

RESEARCH ARTICLE OPEN ACCESS

# Hydrochemical Characteristics of Four Retreating Glacier Forefields Off the Coast of Admiralty Bay (King George Island, Maritime Antarctic): Diverse Sources of Metals and Metalloids

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**Keywords:** Antarctic | anthropogenic influence | climate change | cryosphere | environmental fate | re-emission

## ABSTRACT

This study examines the impact of geological, marine and anthropogenic sources on metal and metalloid concentrations in the forefields of four glaciers (Ecology, Sphinx, Tower and Windy) on King George Island, Antarctic. Water samples were collected at the beginning and end of the hydrological season (austral summer, December 2021 to February 2022), while snow samples were taken from the remaining snow cover at the start of the season. The study area, underlain by the Llano Point and Zamek formations—comprised mainly of basalt and andesite—reveals significant geological contributions of elements such as Fe, Al and Mg due to active weathering processes amplified by glacial retreat. The research highlights how meteorological condition change-induced temperature and precipitation increases accelerate sediment erosion and weathering, mobilising metals and metalloids from glaciers and snowmelt. Significant concentrations of Cr, V and Ba in collected samples align with the local geological substratum. Statistical analyses (Kruskal-Wallis ANOVA) identified notable differences in Mo and Ba levels between glacier forefields, consistent with geological influences, as these elements occur in varying concentrations within the local basaltic and andesitic bedrock. Seasonal variations were also observed, particularly for Mg and K ions, indicating that meltwater dynamics influence element mobilisation throughout the season. Furthermore, Tower Glacier's eastward exposure explains the higher concentrations of Zn and Cd, suggesting atmospheric deposition as a contributing factor. This study underscores the complex interactions between geological, climatic and atmospheric processes, illustrating how geogenic sources and cryosphere degradation influence the chemical landscape of Antarctic glacier forefields.

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## 1 | Introduction

Antarctic is usually included among the few pristine environments on Earth, yet it has been proven that anthropogenic pollution can reach this polar region through atmospheric circulation, dry and wet deposition of pollutants and transport in oceanic currents (Szopińska et al. 2019; Webb et al. 2020). Chemical pollution reaches the Antarctic coast from global sources via long-range atmospheric and oceanic transport (LRAT and LROT, respectively) (Chambers et al. 2018; Souza et al. 2020). During the environmental studies of the Antarctic area, it was also found that local sources, such as shipping, tourism and the operation of polar stations, also contribute to the delivery of pollutants to the environment (Martins et al. 2021; Montone et al. 2010; Szopińska et al. 2016). Such diversity of sources may confound interpretations of pollution levels, as elevated concentrations of metals and metalloids can originate from natural inputs (e.g., mineral dust from local bedrock or sea spray) rather than anthropogenic contamination. This overlap makes it challenging to clearly distinguish between geogenic background levels and human-derived inputs, especially in regions like the Antarctic, where even minor increases in element concentrations are often scrutinised as potential indicators of pollution. Accurate source attribution therefore requires a careful geochemical and statistical assessment, including quantification of natural contributions.

Throughout the globe, intense climate change has been observed over the past decades (Gabov et al. 2017; Lehmann-Konera et al. 2018; Rabassa 2009; Turner et al. 2014). These changes also affect the polar regions, including the Antarctic (Bockheim et al. 2013; Kosek et al. 2018; Potapowicz et al. 2019). As global warming accelerates glacier melt and exposes land surfaces, scientists are increasingly concerned about the issue of chemical pollution remobilised from cryospheric sources in the Antarctic (Bargagli 2008; Grannas et al. 2013). Recent studies further highlight the role of glacial meltwaters as a key vector of trace metal transport into coastal ecosystems, especially in relation to Fe, Mn and Cu dynamics (Forsch et al. 2021; Jones et al. 2025; Krause et al. 2021). Meltwater from glaciers may interact with minerals in the bedrock and remobilise chemicals harmful to Antarctic ecosystems and the surrounding marine environment (Goutte et al. 2015; Potapowicz et al. 2019; Stumpf et al. 2012). Another consequence of increased ice melt in Antarctic catchments is an increase in surface runoff, which results in the transfer of larger amounts of mineral and organic matter into freshwater in the Antarctic (Szopińska et al. 2018). Significant changes in fluvial drainage systems, the landscape, and the chemistry of different parts of the environment are observed in this area (Baroni et al. 2005). This is consistent with the periglacial zone being one of the most rapidly changing environments worldwide (López-Martínez et al. 2012; Oliva et al. 2018; Oliva and Ruiz-Fernández 2017; Ravanel et al. 2017). In the vicinity of the western shore of Admiralty Bay (King George Island, Maritime Antarctica), a rapid glacier retreat has been observed that resulted in the creation of a new ice-free zone with a varied morphology (Dziembowski and Bialik 2022; Sziło and Bialik 2018) and the intensification and high diversity of chemical weathering in the area (Szopińska et al. 2018). Climate change and its consequences encountered in this area

also occurred in other parts of the Antarctic region (Oliva and Ruiz-Fernández 2017).

These pollutants may include both natural and anthropogenic substances deposited as a result of global atmospheric processes and ocean currents. Antarctic sediments contain trace elements like mercury, lead and cadmium, which, when migrating to meltwaters, pose a potential threat to the local flora and fauna (Bargagli 2008; Jara-Carrasco et al. 2015). Studies indicate that processes like chemical weathering can accelerate the release of these substances from exposed rocks and sediments, especially in coastal glacier regions where melting is most pronounced (Grannas et al. 2013).

Current research confirms that the cryosphere contains chemical compounds, elements and ions both from recent emissions (indicating seasonal impact of pollution) (Szopińska et al. 2018) and legacy sources (indicating long-term impact) (Fuoco et al. 2012; Kukucka et al. 2010). Among the chemical entities determined in the Antarctic snow and ice, both inorganic and organic pollutants were found, such as heavy metals, including mercury and lead (Pérez-Rodríguez et al. 2019; Szumińska et al. 2021); inorganic ions (Nędzarek et al. 2015); polycyclic aromatic hydrocarbons (PAHs) (Cao et al. 2018; Fuoco et al. 2012; Szumińska et al. 2021; Vecchiato et al. 2015); organochlorine pesticides (Kang et al. 2012; Schiavone et al. 2009); polychlorinated biphenyls (Fuoco et al. 2012; Vecchiato et al. 2015); per- and polyfluoroalkyl substances (Cai et al. 2012); and polybrominated diphenyl ethers (Hale et al. 2008; Vecchiato et al. 2015).

It is important to note that pollutants released from geological sources can include both low-toxicity elements and highly toxic ones that accumulate in living organisms, affecting local food chains (Bargagli 2008; Goutte et al. 2015; Jara-Carrasco et al. 2015). Antarctic ecosystems are particularly sensitive to changes in toxic substance concentrations, as many species in these regions have low adaptability and metabolic processes specifically suited to extreme environmental conditions (Bargagli and Rota 2024; Bhardwaj et al. 2018; Pearce 2017).

Research shows a strong correlation between the intensity of glacier melting and increased chemical remobilisation (Grannas et al. 2013). In regions where melting is most intense, an increase in heavy metal concentrations and geologically derived organic compounds has been observed. For example, studies by Bargagli and Rota (2024) and Pearce (2017) show that glacier melting and the remobilisation of trace elements into coastal marine ecosystems lead to the accumulation of toxic substances in marine organisms. This is a significant threat to the entire ecosystem, as higher trophic level organisms, such as fish and birds, can accumulate these substances in their tissues, impacting the health and biodiversity of the entire ecosystem (Goutte et al. 2015; Jara-Carrasco et al. 2015; Weber and Goerke 2003).

Based on research conducted in the Antarctic area, it was found that the degradation of the cryosphere due to climate change, including glacier retreat (Pętlicki et al. 2017; Pudełko et al. 2018) and intensive weathering processes (Navas et al. 2017; Oliva and Ruiz-Fernández 2017) may cause the release of pollutants

previously stored in ice (Herbert et al. 2006; Szopińska et al. 2016), permafrost (Oliva et al. 2018; Potapowicz et al. 2019; Szopińska et al. 2019) and sediments (Martins et al. 2002; Pongpiachan et al. 2017; Potapowicz, Szumińska, Szopińska, Bialik, et al. 2020; Potapowicz, Szumińska, Szopińska, Czapiewski, et al. 2020; Wang et al. 2011). Nevertheless, gaps remain in the understanding of specific processes of chemical element remobilisation from the Antarctic geological substrate, including glacial river sediments and permafrost. Therefore, the aim of this study, conducted on the western shore of Admiralty Bay on King George Island, is to perform a detailed analysis of the chemical composition of glacial waters in the context of potential remobilisation from sediments, and in particular to identify potential metals and metalloids of geological origin in such waters. Of particular interest in this study are heavy metals and metalloids, such as arsenic, cadmium, chromium, copper, nickel, selenium and zinc, and other potentially toxic metals such as aluminium, barium, manganese, molybdenum and vanadium, which may pose a threat to Antarctic ecosystems. The novelty of this project lies in combining qualitative and quantitative tools to elucidate sources of metals and metalloids in waters of Antarctic glaciated catchments. Unlike previous studies, this project considers seasonal variations in the concentrations of these elements and the influence of local geological formations, the Llano Point and Zamek formations, which enable the identification of specific geological sources of metals in the region.

## 2 | Materials and Methods

### 2.1 | Study Area, Sample Collection and Storage

The research was conducted in the western sector of Admiralty Bay, King George Island, the largest in the South Shetland Archipelago, located ~770 km southeast of Cape Horn and ~160 km north of the northernmost part of the Antarctic Peninsula (Figure 1a,b). The island is mostly covered by several icefields with large outlet glaciers, with a measured average ice thickness of 250 m in the Arctowski Icefield (Figure 1c) (Blindow et al. 2010). The ice-free areas, which constitute only 10% of the island, consist of coastal oases or nunataks (Marsz 2000).

The climate of the area is characterised by a higher mean air temperature compared to other regions of the Antarctic, with positive air temperatures observed from November to March. Climate fluctuations were observed in this area, with significant regional rapid warming recorded until the end of the 20th century (Kejna et al. 2013; Stastna 2010; Turner et al. 2005) and local cooling during the recent years recorded particularly in the summer months (Oliva et al. 2017; Plenzler et al. 2019; Turner et al. 2016). The average multi-annual temperature noted for the period 2013–2017 was  $-1.7^{\circ}\text{C}$ , with the coldest month being August ( $-6.1^{\circ}\text{C}$ ) and the warmest being February ( $1.5^{\circ}\text{C}$ ) (Plenzler et al. 2019). Oceanic influence, typical for the climate of the Maritime Antarctic, results in high humidity (84%) and high precipitation, with an estimated average of 701 mm. Strong katabatic winds that often reach hurricane force occur often in the area (Kejna et al. 2013).

Climatic fluctuations observed since the last century have resulted in significant landscape changes—especially the evident retreat of glaciers in Admiralty Bay. However, the pace of

glacier mass loss varied during that period, with the fastest rate recorded in the last two decades of the 20th century followed by a steady slowdown in glacier retreat rate, which seems to have resulted from a recent temperature decrease (Pętlicki et al. 2017; Pudełko et al. 2018; da Rosa et al. 2020).

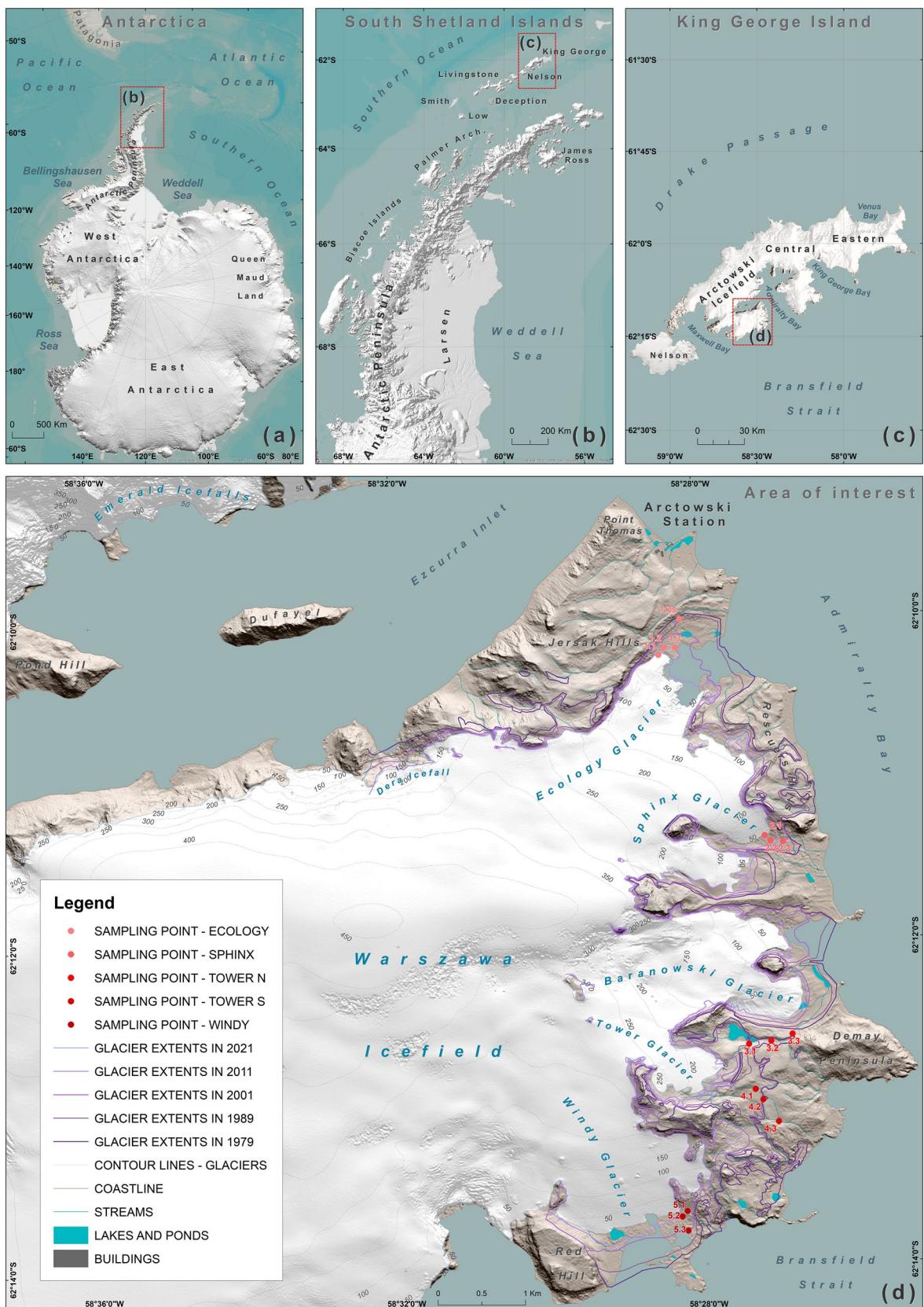
Our sampling design targeted waters originating from four glaciated catchments (Ecology, Sphinx, Tower and Windy; Figure 1d, Table S1) during the melting season. Snow and river water were sampled from ice-free areas in the glacier forefields. Snow sample collection was combined with snow density measurements using snow thickness at five points within a square of  $\sim 2\text{ m}^2$  area and snow cylinder weight ( $d = 0.05\text{ g}$ ) at one of those points. Freshwater samples were collected in the forefields of the four glaciers (Figure 2) at the beginning and end of the austral summer 2021/2022.

Sampling sites were located at various distances from the Polish and Argentinian polar stations in a transect along the coast of the Admiralty Bay. The direct sources of water, as well as metals and metalloids, supply to the fresh- and seawater at the western shore of this bay are rainfall, snowfall (and snow cover melt) and glacier drainage (Gunes and Balci 2022). Therefore, the sampling design matched the research task of showing the contribution of cryosphere degradation by contrasting spring snowmelt and glacier ice melt (the latter bearing the impact on rock weathering due to the longer contact of such waters with mineral grains in sediment) in four non-glaciated catchments. In addition, the locations at different distances from the polar stations made it possible to filter out the direct impact of stations as local sources of pollution.

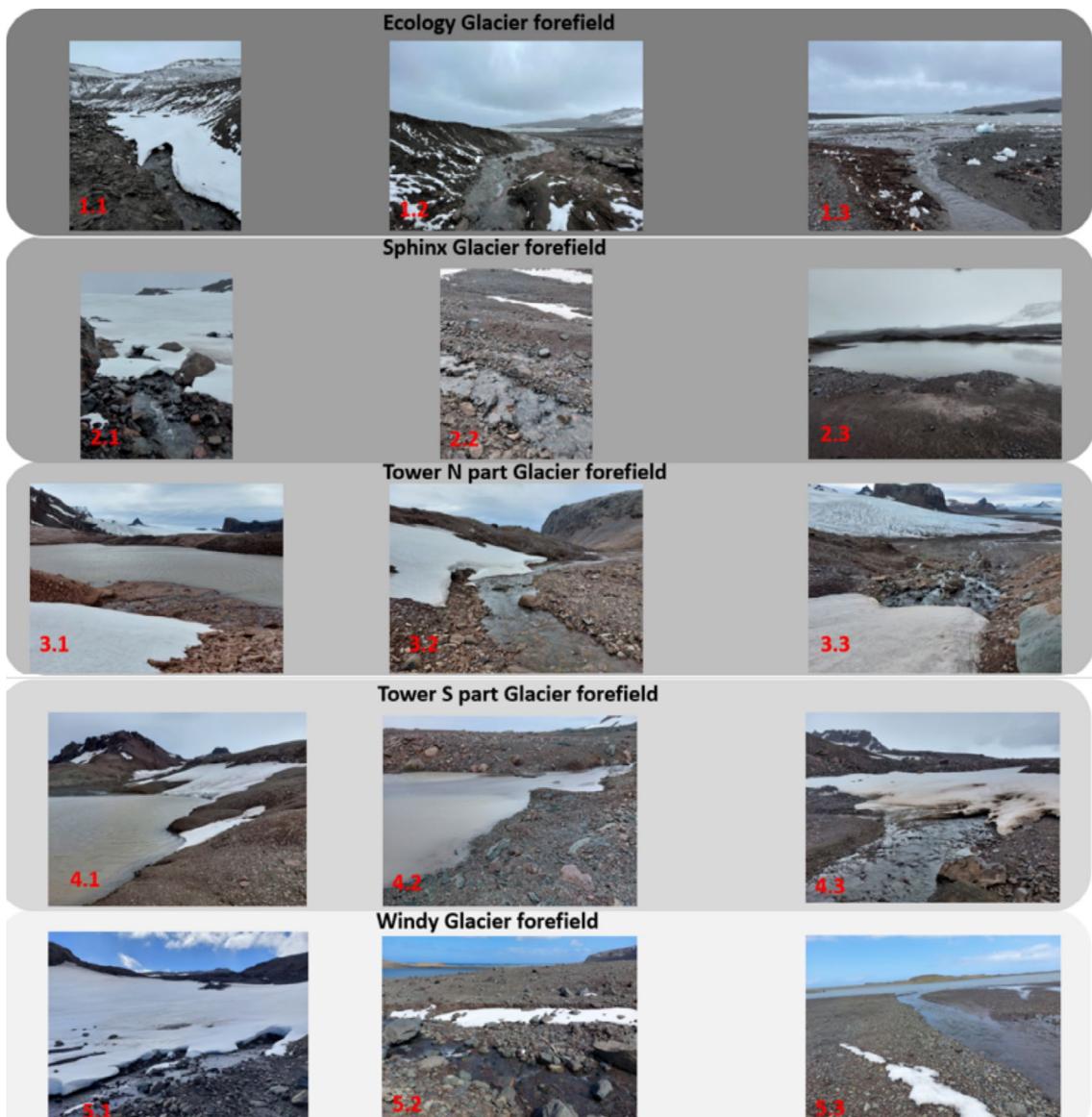
### 2.2 | Sample Preparation and Laboratory Analysis Methods

In order to remove solid particles from the snow, after thawing at  $+4^{\circ}\text{C}$ , the snow samples were vacuum-filtered through Whatman GF/F Glass Microfiber Filters ( $\phi 47\text{ mm}$ ). Temperature and specific electrolytic conductivity ( $\text{SEC}_{25}$ ) were measured with a multi-parameter device CC-105, while pH was measured with a CPC-105 device (both by Elmetron, Poland). Measurements were performed in the field for flowing water and immediately after thawing in the laboratory for snow samples.

Further laboratory analyses were undertaken, following the transport of samples to Poland, in frozen storage. A DIONEX 3000 chromatograph (DIONEX, USA) with a conductometric detector was used for inorganic ions determination. The Dionex IonPac AS22 analytical column separated anions (eluents: 4.5 mM  $\text{Na}_2\text{CO}_3$  and 1.5 mM  $\text{NaHCO}_3$ , flow rate:  $0.3\text{ mL min}^{-1}$ ), and the Dionex IonPac CS16 analytical column separated cations (eluent: 38 mM methanesulphonic acid, flow rate:  $0.36\text{ mL min}^{-1}$ ). TOC was determined in liquid environmental samples using a catalytic combustion method with non-dispersive infrared detection (NDIR) on the TOC-VCSH/CSN Analyser (SHIMADZU, Japan). Ca, Fe, K, Mg, P, S and Si concentrations were determined in water and snow samples by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES 9820 Shimadzu, Japan), while 22 elements: Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, La, Li, Mn, Mo, Na, Ni, Pb, Sb, Se,



**FIGURE 1** | Location of study area and sampling points on the background of (a) the Antarctic Continent (b) the Antarctic Peninsula (c) King George Island and (d) Admiralty Bay and glacier extents between 1979 and 2021 (data taken from Pudełko et al. (2018) for the years 1979–2011, and from Dudek et al. (2025) for the year 2021). [Colour figure can be viewed at [wileyonlinelibrary.com](https://wileyonlinelibrary.com)]



**FIGURE 2** | Sampling points of the studied creeks and forefields of glaciers at the western shore of Admiralty Bay. [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

Sr, V and Zn were determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS 2030 Shimadzu, Japan). Inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) were selected due to their high sensitivity, precision and ability to simultaneously detect multiple elements at trace levels. ICP-OES is based on the measurement of characteristic optical emissions from excited atoms, making it suitable for major and minor elements. ICP-MS, in turn, allows detection of ultra-trace concentrations through mass-to-charge ratio analysis, offering superior detection limits and isotopic resolution. These complementary techniques ensured accurate quantification of both high- and low-abundance elements in environmental water samples. During the analysis, the ICP-MS device worked with the following parameters: collision gas (Ar) flow:  $8.0 \text{ L min}^{-1}$ , auxiliary gas flow:  $0.7 \text{ L min}^{-1}$ ; nebuliser gas flow:  $0.9 \text{ L min}^{-1}$ , collision cell technology (CCT) gas (Helium) flow:  $6.0 \text{ mL min}^{-1}$ , CCT mode + 3 Kinetic Energy Discrimination. For ICP-OES, the parameters were: plasma gas (Ar) flow rate:  $10 \text{ L min}^{-1}$ , auxiliary gas

flow:  $0.6 \text{ L min}^{-1}$ ; nebuliser gas flow:  $0.7 \text{ L min}^{-1}$ , radio frequency power generator:  $1.2 \text{ kW}$ .

### 2.3 | Quality Control

Environmental samples were handled with special care to avoid cross-contamination. Error precision for the ions, all elements, and TOC analyses was 5% according to repeat analyses of mid-range standards, while the detection limits are listed in Table S2. No contaminants were detected above this limit in the analyses of blank deionised water ( $18 \text{ M}\Omega$ ) samples.

Metals and metalloids were determined by ICP-OES and ICP-MS analytical techniques both from Shimadzu—models 9820 and 2030, respectively (Shimadzu, Japan). The analytical accuracy of metal and metalloid determination was checked with certified reference material Trace Metals ICP-Sample 2 (Merck, Germany); CRM recovery ranged from 97% to 103%. Further

QA/QC parameters of the applied methods specific to each analyte are reported in Table S2.

## 2.4 | Statistical Analysis

All correlations and significant differences between subsets of data were explored with non-parametric methods due to the lack of normality in the dataset and for uniformity across the cases for which the log-transformation was not sufficient to fulfil all assumptions of a Pearson correlation or ANOVA. The Kruskal-Wallis ANOVA (K-W ANOVA) is a robust alternative to one-way ANOVA when assumptions of normality and homoscedasticity are not met, allowing us to detect statistically significant differences between two or more sample groups for one variable (Kruskal and Wallis 1952). Principal component analysis (PCA), although not a hypothesis test, is a powerful exploratory technique that reduces data dimensionality and helps identify patterns, gradients and groupings in complex multivariate datasets (Bro and Smilde 2014). Together, these methods facilitated the detection of environmental patterns and underlying factors driving variation in metal and metalloid concentrations. Therefore, Spearman  $\rho$  is reported for correlations, and K-W ANOVA was used for group comparisons. Both were obtained with the use of Statistica v.13 software (TIBCO Software Inc.). Post hoc single comparison  $p$  values were calculated, by default, with the Bonferroni correction.

PCA was performed using R version 3.6.2 (R Core Team 2019) with R Studio, FactoMineR package, with sample type and location as alternating qualitative variables. Quantitative variables were log-transformed (except pH, which is already a logarithm). Only variables with more than  $n/2$  values above the limit of detection (LOD) were included in the PCA. A scree plot showed that a maximum of four principal components (PCs) should be interpreted in this case.

## 3 | Results

### 3.1 | Changes in Meteorological Conditions in the Research Area

Meteorological conditions during the research period were described using data from the meteorological station situated close to the Polish Antarctic Station, including 10-min resolution measurements of air temperature, wind speed at 2 m above ground, and daily precipitation totals, as well as snow cover depth observations. Air temperature and wind speed were measured by an automatic weather station (AWS), and the precipitation total was measured once a day using Hellman's rain gauge. More details regarding the construction and production of individual AWS components are described in a separate article (Plenzler et al. 2025). Additionally, air temperature measurements from AWS Puchalski (located close to AWS Arctowski but at 55 m a.s.l.) and AWS Lions Rump (located at the western shore of King George Bay at 23 m a.s.l., Figure 1) were used. AWA register measurements at 2 m above ground every 10 min; based on those measurements, mean daily and monthly values were calculated.

Based on the data from Puchalski and Lions Rump weather stations, we describe the variability in temperatures due to altitude

and topography at the study sites. In general, mean daily and monthly air temperatures in particular parts of King George Island show similar trends, but their absolute values differ depending on altitude and distance from the coast (Kejna 2008; Plenzler et al. 2019). An important temperature threshold for this research was the freezing point of water. Data from Lions Rump approximate well the meteorological conditions at the forelands of Windy and Tower Glaciers (Figure 1), while data from the Arctowski station approximate best the conditions at Ecology and Sphinx field sites.

Mean monthly air temperature at Arctowski Station was 2.0°C in both December 2021 and January 2022, and it was higher than the 2013–2022 decadal mean for those months (Table 1). December 2021 was the warmest December in the decade 2013–2022. Furthermore, October and November 2021 were also the warmest October and November, respectively, in 2013–2022 (*The Archive of Polish Antarctic Station*). Mean daily air temperature ranged from -0.1°C to 4.6°C at Arctowski (Figure 3), from -0.4°C to 4.7°C at Puchalski and from -0.7°C to 5.5°C at Lions Rump. Mean daily air temperatures at Lions Rump and Puchalski were usually lower than at Arctowski. Mean daily air temperature below 0.0°C occurred only on 31 December at all stations within the study period. 31 December was also the only day when the maximum daily temperature was below 0.0°C (also at all stations).

December 2021 was not only the warmest month during 2013–2022 but also the windiest. Mean monthly wind speed at 2 m above ground at Arctowski Station was 7.1 m/s. Wind speed in January 2022 was slightly below the multiannual mean value (Table 1). Westerly wind predominated at all presented weather stations.

The monthly precipitation total was 35.5 mm in December 2021 and 95.5 mm in January 2022. While the precipitation total for December was similar to the multiannual mean, the January 2022 total greatly exceeded the multiannual mean (Table 1). Also, on 30 November 2021, a high daily sum of 14.2 mm precipitation was observed. The number of days with a sum of precipitation above 0.1 mm was similar to the multiannual value. In the winter of 2021, preceding the fieldwork, the continuous snow cover in the location of the meteorological station at 2 m a.s.l. lasted from the beginning of July to the first decade of September and was 2–28 cm thick. Later, the snow cover formed and disappeared several times, and the last snow cover event appeared during 4–12 October 2021, reaching 13–32 cm snow depth. The majority of precipitation during the investigation period was rainfall. Snowfall was observed several times, but snow cover never formed. Therefore, the sampled snow consisted of remaining patches of snow cover formed last in October.

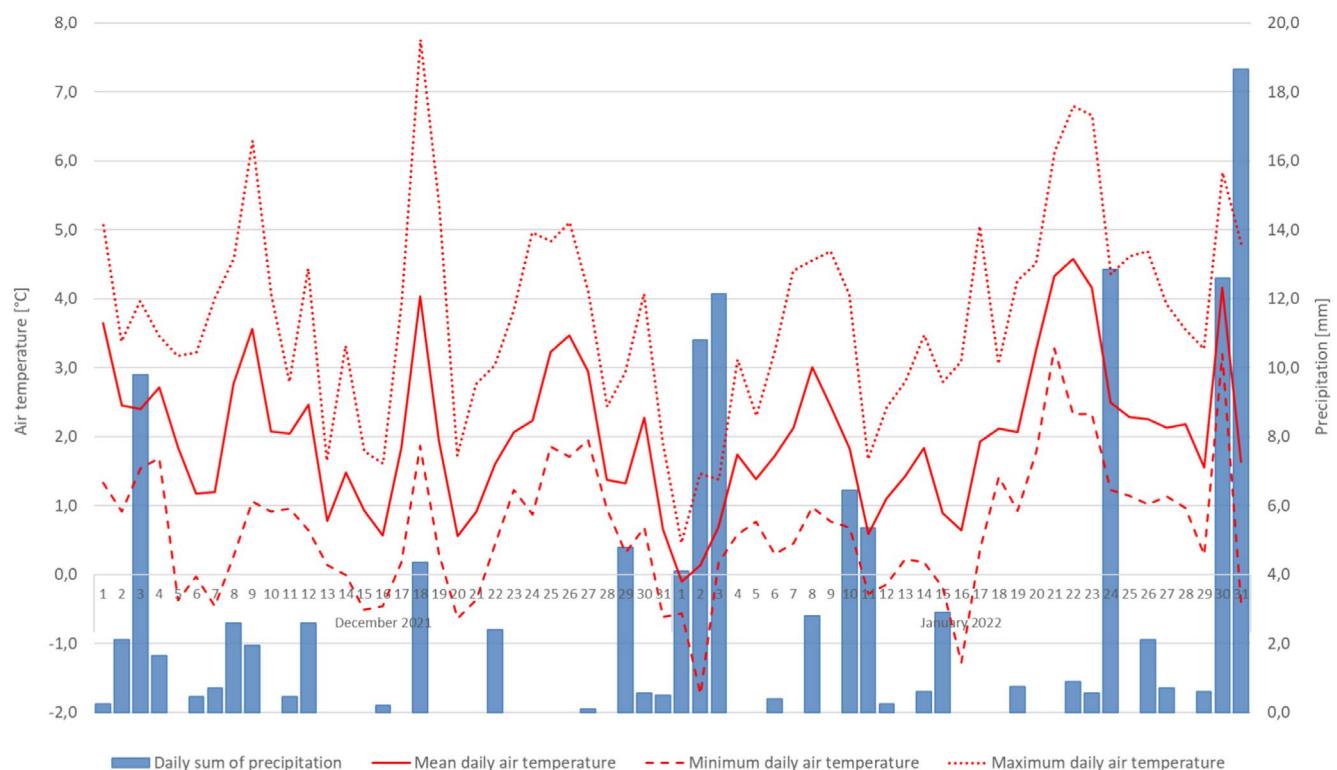
To conclude, in the research period, conditions favourable to freezing of water occurred very rarely; therefore, melt processes predominated throughout the sampling period. Furthermore, the fieldwork period experienced the highest temperatures in the preceding decade and a higher sum of precipitation compared to the previous years. However, neither sampling date was directly preceded by a high precipitation event (cf. Figure 3, Table S1), which reduced the impact of rainwater on stream water composition presented here.

**TABLE 1** | Monthly values of meteorological characteristics in the investigated area during the sampling period (Dec 2021 to Jan 2022) and in the similar period and entire year in the reference period: the preceding decade at Arctowski Station (2013–2022) and a shorter period when measurements are available at the local stations Puchalski and Lions Rump.

	Arctowski 2 m a.s.l. (2013–2022)				Puchalski 55 m a.s.l. (2019–2022)	Lions Rump 23 m a.s.l. (2019–2022)
	Mean monthly air temperature (°C)	Monthly sum of precipitation (mm)	Number of days with daily sum of precipitation > 0.1 mm	Mean monthly wind speed at 2 m a.s.l. (m/s)	Mean monthly air temperature (°C)	Mean monthly air temperature (°C)
Dec 2021	2.0	35.5	17	7.4	1.7	1.7
Jan 2022	2.0	95.5	19	4.1	1.8	1.8
Dec	1.0	36.9 <sup>a</sup>	17 <sup>a</sup>	5.0	1.1	1.3
Jan	1.7	48.7 <sup>b</sup>	20 <sup>b</sup>	4.5	1.8	2.0
Year	-1.2	512.0 <sup>b</sup>	216 <sup>b</sup>	5.7	-1.3	-1.2

<sup>a</sup>Mean for the period 2016–2022.

<sup>b</sup>Mean for the period 2017–2022.



**FIGURE 3** | Daily air temperature and sum of precipitation at Arctowski Station during the research period (Dec 2021 to Jan 2022). [Colour figure can be viewed at [wileyonlinelibrary.com](https://wileyonlinelibrary.com)]

### 3.2 | Physicochemical Parameters, Total Organic Carbon and Inorganic Ion Concentrations as Indicators of Cryosphere Degradation or Other Sources of Metals and Metalloids

The water temperatures in glacial melt streams ranged from 0.8°C to 14°C in both measurement series (in December and in January) (Table 2). The temperature was lowest at the source and increased towards the stream mouth, confirming ice or snow

melt as the dominant water source. Previous research in this area (Potapowicz, Szumińska, Szopińska, Bialik, et al. 2020; Potapowicz, Szumińska, Szopińska, Czapiewski, et al. 2020) and in other periglacial areas (Liu et al. 2005; Marszałek and Górnjak 2017; Yang et al. 2014) showed a similar trend, except for places where tributaries joined the main stream. In such places, the water temperature may deviate from the upward trend. Moreover, compared to the measurements from 2017 (Potapowicz, Szumińska, Szopińska, Bialik, et al. 2020;

**TABLE 2** | Values of measured physicochemical parameters and snow cover density at individual points.

Sample name	T (°C)	pH (-)	SEC (µS/cm)	TOC (mg/L)	Snow density (kg/m³)
1.1 I	1.8	7.59	144.6	<LOD	—
1.1 II	1.6	8.54	33.1	0.094	—
1.1s	—	5.32	15.4	0.150	320
1.2 I	2.7	7.41	151.6	<LOD	—
1.2 II	5.3	7.97	216	0.114	—
1.2s	—	5.17	7.8	0.122	340
1.3 I	5.4	7.29	128.5	0.065	—
1.3 II	5.7	8.9	179.8	0.125	—
1.3s	—	5.22	6.4	0.225	410
2.1 I	0.8	6.87	53.1	<LOD	—
2.1 II	1.1	8.7	20.6	<LOD	—
2.1s	—	5.07	8.1	0.054	800
2.2 I	1.5	7.26	69.3	<LOD	—
2.2 II	2.0	7.58	37.9	<LOD	—
2.2s	—	5.04	8.2	0.077	710
2.3 I	2	7.18	104.2	<LOD	—
2.3 II	7.7	8.05	59.2	0.055	—
2.3s	—	4.99	4.8	0.147	850
3.1 I	3.4	8.1	67.3	<LOD	—
3.1 II	6.3	8.46	64.8	0.069	—
3.1s	—	5.49	23.8	0.543	580
3.2 I	4.9	7.74	81.8	0.079	—
3.2 II	6.5	7.86	71.1	0.077	—
3.2s	—	4.12	7.4	<LOD	560
3.3 I	5.1	7.62	58.8	<LOD	—
3.3 II	7.2	7.82	79.7	0.093	—
3.3s	—	5.46	8.4	0.276	530
4.1 I	4.4	7.8	60.2	<LOD	—
4.1 II	9.7	8.43	115	0.244	—
4.1s	—	5.26	16.8	0.371	470
4.2 I	4.3	7.71	54.7	0.034	—
4.2 II	12.1	8.57	99	<LOD	—
4.2s	—	5.31	19	0.347	400
4.3 I	4.6	7.7	65.1	0.138	—
4.3 II	14	8.71	119.6	0.133	—
4.3s	—	4.77	28.7	0.232	540

(Continues)

**TABLE 2** | (Continued)

Sample name	T (°C)	pH (-)	SEC (µS/cm)	TOC (mg/L)	Snow density (kg/m³)
5.1 I	2.4	8.1	52.6	0.086	—
5.1 II	4.2	8.22	25.1	0.097	—
5.1s	—	4.56	26.6	<LOD	560
5.2 I	3.4	8.15	73	0.033	—
5.2 II	5	7.88	22.2	<LOD	—
5.2s	—	5.33	119.4	0.269	640
5.3 I	3.9	8.5	3.67	0.110	—
5.3 II	7.9	8.8	12,200	0.305	—
5.3s	—	5.87	82.6	0.581	640

Potapowicz, Szumińska, Szopińska, Czapiewski, et al. 2020), when the stream water temperature ranged from 0.1°C to 8.1°C, in the present study, maximum values reached up to 14°C and mean values were nearly twice as high as in 2017, which may be attributed to exceptionally warm summer conditions in 2021/2022 (Castro et al. 2022; Marsz and Styszyńska 2013). The mean water temperature across all studied points was 5.3°C in December and 7.1°C in January, with the highest values recorded near the stream mouths.

Snow density values ranged from 320 to 850 kg/m³ (Table 2). Compared with the snow density values in the polar regions (Kachniarz et al. 2022; Laska et al. 2022; López-Moreno et al. 2020; Wever et al. 2023), the studied snow cover was relatively hard and compact. Such high values indicate significant compaction and ageing of snow cover due to repeated melting and refreezing, likely combined with aeolian redistribution of snow (Moure et al. 2023; Thompson-Munson et al. 2023). The highest snow densities (> 800 kg/m³) were observed in the forefields of the Tower and Windy glaciers, while the lowest values (< 350 kg/m³) occurred near the Ecology Glacier. Moreover, in the Sphinx glacier forefield, the stream current was stronger during the first sampling series than in the other streams, perhaps indicating a higher water supply from melting snow. Furthermore, during the collection of the second series, water flow was significantly lower than before. This difference is likely due to the spring freshet influencing the first series but not the second series. Another factor of note was that precipitation totals in January 2022 greatly exceeded the multiannual mean. Intense rainfall could have accelerated snow and ice melt and contributed to increased discharge from these sources (including ice-cored proglacial moraines). In addition, the groundwater table could also have risen due to rainfall.

In the collected samples, pH ranged from 4.12 to 5.87 in snow and from 6.87 to 8.8 in surface waters (Table 2), indicating a clear difference between acidic to neutral precipitation and neutral to alkaline surface waters. The difference in SEC was less pronounced (Table 2): snow samples noted SECs from 4.8

to  $119.4 \mu\text{S}/\text{cm}$ , while water sample SECs generally ranged from 3.67 to  $216 \mu\text{S}/\text{cm}$ . In most sampling points, surface water conductivity was higher than that of snowmelt, except in the Windy catchment, where similar SEC values were recorded. Furthermore, in the Windy catchment, at least one water sample reached a very high SEC of  $12,200 \mu\text{S}/\text{cm}$ , characteristic of seawater or marine aerosol impact, especially given the proximity of the Windy Glacier forefield to the coast and prevailing westerly winds. Previous studies on catchment types have found that SECs for glacially fed catchments have lower values than for non-glaciated catchments (Potapowicz, Szumińska, Szopińska, Bialik, et al. 2020; Potapowicz, Szumińska, Szopińska, Czapiewski, et al. 2020), which indicates a large share of supraglacial waters in glacial catchment runoffs.

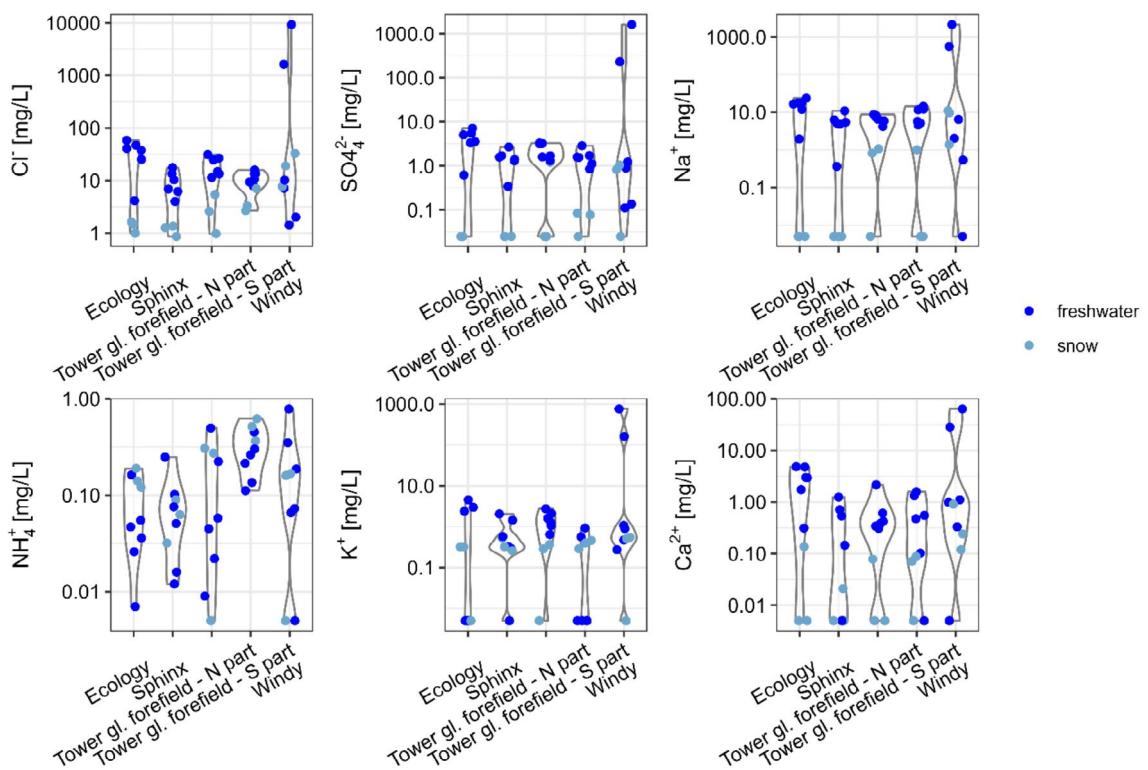
TOC levels were more uniform and reached higher values in snow ( $0.05\text{--}0.581 \text{ mg/L}$ ) than in surface waters ( $0.05\text{--}0.305 \text{ mg/L}$ ), which is a surprising result, and it corroborates the idea that snow cover was a source of TOC in the studied glacier forefields. The maximum TOC value in snow ( $0.581 \text{ mg/L}$ ) was recorded in the forefield of the Windy Glacier (Sample 5.3s), while the lowest values (< LOD) were found in water samples from the Ecology and Tower Glacier catchments.

Our research also confirmed that the most abundant ion (by mass concentration) in the collected samples was chloride, followed by sodium, sulphate, potassium and calcium (Figure 4, Table S3). The highest chloride and sodium concentrations were detected in surface water samples collected

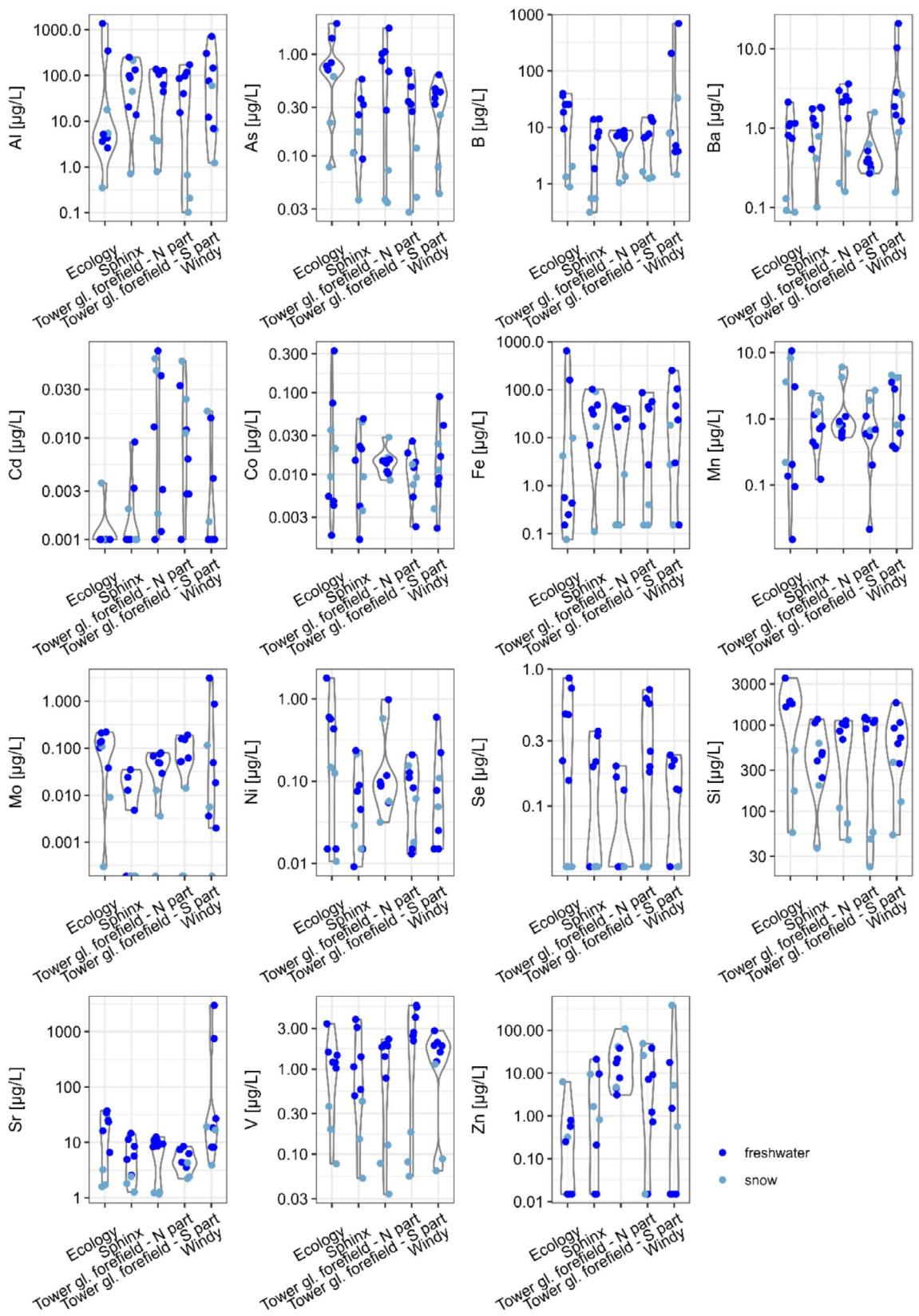
in the lower sections of the Windy Glacier forefield. Two of the samples from the Windy Glacier catchment showed very high salt concentrations, likely impacted by seawater. Among nitrogen species, ammonium was most frequently detected, at concentrations reaching almost  $1 \text{ mg/L}$  (in two points: 4.2 and 5.3) and  $\sim 0.5 \text{ mg/L}$  (in four points: 3.1, 4.2, 4.3 and 5.2), showing a likely influence of fresh bird guano. With the exception of the Windy catchment, all snow samples showed decidedly lower concentrations of  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  than the water samples collected. In the case of the foreland of the Windy Glacier, the influence of seawater that entered the final section of the stream can be seen. In the Windy catchment for all ions, and in the other catchments for  $\text{K}^+$  and  $\text{NH}_4^+$ , there was less clear distinction between snow and freshwater samples, showing that either the sampled water was directly fed by snowmelt (Windy catchment) or that there were abundant sources of  $\text{K}^+$  and  $\text{NH}_4^+$  for the snow cover from wet and dry deposition, perhaps due to the presence of a bird colony observed there. No consistent trend was observed in the concentration of sulphate anions at the beginning and end of the austral summer.

### 3.3 | Measured Levels of Trace Elements in Snow and Glacial Runoff Waters

Predominant metals and metalloids in the collected samples, besides the major ions listed already, were Si, Al, B, Fe and Sr at concentrations ranging from 22.7 to 3520, 0.102 to 1370, 0.313 to 693, 0.075 to 647 and 1.17 to 2980  $\mu\text{g/L}$ , respectively (Figure 5, Table S4). Among the analysed trace elements, silicon



**FIGURE 4** | Major inorganic ion concentrations (of the ions detected in more than  $1/2 n$  samples) in glacial catchments in the Arctowski Station vicinity in the summer 2021/2022. Each violin plot reflects one location (catchment) for data distribution, while shades of blue divide samples into snow and liquid water (assumed freshwater before measurements). [Colour figure can be viewed at [wileyonlinelibrary.com](https://wileyonlinelibrary.com)]



**FIGURE 5** | Elemental concentrations (of the metals and metalloids detected in more than 1/2  $n$  samples) in glacial catchments of the Arctowski Station area (summer 2021/2022). Each violin plot reflects one location (catchment) for data distribution, while shades of blue divide the samples into snow and liquid water (assumed freshwater before measurements). [Colour figure can be viewed at [wileyonlinelibrary.com](https://wileyonlinelibrary.com)]

(Si) exhibited the highest concentrations, with values reaching up to 3520  $\mu\text{g}/\text{L}$  in water samples and 510  $\mu\text{g}/\text{L}$  in snow samples. Aluminium (Al) also showed relatively high levels, with

maximum concentrations up to 1370  $\mu\text{g}/\text{L}$  in surface waters and significantly lower values in snow. Strontium (Sr) concentrations ranged from 1.17 to 2980  $\mu\text{g}/\text{L}$ , with higher values observed in

water compared to snow. Iron (Fe) and boron (B) displayed moderate concentrations, with Fe reaching up to 647 µg/L and B up to 693 µg/L.

In contrast, several metals such as Ag, Bi and Be were frequently below the LOD in most samples. These elements are therefore not discussed further in terms of their environmental impact. Cadmium (Cd) concentrations in snow samples varied from 0.0012 to 0.0718 µg/L, confirming previous findings in similar Antarctic environments. Chromium (Cr), copper (Cu) and lead (Pb) were detected only in selected samples, generally at low concentrations not exceeding 0.08 µg/L for Pb and 1.4 µg/L for Cu. Vanadium (V) concentrations were higher in water samples compared to snow, ranging up to 3.4 µg/L.

Freshwater and snow from the forefields of the Tower (southern part) and Windy glaciers have not been tested for their chemical composition in any previous studies. The values of Fe and Al concentrations in water from these areas are similar to the values for water from the northern forefield of the Tower glacier. However, it is worth noting that the concentrations of these elements in snow samples are much lower, and at three points (4.2s, 4.3s and 5.2s), even below the limit of determination.

The cadmium content in the tested snow samples was within the range of 0.0012–0.0718 µg/L, which is a result comparable to previous studies (Hong et al. 2004; Szumińska et al. 2021). It is worth noting that in the areas closest to the polar station (around the Ecology and Sphinx glaciers), the concentration values in both water and snow were below or slightly above the limit of quantification. Cadmium concentrations near the Baranowski and Tower glaciers were the highest, and in almost all places, higher concentrations in water were observed at the beginning of the summer season.

The concentration levels of heavy metals such as Cr, Cu and Pb exceeded the limits of determination in only a few samples taken along the entire length of the coast, which is why concentrations of these elements cannot be observed in the vicinity of a specific glacier. The Pb concentration did not exceed 0.078 µg/L. For comparison, the Pb concentration in the water from Deception Island was 0.049 µg/L (de Mão Ferro et al. 2013), and in several bays of King George Island, the range was 0.1–0.4 µg/L (Préndez and Adriana Carrasco 2003). The Cr concentration reached the highest value of 0.076 µg/L, while in comparable studies in this area, concentrations in snow amounted to a maximum of 0.14 µg/L (Szumińska et al. 2021). The issue of Cu pollution in the Antarctic environment is also minor, as it affected only a few points, and the concentration of this metal did not exceed 1.4 µg/L.

## 4 | Discussion

### 4.1 | Sources and Environmental Impact of Chemical Constituents in Glaciated Catchments

Based on the obtained values of physicochemical parameters and elemental and ionic concentrations, processed statistically, we evaluate the role played by long-range atmospheric transport (LRAT) in the chemical concentrations remobilised from melting

snow and glacier ice, in contrast to local geological sources (presumably rock weathering). As support for these interpretations, we use meteorological and geological background data.

The results of this study confirm that in areas under the direct influence of aerosols, as well as those exposed to periodic influxes of seawaters, the values of SEC increased (Nędzarek and Pociecha 2010). It has been proven that increased SEC values in the western shore of Admiralty Bay are associated with relatively high concentrations of  $\text{Cl}^-$ ,  $\text{Na}^+$  and  $\text{SO}_4^{2-}$ , which, in terms of percentage contribution to the total ions, are dominant in the waters of this area (Nędzarek et al. 2014; Potapowicz, Szumińska, Szopińska, Bialik, et al. 2020; Potapowicz, Szumińska, Szopińska, Czapiewski, et al. 2020; Szopińska et al. 2018). Previous studies on the chemical composition of Antarctic waters have shown an increase in sulphate aerosol concentrations in spring, attributed to biogenic sources, including phytoplankton activity (Giordano et al. 2017). On the other hand, on the western shore of Admiralty Bay, the concentrations of sulphate anion were stable and independent of the summer months (Nędzarek et al. 2015; Potapowicz et al. 2019; Szumińska et al. 2021). While the marine sources of sulphate ions are varied, the concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  ions may be used as marine origin indicators in our samples. Similar patterns of trace metal behaviour across salinity gradients have been reported in recent studies of polar fjords, where glacial meltwater interacts with marine inputs (Krause et al. 2021).

Differences between early and late outflow samples observed in this study are mainly attributable to the seasonal dynamics of snowmelt and precipitation events. During the early phase of melting, the 'ionic pulse' phenomenon dominated, characterised by the preferential elution of highly soluble sea salt ions (such as  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{Mg}^{2+}$ ) from the snowpack (Grannas et al. 2007; Koerner 1997). These ions were rapidly flushed during initial melting events, resulting in elevated concentrations in early meltwater samples. As the melting season progressed, snow cover depletion and increased exposure of glacial and moraine surfaces led to an increasing contribution from geogenic sources. Weathering of local volcanic rocks enriched the meltwaters in lithogenic elements such as Al, Fe and Si (Birkenmajer 2003; Szumińska et al. 2018). Additionally, intense mid-summer rainfall events likely enhanced chemical weathering and the mobilisation of elements from exposed soils and sediments (Potapowicz, Szumińska, Szopińska, Bialik, et al. 2020; Potapowicz, Szumińska, Szopińska, Czapiewski, et al. 2020). These combined processes explain the temporal shifts in the chemical composition of meltwater and its divergence from the original composition of the snow cover.

The concentrations in snow were distinctly smaller than in surface waters for the elements Al, As, B, Si, Sr and V, which can be interpreted in favour of their local geological origin (consistently with the presence of Al in this group) (Nyamgerel et al. 2025). On the other hand, Cd, Mn and Zn exhibited higher concentrations in snow cover than in surface waters, which speaks of their likely origin from atmospheric deposition (Kozak et al. 2015; Potapowicz, Szumińska, Szopińska, Bialik, et al. 2020; Potapowicz, Szumińska, Szopińska, Czapiewski, et al. 2020; Szumińska et al. 2021). Other elemental concentrations were more similar between the snow cover and surface waters, likely

indicating a mixed origin and the contribution of snow melt to the concentrations in freshwater.

In this study, the concentrations of Al and Fe were relatively high in both water and snow samples. Previous research on non-glaciated catchment areas on the west coast of Admiralty Bay attributed such high concentrations of these elements to the mechanical weathering of local rocks (Birkenmajer 1981, 2003; Szopińska et al. 2018). It was found that a source of Fe in the water may also be pyrite, a mineral commonly found on King George Island (Brown 2002; Hodson et al. 2010; Paulo and Rubinowski 1987). As has been shown in the literature, the extensive, dynamically changing drainage network created by water from melting glaciers enriches the water in Fe and Al while flowing through the sediment (Brown 2002; Tatur and Keck 1990), and these elemental concentrations tend to correlate with Si concentrations in subglacial waters (Stachnik et al. 2019). Our findings are consistent with recent reports of Fe and Mn enrichment in meltwater-dominated drainage networks in Antarctica, supporting the interpretation that glacial processes play a key role in the flux of lithogenic and colloidal metal forms (Forsch et al. 2021; Jones et al. 2025). The plots presented in Figure 5 show that elemental concentrations in liquid water samples were generally higher than those in snow, particularly for Si, Al, Sr and Fe. This distribution also suggests a dominant contribution from local geological sources through rock weathering, consistent across all sampled glacier forefields.

The highest TOC value in snow in Windy Glacier forefield, as opposed to <LOD values in water samples from the Ecology and Tower Glacier catchments, may reflect atmospheric deposition of organic matter or input from bird colonies (Castro et al. 2022). Numerous colonies of pinniped mammals and seabirds were observed near the sampling points. Due to the terrain and access to the waters of the bay, most colonies of these animals were in the forelands of the Tower and Windy glaciers. Adults and hatchlings of the south polar skua (*Stercorarius maccormicki*) also occur along the streams near the Ecology and Tower glaciers, even in the higher parts of the streams. These observations indicate a biological input of organic matter to the snow surface through, among others, guano and dead tissue. Furthermore, surface sediment in the study area may also be an important source of organic carbon in the waters (Bröder et al. 2022). Overall, snow concentrations of TOC were not particularly high for polar snowpacks; similar values have been noted, for example, on an Arctic glacier in Svalbard (K. A. Koziol et al. 2019), in the Warsaw Icefield area on King George Island, Antarctic (Szumińska et al. 2021), or in the vicinity of Chukchi Sea (Alaska) (Zhang et al. 2020). This observation and the uniform concentration levels would indicate atmospheric deposition as the dominant source of TOC.

Seabirds in polar regions are a specific vector for the transfer of biogenic compounds from sea to land, thus influencing the chemical properties of inanimate elements of the environment (Szopińska et al. 2016). It was also confirmed that water near penguin colonies is richer in phosphorus compounds and nitrogen than water farther away from them (Nędzarek 2008). Seabird guano and products resulting from the erosion of ornithogenic soils may settle at the bottom of water bodies (Castro

et al. 2022; Zhu et al. 2006), where they are transported along the streams fed by melting glacial ice and snow (Hodson et al. 2010; Potapowicz, Szumińska, Szopińska, Bialik, et al. 2020; Potapowicz, Szumińska, Szopińska, Czapiewski, et al. 2020; Szopińska et al. 2018). The relatively high concentrations of the  $\text{NH}_4^+$  ion in the studied area were therefore expected because the entire research area is located in ASPA 128, which is characterised by a large number of colonies of birds and pinniped mammals. Similarly to previous studies (Nędzarek et al. 2015), at most points the concentration of this ion did not exceed 0.25 mg/L. Snow samples from the foreland of the Tower Glacier were characterised by high  $\text{NH}_4^+$  concentrations, likely due to contamination of the snow cover with bird guano. Due to the high elevation of the sampling points and distance from the bay, no seal colonies were present there. Compared to other studies (Nędzarek et al. 2015; Szopińska et al. 2018), the lower concentrations of nitrate and phosphate anions observed here were surprising. However, the mentioned studies focused on non-glaciated catchments, which are rich in moss and lichen vegetation (Kappen and Schroeter 2002).

In comparing the relative impact of atmospheric sources and seabird activity on trace metal concentrations, our results suggest distinct patterns between snow and freshwater samples. In snow cover, atmospheric deposition, particularly from snowfall and rainfall events, appeared to be the dominant factor influencing trace metal levels, especially for elements such as Cd, Zn and Pb. These metals are commonly associated with LRAT and wet deposition processes (Mishra et al. 2004; Szumińska et al. 2021). In contrast, in surface waters, the influence of seabird colonies was more pronounced, particularly near ornithogenic areas, where elevated levels of biogenic nutrients and certain metals such as Cu, Zn and Sr were detected. This indicates that while atmospheric inputs primarily shape the initial chemical composition of the snowpack, biological inputs from seabird activity substantially modify the chemistry of meltwaters, especially during peak biological activity periods in summer (Castro et al. 2022; Lu et al. 2012).

Of particular interest are the concentration levels of elements that have a potentially negative impact on the environment. Based on aerosol studies near King Sejong Station on King George Island, elements such as Bi, Cd, Co, Cr, Cu, Ni, V and Zn are classified as pollutants of both local and distant origin, but in both cases of anthropogenic nature (Mishra et al. 2004). Research near the Fildes Peninsula claims that Cr, Pb, Zn and Ni had a volcanic origin, while only Cd and Cu were attributed to anthropogenic sources (Polyakov et al. 2020). Other results show that As, Cd, Cu, Hg, Pb and Zn are common pollutants in the Antarctic, mainly resulting from fuel leaks (Tin et al. 2009). A contribution of multiple sources (both natural and anthropogenic) to determine elemental concentrations is a probable explanation for some of the conflicting evidence.

While the low concentrations in the Ecology glacier forefield rule out a direct impact of the research station on environmental Cd pollution, which is also confirmed by our previous studies (Potapowicz, Szumińska, Szopińska, Bialik, et al. 2020; Potapowicz, Szumińska, Szopińska, Czapiewski, et al. 2020), cadmium concentrations near the Baranowski and Tower

glaciers were the highest. At those locations, higher concentrations in water were observed at the beginning of the summer season. This can be explained by the 'spring pulse' phenomenon, that is, the temporarily concentrated outflow of chemical species from melting snow cover. The decrease in concentration at the end of the summer season suggests that the contribution of glacial erosion of the local substratum to Cd supply to streams is negligible.

During advanced melting stages, the elution patterns of certain metals, including Zn, may be influenced by several mechanisms. First, zinc is often present in snow in more mobile ionic forms or loosely bound to particulate matter, making it more susceptible to rapid elution during early melting events (Grannas et al. 2007; Koerner 1997). Its low concentration at late stages of snowpack melt was confirmed in elution studies (Avak et al. 2019). Second, enhanced atmospheric deposition through rainfall events can introduce additional Zn into surface waters, either directly or by facilitating the mobilisation of Zn from surface sediments and snowpack. Third, differential solubility and complexation behaviour under changing pH and conductivity conditions during melt can selectively enhance Zn release compared to other metals. Zinc exhibits the highest mobility in low-pH, oxidising environments; however, it also becomes easily adsorbed to mineral and organic surfaces (Kabata-Pendias 2010). Such processes may collectively explain the observed elevated Zn concentrations during the mid- to late-melting period.

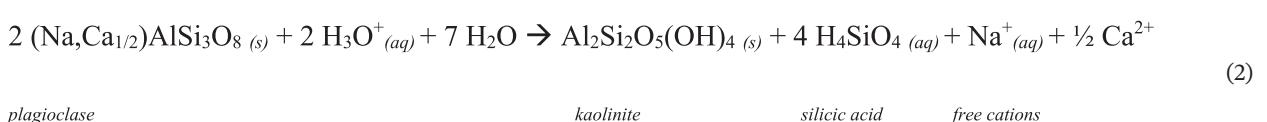
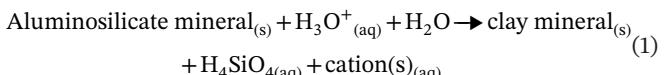
Taking into account that volcanic rocks are common on King George Island and contain relatively high concentrations of Cu and Mn, and that the rock formations underlying the studied glaciers contain Mn, Cr, Cu and Pb (Groeneweg and Beunk 1992; Mozer et al. 2015), the geological factor likely contributed to Cr, Cu, Pb and Mn concentrations in the studied watercourses. However, it was also found that seabirds may be vectors bringing Cu, Zn and Sr into the environment (Lu et al. 2012; Tatur 1989), and their contribution to the collected samples' concentrations of Cu cannot be excluded.

The observed strong relationship between water temperature and metal concentrations suggests that future environmental changes, particularly cryosphere degradation driven by climate warming, could significantly alter the geochemical balance of glaciated catchments. As glacier and snow cover retreat accelerates, enhanced mineral weathering processes and intensified microbial activity may lead to increased mobilisation of metals into freshwater systems (Coulon et al. 2024; Piccione et al. 2024).

## 4.2 | Quantification of the Crustal and Sea Salt Contributions to the Metal and Metalloid Concentration in the Sampled Waters

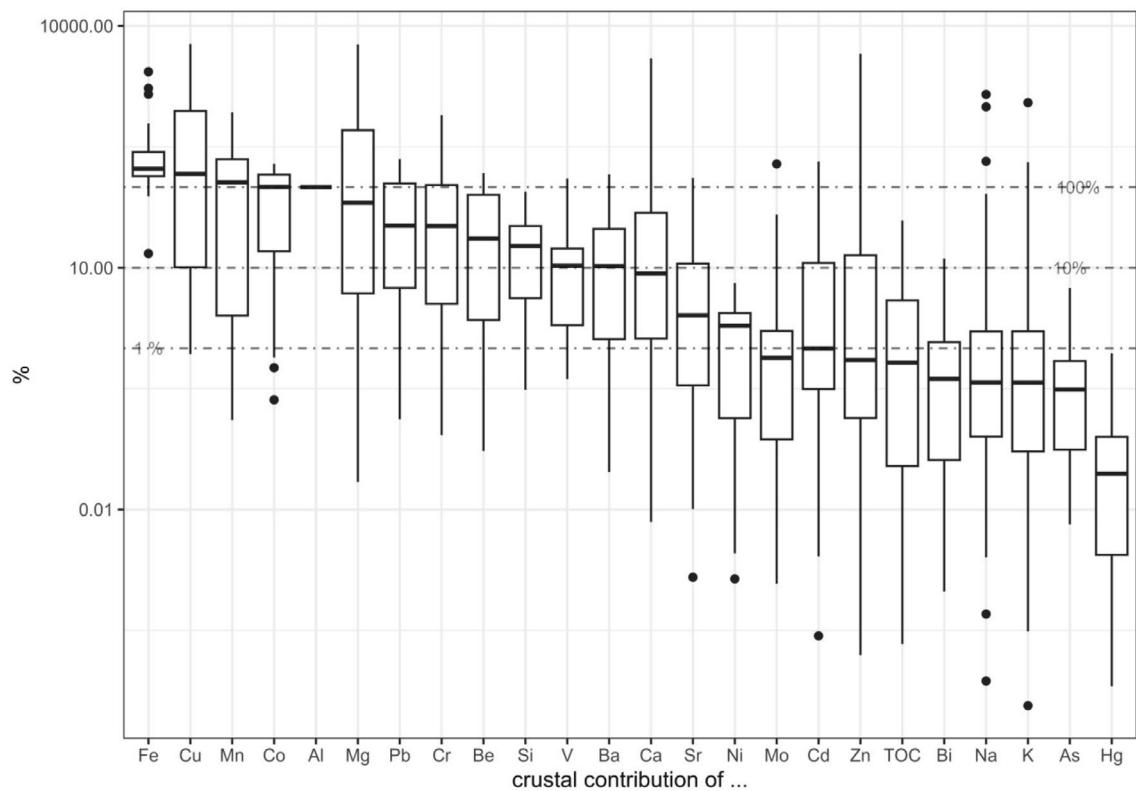
Geologically, the area consists of basalt and andesite lavas with intercalations of, for example, fluvial deposits. All glaciers in this study are underlain by the same rock formations, namely the Llano Point Formation, likely also the Zamek Formation. Windy and Sphinx glaciers also have contact with Palaeogene dykes from the Admiralty Bay Group (surfacing as Blue Dyke, at Agat Point, Sphinx Hill and the Czajkowski Needle; Mozer et al. 2015). The Llano Point and Zamek formations are both composed of mafic volcanic rocks, especially basalt, with a contribution of andesite. From the typical composition of these rock types, it may be deduced that the geological substratum is a likely source of Fe, Ca, Mg, Na, Al, Si, F, and potentially also Zn, Mn, Li, Cr, Co and V, and in andesites also K. Geochemical analysis by Mozer et al. (2015) has revealed that some of the collected samples from the Zamek and Llano Point Formations contained, besides Si, Fe, Al, Mg, Ca and K, detectable concentrations of MnO (up to 0.18%), CrO<sub>2</sub> (up to 0.004%), Sr (up to 728.2 ppm), Ba (up to 311 ppm), V (up to 303 ppm), Cu (up to 167.9 ppm), Zn (up to 69 ppm), Co (up to 26.1 ppm), Ni (up to 22 ppm), As (up to 8.8 ppm), Pb (up to 4.6 ppm), Mo (up to 0.8 ppm), Cd (up to 0.4 ppm) and several rare earth elements and other elements that were not the subject of this study. The Llano Point formation samples were more abundant in K, Ba and Ni, and less abundant in Cs and V than the Zamek Formation; they also exhibited a higher variability in Sr and As concentration than the Zamek Formation.

As both basalts and andesites typically contain plagioclase feldspar, pyroxene and hornblende, a typical weathering reaction shared by these minerals will follow the hydrolysis pattern where free alkaline and alkaline earth cations are released into the aqueous solution (Equation 1). For example, the weathering of plagioclase will result in free sodium and calcium anions in water (Equation 2). The formation of clay minerals favours further ion exchange and adsorption on their internal surfaces. The mobility of other metals and metalloids, especially of Fe and Al, may strongly depend on the availability of organic compounds acting as ligands in organic complexes (VanLoon and Duffy 2017).



This could elevate the availability of potentially toxic elements such as Cd, Pb and Zn, with possible consequences for aquatic organisms sensitive to metal pollution. In the long term, these changes could affect nutrient cycling, water quality and the ecological functioning of freshwater ecosystems in polar regions (Bargagli and Rota 2024; Convey and Peck 2019; Hodson et al. 2008).

To further quantify the contributions of geogenic and marine sources to the observed elemental concentrations, calculations based on Al and Na<sup>+</sup> proportions were performed. The proportions were assumed to follow the rock composition as described by Mozer et al. (2015) and seawater composition by Turekian (1968). To explore the sources of metals and metalloids in the studied environment in a quantitative fashion, we have



**FIGURE 6** | Geogenic (local crustal) contributions to each elemental concentration, based on Al concentration in the samples and the proportion of Al to each element concentration in the local geological substratum (after Mozer et al. (2015)). Please note that the elements presented in the graph are only those for which both source composition and our sample composition information were available.

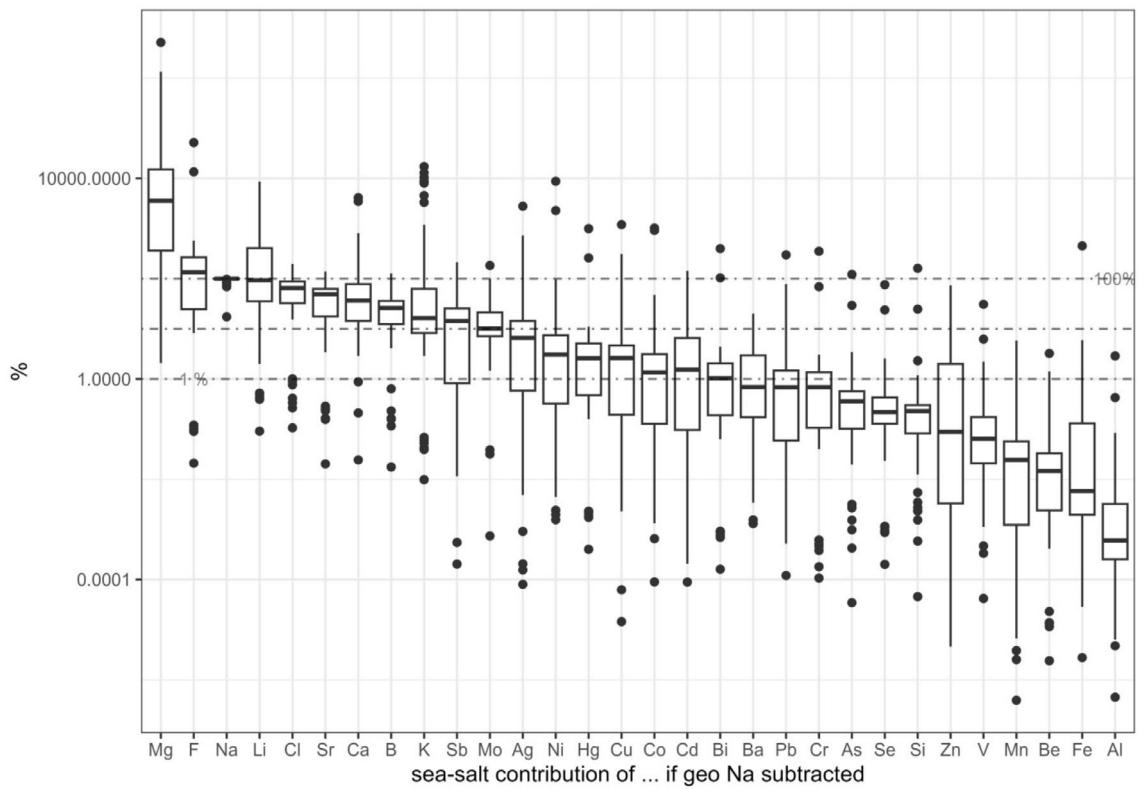
estimated the fractions of each element contributed by these two main natural sources, that is, local geological substratum (crustal or geogenic contribution hereafter) and the sea salt (or seawater). Seawater fractions were based on  $\text{Na}^+$  concentration corrected for geogenic sources, while the crustal contribution was based on the proportion to Al, since its marine source was marginal in the studied samples (a level of magnitude smaller than for Fe). Resulting contribution values exceeding 100% mean probably that the element in our water sample was depleted against source composition, by plant or microbial uptake, or by precipitation of insoluble salts. There is also a possibility that the element adopted as the basis of calculation (Na in the case of sea salt, Al in the case of local crustal contribution) has another significant source in this environment, and therefore all sea-salt or crustal contributions should be shifted towards lower values. This was also the reason for  $\text{Na}^+$  concentration correction for geogenic sources prior to sea-salt contribution calculation.

The calculation of crustal contribution revealed that elements such as Fe, Cu, Mn, Co and Mg (and Al, per assumption) originated mainly from the local rock weathering, while further elements Pb, Cr, Be, Si, V and Ba had a marked local crustal contribution (> 10% median; Figure 6). However, of these elements, Mg should have been contributed in a much larger quantity from the sea salt, and it was likely depleted against both sources; therefore, the estimation of the geogenic source of magnesium should be proportionally reduced (Figure 7). The group of elements with predominantly marine sources in the studied samples therefore comprised Mg, F (Na per assumption), Li and Cl, and, with a median contribution exceeding

10%, also Sr, Ca, B, K, Sb and Mo. For elements with neither of the natural sources providing above 50% contribution, additional sources, including the LRAT, should be considered likely origins. Elements with < 10% sea salt and < 10% crustal contribution encompassed As, Cd, Ni and Zn (as well as Bi and Hg, not detected in the collected samples), which are typically associated with LRAT in both hemispheres (K. Koziol et al. 2021; Mishra et al. 2004; Tin et al. 2009). Similarly, small contributions were evaluated for TOC against crustal source and for Se against sea salt (the other source for either could not be evaluated due to a lack of source composition data). Pb, Cr, Be, Si, V and Ba were also likely contributed mostly by LRAT in the collected pool of samples, yet with a significant (> 10% median and highly variable) portion of local geological input. A similar statement could be made about Sr, Ca, B, K, Sb and Mo supplied from LRAT and secondarily sea salt; yet, Sr and Ca also had a non-negligible share supplied from crustal sources, and for B and Sb, an evaluation of crustal sources was not possible with the existing source data on geological substratum (Mozer et al. 2015).

#### 4.3 | Statistical and Multivariate Data Analysis for Exploration of Metal and Metalloid Sources

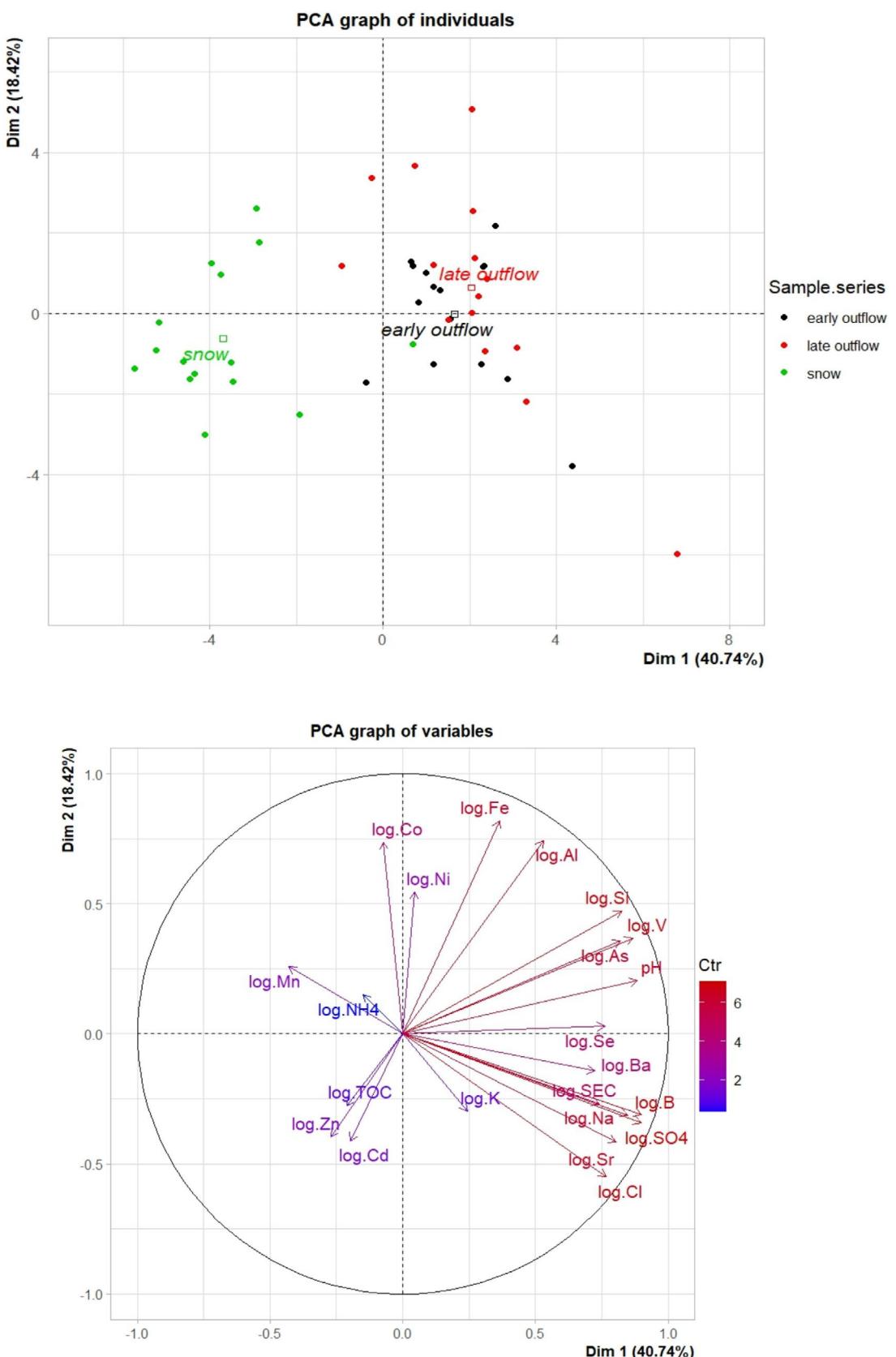
Further information on the studied metal and metalloid sources may be gleaned from their statistical analysis, especially PCA. PCA has shown that a major part of the variance (> 59%) is explained by the first two PCs, defining the plane in which the differences between snow and freshwater samples were the most



**FIGURE 7** | Sea-salt contributions to each elemental concentration, based on the  $\text{Na}^+$  concentration in the samples, less the geogenic contribution of Na calculated before. Seawater proportions of elemental concentrations were based on Turekian (1968).

pronounced (Figure 8). The collected snow samples were characterised by higher Zn, Cd, Mn and TOC concentrations, while the other water samples showed higher SEC and pH, and higher concentrations of sea salt components ( $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and Sr) and of the elements As, B, Ba, Se, Si and V. Sea salt, B and Ba concentrations were the main drivers of variability within the freshwater samples group, while high Fe and Al concentrations also distinguished a group of freshwater samples, indicating two factors influencing the freshwater sample composition: seawater presence (in groundwater, sea spray, etc.) and geological substratum dissolution. The seawater variable cluster contained sodium, chloride and sulphate ions, B, Ba, Se and Sr concentrations, despite the relatively small sea-salt contributions to Ba and Se concentrations estimated from proportion to Na, perhaps indicating another source connected to the marine environment. Geogenic variables encompassed the concentrations of Fe, Al and Si, as well as As and V, and the pH of water, which may have been an additional factor in element solubility. The result for As is surprising due to a relatively small crustal contribution estimated before; however, since As mobility in the aquatic environment increases significantly in reducing environments (Kabata-Pendias 2010), it may be more closely connected to the redox state in the studied waters than source composition. The pH may have been impacted by the alkalinity derived from both rock dissolution and seawater intrusions. The concentrations of Ni and Co in the collected samples shared a notable part of the variability with the geogenic elements Fe and Al, which may indicate a stronger impact of the geogenic source on Ni concentrations than indicated by the quantitative approach used before in this study, or perhaps a similar mobility mechanism in the aquatic environment for these metals (likely chelating).

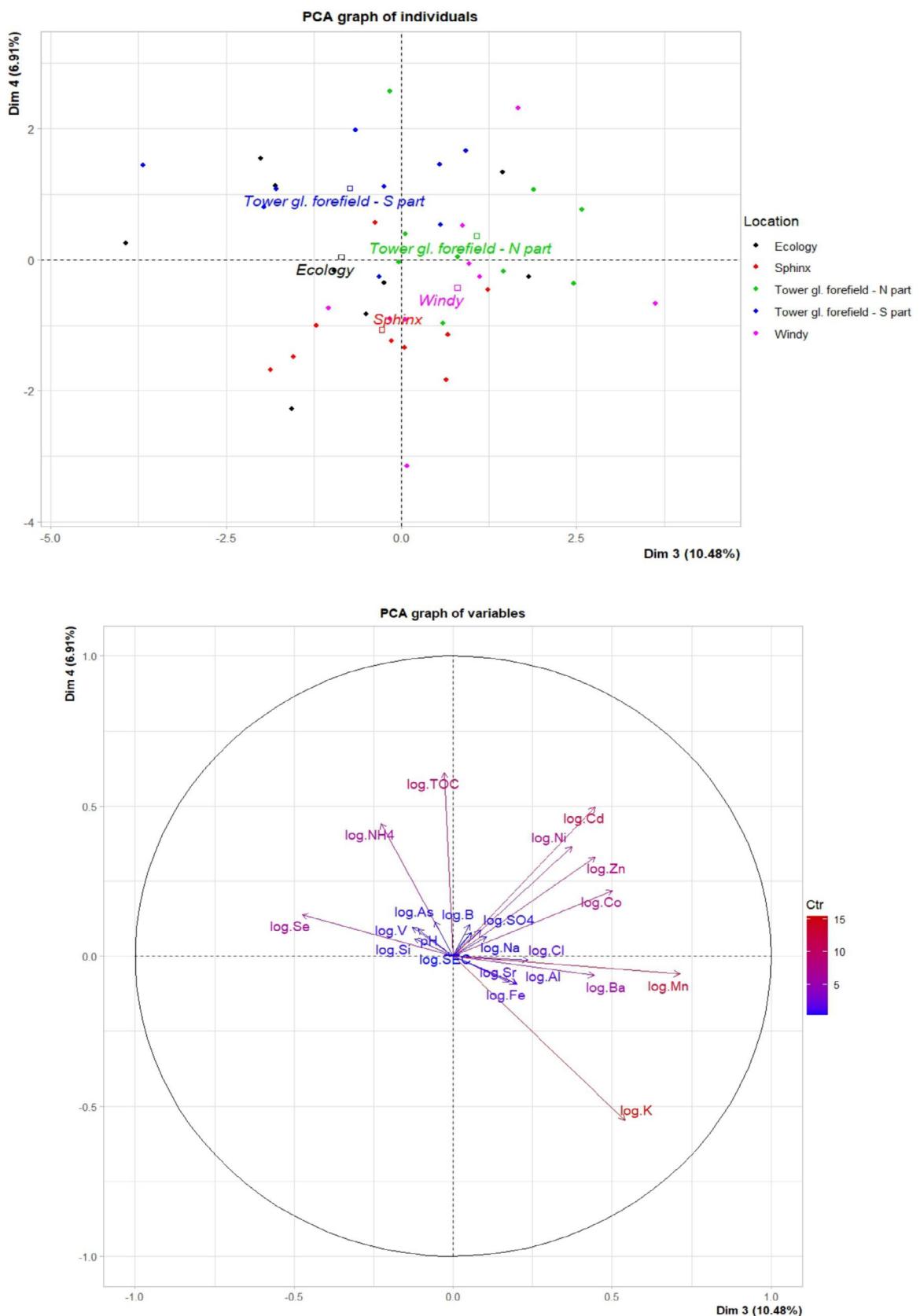
Since the sampled snow was characteristic of remaining snow cover while melting was advanced, the more mobile ions may have already been eluted from it by the time of sampling (Björkman et al. 2014; Kępski et al. 2016). However, Zn and Cd were indicated in an Alpine snowpack study to be readily eluted alongside Na and Sr, indicating that either the elution processes in the Antarctic follow a different pattern than in the European Alps (Avak et al. 2019) or their deposition onto snowpack was ongoing. For example, rainfall in December could be a continuous source of atmospheric Zn, as this element has been shown to be abundant in rainfall of a remote Arctic site (Kozak et al. 2015); another source could have been the bird vector effect mentioned before (Tatur 1989). Interestingly, the early and late outflow (the two series of collected freshwater samples) did not differ markedly in the PCA graph, with the slight distinction provided by more sea salt ions in the early outflow and more geogenic elements in the late outflow. While this is a typical difference between such waters, it is surprising that even early outflow did not resemble the snow cover in chemical composition. Chemical analysis of surface waters revealed significant relationships between water temperature and the concentrations of various metals, metalloids and ions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , Al, As, B, Fe, Li, Mo, Se, Si, Sr and V), indicating the important role of temperature in geochemical processes. Spearman's correlation coefficients for these elements showed significant positive correlations ( $p < 0.05$ ), suggesting that higher temperatures may accelerate chemical reactions such as mineral weathering, microbial processes, or other mechanisms that release elements from the geological substrate. This hypothesis is further supported by positive correlations of pH ( $\rho = 0.421$ ,  $p < 0.05$ ) and specific electrical conductivity (SEC) ( $\rho = 0.508$ ,  $p < 0.05$ ) with



**FIGURE 8** | PCA results for the analysed variables, presented in the plane defined by PCs 1 and 2. Top: Cases divided by sample series. Bottom: Variable graph within the same space. [Colour figure can be viewed at [wileyonlinelibrary.com](https://wileyonlinelibrary.com)]

temperature, consistent with the release of alkalis elements in warmer conditions, probably due to ongoing chemical weathering. These phenomena reflect the complexity of interactions

between temperature and the chemical dynamics of surface waters, highlighting the significance of thermal and geochemical processes in shaping water chemistry. PCs 3 and 4 together



**FIGURE 9** | PCA results for the analysed variables, presented in the plane defined by PCs 3 and 4. Top: Cases divided by sample location. Bottom: Variable graph within the same space. [Colour figure can be viewed at [wileyonlinelibrary.com](https://wileyonlinelibrary.com)]

explained ~17% of total variance and differentiated between sample locations (Figure 9). Most Sphinx and Windy samples were characterised by relatively high concentrations of K, Mn

and Ba, aligning with the probable Llano Point Formation impact on their composition, while for Tower southern forefield and Ecology samples, high TOC,  $\text{NH}_4^+$  and Se concentrations

were more characteristic. Tower northern forefield samples tended to exhibit higher concentrations of Mn, Ba, Co, Zn, Ni and Cd, though this distinction was fuzzy. Ecology and Sphinx glaciers, situated in proximity to the research station, exhibited relatively low concentrations of most determined elements and ions, with two notable exceptions: Cu, which was present in relatively high concentrations in the forefield of Ecology Glacier and Mo, for which concentrations at the same site fell within the medium range of the collected dataset. These observations suggest that local anthropogenic contamination likely does not play a significant role in shaping the elemental composition of these glaciers. However, the observed Mo concentrations warrant further consideration, as this element may originate from both geological sources and LRAT associated with coal combustion, as highlighted by Harkness et al. (2017) and discussed in Spolaor et al. (2021). Given that Mo has been detected in local rock formations, it is plausible that its presence is geogenic; however, its relatively low crustal contribution calculated for the sampled waters suggests that other sources, such as LRAT, may also be relevant. Additionally, Mo may have been remobilised during the more alkaline conditions observed in the late outflow season, due to its higher mobility in alkalis and oxidising environments (Kabata-Pendias 2010). Thus, the observed Mo levels are likely a result of mixed inputs, with both local and distant origins contributing to their occurrence.

The significant differences between the studied glaciers were further tested by K-W ANOVA. The entire Tower glacier forefield was significantly more exposed to Cd concentrations than Ecology glacier ( $p=0.0012$ , post hoc  $p=0.024$  and  $p=0.017$  for Tower S and N, respectively) and the northern Tower forefield was more exposed to Zn concentrations ( $p=0.0125$ , post hoc  $p=0.011$  for Tower N to Ecology glacier difference), which can be interpreted in favour of Cd and Zn origin from LRAT with eastern winds because of the direct exposure of the Tower Glacier to this direction but also aligns with the potential transport of these metals by the bird vectors, since the Tower glacier forefield hosts a bird colony. An increased number of Antarctic skuas was observed in this area during sampling compared to other areas. The latter idea is supported by the significant difference also noted for the concentration of  $\text{NH}_4^+$  ( $p=0.0192$ ) between Tower S part and Ecology or Sphinx glacier, with the Tower S forefield noting higher concentrations (post hoc  $p=0.043$  and  $p=0.024$  for Ecology and Sphinx, respectively). The northern part of the Tower glacier forefield also showed significantly higher Li concentrations than Sphinx glacier ( $p=0.0048$ , post hoc  $p=0.010$ ). Other significant differences between glaciers in our dataset included Ba ( $p=0.0214$ ; with Windy glacier showing higher values than Tower S forefield; post hoc  $p=0.039$ ) and Mo concentrations ( $p=0.0232$ , Ecology glacier showing higher values than Sphinx glacier; post hoc  $p=0.014$ ), which may have resulted from the differences in minor components in the local geological substratum composition, for example, the Llano Point formation being slightly more abundant in Ba than Zamek Formation, or even within-formation elemental concentration variability (Mozer et al. 2015).

To explore the potential impact of rock dissolution during the austral summer, we also sought significant differences between the chemical parameters of early and late outflow samples (with K-W ANOVA).  $\text{K}^+$  concentrations showed such significant differences ( $p=0.0106$ , post hoc  $p=0.011$ ), and  $\text{Mg}^{2+}$  also exhibited

a marginal significance level ( $p=0.0076$ , post hoc Bonferroni-corrected  $p=0.062$ ). The late outflow was also significantly more alkaline (pH K-W ANOVA  $p=0.001$ ), and more abundant in TOC than the early outflow (K-W ANOVA  $p=0.046$ ), and the water was warmer later in the season (temperature K-W ANOVA  $p=0.007$ ). All these factors may change elemental mobility; the TOC may either originate from leaching soils and sediments or from autotrophic production on site, and it could have been a chelating agent playing a role in metal mobility in the studied waters.

## 5 | Conclusions

This study provides valuable insights into the hydrochemical dynamics of glacier forefields on King George Island, directly addressing the research objective of evaluating the influence of geological formations and cryosphere degradation on the mobilisation of metals and metalloids in this unique Antarctic environment. The Llano Point and Zamek formations, composed predominantly of basalt and andesite, play a significant role in the chemical weathering processes intensified by glacial retreat. High concentrations of Fe (ranging from 0.075 to 647  $\mu\text{g/L}$ ) and Al (0.102 to 1370  $\mu\text{g/L}$ ) in surface waters confirm the weathering of these formations as a key driver of the hydrochemical patterns observed in the region. Similarly, elevated levels of Cr (up to 0.076  $\mu\text{g/L}$ ), V (up to 303 ppm in substratum, up to 5.62  $\mu\text{g/L}$  in water) and Ba (up to 311 ppm in substratum and 20.8  $\mu\text{g/L}$  in water) further underscore the geogenic origin of these elements, aligning with the research aim to identify specific geological sources of trace metals. Other elements associated mainly (> 50% median) with the crustal source were Cu, Mn, Co, Mg, and a marked proportion (> 10% median) of Pb, Be, Si (and Cr, V) concentrations was also estimated as supplied from local geological substratum.

Statistical analyses validate the significant spatial and seasonal variability in chemical composition across glacier forefields, supporting the study's objective to explore how meltwater and geological interactions shape element mobilisation. K-W ANOVA revealed distinct differences in Cd concentrations between the Tower Glacier forefield and other sites, attributed to its exposure to eastern winds and the role of atmospheric deposition. Significant variability in Zn levels and  $\text{NH}_4^+$  concentrations further supports the interplay of atmospheric and biological inputs in shaping chemical profiles, particularly in areas influenced by seabird colonies. Seasonal differences in ion concentrations, such as the marked increases in K levels during late meltwater flows, highlight the role of warmer temperatures in enhancing geochemical processes, consistent with the study's focus on seasonal variability.

PCA indicated that over 59% of the variance in chemical composition is driven by geological and marine influences, confirming the importance of local bedrock in element mobilisation. Freshwater samples were enriched in geogenic elements, including Fe, Al and Si, while snow samples exhibited elevated levels of Zn, Cd and TOC, reflecting the combined effects of atmospheric deposition and biological activity. The clustering of Fe, Al and Si in PCA analyses aligns with their geogenic origin, directly linking their mobilisation to the Llano Point and Zamek Formations. Additionally, the association of Zn and Cd with  $\text{NH}_4^+$  highlights the connected contributions of seabird colonies and LRAT.

Spatial differences in Ba concentrations, particularly in the Windy Glacier forefield (up to 20.8 µg/L), align with the mineralogical composition of the formations in the study area, confirming geological inputs as a dominant source. Similarly, the Tower Glacier forefield, characterised by elevated Cd (0.0718 µg/L) and Zn (1.4 µg/L) levels, demonstrates a combination of atmospheric deposition and biological inputs. Correlations between these elements and NH<sub>4</sub><sup>+</sup> (Spearman's  $\rho > 0.4$ ,  $p < 0.05$ ) further emphasise the significance of external influences, consistent with the research objective of identifying geogenic and non-geogenic contributions.

This study also underscores the ecological implications of cryosphere degradation, a key focus of the research. The seasonal 'spring pulse' phenomenon, evident in early meltwater samples, leads to temporary peaks in trace metal concentrations, such as Cd, posing potential risks to local ecosystems. Statistical analyses reveal significant correlations between water temperature and concentrations of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, and geogenic elements such as Fe and Si (Spearman's  $\rho > 0.5$ ,  $p < 0.05$ ), highlighting the role of warming temperatures in accelerating chemical mobilisation processes. Non-negligible concentrations of potentially toxic elements (such as Al, As, Mo, Se and V) may also be mobilised from the studied Maritime Antarctic catchments in the higher water temperatures.

This research achieves its stated objective of elucidating the contributions of geological, other natural and anthropogenic factors in shaping the hydrochemistry of Antarctic glacier forefields. By integrating statistical analyses with geochemical observations, the study provides a robust framework for assessing the impacts of cryosphere degradation upon freshwater composition in glacial catchments. The findings underscore the urgency of continued monitoring and research, particularly in the face of rapid glacial retreat and its implications for geochemical cycles and ecosystem health in the Maritime Antarctic.

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## Data Availability Statement

The data that support the findings of this study are available in Supporting Information S1 of this article.

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## Supporting Information

Additional supporting information can be found online in the Supporting Information section. **Table S1:** Information on sampling sites and dates for collected water samples. **Table S2:** Analytical parameters used for the determination of elements in water samples. **Table S3:** Ion concentrations determined in water samples from various locations. **Table S4:** Results of trace element analysis in the collected water samples.