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Seasonal and Spatial Differences in Metal and Metalloid Concentrations in the Snow Cover of Hansbreen, Svalbard

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Metals and metalloids in snow on glaciers, depending on the season of deposition, may come from various sources: local rock dust (erosion of the geological substratum), marine aerosol, local human activity (e.g., impurities in combusted fuel and waste incineration), and long-range atmospheric transport. Hansbreen, a glacier located close to the Polish Polar Station in southern Svalbard, is a perfect site to study metals and metalloids: it has a complex geological substratum, has a year-round presence of a small group of people, and is near the coast. We analyzed a snapshot of metal and metalloid concentrations in snow samples from shallow cores corresponding to autumn, winter, and spring deposition on Hansbreen. Eighteen cores of snow were collected across the glacier, revealing the influence of potential local sources of metals and metalloids. In these samples, we predominantly found Na, Mg, and K, followed by Zn, Ca, Al, and Fe. Heavy metals, such as Bi or Hg, were also detected. Cluster analysis of the determined elemental concentrations divided them into three distinct groups: Group 1: Ag, As, Bi, Cd, Hg, Mo, Sb, Se, and Zn—the most diverse cluster, representing mostly long-range transported volatile elements, with possible extra local geological sources; Group 2: Al, Fe, Cu, and Mn—elements with crustal sources; and Group 3: Na, Ca, Mg, K, and Sr—with the main source in sea spray aerosol. The latter interpretation was confirmed by the calculation of sea salt contribution based on the composition of mean seawater and the positive significant correlation between their concentrations and the electrical conductivity of snow samples. In the study site, snow was up to six times more efficient in bringing metal pollution into terrestrial environment, when compared to rain.

Keywords: Svalbard, Arctic, spatial distribution, snow, heavy metals, trace elements

INTRODUCTION

Metal and metalloid impurities in the Arctic snow may come from both local and distant sources, and only some are supplied by human activities (Kozak et al., 2015). Pollutants can be delivered to Svalbard along fast and slow transport routes, and the cold climate favors accumulation of some contaminants (Ruman et al., 2012). Metals and metalloids can occur from background to excessive levels in the Arctic environment and cause harmful effects in people and animals at the latter

(AMAP, 2005). Arctic snow captures atmospheric dust efficiently, through dry and wet deposition, and thus forms an archive of the seasonal contamination of the Arctic atmosphere. It transfers the pollutants to glacier surfaces, where they may be incorporated into ice (Lehmann-Konera et al., 2017) and cryoconite matter (Łokas et al., 2016). Snow upon glaciers in Svalbard has only rarely been sampled for metal and metalloid concentrations (beyond the major ion chemistry, as performed by, e.g., Virkkunen et al., 2007; Nawrot et al., 2016) and when it was sampled, the focus was either on one element, usually mercury (Ferrari et al., 2008; Larose et al., 2010), or on one location (Spolaor et al., 2020a). There has also been a study conducted on firn cores across one Svalbard glacier (Singh et al., 2015). Further studies report on the elemental composition of ice samples (Yevseyev and Korzun, 1985; Simoes and Zagorodnov, 2001; Drbal et al., 1992; Lehmann et al., 2016).

The spatial distribution of elemental deposition upon glacier surfaces may be modified by the influence of local sources of metals and metalloids, snow redeposition patterns (e.g., Grabiec et al., 2011), and other postdepositional processes (Larose et al., 2010; Avak et al., 2019). Here, we focus on the spatial distribution of elemental impurities in the snow on one glacier in southern Svalbard, in light with these processes. The site is located in the vicinity of the Polish Polar Station, a well-monitored area which may be considered a natural science laboratory for complex system observations. The area is subject to intensive glaciological research (Błaszczuk et al., 2019), especially Hansbreen (Kosiba, 1963; Pälli et al., 2003; Grabiec et al., 2006; Oerlemans et al., 2011; Petlicki et al., 2015; Laska et al., 2017; Decaux et al., 2019), which forms a perfect basis for the understanding of biogeochemical processes in glacial environments. This can be also enhanced through comparisons with metal and metalloid distribution, as was investigated in various environmental components of the area, such as surface waters (e.g., Kosek et al., 2019), plant tissue (e.g., Wojtuń et al., 2018), or fjord sediments (Frankowski and Ziola-Frankowska, 2014; Zaborska et al., 2017). In the context of glaciers, cryoconite matter has been subject to metal content studies (Łokas et al., 2016), as was the aluminum export from the nearby Werenskiöldbreen (Stachnik et al., 2019). Since the deposition of chemical elements may change seasonally (as was observed, e.g., for Ni and Pb by Berg et al. (2004)), additional temporal information is added in this study through the subdivision of the collected snow cores into layers. These correspond to a snapshot of autumn, winter, and spring deposition of metals and metalloids in the accumulation season of 2017/2018.

METHODS

Field Site

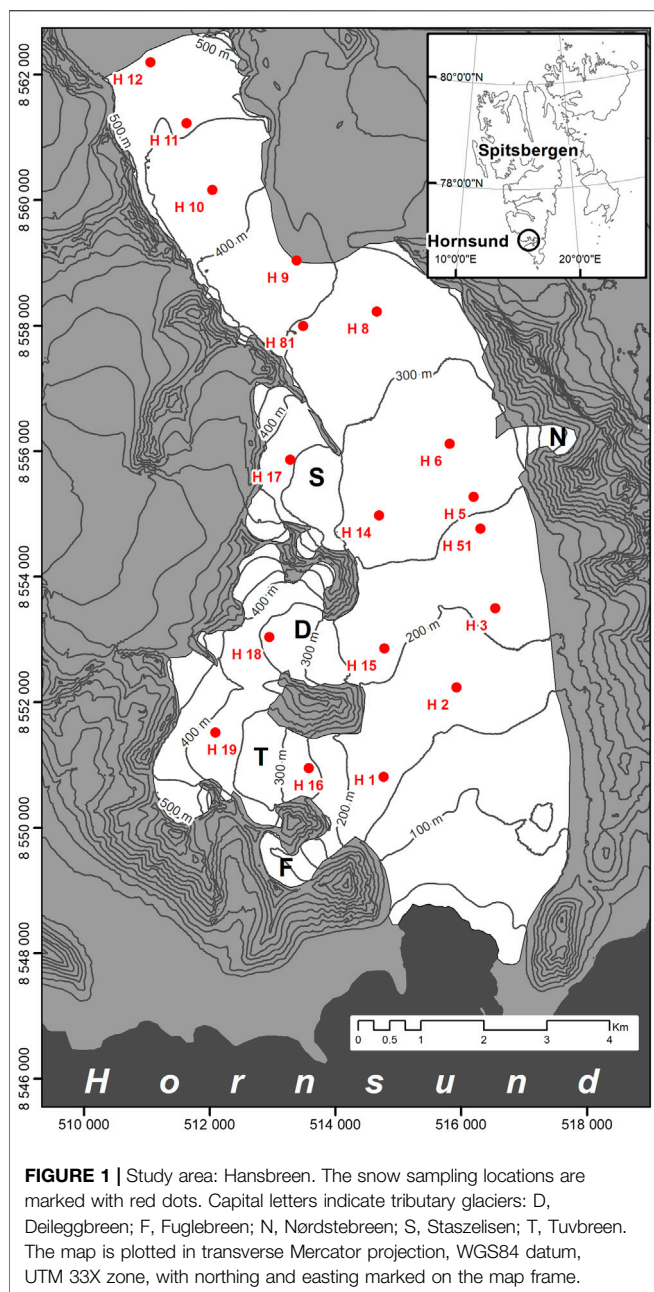
Hansbreen is a medium-sized tidewater glacier (56 km²) located in SW Spitsbergen (Wedel Jarlsberg Land). It is approximately 16 km long and 2.5 km wide on average; it terminates into Hansbukta (Hornsund). Bordered by mountains, it is nevertheless linked to other glaciers (Paierlbreen,

Vrangpeisbreen, and Werenskiöldbreen) (Szafraniec, 2002; Grabiec et al., 2011). Four tributary glaciers (Staszelisén, Deileggbreen, Tuvbreen, and Fuglebreen) are located in its western bank and one small tributary glacier in its eastern bank (**Figure 1**). The glacier's elevation range is ca. 550 m (Grabiec et al., 2012).

Every year on Hansbreen, new firn is built from the remaining snow cover (Błaszczuk et al., 2019; Uszczyk et al., 2019), yet the entire glacier records a negative mass balance due to the losses from ice melt and calving. The maximum depth of the snow cover at the end of accumulation season (April/May) occurs in the highest parts of the glacier (upglacier from H10, **Figure 1**). During the last 8 years, it reached 5.99 m in the accumulation season of 2010/2011. At the same point in the season, the minimum snow cover depth of 0.66 m was noted in 2012/2013 in the lower parts of Hansbreen (downglacier from H2, **Figure 1**). On average, the end-of-accumulation-season snow cover depth was 2.58, 2.01, and 2.22 m (in the 2010/2011, 2012/2013, and 2013/2014, respectively) (Grabiec, 2017). In general, the distribution of snow cover is linked to weather conditions (solid precipitation and temperature). Therefore, the altitude of the glacier determines the snow cover pattern and the snow cover thickness is modified further by the wind. As indicated by Grabiec et al. (2006), the eastern part of the glacier, which has relatively low accumulation, is the place where strong winds occur. Contrastingly, the west side (including tributary glaciers) is the typical place for the higher accumulation of snow cover.

The snow density on Hansbreen depends on snow depth (Uszczyk et al., 2019) and weather conditions (Grabiec et al., 2011; Łupikasza et al., 2019). The highest snowpack density occurred in the higher parts of the glacier, while the low density was nearer its front. A significant factor influencing the snow cover structure and its density is rain-on-snow events (Łupikasza et al., 2019). These events (more frequent than winter thaws) increase the density of snowpack through the formation of hard ice layers and may also leave a chemical footprint (Spolaor et al., 2020b). According to observations in 2010 and 2014 (Laska et al., 2016, 2017; Uszczyk et al., 2019), the snow cover density reached on average 398 kg/m³ at the end of accumulation season and 528 kg/m³ in the ablation season.

Hansbreen terminus lies approximately 3 km from the Polish Polar Station Hornsund, the only human settlement within a radius of 100 km (approximately 10 permanent staff live there). The biggest centre of human activity in Svalbard, Longyearbyen, is located about 140 km north from the study site. Its pollution sources include an airport, a functioning coal mine, local coal-fired power plant, a landfill and untreated sewage outflow (Granberg et al., 2017), a harbor, and local road and snowmobile traffic (e.g., Reimann et al., 2009). Barentsburg, another important settlement in Svalbard, lies over 120 km north from Hansbreen, harboring an active coal mine, a heliport, and a dumpsite where garbage has been burnt repeatedly (Granberg et al., 2017). The local human activity in Hornsund is from the small year-round team and up to 42 people during the peak research season (parts of the summer). It causes the following contamination sources: two arrivals of a supply



ship, a diesel power plant, waste incineration, and sewage processing; ship traffic also exists in the nearby Hornsund fjord. In the spring, there is occasional local snowmobile traffic for research purposes.

The glacier is surrounded by diverse geological formations, with ore-bearing veins, which may be a source of metals and metalloids such as Al, As, Bi, Ca, Cd, Co, Cu, Fe, Mg, Mn, Ni, Pb, S, and Zn (Birkenmajer, 1990; Kieres and Piestrzyński, 1992; Czerny et al., 1993). In the wider area (within 15 km radius), there exist geological sources of Al, B, Ba, Be, Ca, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Na, Nb, Pb, Rb, Sn, Sr, Ta, Th, Ti, U, V, Zn, Zr, and rare-earth elements (cf. Koziol et al., 2020; Spolaor et al., 2020a).

Sampling

Snow samples were collected on 22nd and 25th April 2018. The air temperature during those field trips was approximately -5 and -10°C , respectively; on both days, there was a moderate wind speed of 5 m/s and little-to-no direct solar radiation. A snow core, with 9 cm diameter, was hand-drilled at each point shown on the map in **Figure 1**. To avoid external contamination entering the snow samples, an outer layer of the collected core was scraped with a precleaned polyethylene scraper. Only selected layers from the core were sampled, representing the bottom, middle, and top of the annual snowpack, which most likely belonged to the seasons autumn 2017, winter 2017/2018, and spring 2018, respectively. In particular, the autumn samples were characterized by an increased density (as compared to the rest of the snow core). The sampled layers spanned between 9 and 32 cm, averaging 17 cm (± 4.3 , 1 SD), while their density ranged from 0.287 to 0.655 g cm^{-3} (mean: $0.460 \pm 0.0874\text{ g cm}^{-3}$). Each sampled layer differed from its neighboring layers in terms of hardness and/or grain size. The total thickness of the snow cover has been measured at each sampling site with a graduated avalanche probe, averaging 202 cm (± 51.7 , 1 SD; full range: 115–337 cm).

Laboratory Analysis

We analyzed potassium, calcium, magnesium, and iron, with inductively coupled plasma optical emission spectrometry (ICP-OES 9820, Shimadzu, Japan). Twenty-one other elements (Ag, Al, As, Ba, Bi, Cd, Co, Cr, Cu, Hg, Li, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, V, and Zn) were analyzed using inductively coupled plasma mass spectrometry (ICP-MS 2030, Shimadzu, Japan). Before analysis, the samples were acidified with high-purity nitric acid and trace metal basis (Sigma-Aldrich). Analyses were run in triplicate (with a mean CV 3.82% and 6.43% for ICP-OES and ICP-MS measurements, respectively). The specific measurement conditions and parameters are listed in **Supplementary Table S1** (Supplementary Information). All measurements were quality-assured. The ICP-MS was calibrated with the ICP IV multielement standard (Merck) and the single-element standards of As, Sb, Se, Mo, and V (Sigma-Aldrich). Solutions of Sc, Rh, Tb, and Ge in suprapure 1% HNO_3 (Merck) were applied as internal standards. Samples were diluted (if necessary) using deionized water (from Milli-Q Direct 8 Water Purification System, Merck Millipore). The ICP-OES was calibrated with single-element standards (Sigma-Aldrich) of 1000 mg L^{-1} . Analytical accuracy was verified with two certified reference materials (CRMs): Trace Metals ICP-Sample 1 and Trace Metals ICP-Sample 2 (Sigma-Aldrich). CRM recovery ranged from 96% to 104%. Further analytical parameters, including the detection and quantification limits of the method, are listed in **Supplementary Table S2** (Supplementary Information).

Total organic carbon (TOC) was determined through catalytic oxidation with oxygen at 680°C , with a nondispersive infrared spectroscopy detector (Analyser TOC-VCSH/CSN, Shimadzu). The pH and electrical conductivity were measured with a microcomputer pH meter and conductivity meter (inoLab® Multi 9310 IDS pH), fitted with a Tetra-Con® 925 conductivity sensor and a SenTix®940 electrodes. The

analytical qualitative parameters of the basic physicochemical characteristics are given in **Supplementary Table S3** (Supplementary Information). Metal and metalloid concentrations measured have been corrected by the subtraction of a mean blank value, calculated from five procedural blanks. In the rest of the assays, the blank correction was not required, as background contamination was negligibly low.

Statistical Procedures

Before statistical analyses, results below the limit of detection were assigned 1/3 of its value (to approximate their probable level according to the data distribution curve, approximated best as log-normal for most of the studied variables). All statistical analyses were performed using Statistica, version 13.3 (TIBCO). The first tool used to explore our data was cluster analysis applied to variables. The cluster analysis procedure links elements with concentrations of the most similar variability. In brief, concentrations of elements are standardized (transformed to have a mean of 0 and standard deviation of 1), which means that the concentrations of predominant and minor chemical components of the snow samples can be safely compared. Then, they are plotted upon a dendrogram, and the closer they are on the graph, the more similar is their distribution around their mean. Admittedly, the mean and standard deviation are parameters typical for normally distributed datasets, yet as an exploratory method, cluster analysis can also be used for non-normal data distributions. For the clustering, we used Ward's method, with squared Euclidean distance. The correlations mentioned further in the text were calculated using two nonparametric indices, Spearman rank ρ , and Kendall τ , due to the non-normal distribution of data.

RESULTS AND DISCUSSION

Cluster analysis results (**Figure 2**) show, at a 33% relative distance level (a typical cutoff point for the most similar items), there are three distinct groups of metals and metalloids: cluster 1: Ag, Bi, Cd, Sb, As, Hg, Zn, Se, and Mo; cluster 2: Al, Cu, Fe, and Mn; cluster 3: Ca, K, Mg, Sr, and Na. Since the snow in the area has been shown to contain a relatively high proportion of sea spray aerosols (Nawrot et al., 2016), cluster 3 is likely connected to this source. Cluster 2 is likely representing local geological substratum variability, with the local metamorphic rocks containing ore-bearing veins with Cu and Fe, while Al and Mn are also generally abundant elements of the Earth's crust (Birkenmajer, 1990; Kieres and Piestrzyński, 1992; Czerny et al., 1993). Cluster 1 is the most diverse, with elements at very low concentrations, some of which are typically transported to Svalbard from remote anthropogenic sources (e.g., Hg and Cd; Carlsson et al., 2016). Furthermore, the elements in this cluster have volatile forms, which are easily transported over long distances (especially Hg, Zn, As, Cd, Sb, and Se, and likely also Ag, Bi, and Mo; Steinnes and Friedland, 2006). However, in the Hansbreen surroundings, both Hg and Cd, as well as Ag, As, Bi, Sb, and Zn, all occur in ore-bearing veins on the western side of Hansbreen (Kieres and Piestrzyński, 1992),

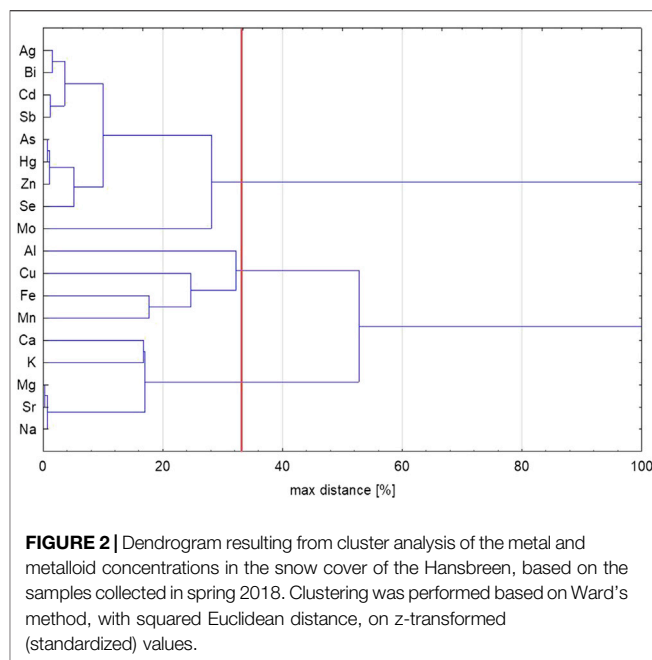


FIGURE 2 | Dendrogram resulting from cluster analysis of the metal and metalloid concentrations in the snow cover of the Hansbreen, based on the samples collected in spring 2018. Clustering was performed based on Ward's method, with squared Euclidean distance, on z-transformed (standardized) values.

either as their minerals or as admixtures (Cd mainly in sphalerite, Ag in galena, Hg in sphalerite, pyrite, and pyrrhotite). Interestingly, Se occurred as an admixture in rock samples from ore-bearing veins (especially of pyrite, pyrrhotite, and galena), yet at a much lower content level (at least 10 times less than the other elements in the cluster). Furthermore, there was no significant mineral source of Mo found in those rocks, despite this element being included in the geological composition study (Kieres and Piestrzyński, 1992).

The spatial and temporal distribution of elements from each cluster is exemplified by one of the cluster members in **Figure 3**. Additional information on the seasonal distribution of elemental concentrations and on elemental fluxes calculated in this study is also given in **Supplementary Tables S4 and S5**, respectively (Supplementary Information). The sea spray cluster 3 was characterized by generally lower concentrations of its elements in the winter season layers (**Figure 3A**), while the highest concentrations of these elements were noted in the spring layers nearest to seawater (Burgerbukta to the east). The concentrations of elements from cluster 3 decreased also up the glacier, which could reflect a decreasing supply of sea spray from the Hornsund fjord. The rock dust in cluster 2 showed a more even distribution of concentrations across the glacier (**Figure 3B**). Occasionally, elevated concentrations of its elements could be found, especially in the autumn layer. Such concentrations could be interpreted as an effect of rock dust abundance in the period when snow cover only starts forming and does not cover fully the mountain slopes or the moraines. The volatile element cluster 1 (**Figure 3C**) was patchily distributed, with higher concentrations on the western side of the glacier, where the snow cover was accumulated by wind redeposition (Grabiec et al., 2006), and at higher elevations, perhaps due to the

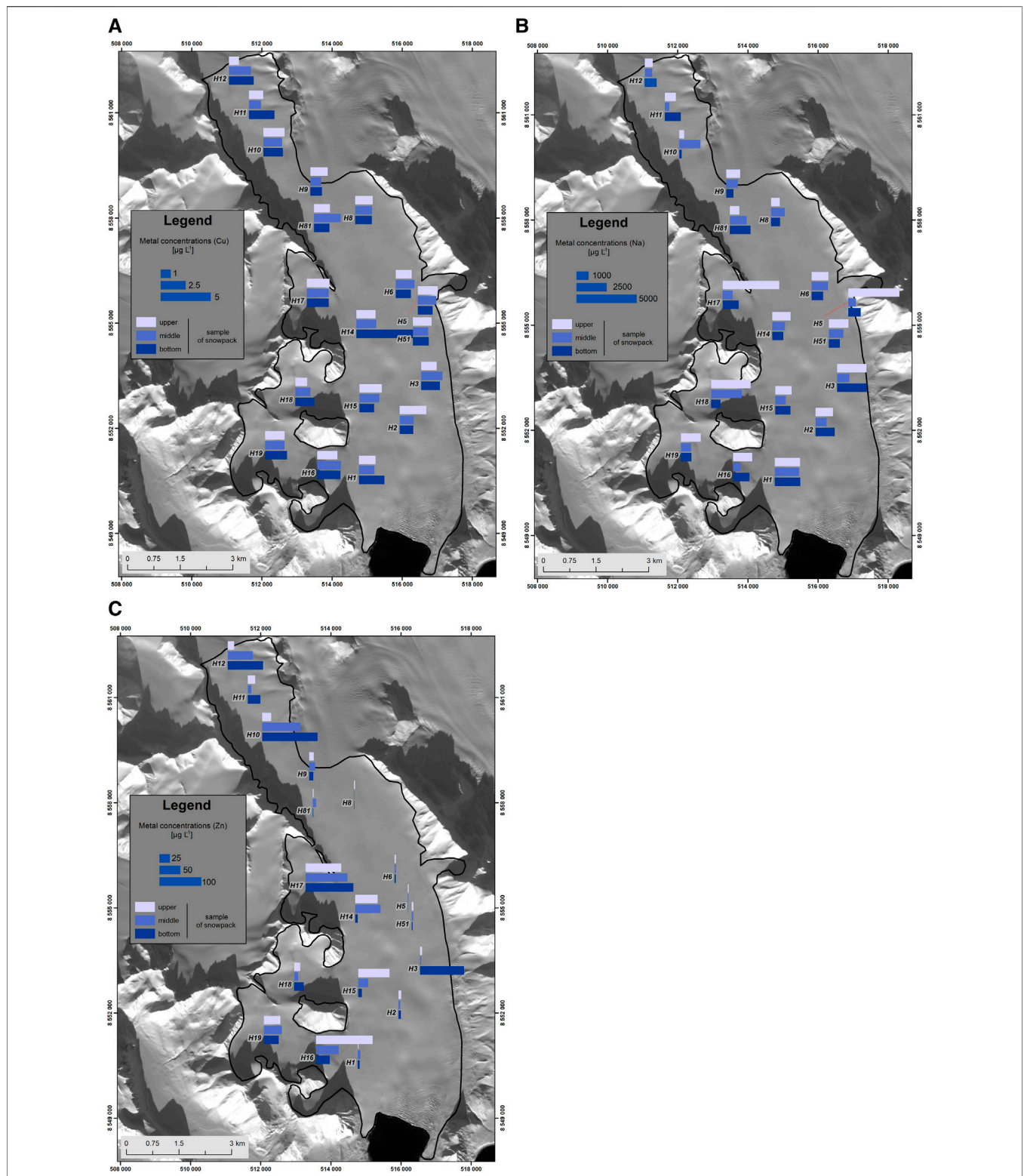


FIGURE 3 | Spatial and interlayer distribution of selected metal concentrations [$\mu\text{g L}^{-1}$] in the snow cover of Hansbreen in the accumulation season of 2017/2018. Each figure concerns a member of a different variable cluster in **Figure 2**: **(A)** Na, **(B)** Cu, and **(C)** Zn. All maps are plotted in the WGS84 datum, in transverse Mercator projection, UTM 33X zone, with northing and easting marked on the map frame.

TABLE 1 | Sea salt contribution (ssC) to the elemental composition of snow on Hansbreen, calculated from the proportional concentration of each element to sodium.

ssC [%]	Q ₂	Q ₁	Q ₃	min	max
Ag	0.03	0.01	0.2	0	2.5
Al	0	0	0	0	0.01
As	0.11	0.04	0.23	0	1.04
Bi	0	0	0	0	0
Ca	308	236	395	61.5	763
Cd	0.02	0.01	0.03	0	0.07
Cu	0.01	0	0.01	0	0.02
Fe	0.01	0.01	0.01	0	0.03
Hg	0.04	0.02	0.06	0	7.1
K	26	18.1	39.7	6.2	58.7
Mg	61.3	57.6	66.4	46.3	103
Mn	0	0	0.01	0	0.02
Mo	0.28	0.16	0.78	0.03	22.5
Sb	0.01	0.01	0.02	0	0.11
Se	0.01	0.01	0.03	0	0.07
Sr	39.1	32	44.1	12.1	58.1
Zn	0.01	0	0.02	0	0.21

The data in the table describe the distribution of sea salt contribution across the whole glacier and seasons (vertically distributed samples within the snow core, i.e., $n = 54$ snow samples for each element). Q_{1-3} are quartiles, i.e., $Q_2 = \text{median}$; min and max show the full range of sea salt contribution calculation results. Values below the limit of detection were excluded from ssC calculations. Fractions $>100\%$ signify depletion in a certain element against the typical composition of seawater.

exposure to long-distance-transported air pollution. However, this side of the glacier is also closer to the elemental sources in rock dust, so their concentrations may only be elevated very near to such areas (due to the generally lower concentrations of these elements in the said rocks and their irregular spatial distribution as ore-bearing veins).

To further explore the possible sources of various elements in the snowpack, we calculated correlation coefficients between their concentrations and the pH, electrical conductivity, and total organic carbon (TOC) concentration in the collected samples. Both Spearman ρ and Kendall τ showed the same pairs of variables to correlate significantly at the p level <0.05 (and only the correlations with electrical conductivity were significant at $p < 0.01$). Electrical conductivity correlated positively and strongly with the concentrations of Ca, K, Mg, Na, and Sr, grouping again the sea salt-related elements in one cluster. Also, the concentration of Fe correlated negatively with pH of the samples, likely indicating the origin of Fe from sulphide minerals, which oxidate producing SO_4^{2-} ions which acidify the snow (Moses et al., 1987). If we assume that TOC concentration is a sign of likely pollution from snowmobile tracks, then this factor appears as unimportant in shaping the metal and metalloid composition of snow upon the glacier: the highest positive Spearman ρ between any metal concentration and TOC equaled 0.096 for Mo.

Multiple elements seem to be supplied from sea spray on this glacier, which merits the calculation of sea salt contribution (ssC) into the elemental concentrations in the snow cover. This has been performed assuming that all Na

was derived from sea salt and that sea spray has the same salt composition as average seawater (Turekian, 1968) (Table 1). In this procedure, all data records with values below the detection limit were omitted. The occurrence of sea salt contributions exceeding 100% indicates either that there were extra sources of Na besides sea salt or that Na may be enriched in sea spray, as compared to mean seawater composition, or else that these elements' concentrations were depleted postdepositionally. The elements with the highest sea salt contributions were Ca, Mg, Sr, and K (median ssCs $>25\%$), which confirms the origin of the first variable cluster in Figure 2 from sea spray. In isolated cases (maximum ssCs $>5\%$), sea spray seemed to be a significant source of also Mo and Hg.

Crustal fractions of elements were also estimated (Supplementary Table S6, Supplementary Information), assuming all Al was of crustal origin, and using geochemical background composition after the Geochemical Atlas of Svalbard (Ottesen, 2015). Whenever the Geochemical Atlas supplied two different values derived from two different analytical methods, we used the concentrations determined by the analytical method most similar to the one used here. The calculations highlighted the crustal origin of Fe in the collected samples; in certain samples, Mg and As could also be supplied from the general geochemical crustal background (max crustal fractions $>5\%$). However, the very low crustal fractions of other elements calculated in this way do not exclude their origin from local ore-bearing veins. This is because the locally occurring veins would not influence the Svalbard-wide geochemical background concentrations, which were the basis for the calculations. The low crustal fractions of calcium support the interpretation that Ca from rock dust was negligible in the collected snow samples.

Since the deposition of impurities in snow is generally considered very efficient (Błaś et al., 2010), we compare the obtained median concentrations in the snow with the median concentrations measured in the rain at the nearby Polish Polar Station Hornsund (Kozak et al., 2015). Available for comparison were the concentrations of Al, As, Cu, Mn, Se, Sr, and Zn. All these elements were found at higher median concentrations in the snow on Hansbreen, exceeding the concentrations in rain from 1.02 to 5.88 times (for Zn and Al, respectively). The maxima of metal and metalloid concentrations in summer precipitation, published by Koziol et al. (2020), were also mostly lower than maximum concentrations in the snow studied here (for Al, Cu, Sb, and Se). Mn, Sr, and Zn showed the opposite proportion, but the difference between the two maxima was very small for Zn. Overall, the snow cover seems a more important medium than rain for the transfer of metal and metalloid impurities from the atmosphere to the terrestrial system on this glacier. The snow cover also holds such impurities for longer and may release them in different temporal patterns, depending on their abundance in the snowpack (Avak et al., 2019). Thus, snow appears to be a crucial component for the supply of metals and metalloids to

the surface waters of the area, which warrants its further investigations to understand the element mobility and long-term concentration changes.

CONCLUSION

We investigated the concentrations of metal and metalloid impurities in the annual snowpack on a glacier in southern Svalbard, focusing on their spatial variability. We attempted to determine their main sources by the application of statistical analysis and a comparison to seawater and crustal composition. As a result, we found that Na, Mg, Ca, K, and Sr had a significant source in the sea spray aerosol. Al, Fe, Cu, and Mn could be attributed to crustal sources. Multiple elements likely come from long-range transport, with potential secondary sources in the local geological substratum (ore-bearing veins): Ag, As, Bi, Cd, Hg, Sb, Se, and Zn; however, Mo is likely to come from atmospheric transport alone. In comparison to summer rains, snowfall showed higher median concentrations of metals and metalloids (between one and six times higher). The studies on metal and metalloid admixtures in the Arctic snow are important means of measuring the supply of impurities to surface waters and downstream ecosystems, and their long-term changes should be studied in the future.

DATA AVAILABILITY STATEMENT

The datasets generated for this study can be found in the Open Science Framework repository [<https://osf.io/yypskz>] and in Supplementary Information.

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AUTHOR CONTRIBUTIONS

KK and ŻP developed the concept of the paper. KK wrote the main body of the manuscript and prepared the sampling kit. AU collected the samples, prepared maps, and provided field site description. FP and MF analysed the samples (for basic parameters and metal/metalloid concentrations, respectively) and wrote the description of the analytical methods. All authors participated in the final discussion of the results and checked the final version of the manuscript.

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SUPPLEMENTARY MATERIAL

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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