin. An extra consideration is that in the southern region of the 299 archipelago, the higher sea spray input could partially mask the nss- SO_4^{2-} signal, which is a derived 300 variable, because the larger uncertainty for greater Na⁺ concentrations would disproportionately affect 301 estimations of $nss-SO_4^{2-}$ at these sites. 302

303

Bulk ionic loads of SO_4^{2-} in the snow pits were significantly and positively correlated with those of NO_3^{-} 304 $(\rho_{\text{load}}=0.55)$ and NH₄⁺ $(\rho_{\text{load}}=0.68)$, but the correlations between weighted mean ionic concentrations 305 306 were not significant, hinting at co-deposition (wet) rather than shared sources (Table 4). These species are known to form secondary aerosols (Karl et al., 2019; Schaap et al., 2004) and thus their proportions 307 308 in aerosols may differ significantly from those in their source emissions. It is also possible that nitrogen 309 species underwent further post-depositional photochemical reduction and evasion, thereby reducing their 310 concentrations in snow (Curtis et al., 2018). Finally, we remark here that the snow pit sampling was done 311 in April, earlier than the beginning of the oceanic algal bloom in the surrounding Svalbard basin, which 312 could have led to underrepresentation of biological emissions from late spring in our samples.





Spatial variations of ammonium loads (NH_4^+) across Svalbard glaciers mirrored the pattern shown by sea 314 315 salt ions, with higher loads in the Hornsund region and lower loads in other areas. This was also reflected by significant correlations between bulk loads of NH₄⁺ with those of Na⁺ and Cl⁻ ($\rho_{load} = 0.64$ and 0.73, 316 respectively), and with Na⁺, K⁺ and Mg²⁺ by concentration ($\rho_{conc} = 0.47, 0.62$ and 0.47, respectively), the 317 latter relationships suggesting that some ammonium is deposited as coatings on crustal aerosols 318 (Eastwood et al., 2009). Ammonium has been linked to biogenic, forest fire, and anthropogenic 319 agricultural emissions (Trachsel et al., 2019). The higher annual snowpack load of NH_4^+ , determined in 320 the Hornsund region is more likely connected with biological sources than anthropogenic activities, 321 322 although some contribution from biomass burning events cannot be excluded. The marine primary 323 productivity in spring 2016 (April and May) was higher in the south-eastern ocean sector of the Svalbard 324 archipelago (Figure S4), which could partially explain the higher NH_4^+ load. This would also explain the 325 correlation between ammonium and sea-salt ions (Table 4). Locally, especially for HB, there may be 326 extra NH₄⁺ emissions from bird colonies (Keslinka et al., 2019; Wojczulanis K. et al., 2008).

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328 Unlike NH_4^+ , the bulk loading of NO_3^- in snow was highest in northwestern Spitsbergen (Ny-Ålesund 329 area), when compared to other parts of Svalbard. Deposition of NO3 in Arctic snow is often associated 330 with the long-range atmospheric transport of NO_x and related N species from anthropogenic source 331 regions at lower latitudes (Björkman et al., 2014; Fibiger et al., 2016; Vega et al., 2015a). Differences in 332 NO₃ loads in snow in various parts of Svalbard might therefore reflect differences in the transport 333 pathways of precipitating air masses, including formation of secondary aerosols, or post-depositional 334 processes, rather than local emissions. While local shipping routes and the settlement of Ny Ålesund itself may contribute NO_3 emissions (Winther et al., 2014), the highest share of the total ionic load of 335 NO3⁻ was found in the accumulation zone of HDF (9% of the total ionic load; Figure S1). Given that 336 337 HDF is the most remote site from Ny Ålesund relative to KVG or ALB, it should not capture a high share of local pollution. The highest correlation coefficient for NO₃, both in terms of concentrations and 338 loads, was found with nss-Ca²⁺. This would support both the formation of calcium nitrate in the 339 atmosphere (Gibson et al., 2006) or post-depositional processes removing the NO₃⁻ from layers poor in 340 341 Ca^{2+} , since calcium has been hypothesised to stabilise the nitrate in snowpack against post-depositional losses (Kekonen et al., 2017). 342

343

344 4.2. Chlorine depletion

Although Na⁺ and Cl⁻, the main species of sea salt, were significantly correlated ($\rho_{conc} = 0.95$), the values of the Cl⁻/Na⁺ ratio in snow were lower than that in seawater on most studied glaciers, except those near Hornsund (Figure 3), suggesting a Cl⁻ deficit at the more northerly sites. A possible explanation of this Cl⁻ deficit might be de-chlorination of the sea spray aerosol during transport or, less likely, at the snowatmosphere interface. This reaction occurs between sea salt particles, containing NaCl, and NO₃⁻, SO₄²⁻, or organic acids to release gaseous HCl (Zhuang et al., 1999). We calculated the percentage of Cl⁻





depletion ($C\Gamma_{dep}$) as $C\Gamma_{dep} = (C\Gamma_{ss} - C\Gamma_{meas}) / C\Gamma_{ss} \times 100\%$, where $C\Gamma_{ss} = 1.174 \text{ Na}^+_{meas}$, and $C\Gamma_{meas}$ and Na⁺_{meas} are the measured equivalent concentrations (Yao et al., 2003). Except for site HDF2 ($C\Gamma_{dep} = 2\%$), the lowest mean $C\Gamma_{dep}$ values were obtained for Hornsund glaciers (WB, HB: 10–19%), while values at other glacier sites ranged between 21 and 75% (Table 2). This suggests that sea-salt aerosols travel along a route from southern to northern Svalbard, which gives more time for $C\Gamma$ depletion in the ionic mixtures reaching more northerly locations.

357

358 4.3. Bromine enrichment

359 In addition to Cl, snowfall can scavenge Br (Peterson et al., 2019; Spolaor et al., 2019), and Br loads on 360 Svalbard glaciers surveyed in April 2016 were positively and significantly correlated with those of 361 primary sea salt ions Na⁺ ($\rho_{load} = 0.48$), Cl⁻ ($\rho_{load} = 0.53$) and Mg²⁺ ($\rho_{load} = 0.51$) (Table 4). Correlations between weighted mean concentrations were not significant, however, suggesting departures of the Br 362 363 concentrations in snow from typical seawater ionic ratios at some glacier sites. A Br enrichment factor (Br_{enr}) can be calculated as $Br_{enr} = Br / (0.0065 Na^{+})$, where 0.0065 is the $Br : Na^{+}$ seawater mass ratio 364 365 (Maffezzoli et al., 2017). The Brenr reflects specific processes (in particular sea ice Br emission) that affect the Br concentration and load in the snowpack (Spolaor et al., 2014). Results of our calculations 366 367 (Table 2, Figure S5) show that on glaciers of the Hornsund area (HB and WB) and NW Spitsbergen 368 (KVG, ALB and HDF), the mean Br_{enr} values are often, but not always, < 1, indicating some Br^{-} 369 depletion, in agreement with the findings of (Jacobi et al., 2019) for glaciers in the Ny Ålesund area. The 370 depletion could be a result of snowpack Br re-emission, but this seems unlikely since field measurements 371 near Ny-Ålesund found no evidence of such volatilization of snow-bound Br (Spolaor et al., 2019).

372

373 Alternatively, Br depletion could occur through BrO loss from marine aerosols and subsequent 374 deposition of these Br-depleted aerosols in snow. In contrast to southern and northwestern Spitsbergen, glaciers in central Spitsbergen (LF) and in Nordaustlandet (AF), showed Br_{enr} values > 1. These glaciers 375 376 lie relatively close to areas to the east of the archipelago that are often covered by first-year sea ice. 377 Newly-formed sea ice has been shown to release gas phase Br into the polar atmosphere, thus supplying an extra Br source in addition to sea spray (Spolaor et al., 2016). The spatial distribution of the Br-378 379 enriched snow pit sites supports this : sites closest to areas covered by first-year sea ice have the largest 380 Br enrichments, and the latter decrease with greater distance from the eastern shores of Svalbard (Figure 381 S5). A survey of the average sea ice coverage in the period March-May 2016, which is relevant to the Br 382 enrichment phenomenon (data by Norwegian Meteorological Institute) confirms that the north-eastern and eastern shore of Svalbard were indeed covered much more frequently by close and open drift ice 383 384 than the south or north-west.

385

386 4.4 Distribution pattern of $\delta^{18}O$ and $\delta^{2}H$





As described earlier, the SWE-weighted mean δ^{18} O and δ^{2} H values in glacier snow pits decreased significantly with increasing latitude across Svalbard, the least negative values occurring on glaciers of the Hornsund region, and the most negative in Austfonna (Table 2). This pattern follows the climate gradient across the archipelago, milder in the south, colder in the north. Part of the south-north contrast in δ values could be explained by the lower mean altitude of glacier sites in the Hornsund region compared to some of the higher-elevation sites further north on Spitsbergen or on Austfonna, and the relationship with elevation was similar for both isotopic ratios in the collected dataset.

The deuterium excess ($d = \delta^2 H$ -(8* $\delta^{18}O$)) is mainly influenced by the source region of the precipitating 394 moisture and in particular by the sea surface temperature. In addition, d is also influenced by the 395 396 temperature gradient between the moisture source and precipitation area. The SWE-weighted mean d397 values in Svalbard snow pits varied within a relatively narrow range of 6.74‰ (from 10.10 to 16.84 ‰), 398 and similarly to δ^{18} O, showed no clear gradient with elevation or longitude. Deuterium excess showed a 399 significant correlation with latitude, at $\rho = 0.60$ (p < 0.01). A more detailed analysis of d by latitude showed that only beyond 79.2 °N, i.e. in Austfonna snow pits, was d significantly different than at other 400 sites (Kruskal-Wallis test, z = 4.23, p < 0.04). This is consistent with lower temperatures and evaporation 401 402 rates in the more northern waters around Svalbard, and suggests that snowfall on AF is at least partly 403 affected by a different, more northerly moisture source than the rest of the archipelago.

404

405 4.5 Effect of elevation: a case study of Na

406 The glacier survey carried out during the C2S3 project afforded the opportunity to investigate the 407 possible effect of elevation on the ionic composition of the snowpack. To do this, we compared the bulk 408 load and SWE-weighted mean concentration of Na⁺ across all studied snow pits, ordered by elevation (Figure 4). Overall, both Na⁺ loads and concentrations decreased with increasing altitude ($\rho_{load} = -0.24$, p 409 >0.05; $\rho_{conc} = -0.72$, p < 0.05). This likely reflects greater local sea spray aerosol deposition at lower, 410 compared to higher, glacier sites. We then computed linear (Pearson) correlation coefficients (R, with 411 associated p-values) between log-transformed Na⁺ loadings (log(Na_{toad})) and δ^{18} O for all snow pits in the 412 accumulation zones of glaciers (Figure 5). The calculation was performed with all snow layers. The Na⁺ 413 load was used as sea-spray tracer, while the δ^{18} O was assumed to vary with moisture source between 414 discrete snowfall events. We found that the positive correlation between $log(Na_{load})$ and $\delta^{18}O$ increased 415 with elevation from R = 0.1 (HB3; 396 m a.s.l.) to R = 0.65 (LF3; 1193 m a.sl.), and reached a 95 % 416 417 threshold of significance (R > 0.3) for glaciers sites above 600 m a.sl. (KVG, AF, LF and HDF; Figure 418 5). The average distance was a comparatively negligible factor in explaining the correlation between $\log(Na_{load})$ and $\delta^{18}O$. 419

420

421 The increase in strength and significance of the $log(Na_{load})-\delta^{18}O$ correlation with altitude might be 422 explained by different contributions of locally-emitted ssNa⁺, relative to those of Na⁺ from more distant 423 sources. Sites located at lower altitudes are proportionally more affected by local sea spray deposition,





with or without snowfall. Conversely, sites at higher elevations likely receive a larger share of their ionic 424 load from more distant sources, and by wet deposition through snowfall. At the four sites (KVG, AF, LF 425 and HDF) where the log(Na_{load})- δ^{18} O correlation was significant, increases in δ^{18} O in snow layers were 426 often associated with higher Na⁺ concentrations. The isotopically heavier (less negative) δ^{18} O values 427 suggests that the co-registered Na⁺ enhancements were associated with precipitation of relatively warm 428 429 air, probably advected from lower latitudes. Air masses arriving from the south travel across the ocean for an extended time, which can enrich them in sea spray aerosol and hence in Na⁺. It is also possible that 430 the poorer $\log(Na_{load}) - \delta^{18}O$ correlation at lower altitude glacier sites is partly due to stronger post-431 depositional modification of isotopic and ionic signals in snowpack related to more frequent melt-432 433 refreeze episodes.

434

435 5.Summary and Conclusion

We have quantified and described, for the first time, the spatial distribution of major ion loads (Ca^{2+}, K^+ , 436 Na^{2+} , Mg^{2+} , NH_4^+ , SO_4^{2-} , Br^- , Cl^- and NO_3^-) and variations of $\delta^{18}O$ and $\delta^{2}H$ in the snowpack on glaciers 437 across Svalbard for a single accumulation season (2015-2016). The highest total ionic loads were found 438 in the southern region of Spitsbergen (Hornsund area), and exceeded 8 g m⁻². Conversely, the lowest total 439 ionic loads (≤ 0.6 g m⁻²) were found at sites in central or northwestern Spitsbergen (LF and HDF). Sea 440 salt ions (Cl⁻, Na⁺ and SO₄²⁻) dominated the ionic loads at all sites, but their share was highest at sites 441 near Hornsund, for e.g., 48% Cl⁻, compared to only 29% on Holtedahlfonna. Relatively elevated 442 Ca²⁺/Mg²⁺ ratios in snow at all sites indicated non-sea-salt Ca²⁺ inputs, most likely in the form of 443 444 carbonate dust. Unlike other ions, NO₃⁻ had the highest loads in glaciers of northwestern Spitsbergen, and the lowest at LF. The nitrogen species, NO_3^- and NH_4^+ , showed distinct spatial distribution patterns. The 445 446 highest NO₃ loads were found in the northwestern part of Svalbard, while the highest NH_4^+ loads were in 447 the southwest. Bromide (Br) was most enriched in snow relative to seawater at AF and LF, the glacier sites located closest to areas with first-year sea ice cover. This supports first-year sea ice being an 448 449 important source of non-sea salt Br in the polar atmosphere.

450

An increasing, positive correlation between log(Na_{load}) and $\delta^{18}O$ as a function of elevation sites suggests 451 that locations above 600-700 m a.s.l. are influenced by a proportionally higher share of ions from distant 452 453 sources, while the lower sites are exposed to more local sources, especially sea spray. These findings 454 confirm that the optimal sites to study the effects of long-range pollution deposition in Svalbard are those 455 found at higher elevations sites, such as the accumulation zones of HDF or LF, because they are the least impacted by the local aerosol emissions. The current study gives the first picture of the ionic composition 456 457 in the Svalbard snowpack in different regions across the archipelago, in the context of which processes are relevant in controlling the annual snowpack chemical composition there, especially the influence of 458 459 local and long-range transport.





461 Acknowledgements

462	The work developed here was supported through grants 246731/E10 and 257636/E10 from the Svalbard
463	Science Forum /(Research Council of Norway), by the Gothenburg Centre of Advanced Studies, BECC -
464	Biodiversity and Ecosystem Services in a Changing Climate, Gothenburg Air and Climate Centre,
465	International Arctic Science Committee - Cryosphere working group and the Norwegian Polar Institute.
466	Part of fieldwork has been conducted thanks to the funds of the Leading National Research Centre
467	(KNOW) in Poland, received by the Centre for Polar Studies for the period 2014-2018. This research
468	was also partially supported within statutory activities No 3841/E-41/S/2020 of the Ministry of Science
469	and Higher Education of Poland. The project has received further funding from the European Union's
470	Horizon 2020 research and innovation programme under grant agreement no. 689443 via project iCUPE
471	(Integrative and Comprehensive Understanding on Polar Environments).
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652 TABLES

Table 1. Table 1. laciers and sampling sites included in this study with their main characteristic. AWS: atmospheric weather station; UiO: University of Oslo; ThèMA: Thèoriser & Modèliser pour Amènager, University of Franche-Comté; NPI: Norwegian Polar Institute; IMAU: Institute for Marine and Atmospheric Research, Utrecht University; UoS: University of Silesia, IG PAS – Institute of Geophysics, Polish Academy of Sciences; CNR – Consiglio Nazionale delle Ricerche. . The seven glaciers were considered at three different altitudes: 1) lower ablation zone; 2) ELA; 3) upper accumulation zone. Exceptionally, two snow pits (KVG 1 and KVG 1.5) were dug in the ablation zone of Kongsvegen glacier.

660

Table 2. Total load (mg m⁻²) of major ions, calculated as the sum of loads in all layers of each snow pit. Sea salt sulphate (ss-SO₄²⁻) and non-sea-salt sulphate (nss-SO₄²⁻) are expressed as mg m⁻², while chloride depletion (Cl⁻_{dep}) is given as a percentage and bromide enrichment (Br_{enr}) refers to an enrichment compare to sea water. Average SWE-weighted stable water isotope ratios (δ^{18} O and δ^{2} H) and average deuterium excess (*d*) are also reported.

666

667 **Table 3.** Chemical loads (mg m⁻²) of selected elements from the 2016 sampling and earlier studies

at Lomonosovfonna summit (LF3), corresponding to the concentrations given in Fig. 4.

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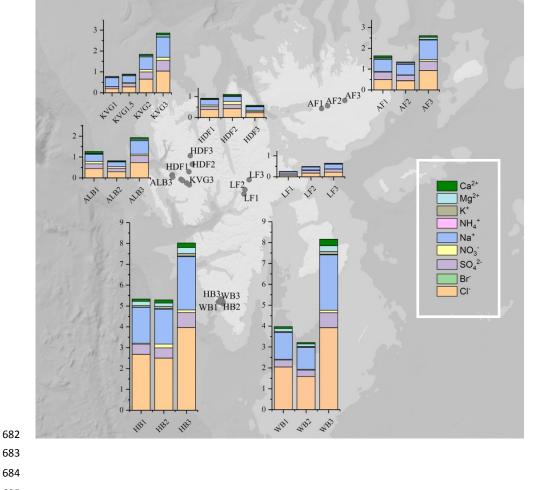
Table 4. Spearman rank order correlations for all 7 glaciers (n=22 locations) with a p < 0.05: a) of total loads (mg m-2) of major ions (calculated as the sum of loads in all layers of each snow pit), b) of volume-weighted average concentrations of each snow pit, calculated by dividing the total load of each snow pit by its total water equivalent. Non-sea-salt (nss) components were calculated based on the seawater ratios to Na⁺ (0.038 and 0.252, respectively, for Ca²⁺ and SO₄²⁻ in mg L⁻¹; Millero et al. 2008); ns = not significant with p-value > 0.05.





676 FIGURES

- Figure 1. Total snowpack loads (mg m⁻²) of major ions in 22 snow pits collected on glaciers during the C2S3 678
- 679 project. Seven glaciers were sampled in three snow pits in the lower ablation zone (1), near the equilibrium
- 680 line (2) and in the upper accumulation zone (3), except on Kongsvegen glacier (KVG) where there was an
- 681 extra snow pit sampled within the ablation zone. Glacier site abbreviations are given in Table 1.

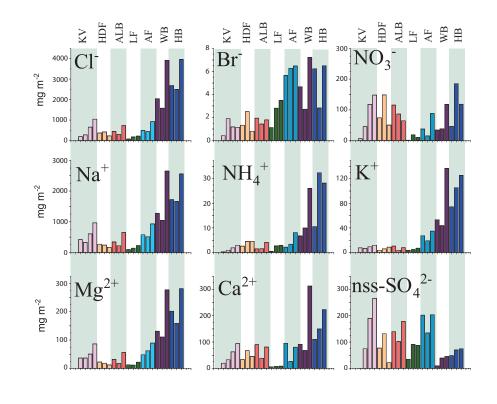


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- Figure 2. Calculated ionic loads in the snowpack (mg m⁻²) at the 7 glacier sites sampled during the C2S3
 project. Snow pits for each glacier are marked with the same colour and ordered from lower (left) to higher
 altitudes (right). For the KGV another snow pit was dug between glaciers zone 1 and 2.

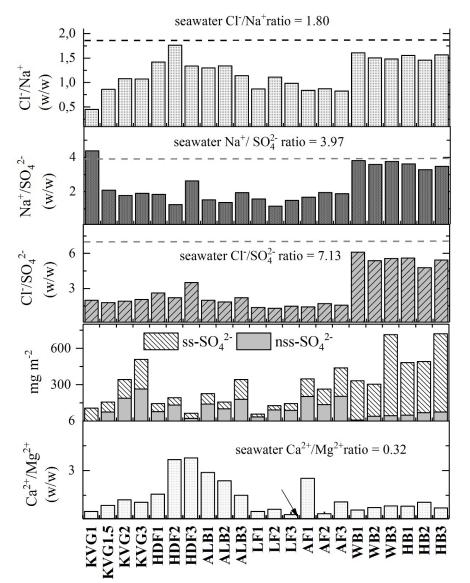






- **Figure 3.** Panels from top: 1) Cl⁻/Na⁺; 2) Na⁺/SO₄²⁻; 3) Cl⁻/SO₄²⁻; 4) the total loads of sea-salt sulphate (ss-SO₄²⁻) and non-sea-salt sulphate (nss-SO₄²⁻), and 5) Ca²⁺/Mg²⁺ - for all glaciers investigated during the C2S3 project (in the spring 2016).
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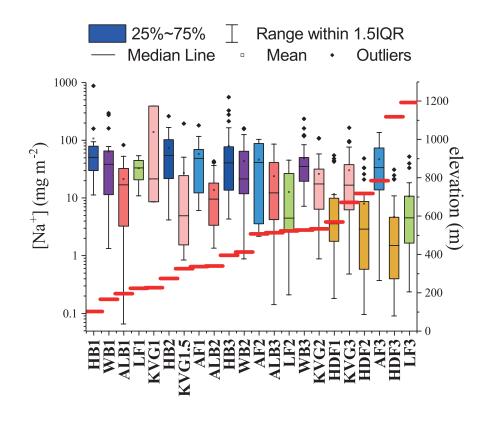
707







- 710 Figure 4. Sodium load in snow pits ordered by increasing elevation in m a.s.l., indicated by the red lines.
- 711 The colours identify areas where the snow pits have been excavated: each colour represents a separate glacier
- 712 (HB blue; WB purple; ALB red; LF green; KVG pink; AF light blue; HDF orange). IQR =
- inter-quartile range, i.e. the difference between the value of quartiles 3 and 1.

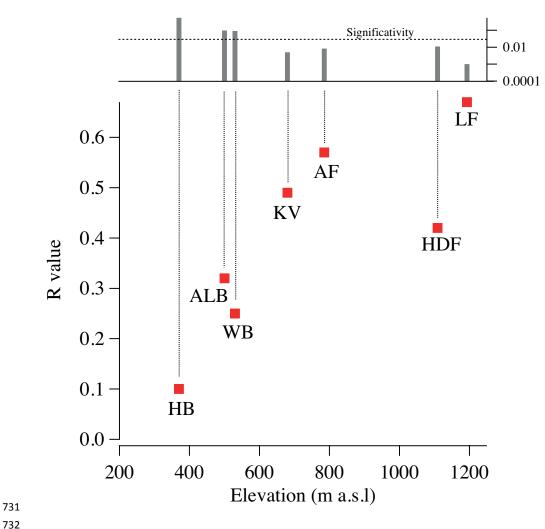






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726 Figure 5. The correlation coefficient between oxygen isotope ratio ($\delta^{18}O$) and log[Na_{load}] increases with elevation. The left axis represents the correlation coefficient (R) between log[Na_{load}] and δ^{18} O, using the 727 728 entire dataset for each snow pit (i.e. all layers have been used for the statistical correlation). The x axis 729 indicates the altitude of the snow pit. The upper panel shows the p-value: correlations have been considered 730 statistically significant if p < 0.05.





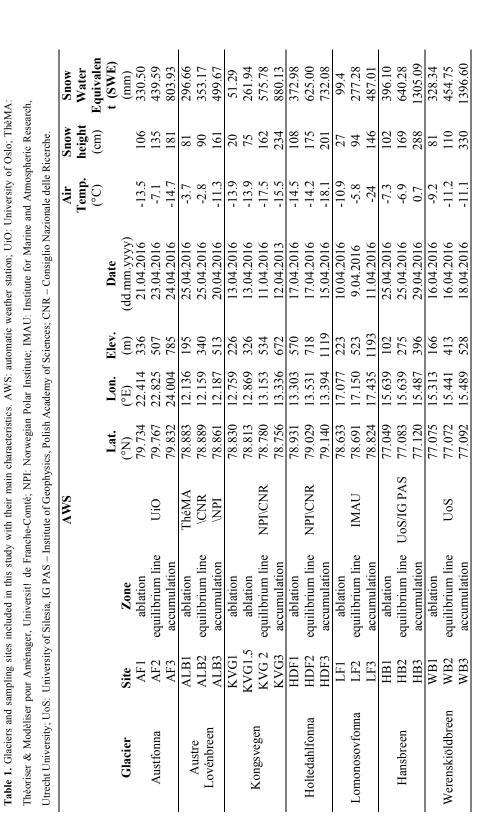
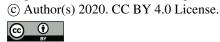




Table 2. Total load (mg m⁻²) of major ions, calculated as the sum of loads in all layers of each snow pit. Sea salt sulphate (ss-SO₄²) and non-sea-salt sulphate (nss-SO₄²) are expressed as mg m⁻², while chloride depletion (Cl^{dep}) is given as a percentage and bromide enrichment (Br_{eur}) refers to an enrichment compare to sea water. Average SWEweighted stable water isotope ratios (δ^{18} O and δ^{2} H) and average deuterium excess (*a*) are also reported.

	CI-	Br^{-}	SO_4^{2-}	NO_3^{-1}	\mathbf{Na}^+	$\mathbf{NH_4}^+$	\mathbf{K}^+	${ m Mg}^{2+}$	Ca^{2+}	-SS-	-SSU	Cl ^{dep} %	$\mathbf{Br}_{\mathrm{enr}}$	δ^{18} O	δ ² H	р
										SO_4^{2-}	SO_4^{2-}	ſ				
KVG1	190		96	9	421	0.3	7	37	20	106	pu	75	0.2	-9.69	-66.17	11.37
KVG1.5	281		157	45	327	0.9	9	36	33	82	75	52	1.0	-11.32	-78.25	12.34
KVG2	652		342	118	605	1.9	6	51	63	152	190	40	0.3	-12.51	-88.62	11.48
KVG3	1039		509	148	967	2.9	12	86	94	244	266	40	0.2	-12.72	-89.50	12.25
HDF1	373		144	74	267	2.6	4	23	33	68	79	21	0.9	-13.51	-94.37	13.75
HDF2	423		192	148	240	4.5	9	18	67	61	131	7	1.7	-13.91	-99.15	12.10
HDF3	227		65	51	170	4.5	6	12	45	43	22	25	0.8	-15.18	-104.51	16.97
ALB1	446		226	115	343	1.5	10	31	90	86	139	27	0.9	-11.22	-75.17	14.59
ALB2	294		158	87	221	1.6	4	17	38	56	107	25	1.2	-12.19	-83.11	14.40
ALB3	729		342	64	648	4.2	8	56	81	158	165	36	0.4	-12.40	-85.40	13.79
LF1	75	1.1	59	1	95	0.4	З	12	9	31	48	51	2.1	-11.61	-82.79	10.10
LF2	174		127	18	141	2.6	S	12	7	53	127	38	3.2	-14.54	-105.44	10.90
LF3	216		144	10	225	2.9	7	22	6	56	93	45	2.7	-15.14	-110.42	10.69
AF1	498		348	38	578	2.2	27	48	95	127	173	53	1.6	-14.34	-100.76	13.94
AF2	438		263	15	509	3.4	19	62	26	147	153	51	2.0	-16.00	-111.15	16.84
AF3	928		439	88	933	8.1	35	89	81	185	206	54	1.5	-13.89	-96.89	14.24
WB1	2041		332	34	1278	6.7	53	131	91	340	15	10	0.6	-10.17	-70.62	10.75
WB2	1584		304	38	1051	9.9	44	110	68	220	24	16	0.4	-10.25	-70.14	11.90
WB3	3922		713	118	2649	26.1	137	277	313	671	37	17	0.5	-9.54	-63.64	12.66
HB1	2680		482	46	1722	10.5	74	201	110	475	47	13	0.6	-11.14	-75.93	13.19
HB2	2499		490	185	1667	32.5	105	159	150	350	73	19	0.3	-10.69	-73.34	12.17
HB3	3964		719	118	2557	28.2	125	281	223	751	107	13	0.4	-11.25	-77.62	12.35



https://doi.org/10.5194/acp-2020-740

Preprint. Discussion started: 2 September 2020







Table 3. Loads (mg m⁻²) of selected major ions from the 2016 sampling and from earlier studies at Lomonosovfonna summit (LF3), corresponding to the (Virkkunen et al., 2007) Study $\overset{nSS-}{\mathrm{SO}_{4}}^{2+}$ NO3⁻ 27.3 33.5 52.3 27.2 11.4 Ca^{2+} 126.7 \mathbf{Na}^+ Year 2002 2009 concentrations given in Fig. 4.

(Vega et al., 2015), Vega C. (unpublished data)

34.1 93.0 48.1

7.2

262.9 222.2

24.3 46.2

80.1 n.a.

> 2010 2011 2016

n.a. 7.1

This study

Vega C. (unpublished data) Vega C.(unpublished data)

37.1 n.a.





a												
		CI	Br'	SO_4^{2-}	NO ³⁻	Na^+	$\mathbf{NH_4}^+$	$\mathbf{K}^{\scriptscriptstyle +}$	Mg^{2+}	Ca^{2+}	nss- SO4 ²⁻	
	Br'	0.53									r	
	SO_4^{2-}	0.93	09.0									
	NO ^{3⁻}	0.55	su	0.55								
	\mathbf{Na}^+	0.94	0.48	0.92	0.44							
	${ m NH_4}^+$	0.73	0.62	0.68	ns	0.64						
	\mathbf{K}^{+}	0.82	0.61	0.81	su	0.85	0.75					
	${ m Mg}^{2+}$	0.90	0.51	0.88	ns	0.98	0.62	0.82				
	Ca^{2+}	0.86	su	0.83	0.69	0.82	0.61	0.76	0.71			
	nss- SO. ²⁻	su	su	su	su	su	su	su	su	su	su	
	nss-Ca ²⁺	0.76	su	0.75	0.77	0.68	0.56	0.66	0.56	0.96	su	
(q												
		CL	Br	$\mathrm{SO_4}^{2-}$	NO ₃ -	\mathbf{Na}^+	$\mathrm{NH_4}^+$	$\mathbf{K}^{\!\!+}$	${{{{\rm Mg}}^{{\rm 2}{\rm +}}}}$	Ca^{2+}	nss- SO4 ²⁻	
	Br'	su										
	SO_4^{2-}	0.75	0.58									
	NO_3^-	su	-0.48	su								
	\mathbf{Na}^+	0.95	su	0.80	su							
	$\mathbf{NH_4}^+$	su	su	su	us	0.47						
	\mathbf{K}^{+}	0.83	0.46	0.73	su	0.88	0.62					
	${ m Mg}^{2+}$	0.92	su	0.78	su	0.98	0.47	0.86				
	Ca^{2+}	0.85	su	0.64	0.44	0.76	su	0.62	0.70			
	nss-SO ₄ ²⁻	ns	su	su	su	su	su	su	su	ns	ns	
	nss-Ca ²⁺	0.67	ns	0.45	0.56	0.54	su	su	0.47	0.91	ns	