

# Do morphometric parameters and geological conditions determine chemistry of glacier surface ice? Spatial distribution of contaminants present in the surface ice of Spitsbergen glaciers (European Arctic)

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**Abstract** The chemism of the glaciers is strongly determined by long-distance transport of chemical substances and their wet and dry deposition on the glacier surface. This paper concerns spatial distribution of metals, ions, and dissolved organic carbon, as well as the differentiation of physicochemical parameters (pH, electrical conductivity) determined in ice surface samples collected from four Arctic glaciers during the summer season in 2012. The studied glaciers represent three different morphological types: ground based (Blomlibreen and Scottbreen), tidewater which evolved to ground based (Renardbreen), and typical tidewater glacier (Recherchbreen). All of the glaciers are functioning as a glacial system and hence are subject to the same physical processes (melting, freezing) and the process of ice flowing resulting from the cross-impact force of gravity and topographic

conditions. According to this hypothesis, the article discusses the correlation between morphometric parameters, changes in mass balance, geological characteristics of the glaciers and the spatial distribution of analytes on the surface of ice. A strong correlation ( $r = 0.63$ ) is recorded between the aspect of glaciers and values of pH and ions, whereas dissolved organic carbon (DOC) depends on the minimum elevation of glaciers ( $r = 0.55$ ) and most probably also on the development of the accumulation area. The obtained results suggest that although certain morphometric parameters largely determine the spatial distribution of analytes, also the geology of the bed of glaciers strongly affects the chemism of the surface ice of glaciers in the phase of strong recession.

**Keywords** Svalbard archipelago · Surface ice · Heavy metals · Anthropogenic pollutants · Environmental contamination · Glaciers

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## Introduction

Anthropogenic contaminants transported through the atmosphere (e.g. persistent organic pollutants, heavy metals, SO<sub>x</sub> and NO<sub>x</sub> particles) can be deposited in various components of the ecosystem as a result of wet and dry deposition (Macdonald et al. 2000; Bidleman et al. 2010; Weber et al. 2010; Ruman et al. 2012; Kozak et al. 2013). A number of scientists focus on the presence of pollutants not only in biotic samples (Braune et al. 2005; Evans et al. 2005; Letcher et al. 2010; Rigét et al. 2010) but also in abiotic samples (Herbert et al. 2005; Ferrari et al. 2008; Hung et al. 2010).

According to Chapman (2007), contamination may be understood both as a presence of substances where they normally would not occur or at concentrations exciding natural background. Contaminants which presence in the environment

may result in adverse biological effects to residential communities are defined as pollutants.

Studies regarding contamination of samples collected from the abiotic environment of glacial catchment (Wadham et al. 1998; Hodson et al. 2002; de Caritat et al. 2005; Dragon and Marciniak 2010; Larose et al. 2010) are considerably scarcer than those referring to the presence of anthropogenic pollutants in biota. Works discussing the accumulation of chemical substances in glaciers refer to the issue of environmental changes in earlier periods and particularly involve the analysis of ice cores (Watanabe et al. 2001; Isaksson et al. 2003; Moore et al. 2005; Kwok et al. 2013). Studies of ice cores show that the phenomenon of deposition of atmospheric pollutants on glaciers has continued for a long time and is still a valid problem in the environment (Ruggirello et al. 2010). Two papers (Kwok et al. 2013; Lehmann et al. 2014) analyse the spatial distribution of pollutants in various elements of the glacial catchment. These two works prove that glaciers accumulate contaminants and redistribute them with ablation in water. According to Moore et al. (2005), the percolation phenomenon observed in glaciers causes a problem in the interpretation of results obtained from ice cores. Moreover, both ions and other contaminants (e.g. metals, particulate matter) may be easily removed from ice during melting and carried downward to fjord or ocean (Moore et al. 2005). Another most frequently discussed aspect involves modern processes/changes occurring within glaciers under the influence of inflowing contaminants (Pulina 1991; Głowacki and Leszkiewicz 1994; Głowacki 2007).

The issues discussed in the world literature show a considerable importance of glaciers in global circulation of water and anthropogenic pollutants present in water. The pollutants are reaching glacier surface as a result of wet or dry deposition, crystallisation of snow or other solid forms of precipitation remaining in constant movement. The processes are determined by external factors, but they also strongly affect the environment, making glaciers open dynamic systems (Jania 1997). An important feature of glaciers is also circulation of the mass of ice, snow, water and mineral matter (and therefore their components of natural origin and deposited pollutants). The functioning of a glacier is determined by the energy circulation (exchange) occurring through accumulation, glacier movement and ablation. It is of importance in the case of processes influencing the division of the present chemical compounds between the solid and liquid phases (and their redistribution between the phases). Input and output routes of deposited substances in an open glacial system with supporting processes are presented in Fig. 1.

Glacier runoff is a factor affecting not only the hydrology of rivers but also circulation within the neighbouring seas and fjords, contributing to changes in stratification within the

water column (Hagen et al. 2003). Dynamic changes in the mass balance of glaciers determine the rate of release of pollutants deposited on their surface over the years (Głowacki 1998).

Glaciers as the most visible part of the environment of the Svalbard Archipelago play a special role in the environment. Approximately 60 % of the total area of the Archipelago amounting to more than 62.248 km<sup>2</sup> is occupied by 1615 glaciers (Hagen et al. 1993; AMAP 2005; IPCC 2013 et al. 2013). Therefore, they can also be considered as the major geomorphological factor of this region (Hagen et al. 2003). Among all of its geocomponents, glaciers respond the fastest and strongest to climate changes. They are the major component of the environment, regulating water circulation in the Arctic (Głowacki 1998).

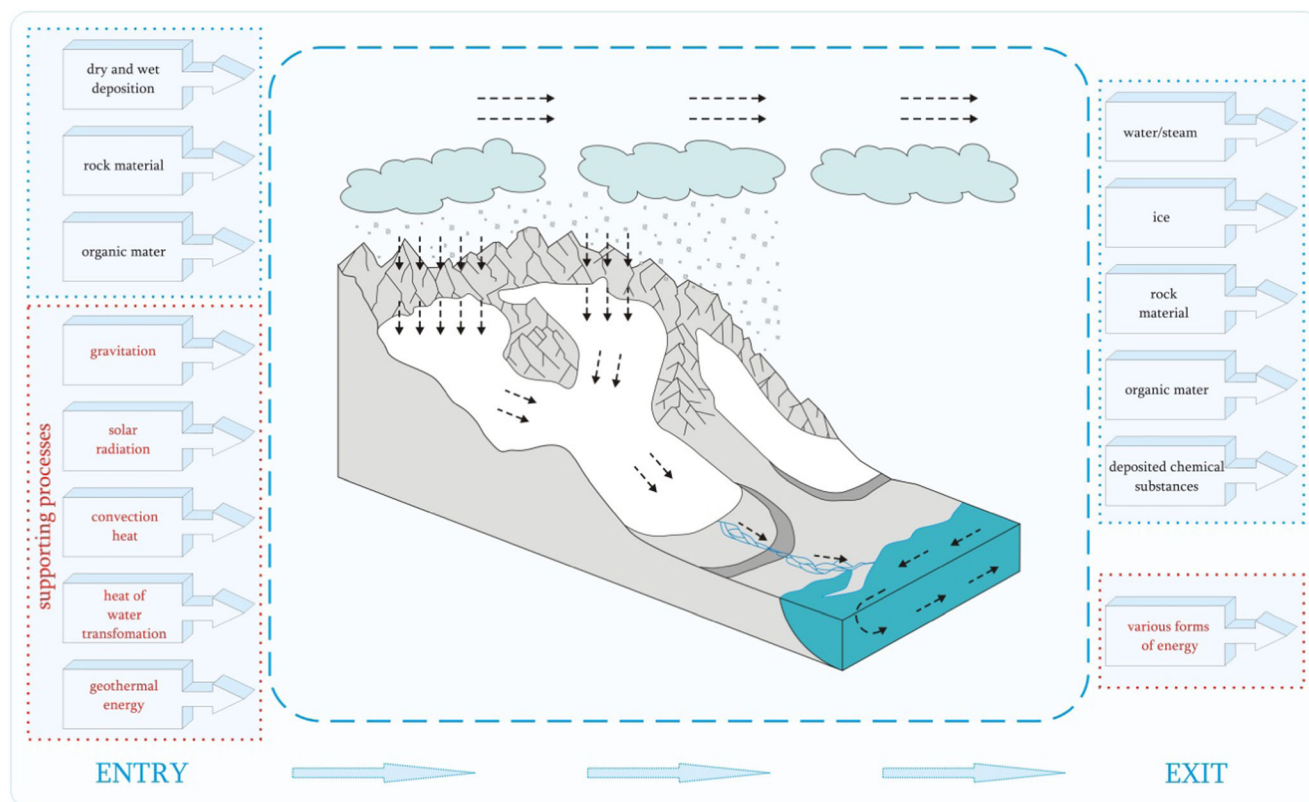
The majority of the glaciated area of Svalbard is covered by single ice streams connecting in areas devoid of ridges and nunataks (Hagen et al. 2003). In geophysical terms, approximately 90 % of Spitsbergen glaciers are considered as polythermal (subpolar). They play an indicator role based on their response to changing climate conditions. The glaciers are affected not only by varying air temperature but also by the variable amount and structure of precipitation. In contrast to glaciers with cold thermal regime, the internal hydrothermal structure of polythermal glaciers is influenced by not only solid but also liquid precipitation (Głowacki 2007; Fookes 2008; Hagen et al. 1993).

The objective of this paper is to define the chemical features of glacier surface ice with contaminants (heavy metals, ions, and dissolved organic carbon (DOC)) based on the example of four polythermal glaciers (Blomlibreen, Scottbreen, Recherchebreen and Renardbreen) located in the SW Svalbard area. The second objective is to determine the possible influence of morphological parameters and geological characteristics of glacier bed on the concentration levels of chemical substances on the surface of Arctic glaciers. To achieve this purpose, obtained results of chemical analysis were used as a source of data for a glacial system which is represented by all studied glaciers. The analyses were conducted on 17 samples of surface ice collected from four open glacial systems, differing in terms of slope inclination, exposition of the ice tongue, glacial mass balance (rate of loss of water by a glacier influencing transport of contaminants) and directions of inflow of air masses in the area.

## Materials and methods

### Study area

Spitsbergen, the largest island of the Svalbard Archipelago, was selected as the study object due to its high degree of



**Fig. 1** Routes of transport in an open glacial system (after Jania 1988, modified)

glaciation (68.1 %), exceeding not only the degree of glaciation of the island (55 %) but also the entire archipelago of Svalbard (59 %) (Jania et al. 2004).

The region of South Bellsund (“Calypsobyen” research station), where studies on glacial and periglacial environments have been conducted since 1986 by scientists from the Maria Curie-Skłodowska University in Lublin, Poland, was selected as the area representative of circulation conditions and types of glaciers (polythermal, ending on land and in the sea, valley) occurring most frequently in the area of West Spitsbergen (Fig. 2).

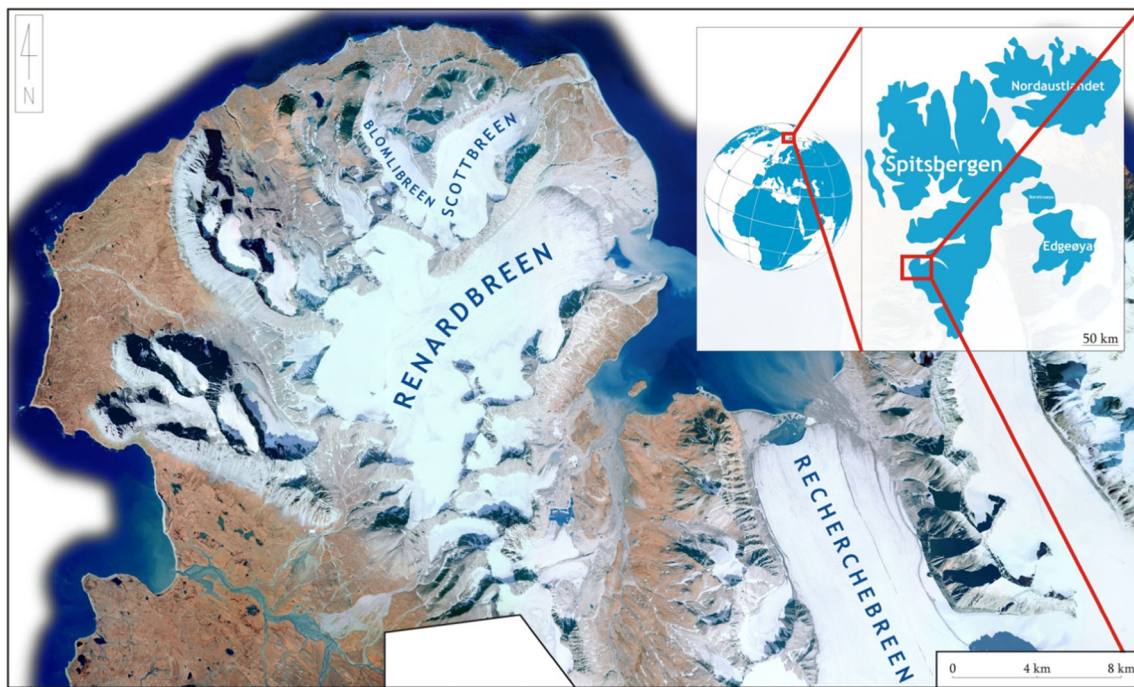
Long-term observations and measurements conducted in the area of South Bellsund permitted the selection for the study of particular glaciers representing four types of glaciers. Blomlibreen is the smallest of the studied glaciers and the most exposed to the direct influence of the Atlantic Ocean winds. Scottbreen is a polythermal glacier of the valley type. Renardbreen is a polythermal glacier of the valley type. Recherchebreen is a polythermal surging glacier of the valley type with a narrow belt of the marine bay forming a closed lagoon at the direct forefield of the glacier.

Table 1 presents and compares basic information concerning morphological parameters of each of the glaciers.

### Atmospheric conditions

Specific atmospheric conditions and the physicochemical properties of pollutants contribute to their accumulation in the Arctic (Macdonald et al. 2000; Stohl 2006). Long-range transport of atmospheric pollutants is a well-known phenomenon described by many scientists (Barrie 1986; Lohmann et al. 2007; Hung et al. 2010; Hallanger et al. 2011). Meteorological observations at summer station Calypsobyen were only conducted during the expedition periods, from July to September. Mędrek et al. (2014) provide the following meteorological parameters for the multiannual 1986–2011: mean air temperature (5.0 °C), mean total precipitation (32.4 mm) and mean wind velocity (4.3 m/s). For comparison, the values of these parameters in Calypsobyen in summer of 2012 were as follows: mean air temperature 4.6 °C, total precipitation 26.4 mm and mean wind velocity 3.6 m/s.

The direction of inflow of air masses may influence the presence and concentration levels of chemical compounds present on the surface of glaciers. Air masses inflowing from the Atlantic may transport atmospheric pollution from Eurasia. In contrast, air masses coming from the interior of the island may transport contaminants of local origin from permanent settlements in Svalbard and cruise ships (Ruman et al. 2012). Another factor crucial for the reception of chemical substances transported by air masses is the aspect of a



**Fig. 2** Map of the Bellsund Fiord (SW part of Spitsbergen) with location of the studied glaciers (sampling points are presented in Figs. 6 and 7) (*base map after*)

given glacier. Figure 3 shows the percentage of the prevailing wind direction following the flow of air masses in the period prior to sampling on the studied glaciers.

Similarities in the prevalent wind direction of inflow of air masses observed for Blomlibreen and Renardbreen as well as for Scottbreen and Recherchebreen result from similar periods of collection of ice surface samples on glaciers. Figure 3 shows that both the Blomlibreen and Renardbreen glaciers were under the influence of air masses predominantly coming from WNW (14 %) and NW (14 %). Percentage contribution of winds coming from directions of ENE, E, SSE, S and SSW ranged between 6 and 9 %. Both glaciers hardly ever were under the influence of winds coming from directions such as N, NNE, NE, ESE, SE, SW, WSW, W and NNW (1–5 %), whereas Scottbreen and Recherchebreen were mostly under the influence of air masses coming from ENE (16 and 19 %, respectively) and NW (15 and 14 %, respectively) directions. For Scottbreen, however, we observe also a significant influence of WNW (11 %) and E (10 %), while for Recherchebreen the percentage contribution of only the E wind direction reaches 12 % (WNW 7 %). Percentage contribution of winds coming from directions of N, NNE and NE ranged between 6 and 8 %. These two glaciers hardly ever were under the influence of winds coming from directions such as ESE, SE, SSE, S, SSW, SW, WSW, W and NNW (1–5 %).

Considering the aspects of the Blomlibreen (NNW) and Renardbreen (NE) glaciers, Blomlibreen was considerably more exposed to the influence of air masses inflowing in the period prior to sampling than Renardbreen. The aspects of the

other two glaciers, namely Recherchebreen (NW) and Scottbreen (NE), suggest higher exposure of Recherchebreen to the influence of air mass influx prior to sampling (Table 1).

Both the mean air temperature and annual precipitation in 2012 are much lower than the average of the last 25 years. Figure 4 shows the fluctuations in air temperature in the summer of 2012. The figure also indicated the time of sampling the ice surface, the temperature of the air and rainfall events which then occurred.

As shown in Fig. 4, samples of the ice surface were taken in two periods: at the end of July and in mid-August. Either samples taken from glaciers Recherchebreen, Scottbreen and Renardbreen were collected when jumps of the air temperature were observed. The highest maximum temperature (8–10 °C) was observed in mid-July (21–23, 2012) which was accompanied by rainfall events. During these 3 days, a total of 58 % of the rain fell in the entire measurement period from 12 July to 25 August 2012. Between collection of samples from Recherchebreen and Scottbreen, small precipitation occurred (CS\_6), while before collection of samples from Renardbreen and Blomlibreen, a second rise of temperature occurred (9–11 August 2012), as is shown in Fig. 4. Few events of wet precipitation took place. However, maximum temperature did not reach 10 °C, and the rainfalls were not as intense as the ones which occurred in mid-July. Since 19–23 August 2012, a gradual decline of temperature, below 4 °C, is noticed. Summarizing, before each sampling period, maximum air temperatures (>8 °C) are observed, which favours melting of glaciers and rainfall events, which favours flushing the

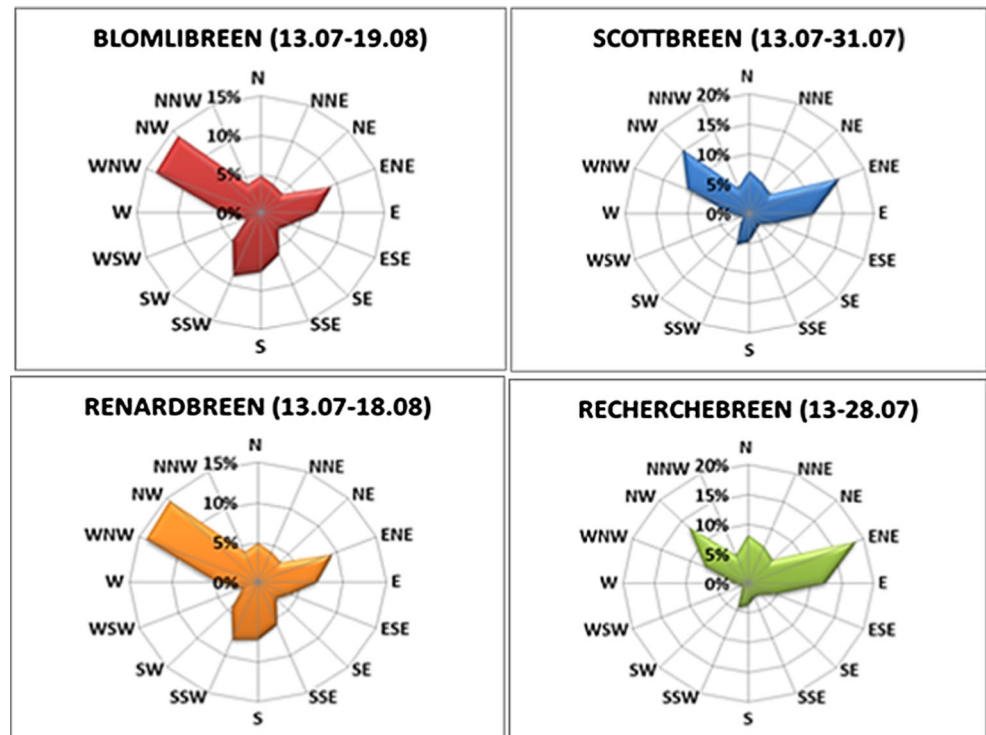
**Table 1** Morphological characteristics of the glaciers

Parameters	Blomlibreen	Scottbreen	Renardbreen	Recherhebreenn
Glacier basin area	Morphometric			
Glacier area	Approx. 2.5 km <sup>2</sup>	Approx. 6 km <sup>2</sup>	39 km <sup>2</sup>	n.d.
Length	1.8 km <sup>2</sup> (2012)	4.4 km <sup>2</sup> (2012)	27 km <sup>2</sup> (2012)	120.2 km <sup>2</sup> (2009)
Width	2900 m (2012)	3500 m (2012)	8300 m (2012)	22,800 m (2009)
Max. elevation [m a.s.l.]	480 m	900 m	2500–8000 m	3000–4500 m
Min. elevation [m a.s.l.]	640	700	654	800
ELA (equilibrium line altitude)	240 (2013)	120 (2012)	30 (2012)	0
Accumulation area	530 (2012)	400 (2003), 530 (2012)	420–460 (2005–2007)	370 (1993)
AAR (accumulation area/ablation area)	n.d.	1.6 km <sup>2</sup>	14.2 km <sup>2</sup>	n.d.
Aspect	n.d.	0.36	0.52	n.d.
Max. thickness [m]	NNW (accumulation area), NNW (tongue)	N (accumulation area), NE (tongue)	N-S (accumulation area), NE (tongue)	NW
Volume	n.d.	NE (tongue)	341 m (2009)	430 m (1982)
Average slope	0.15 km <sup>3</sup> (1990)	Circa 160 m (2009)	Approx. 4.8 km <sup>3</sup> (2009)	37 km <sup>3</sup> (1960)
Flow velocity [m y <sup>-1</sup> ]	Approx. 5°	Approx. 5°	4.02°	Approx. 1.49°
	<1	Circa 1	Circa 40 (end of LIA); 9.6 (2005–2012)	<40
	Mass balance and geometric changes			
Net mass balance	n.d.			n.d.
Average terminus position change [m y <sup>-1</sup> ]	n.d.	-0.81 e.w. (1990–2012)	-0.41 e.w. (2005–2008)	-380–(-40) (1838–2012)
	-4 (1936–2012)	-15 (1895–2012)	-14–(-17) (1895–2012)	+110 (1936–1945)
Observed surges (year)	n.d.			1838, 1945
Area changes	-0.7 km <sup>2</sup> (1936–2012)	Circa 1880	End of LIA	-16.5 km <sup>2</sup> (1838–2012)
Thickness changes (m) of:	~1.4 (2012–2013)	-1.52 km <sup>2</sup> (1895–2012)	-6.65 km <sup>2</sup> (1895–2012)	-40–(-20) (1936–1990)
Accumulation area (>350 m a.s.l.)	~0.6 (2012–2013)	-57 (1936–2005) -58 (2005–2012)	-47–(-40) (1936–2005) -20 (2005–2012)	-20–(-10) (1936–1990)
		0 (1936–1990) -1 (1990–2005)	+34–+69 (1936–1990) -10–(-2) (1990–2005)	
Morphological	Glacier type	Valley, subpolar high latitudes, ground based	Valley, subpolar high latitudes, previously tidewater, ground based	Valley, subpolar high latitudes, tidewater, calving
Thermal regime	Polythermal	Polythermal	Polythermal	Polythermal
Drainage	Supraglacial, inglacial, subglacial	Supraglacial, inglacial, subglacial	Subglacial, inglacial, supraglacial	Subglacial, supraglacial

Baranowski 1977; Blaszczyk et al. 2009; Gajek 2007; Gajek et al. 2008a, b; Gajek et al. 2009; Grabiec et al. 2010a, b; Grabiec et al. 2011; Hagen et al. 1993; Hoel and Werenskiold 1962; Jania 1988; Jania et al. 2010, Liestøl 1993; Macheret et al. 1982; Mangerud and Landvik 2007; Nuth et al. 2007; Nuth et al. 2010; Reder and Zagórski 2007; Zagórski and Bartoszewski 2004; Zagórski et al. 2012; Zagórski et al. 2008a, b. Calculation of average slope of Recherhebreenn were as follows:  $\Delta h = 250 \text{ m} - 90 \text{ m} = 160 \text{ m}$ ;  $L = 4800 \text{ m}$ ;  $S = \Delta h/L = 0.033$ ;  $0.033 \times 100 \% = 3.33 \%$ ; 100 % corresponds to 45° and consequently 3.33 % corresponds to 1.49°

n.d. no data, LIA little ice age, e.w. water equivalent

**Fig. 3** Percentage of the prevailing wind direction during the period prior to sampling on glaciers



chemical compounds from the surface of the glaciers to its downward parts.

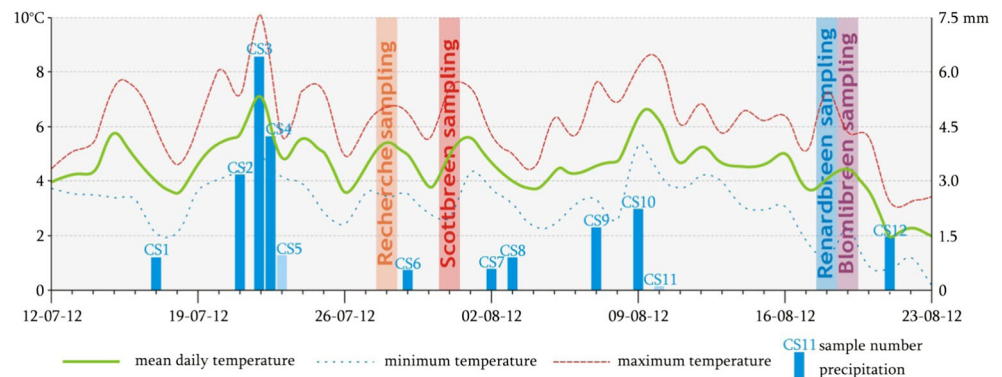
### Sampling and weather data collection

Glacier ice samples were collected along the longitudinal profile of the glaciers on 28 July (Recherchebreen), 31 July (Scottbreen), 18 August (Renardbreen), and 19 August (Blomlibreen).

During field sampling, extreme care was taken to avoid contamination. Personnel taking the samples wore polyethylene gloves. Surface ice sampling sites were carefully selected far enough away from any possible contamination sources nearby (e.g. ablation poles, frequented path on the glacier). Surface ice samples were obtained by scraping the ice surface

to the depth of 5 cm from the surface of 50 cm × 50 cm in the zone of extensive glacier ablation, below the seasonal equilibrium line altitude (ELA) (530 m as.l.). In the field, samples were packed in string plastic bags which earlier were washed with deionised water. After collecting, the ice samples were left for melting in the field laboratory of Calypsobyen station for 24 h. Subsequently, samples were placed in polyethylene containers also washed earlier with deionised water. In order to avoid losses of analytes to headspace, the samplers were filled without air bubbles. The study involved the analysis of blank samples to exclude the impact of the samplers to which rain and ice surface were collected. Blank samples were prepared in the laboratory of Faculty of Chemistry of Gdansk University of Technology with use of the same string bags and containers as in the field. To prepare a blank sample of

**Fig. 4** Fluctuations of mean air temperature, minimum and maximum temperature and volume of wet precipitation during the summer season of 2012 (in CS\_5 and CS\_11 samples, no chemical analyses were performed due to loss of samples in transport)



surface ice, the string bag was filled with deionised water and left for 24 h, and next deionised water from the string bag was placed in the polyethylene container. The blank sample for rain was gained by flushing using a Hellmann rain gauge with deionised water and collecting this water in a polyethylene container.

A portable weather station (Campbell Scientific, CR10X, Datalogger for Measurement and Control) and rain gauge were placed approximately 200 m from the seashore at an altitude of 23 m a.s.l. Precipitation and ice surface samples were collected during the summer season of 2012. Precipitation samples were collected to a sampler placed in a Hellmann rain gauge (200 cm<sup>2</sup>—surface of the inlet ring) from July 13 to August 24 on the seaside terrace in the vicinity of the “Calypsobyen” station.

**Analytical methods**

Determination of the pH and specific electrolytic conductivity (SEC) of the collected ice surface samples was conducted in the field laboratory of the Calypsobyen polar station within 24 h after sampling. The samples were then transported to the laboratories in Poland and stored at a temperature of 4 °C prior to analysis. In order to minimize the storage time, analyses were performed immediately after the delivery of the samples to the laboratory according to analysis data presented in Table 2. Before analysis, the samples were filtered through 0.45-µm filters. Basic ions and DOC were determined in the laboratory of the Department of Analytical Chemistry of the Gdańsk University of Technology. Analyses of metals were conducted in the laboratory of the Department of Hydrography of the Maria Curie Skłodowska University in Lublin.

Physicochemical parameters such as pH and specific electrolytic conductivity were determined by the electrochemical method with the application of a microcomputer pH/conductometer CPC-411 by Elmetron, electrode type EPS-1 and conductivity sensor EC 60.

Quantitative analyses of inorganic compounds were conducted immediately after delivering samples to the laboratories. Basic anions (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup>) and cations (Li<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>) were determined by means of ion chromatography (ICS 3000 Dionex). The determination of various groups of analytes involved the application of demineralised water type Mili-Q (Mili-Q ® Ultrapure Water Purification Systems, Millipore® production). Metals such as Li, Be, B, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Cd, Cs, Ba, La, Ir, Pb, Th and U were determined by inductively coupled plasma mass spectrometry (Thermo Scientific XSERIES 2 ICP-MS). Concentration levels of sum parameter for carbon bound in organic compounds were determined by the method of catalytic combustion (oxidation) using

**Table 2** Validation parameters, technical specifications used in the analytical procedures

Parameter	Measurement range	LOD	LOQ	Measurement instrumentation
Anions [µg/L]	0.06–500	0.055–0.09	0.027–0.17	DIONEX 3000 chromatograph (DIONEX, USA) Column: Ion Pac® AS22 (2 × 250 mm); suppressor: ASRS-300, 2 mm, mobile phase: 4.5 mM CO <sub>3</sub> <sup>2-</sup> , 1.4 mM HCO <sub>3</sub> <sup>-</sup> , flow rate: 0.38 mL/min, detection: conductivity
Cations [mg/L]	0.03–500	0.01	0.030	Column: Ion Pac® CS14 (3 × 250 mm); suppressor: CSRS-300, 2 mm, mobile phase: 38 mM metasulfonic acid, flow rate: 0.36 mL/min, detection: conductivity
Metals [µg/L] Be, Ga, Rb, Cd, Cs, La, Ir, Tl, Th, U Li, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Ba, Pb, Bi Fe, Sr, Bi	0.01–1000 0.1–1000 1.0–1000	0.01 0.1 1.0	0.030 0.3 3.0	Thermo Scientific XSERIES 2 ICP-MS Germany, Collision Cell Technology, cool gas flow Ar: 12 L/min, cell gas flow He/H: 5.5 mL/min
Dissolved organic carbon [mg/L]	0.030–10.0	0.030	0.100	TOC analyser (TOC-VCSH/CSN, Shimadzu, Japan) potassium hydrogen phthalate standard

Limit of detection (LOD) was calculated based on the standard deviation of the response (s) and the slope of the calibration curve (b) according to the formula: LOD = 3.3 (s / b). Limit of quantitation (LOQ) was calculated based on the standard deviation of the response (s) and the slope of the calibration curve (b) according to the formula: LOQ = 10 (s / b)

an NDIR detector (Total Organic Carbon Analyzer TOC-VCSH/CSN, Shimadzu).

### Quality assurance/quality control

The analytical procedures applied in the determination of individual components in environmental samples with various matrix compositions should be validated against certified reference materials. The data obtained in the research were subjected to strict quality control procedures.

Prior to measurements, the pH-electrode three-point calibration with temperature compensation was performed. For electrode calibration, buffer solutions (traceable to SRM from NIST and PTB, pH 4.01 (phthalate), pH 7.00 (phosphate), pH 9.00 (borate), pH 4.01/pH 7.00/pH 9.00 (25 °C) Certipur®) of Merck Millipore were used.

Analyses of ions were performed with the application of Standard Reference Material NIST for cations (1000 mg/L: Na<sup>2+</sup> and NH<sub>4</sub><sup>+</sup> in H<sub>2</sub>O; 1000 mg/L: Li<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> in HNO<sub>3</sub> 0.5 mol/L) and anions (1000 mg/L: F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> in H<sub>2</sub>O) by Merck (Germany).

The analysis of metals involved the application of Standard Reference Material NIST 1643e Trace Elements in Water and Reference Material EnviroMAT ES-L-2 CRM, ES-H-2 CRM SCP SCIENCE. The calibration of the apparatus was based on reference materials by Inorganic Ventures Analytik CCS-4, CCS-6, CCS-1 and IV-ICPMS-71A. Potassium hydrogen phthalate by Nacalai Tesque (Japan) was used for the calibration of the TOC analyser.

### Results and discussion

According to AMAP (2005), accelerated melting of glaciers would result in the release of a more concentrated pulse of stored contaminants. In this study, we present the results of measurements of the physicochemical parameter (pH, SEC) and chemical parameter (DOC) as well as concentration levels of chemical compounds such as ions ( $\sum$ cations,  $\sum$ anions) and metals ( $\sum$ metals) in surface ice samples collected on four polythermal glaciers: Scottbreen and Blomlibreen (Fig. 6) and Renardbreen and Recherchebreen (Fig. 7a, b).

During sampling, it was noticed that all of the samples from Scottbreen and Blomlibreen were collected below the seasonal ELA (530 m a.s.l.) in the summer season of 2012 (Table 1). Data on ELA for Renardbreen and Recherchebreen during the collection of samples are not available. Domination of surface runoff process together with wet deposition of chemical substances were observed during the summer season of 2012.

Results of the parameters (pH, SEC, DOC) and analyte contents ( $\sum$ cations,  $\sum$ anions,  $\sum$ metals) determined in surface

ice samples collected from the glaciers studied (Blomlibreen, Scottbreen, Renardbreen, Recherchebreen) and wet precipitation are presented in Table 3.

pH values of precipitation ranged from 5.98 to 7.93, while lower pH ranges were observed in surface ice samples of Scottbreen (5.65–6.11) and Recherchebreen (5.67–6.55). Higher pH ranges were noticed in ice of samples collected from Blomlibreen (6.12–6.43) and Renardbreen (6.25–7.03). However, on the surface of Scottbreen and Blomlibreen, pH differs insignificantly from 5.65 to 6.43. pH values of Renardbreen (old tidewater glacier) and Recherchebreen (current tidewater glacier) show a broader range from 5.67 and 7.03. The highest pH value from all of the studied glaciers was detected in Renardbreen, and the lowest one in Scottbreen and Recherchebreen.

Specific electrolytic conductivity in wet precipitation ranged from 27.8 to 128.3  $\mu$ S/cm. On the studied glaciers, specific electrolytic conductivity in surface ice samples varied significantly between 4.50 and 21.2  $\mu$ S/cm. The highest values exceeding 10  $\mu$ S/cm, related to high amounts of ions, are detected in the lower part of Renardbreen (10.4  $\mu$ S/cm) and upper part of Blomlibreen (11.1  $\mu$ S/cm) and Recherchebreen (21.2  $\mu$ S/cm). Glacier ice is distinguished by very low levels of specific electrolytic conductivity. Due to the cryochemical process, frozen ice is devoid of a certain part of ions which may leave the glacier with meltwaters as a result of spring thaw (Moore et al. 2005).

Ion levels determined in surface ice samples were the lowest ( $\sum$ cations = 0.015 meq/L,  $\sum$ anions = 0.022 meq/L) in the case of Scottbreen. Interestingly, concentration ranges of ions were similar in Blomlibreen and Recherchebreen. The highest levels of ions ( $\sum$ cations = 0.279 meq/L,  $\sum$ anions = 0.236 meq/L) were detected in the upper part of Renardbreen (REN\_1). This sampling point was located in the shallow area which favours accumulation of ions in this part of the glacier. However, it is also possible to be the result of a different aspect of the accumulation area of the glacier. The aspect of glaciers should be considered in the interpretation of contributions of particular ions.

$\sum$  of metals present in wet precipitation ranged from  $27.2 \times 10^{-3}$  to  $130.4 \times 10^{-3}$  meq/L. Values of metals are higher in samples collected from the lower parts of the surface of Blomlibreen, Scottbreen and Renardbreen. They vary from  $0.779 \times 10^{-3}$  to  $1.81 \times 10^{-3}$  meq/L. These glaciers have a similar average slope of 4° (Renardbreen) and 5° (Blomlibreen, Scottbreen). There is a possibility of metal washout from particulate matter and mineral dust deposited on the glacier surface with surface runoff. In case of glaciers with a far lower average slope value (approximately 1.45°), e.g. Recherchebreen, the opposite situation is observed. In the upper part of the glacial tongue, the concentration of metals is the highest ( $2.05 \times 10^{-3}$  meq/L) among all of the studied glaciers.



**Table 3** Minimum and maximum values of determined parameters and analytes in samples of glacier ice collected from the surface of the studied glaciers and in wet precipitation samples

GLACIER	RANGES OF DETERMINED PARAMETERS/ANALYTES					
	pH [-]	SEC [μS/cm]	Σ of cations [meq/L]	Σ of anions [meq/L]	Σ of metals <sup>h</sup> [meq/L]	DOC [mg/L]
Precipitation (n=9)	5.98-7.93	27.8-128.3	-	-	27.8-130.4	-
Blomlibreen (n=3)	6.12-6.43	7.16-11.1	0.070-0.162	0.070-0.150	0.424-0.779	<LOD-0.100
Scottbreen (n=7)	5.65-6.11	4.50-8.35	0.015-0.069	0.022-0.073	0.753-1.78	<LOD
Renardbreen (n=4)	6.25-7.03	5.38-10.4	0.053-0.279	0.053-0.236	0.340-1.81	<LOD-0.375
Recherchebreen (n=3)	5.67-6.55	4.73-21.2	0.040-0.184	0.050-0.141	0.171-2.05	<LOD-0.566

For easier comparison, the values were multiplied by 1000

n number of examined samples

Dissolved organic carbon constituting a summarized parameter of all carbon atoms originating from organic matter has rather low levels. In ten samples collected from the glaciers studied, the values of DOC were below the limit of detection (0.030 mg C/L). The highest and the lowest DOC values determined on Recherchebreen reached 0.070 and 0.566 mg C/L, respectively. The glacier is located in close vicinity of the Observatoriefjellet mountain with a bird (*Alle alle*) habitat, possibly constituting a source of organic pollution.

Mean values of pH, SEC, DOC and total ions and metals determined in surface ice samples collected from the studied Arctic glaciers are presented and compared by means of a radar chart in Fig. 5. The values presented in the diagrams show both the largest similarities and differences in the chemism of surface ice samples on particular types of glaciers.

In spite of vast differences in the morphological characteristics of glaciers (Table 1), Fig. 5a shows similarities in mean values of pH and specific electrolytic conductivity, whereas the highest mean values of SEC (10.5 μS/cm) are recorded on the Recherchebreen glacier.

In comparison to the remaining glaciers, Scottbreen is distinguished by the lowest mean values of pH (5.86), SEC (6.10 μS/cm) and both the Σ of cations and anions (0.047 and 0.051 meq/L, respectively) and DOC (<LOD). Blomlibreen shows the lowest mean value of Σ of metals (0.562 × 10<sup>-3</sup> meq/L) among all of the glaciers, and Scottbreen also has one of the lowest values of DOC (0.100 mg C/L). Evident similarities are observed in mean values of pH and SEC between Blomlibreen, Scottbreen, and Renardbreen (Fig. 5a); DOC between Renardbreen and Recherchebreen (Fig. 5b); Σ of ions between Blomlibreen, Renardbreen and Recherchebreen (Fig. 5c); and Σ of metals between Scottbreen, Renardbreen and Recherchebreen (Fig. 5d).

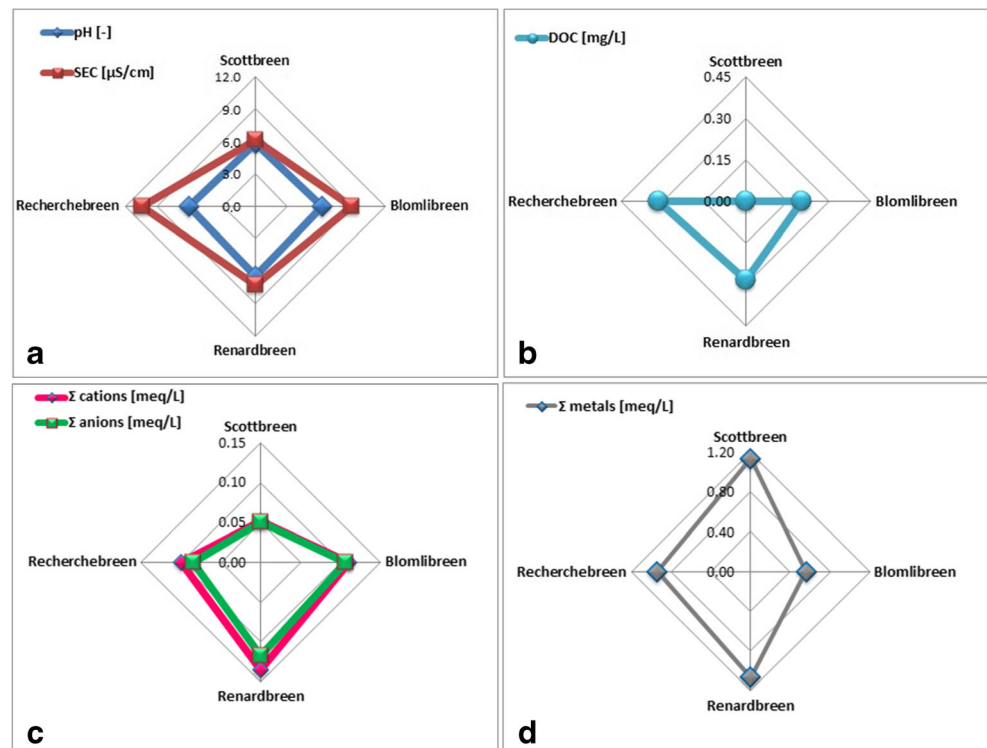
High values of SEC as well as Σ of metals clearly indicate a significant contribution of wet precipitation as a source of pollution. The potential effect of morphological parameters and geological conditions on the chemism differentiation of glacier surface is discussed in detail in chapters “Relations of physicochemical parameters/analytes to morphological parameters” and “Metals and geological conditions”.

### Spatial distribution of analytes

Due to the common accumulation area of Scottbreen and Blomlibreen, observing a lot more similarities in the chemism of the surface ice samples collected from both glaciers could be expected. Meanwhile, the mean values of the determined physicochemical parameters and analytes do not confirm the effect of this condition on the obtained results. With the exception of the mean value of Σ of metals, the remaining mean values determined in Blomlibreen ice samples are always higher than the ones from Scottbreen. A substantial difference in mean values of Σ of metals on the surface of these two glaciers with the same glaciological bed suggests a significant effect of wet and dry deposition of atmospheric pollutants and long-range atmospheric transport on this state.

In the summer season of 2012, the accumulation area did not develop on Scottbreen and Blomlibreen and the dominant process was surface runoff. Therefore, no percolation process occurred, and ablation of the glaciers in their longitudinal profile was observed (field observation). In comparison to Renardbreen and Recherchebreen, Scottbreen and Blomlibreen show similarities such as glacier area (<5 km<sup>2</sup>), total length (3500 and 2900 m, respectively), seasonal ELA (530 m a.s.l. in 2012), volume of ice (0.5 and 0.15 km<sup>3</sup>, respectively), average slope (5°) and flow velocity (<1 m year<sup>-1</sup>) (Table 1). These morphological parameters may have an effect on the different transport of impurities on their surface in

**Fig. 5** Mean values of physicochemical parameters (**a** pH, SEC; **b** DOC) and analytes (**c**  $\Sigma$ cations,  $\Sigma$ anions; **d**  $\Sigma$ metals (multiplied by 1000) determined in ice glacier samples collected from the area of Bellsund Fiord (Spitsbergen)



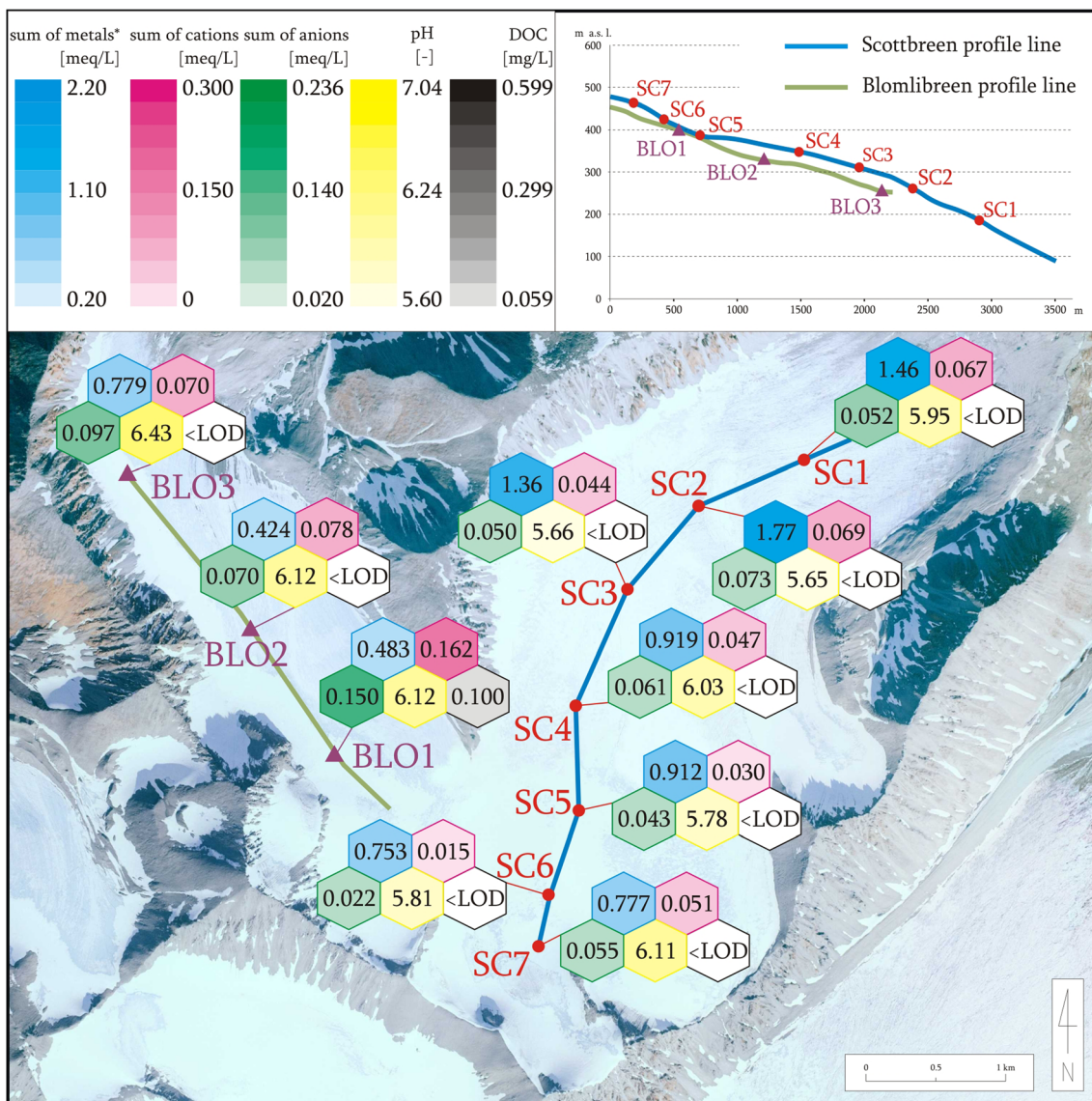
comparison to two larger glaciers which are studied in this article (Renardbreen and Recherchebreen). Moreover, both of the glaciers have polythermal regime, but they also represent the same morphological type (valley, subpolar high latitudes, ground based) with fully functioning drainage (supraglacial, inglacial, subglacial). Figure 6 presents sampling sites on the surface of two glaciers with a common accumulation area (Scottbreen and Blomlibreen). The most significant differences between these two glaciers concern the width of the glaciers (900 and 480 m, respectively) and the aspect of the tongue (NE, NNW). The diagram in Fig. 6 additionally presents the height of the glacier on which samples were collected, as well as their location on the longitudinal profile of the glaciers. Results of analyses for each sampling site are assigned to each of them.

Parameters such as glacier area, width, ELA, area of accumulation and its aspect and glacier tongue aspect may constitute factors influencing the intake of impurities. In this type of catchment (partially glaciated), glacier ablation may constitute up to 70–80 % of the total outflow (Bartoszewski et al. 2006). On both of the glaciers at the beginning of the summer season of 2012, the melting process must have been active, causing flushing of chemical substances from the surface of the glaciers to lower parts of the glacial catchment. The equilibrium line of glaciers was situated higher than the climatic equilibrium line of glaciers from the Wedel Jarsberg Land area (312 m a.s.l.) (Hagen et al. 1993). This resulted in development of the ablation area on the glaciers and low values of chemical compounds in the surface ice samples. Therefore,

the levels of DOC determined in surface samples range from <LOD to 0.100 mg/L in only one sample (BLO\_1).

An increase in total metals with a decrease in the height of glaciers was observed in both the glaciers. The concentration of metals in samples collected on Blomlibreen is twice as low as on Scottbreen, whereas the sampling site corresponds with the height of collection of samples on the adjacent glacier. Although higher levels of metals are recorded in the lower part of both the glaciers, their concentrations do not increase consistently with a decrease in altitude (e.g.  $\Sigma$ metals of SC\_3 <  $\Sigma$ metals of SC\_2 >  $\Sigma$ metals of SC\_1). The extremely visible difference in the levels of metals on the surface of the Scottbreen and Blomlibreen glaciers may result from the aspect of the accumulation area. The aspect of glaciers determining the exposition of ice to air masses probably affects the amount of impurities deposited on its surface due to wet and dry deposition and long-range atmospheric transport (LRAT).

Renardbreen and Recherchebreen are also polythermal glaciers. However, they differ from Scottbreen and Blomlibreen as well as from each other. The Recherchebreen glacier is a tidewater calving glacier. Renardbreen previously represented this type of glacier, but it is currently a ground-based glacier with fully functioning drainage, similarly as the Blomlibreen and Scottbreen glaciers. The lengths of Renardbreen and Recherchebreen are different (8300 and 22,800 m, respectively). Due to this difference, samples were collected from the same length of both glaciers in the longitudinal profile of the glaciers as shown in Fig. 7.



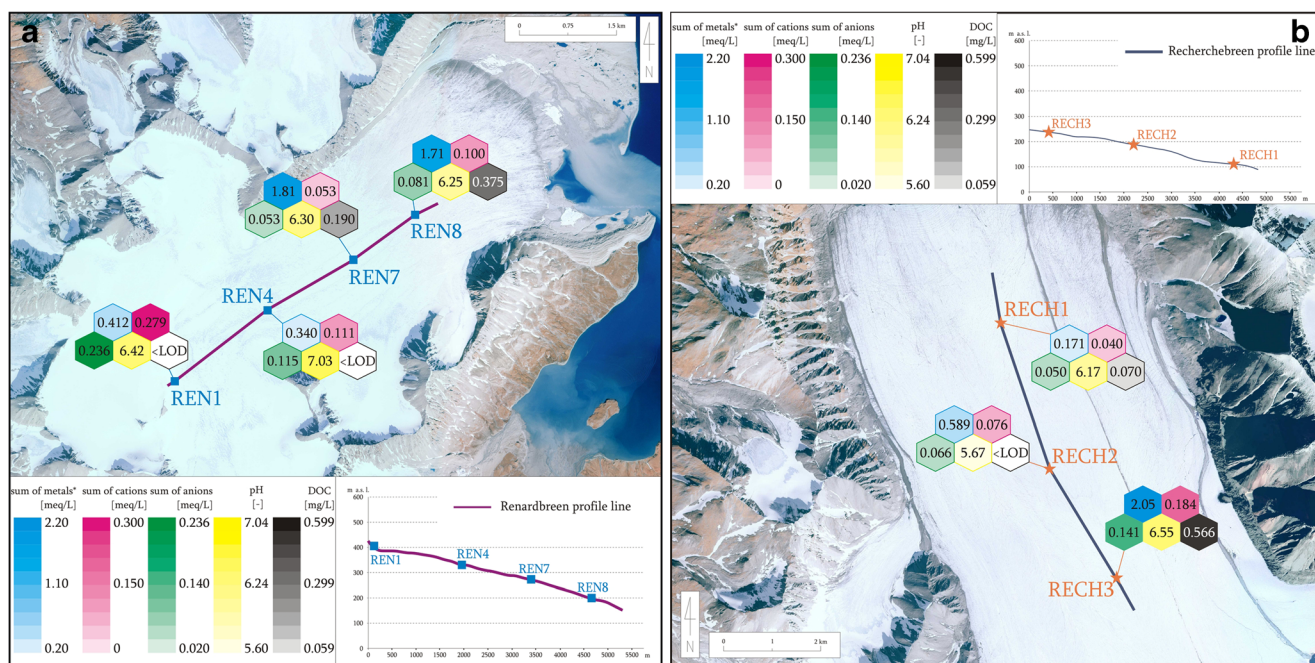
**Fig. 6** Map of Scottbreen (SC<sub>1–7</sub>) and Blomlibreen (BLO<sub>1–3</sub>) including the sampling site points and results of pH, SEC, Σcations, Σanions, Σmetals (\*multiplied by 1000) and DOC obtained based on analyses for each of them (base map: ASTER 23.07.2006, copyright: University of Silesia)

As presented in Fig. 7a, the results obtained for samples collected from Renardbreen show the same tendency of an increase in concentrations of chemical substances (Σmetals, DOC) with a decrease in the altitude of the glacial tongue altitude as in the case of Blomlibreen and Scottbreen. This phenomenon could be related to the slope of these glaciers (Table 1) favouring the accumulation of chemical substances in the lower parts of the glaciers.

The higher amount of ions in sample (REN\_1) is related to the fact that the sampling point was located in the shallower surface ice in the vicinity of the nunatak. This sample and REN\_4 are richer in ions than are layers of ice in the lower part of the glacier. Moreover, the different aspects of the accumulation area and glacial tongue, sheltered from winds on

both sides by mountain ranges, also have an effect on wet and dry deposition of chemicals on the surface of the glacier. However, in samples collected from the lower part of Renardbreen, an increase in ions and DOC with a decrease in altitude and the reverse situation in the case of Σmetals are observed. The occurrence of higher levels of Σmetals and DOC not only is a result of transport of these analytes with surface runoff and deposition in the lower part of Renardbreen but also is related with the presence of the bird (*Alle alle*) colony located in the close vicinity of Renardbreen on Activekammen.

Also in the case of Recherchebreen, observed during field work, the bird (*Alle alle*) colony on the Observatorfjellet has influence on the results of Σmetals and DOC. Next to wet and



**Fig. 7** Map of **a** Renardbreen (REN\_1,4,7,8) (on the *left*) and **b** Recherchebreen (RECH\_1–3) (on the *right*) including the sampling sites and results of pH, SEC,  $\sum$ cations,  $\sum$ anions,  $\sum$ metals (\*multiplied

by 1000) and DOC obtained based on the analysis for each of them (*base map*: ASTER 23.07.2006, copyright: University of Silesia)

dry deposition of atmospheric pollutants, this is probably one of the main causes of the highest levels of DOC detected on Recherchebreen (RECH\_3–0.566 mg/L) (Fig. 7b). Almost no slope in analytes determined on the surface of ice of Recherchebreen takes a completely different spatial distribution. The highest levels of SEC (21.2  $\mu$ S/cm) and  $\sum$ metals, as well as one of the highest levels of ions, are present in sample RECH\_3 collected in the upper part of the glacier. Considerably higher levels of metals present in the upper part of Recherchebreen may be also determined by other morphometric factors than glacier slope, such as the aspect of the tongue and also completely different geomorphological conditions and types of rocks surrounding the glacier. A decrease in  $\sum$ cations,  $\sum$ anions,  $\sum$ metals and DOC with a decrease in altitude of the glacial tongue is also observed on Recherchebreen. This is a completely reverse situation than in the case of Blomlibreen, Scottbreen and Renardbreen. Due to lower slope of the Recherchebreen (approx. 1.5°), process of wet and dry deposition dominates over process of surface runoff. Higher levels of heavy metals and DOC, next to morphological aspects, contribute also to their hydrophobic properties, which favours their accumulation in the sampling points located at higher altitudes. The main difference between Recherchebreen and the remaining studied glaciers is its morphological type as well as the fact that surface ice samples collected on the Recherchebreen glacier were collected only in the lower part of this glacier (Table 1).

### Relations of physicochemical parameters/analytes to morphological parameters

The glaciers studied significantly differ from each other, as illustrated in Table 1 presenting all morphological parameters of Blomlibreen, Scottbreen, Renardbreen and Recherchebreen. All of the glaciers, however, are subject to the same physical processes (melting, freezing) and the process of ice flowing resulting from the cross-impact force of gravity and topographic conditions, where snow accumulates forming glaciers. Due to this, the authors decided to treat the studied glaciers as a single object representative of Arctic glaciers. This procedure aims to establish a link between the morphological parameters and the chemistry of Arctic glaciers.

In this article, an attempt was made to find a relation between the determined levels of physicochemical parameters and analytes in surface samples of the studied glaciers and the morphological parameters, changes in mass balance and geometry of glaciers (Table 1), considered in Tables 4 and 5.

Tables 4 and 5 compare all of the obtained data with the morphological parameters of Scottbreen, Blomlibreen, Renardbreen and Recherchebreen provided in Table 1. Data presented in Tables 4 and 5 permit the identification of the morphological parameters of glaciers which may be referred to other Arctic glaciers.

The results of the correlation calculated for the remaining morphometric parameters and determined

**Table 4** Correlations of results of chemical analyses with morphometric parameters of the studied glaciers

Nr	MORPHOMETRIC PARAMETERS	pH[-]				SEC [μS/cm]			
		„a” factor	„b” factor	r	Correlation	„a” factor	„b” factor	r	Correlation
1	Glacier area [km <sup>2</sup> ]	0.001	6.09	0.14	-	0.030	6.75	0.33	-
2	Length of the glacier [m]	0.009×10 <sup>-3</sup>	6.05	0.18	-	0.002×10 <sup>-1</sup>	6.24	0.33	-
3	Width of the glacier [m]	0.001×10 <sup>-1</sup>	5.89	0.56	+	0.003×10 <sup>-1</sup>	7.04	0.13	-
4	Max. elevation [m a.s.l.]	-0.002	7.33	0.26	-	0.014	-2.14	0.19	-
5	Min. elevation [m a.s.l.]	0.009 ×10 <sup>-1</sup>	6.21	0.21	-	-0.004	8.03	0.08	-
6	Aspect [°]	-0.002	6.60	0.63	+	-0.008×10 <sup>-2</sup>	7.66	0.03 <sup>10-1</sup>	-
7	Volume [km <sup>3</sup> ]	0.002	6.10	0.09	-	0.096	6.88	0.34	-
8	Average slope [°]	-0.559	6.35	0.20	-	-0.996	11.8	0.33	-
9	Flow velocity [-]	0.004	6.08	0.16	-	0.089	6.75	0.33	-
		DOC [mg/L]				Σmetals [meg/L]			
		„a” factor	„b” factor	r	Correlation	„a” factor	„b” factor	r	Correlation
1	Glacier area [km <sup>2</sup> ]	0.001	0.192	0.31	-	-0.002×10 <sup>-4</sup>	0.989	0.01	-
2	Length of the glacier [m]	0.008×10 <sup>-3</sup>	0.162	0.33	-	-0.003×10 <sup>-5</sup>	0.987	0.04	-
3	Width of the glacier [m]	0.004×10 <sup>-2</sup>	0.116	0.36	-	0.002×10 <sup>-2</sup>	0.927	0.08	-
4	Max. elevation [m a.s.l.]	0.007×10 <sup>-1</sup>	0.236	0.28	-	0.001	0.319	0.09	-
5	Min. elevation [m a.s.l.]	-0.011×10 <sup>-1</sup>	0.327	0.55	+	-0.002	1.13	0.21	-
6	Aspect [°]	-0.002×10 <sup>-1</sup>	0.296	0.12	-	-0.003×10 <sup>-1</sup>	1.05	0.06	-
7	Volume [km <sup>3</sup> ]	0.003	0.206	0.29	-	-0.001	0.992	0.02	-
8	Average slope [°]	-0.002×10 <sup>-1</sup>	0.296	0.13	-	0.006	0.962	0.01	-
9	Flow velocity [-]	0.011	0.215	0.24	-	-0.006×10 <sup>-1</sup>	0.990	0.01	-
		Σcations [meg/L]				Σanions [meg/L]			
		„a” factor	„b” factor	r	Correlation	„a” factor	„b” factor	r	Correlation
1	Glacier area [km <sup>2</sup> ]	0.003 ×10 <sup>-1</sup>	0.079	0.31	-	0.001 ×10 <sup>-1</sup>	0.079	0.11	-
2	Length of the glacier [m]	0.002×10 <sup>-3</sup>	0.073	0.21	-	0.009×10 <sup>-4</sup>	0.076	0.13	-
3	Width of the glacier [m]	0.001×10 <sup>-2</sup>	0.054	0.44	+/-	0.001×10 <sup>-2</sup>	0.059	0.39	-
4	Max. elevation [m a.s.l.]	-0.002×10 <sup>-1</sup>	0.201	0.14	-	-0.002×10 <sup>-1</sup>	0.231	0.22	-
5	Min. elevation [m a.s.l.]	-0.001 ×10 <sup>-1</sup>	0.102	0.18	-	-0.006×10 <sup>-2</sup>	0.089	0.09	-
6	Aspect [°]	-0.002 ×10 <sup>-1</sup>	0.150	0.46	+/-	-0.002 ×10 <sup>-1</sup>	0.132	0.45	+/-
7	Volume [km <sup>3</sup> ]	0.007×10 <sup>-1</sup>	0.082	0.15	-	0.003×10 <sup>-1</sup>	0.081	0.07	-
8	Average slope [°]	-0.011	0.135	0.23	-	0.006	0.079	0.16	-
9	Flow velocity [-]	0.001	0.079	0.20	-	0.004 ×10 <sup>-1</sup>	0.079	0.13	-

physicochemical parameters and analytes of the studied glaciers are presented in Table 4. The visualisation of the correlation degree of the data obtained with glacier parameters is considered as follows: + ( $r > 0.5$ )—no justification for rejecting the hypothesis; +/- ( $r = 0.4–0.5$ )—suspected relation; - ( $<0.4$ )—no relation.

Based on the values of correlations between results of chemical analyses and morphometric parameters of glaciers (presented in Table 4), it is possible to prove a considerable impact on the physicochemical parameters and concentration levels of chemical substances on the glaciers confirmed by strong correlations between pH and glacier width or aspect

**Table 5** Correlations between chemical parameters and mass balance and geometric changes of the glaciers

Nr	MASS BALANCE AND GEOMETRIC CHANGES	pH [-]				SEC [ $\mu\text{S}/\text{cm}$ ]			
		„a” factor	„b” factor	r	Correlation	„a” factor	„b” factor	r	Correlation
1	Avg. terminus position change [ $\text{m}\text{y}^{-1}$ ]	$-0.003 \times 10^{-2}$	6.12	$0.04^{10^3}$	-	-0.017	6.84	0.01	-
2	Area changes [ $\text{km}^2$ ]	-0.015	6.05	0.23	-	-0.21	6.52	0.31	-
3	Thickness changes of ablation area (<350 m a.s.l.)	0.005	6.33	0.32	-	0.057	9.85	0.31	-
4	Thickness changes of accumulation area (>350 m a.s.l.)	-0.015	6.06	0.23	-	-0.210	6.72	0.30	-
1	Average terminus position change [ $\text{m}\text{y}^{-1}$ ]	DOC [ $\text{mg}/\text{L}$ ]				$\Sigma$ metals [ $\text{meg}/\text{L}$ ]			
		„a” factor	„b” factor	r	Correlation	„a” factor	„b” factor	r	Correlation
		$-0.005 \times 10^{-1}$	0.114	0.43	+/-	$0.001 \times 10^{-1}$	0.991	0.02	-
2	Area changes [ $\text{km}^2$ ]	-0.011	0.158	0.36	-	-0.001	0.978	0.01	-
3	Thickness changes of ablation area (<350 m a.s.l.)	$0.042 \times 10^{-1}$	0.138	0.37	-	0.010	0.609	0.35	-
4	Thickness changes of accumulation area (>350 m a.s.l.)	-0.012	0.164	0.38	-	-0.004	0.969	0.03	-
1	Avg. terminus position change [ $\text{m}\text{y}^{-1}$ ]	$\Sigma$ cations [ $\text{meg}/\text{L}$ ]				$\Sigma$ anions [ $\text{meg}/\text{L}$ ]			
		„a” factor	„b” factor	r	Correlation	„a” factor	„b” factor	r	Correlation
		$-0.007 \times 10^{-2}$	0.084	0.09	-	$-0.007 \times 10^{-3}$	0.083	0.01	-
2	Area changes [ $\text{km}^2$ ]	-0.034	0.827	0.30	-	-0.002	0.075	0.17	-
3	Thickness changes of ablation area (<350 m a.s.l.)	0.001	0.121	0.29	-	$0.008 \times 10^{-1}$	0.115	0.35	-
4	Thickness changes of accumulation area (>350 m a.s.l.)	-0.003	0.075	0.24	-	-0.002	0.077	0.16	-

and DOC and minimum glacier elevation. Moreover, there is a noticeable relation in case of lower moderate correlation ( $r < 0.50$ ) recorded between  $\Sigma$ ions and glacier aspect and  $\Sigma$ cations and glacier width. The lowest values of moderate correlation ( $r < 0.40$ ) are considered as morphometric parameters with no relation to the chemistry of surface ice on the glaciers.

Notice that  $\Sigma$  of metals has the lowest correlation with any of the morphometric parameters. Except for the weak correlation ( $r = 0.21$ ) between  $\Sigma$  metals and minimum glacier elevation, the remaining correlations are substantially below 0.10. This suggests none or very weak impact of morphometric parameters on the occurrence of metals on the glacier surface, at least during the summer season.

The changes in mass balance and geometry of the glaciers are very evident due to the fast and strong response of small

Arctic glaciers to climate warming (ACIA 2005). Due to the intensive melting of glaciers, many of them may become redistributors of anthropogenic pollutants accumulated in the ice layers of these cryosphere elements over the years.

The remaining results of correlation determined for parameters referring to changes in the glacial mass balance and determined physicochemical parameters and analytes of the studied glaciers are presented in Table 5. The degree of correlation between the obtained data and glacier parameters is considered as follows: + ( $r > 0.5$ )—no justification for rejecting the hypothesis; +/- ( $r = 0.4-0.5$ )—suspected relation; - ( $<0.4$ )—no relation.

Table 5 shows a moderate correlation ( $r = 0.43$ ) for DOC and average terminus position change. This suggests suspected impact of this parameter on the determined levels of DOC in surface ice samples. Lower values of moderate

correlation ( $r < 0.40$ ) are considered parameters with no relation to the chemistry of surface ice on the glaciers.

Figure 8 presents graphs of the relations between the determined physicochemical parameters and analytes and elements of morphological characteristics of the glaciers. The graphs show the mean values of the determined parameters and analytes for each glacier: Blomlibreen (BLO), Scottbreen (SCO), Renardbreen (REN) and Recherchebreen (RECH), on the background of their morphological parameters.

Among all of the elements of morphological characteristics of the glaciers mentioned in Table 1, the strongest correlations between physicochemical parameters and analytes are observed in the case of the glacier aspect. According to the data in Table 4, aspect is a parameter with a potential impact on  $\Sigma$  of ions. This parameter determines the glacier exposure to incoming air masses which may transport pollutants from both local sources and further areas of the northern hemisphere.

The parameter with the second strongest correlation with the chemistry of the glaciers is glacier width. It probably insignificantly affects the determined pH (Table 4) as well as  $\Sigma$ cations and  $\Sigma$ anions whose correlation with this parameter is lower than  $r = 0.40$ . Apart from wet and dry deposition, the source of cations and anions may also be weathering of rock debris and dust present on the glacier surface.

Another parameter is minimum elevation of the glacier. It probably affects values of DOC. It is possible that organic substances are flowing down with melting or precipitation waters to the lower parts of the glacier. It is also possible that glaciers distinguished by a low value of minimum elevation are much more accessible to a wide range of animals living in the vicinity of the glacier. Correlations between minimum elevation and  $\Sigma$  of metals as well as SEC are weak ( $r = 0.21$

and  $r = 0.08$ , respectively). The variations of metals and specific electrolytic conductivity on the surface of the glaciers cannot be explained by this parameter.

### Metals and geological conditions

The Blomlibreen, Scottbreen and Renardbreen glaciers are located within the Renardbreen Block, divided by secondary faults with north-south orientation. The Renardbreen Block is predominantly developed by Proterozoic sediments represented by the Bergskarget Formation (Deilegga Group) and two-part Kapp Lyell Formation (Birkenmajer 1975, 2004; Czerny et al. 1993 ). The Bergskarget Formation is particularly represented by a complex of green and black phyllites and chlorite slates with dolostone and quartite interclastations. The Kapp Lyell Formation is composed of yellow and green diamictites particularly containing quartite and carbonate, rarely granite interclastations, deposited in the silicocarbonate matrix with admixtures of white mica.

Table 6 presents data concerning the spatial distribution of metals on the glaciers, and geological data of the bedrock underlying the glaciers.

The common feature of the rocks of the Kapp Lyell Formation is pyritic mineralisation ( $FeS_2$ ) of the matrix, particularly intensive in diamictites with granite clasts also enriched in pyrite (Dallmann et al. 1990). The recorded high concentrations of iron and zinc ions in the horizontal distribution within the glaciers of the Renardbreen Block are closely associated with the geochemical conditions of the bedrock. The increased content of zinc suggests hydrothermal activity related to tectonic discontinuities within the tectonic block. In the vertical distribution of concentrations of metals, increasing metal

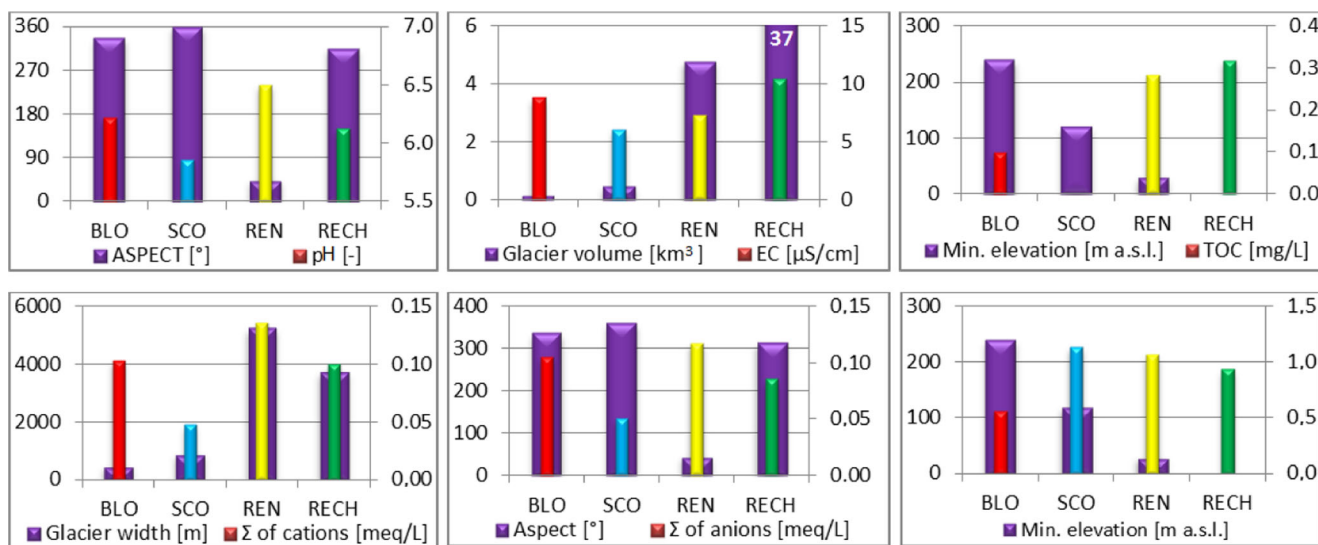


Fig. 8 Relations between elements of morphological characteristics of the glaciers and the determined physicochemical parameters and analytes

concentrations in the terminal parts of the glaciers draw attention (particularly in the case of Scottbreen and Renardbreen). Polythermal glaciers such as the analysed objects are distinguished by thermal complexity involving freezing of the cold terminus to the bedrock and retaining warm thermal regime in the accumulative part (Baranowski 1977; Grabiec et al. 2009, Grabiec et al. 2010a, b). Such thermal distribution and increased friction of the glacier against the bedrock in the terminal zone cause an increase in the emergence velocity. This results in the development of strike-slip dislocations within the terminal zone—small faults perpendicular to the movement of the glacier along which the mineral material of the bedrock is transported towards the surface of the glacier. This hypothesis is confirmed by the observation of metal concentrations in the ablation zone of the glacial tongue of Recherchebreen decreasing with altitude. It is a glacier entering the sea, supported by

the bottom (Glazovsky et al. 1991; Hagen et al. 1993). In such a case, friction against the bedrock in the terminal zone is considerably reduced, intensive tension occurs and movement vectors are directed downwards (Jania 1988, 1997). In the ablation part of the glacial tongue of Recherchebreen, the factor determining the spatial distribution of metals should be sought for not in the tectonics of the glacier's terminus, but in the surface distribution of sources of supply of mineral material. The surface of the Recherchebreen glacier includes belts of medial moraines consisting of material originating from exarational destruction of nunataks separating the supply glaciers. The course of the belts of medial moraines, as well as foliation folds visible in satellite and aerial images (ASTER 10 July 2006; GoogleMaps 2012), suggests a completed active surge phase (Post 1969; Sharp 1988; Jania 1988) resulting in tension of the glacier terminus (thinning and elongation of the glacier with the

**Table 6** Ranges of metals recorded on the glaciers and characteristics of rocks developing the bed of glaciers

No.	Rocks		High ranges of metal concentration	Low ranges of metal concentration
1	Blomlibreen			
	30—diamictite (mainly quartzite clasts SiO <sub>2</sub> )	BLO_3	1–15 µg/L Fe < Mn 15–25 µg/L Zn	<1 µg/L Pb < B < Al < Ni < Cu < Ba
	27—diamictite (mainly dolomites clasts CaMg(CO <sub>3</sub> ) <sub>2</sub> )	BLO_2	1–15 µg/L Fe < Zn	<1 µg/L Pb < Ni < B < Mn < Cu < Ba < Sr
	31—diamictite (mainly dolomite and quartzite clasts- CaMg(CO <sub>3</sub> ) <sub>2</sub> , SiO <sub>2</sub> )	BLO_1	1–15 µg/L Sr < Fe < Zn	<1 µg/L Al < Ni < Pb < B < Ba < Cu < Mn
2	Scottbreen			
	30—diamictite (mainly quartzite clasts) SiO <sub>2</sub>	SC_7	1–15 µg/L Sr < Zn < Fe	<1 µg/L Pb < Rb < Ni < Al < Cu < Mn < Ba
	31—diamictite (mainly dolomite and quartzite clasts SiO <sub>2</sub> )	SC_6	1–15 µg/L Zn < Fe	<1 µg/L Al < Pb < Ni < Cu < Ba < Mn < Sr
		SC_5	1–15 µg/L Zn < Fe	<1 µg/L Pb < Al < Ni < Cu < Ba < Mn < Sr
	27—diamictite (mainly dolomites clasts) CaMg(CO <sub>3</sub> ) <sub>2</sub>	SC_4	1–15 µg/L Zn < Fe	<1 µg/L Pb < Ni < Cu < Al < Ba < Mn < Sr
		SC_3	1–15 µg/L Ba < Sr < Zn 15–25 µg/L Fe	<1 µg/L Cr < Pb < Rb < Ni < Al = Cu < Mn
		SC_2	1–15 µg/L Al < Sr < Zn 15–25 µg/L Fe	<1 µg/L Cr = Se < Pb < Rb < B < Mn < Ni < Ba = Cu
		SC_1	1–15 µg/L Zn 15–25 µg/L Fe	<1 µg/L Pb < Cr = Rb < Se < Mn < Ni < Cu < Al < Sr
3	Renardbreen			
	30—diamictite (mainly quartzite clasts SiO <sub>2</sub> )	REN_1	1–15 µg/L Zn	<1 µg/L Pb < Al < B < Ni < Cu < Sr < Ba < Fe < Mn
	31—diamictite (mainly dolomite and quartzite clasts CaMg(CO <sub>3</sub> ) <sub>2</sub> )	REN_4	1–15 µg/L Zn	<1 µg/L Pb < Fe < B = Al < Rb < Ni < Cu < Mn < Ba < Sr
	28—phillite with clasts	REN_7	1–15 µg/L Ni < Ba < Cu < Fe < Sr	<1 µg/L Cr < Rb < Pb < B < Al < Mn
	29—diamictite (mainly limestone clasts CaCO <sub>3</sub> )	REN_8	1–15 µg/L B < Al < Ni < Cu < Ba < Sr < Mn 15–25 µg/L Zn	<1 µg/L Cr < Rb < Pb < B < Al < Mn
4	Recherchebreen			
	38—diamictite (Konglomeratfjellet),	RECH_3	1–15 µg/L Al < B < Ni < Ba < Cu < Sr < Mn 15–25 µg/L Zn	<1 µg/L U < Pb < Cd < Cr < Rb < Fe
	36—carbonate rocks (dolostone, limestone CaMg[CO <sub>3</sub> ] <sub>2</sub> )			
	50—dolostone- (CaMg[CO <sub>3</sub> ] <sub>2</sub> )	RECH_2	1–15 µg/L Sr < Mn < Ni < Zn	<1 µg/L Be = U = Pb < Rb < Al < B < Fe < Cu < Ba
	49, 50—Fe-ore-bearing dolostone CaMg[CO <sub>3</sub> ] <sub>2</sub>	RECH_1	1–15 µg/L Zn	<1 µg/L Cd < Rb < Al < Li < Fe < Sr < Mn < Cu < Ba < Co = Ni
	49—augengneiss and feldspathic quartzite,			
	50—massive dolomites CaMg(CO <sub>3</sub> ) <sub>2</sub>			
	51—limestone CaCO <sub>3</sub>			
53—phillite- (KAlSi <sub>3</sub> O <sub>8</sub> -NaAlSi <sub>3</sub> O <sub>8</sub> -CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> )				

Dallmann et al. 1990; Birkenmajer 2004; Kowallis and Craddock 1982



**Table 7** Concentration ranges of metals detected in the samples of ice collected from the surface of the studied glaciers

Metals	Precipitation (n=5) 13-24.07	Recherchebreen (n=3) 28.07	Scottbreen (n=7) 31.07	Scottbreen (n=10) (Chmiel et al. 2009)	Precipitation (n=8) 13.07-10.08	Renardbreen (n=8) 18.08	Blomlibreen (n=3) 19.08
Concentration Ranges ( $\Sigma$ metals) [ $\mu\text{g/L}$ ]=ppb							
<b>Li<sup>11</sup></b>	0.04-0.46 (0.89)	<LOD	<LOD	n.d.	<LOD-0.46 (1.05)	<LOD	<LOD
<b>Be<sup>12</sup></b>	<LOD	<LOD-0.02	<LOD	n.d. <sup>13</sup>	<LOD	<LOD	<LOD
<b>B</b>	2.91-6.59 (22.84)	0.25-2.31	<LOD- 0.26	n.d.	2.86-7.93 (39.84)	0.08-1.09	0.20-0.25
<b>Al</b>	0.94-3.11 (8.83)	0.18-1.41	0.11-2.85	n.d.	0.94-3.12 (16.51)	0.11-1.15	<LOD-0.27
<b>V</b>	<LOD-0.42 (0.53)	<LOD	<LOD	n.d.	<LOD-0.51 (1.32)	<LOD	<LOD
<b>Cr</b>	0.29-1.21 (3.64)	<LOD-0.16	<LOD- 0.10	n.d.	0.29-1.35 (6.60)	<LOD-0.12	<LOD
<b>Mn</b>	0.32-7.56 (16.26)	1.11-5.20	0.22-0.92	<50	0.32-11.60 (41.17)	0.53-3.22	0.56-1.33
<b>Fe</b>	1.41-28.32 (41.41)	0.30-0.75	10.86- 17.20	<10-100	1.41-28.32 (77.98)	0.10-1.98	1.12-1.31
<b>Co</b>	0.31-0.85 (2.67)	<LOD	<LOD	n.d.	0.31-0.85 (4.12)	<LOD	<LOD
<b>Ni</b>	0.42-1.30 (3.91)	1.27-2.34	0.13-0.72	n.d.	0.42-1.86 (8.92)	0.29-1.51	0.19-0.27
<b>Cu</b>	n.d.	0.65-3.25	0.27-0.87	<1	n.d.	0.41-1.94	0.57-0.64
<b>Zn</b>	n.d.	11.16-23.35	2.13-12.90	1-10	n.d.	6.32-40.91	6.95-17.11
<b>As</b>	<LOD-0.10 (0.10)	<LOD	<LOD	n.d.	<LOD-0.15 (0.25)	<LOD	<LOD
<b>Se</b>	n.d.	<LOD	<LOD- 0.15	n.d.	n.d.	<LOD	<LOD
<b>Rb</b>	n.d.	0.11-0.26	<LOD- 0.19	n.d.	n.d.	<LOD-0.30	<LOD
<b>Sr</b>	7.57-14.38 (51.01)	1.00-3.89	0.65-3.08	n.d.	7.57-14.38 (83.51)	0.51-2.17	0.80-1.01
<b>Cd</b>	0.11-0.36 (1.16)	<LOD-0.10	<LOD	<1	0.11-0.74 (2.68)	<LOD	<LOD
<b>Cs</b>	<LOD-0.06 (0.07)	<LOD	<LOD	n.d.	<LOD-0.06 (0.07)	<LOD	<LOD
<b>Ba</b>	n.d.	0.86-3.14	0.30-1.44	n.d.	n.d.	0.60-1.90	0.41-0.85
<b>La</b>	<LOD-0.06 (0.11)	<LOD	<LOD	n.d.	<LOD-0.06 (0.15)	<LOD	<LOD
<b>Ir</b>	<LOD	<LOD	<LOD	n.d.	<LOD	<LOD	<LOD
<b>Pb</b>	0.22-2.90 (5.49)	0.02-0.04	0.04-0.17	<1-10	0.22-2.90 (7.51)	0.04-0.45	0.14-0.22
<b>Th</b>	<LOD	<LOD	<LOD	n.d.	<LOD	<LOD	<LOD
<b>U</b>	<LOD-0.06 (0.07)	0.02-0.02	<LOD	n.d.	<LOD-0.06 (0.07)	<LOD	<LOD

Literature data from polar summer 2005 available for Scottbreen glacier are added for comparison (Chmiel et al. 2009). No data Yellow not detected on the surface of any of the glaciers, Green detected only on Recherchebreen

movement vector directed downwards). The diversity of rocks within the Recherchebreen basin, complex lithology of the tectonic units of the Chamberlindalen Block and Martinfjella Block and intensive mineralisation of rocks with ore minerals (iron, lead, zinc and manganese compounds) account for the spatial and qualitative differentiation of metals within the terminus of Recherchebreen.

Table 7 presents the ranges of concentration levels of particular metals present in the samples of wet deposition and surface ice samples collected from four glaciers (Blomlibreen, Scottbreen, Renardbreen and Recherchebreen).

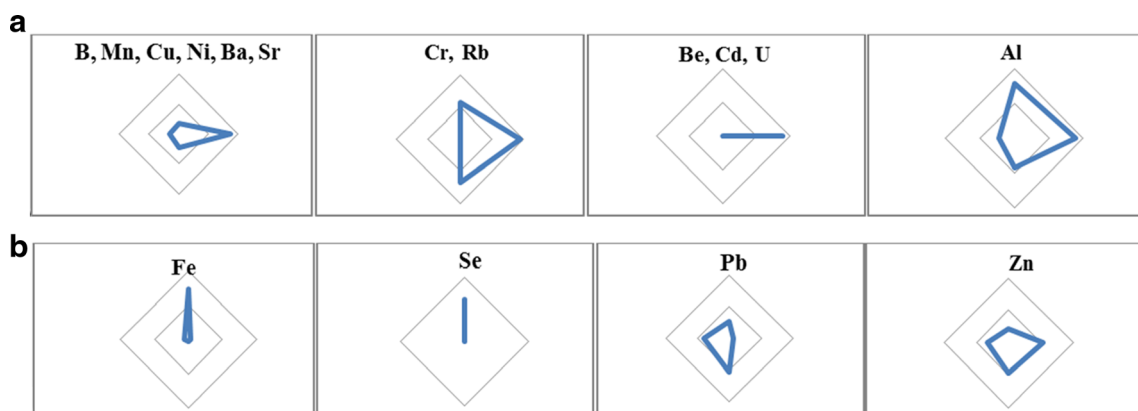
The contribution of metals present in the collected precipitation samples was adapted to the time of collection of ice surface samples from particular glaciers and was divided into two periods (18–24 July and 18 July to 10 August). Values of metals such as Be, Ir and Th analysed in atmospheric precipitation samples collected between 18 and 24 June were <LOD. The remaining metals detected in the samples during that time were within the following ranges: <1 µg/L (Cs, U, As, La, V, Li); 1–15 µg/L (Cd, Co, Cr, Ni, Pb, Al); 15–25 µg/L (Mn, B) and 25–55 µg/L (Fe, Sr). In the second period from 18 July to 10 August, also no occurrence of three metals (Be, Ir, Th) was detected. After 24 July, however, an increase in concentrations of particular metals in precipitation was observed. Due to this, in the period from July 18 to August 10, the concentration ranges of a particular sum of metals changed as follows: <1 µg/L (Cs, U, La, As); 1–15 µg/L (Li, V, Cd, Co, Cr, Pb, Ni); 15–25 µg/L (Al); 25–55 µg/L (B, Mn) and 55–350 µg/L (Fe, Sr).

The results presented in Table 7 suggest that wet deposition of metals occurring in atmospheric precipitation has a considerable role in supplying metals to the glaciers. These analytes may flow down the glacier, mix with ablation waters and leave the glacier surface with glacial runoff. Another possibility for them is to permeate to the inner layers of ice, and accumulate there, or to join the drainage waters of the polythermal glaciers.

Figure 5d shows that the total values of  $\Sigma$ metals for Scottbreen, Renardbreen and Recherchebreen were very similar. In order to better visualise the obtained results listed in Table 7, we presented  $\Sigma$  of particular metals in radar graphs in Fig. 9 with the following directions corresponding to the studied glaciers (←Blomlibreen; ↑ Scottbreen; →Recherchebreen; ↓ Renardbreen).

Figure 9 serves exclusively as the function of visualization of the contribution pattern of metals occurring in the surface ice samples collected from the glaciers. It is not intended to present their values. Although metals occur in samples at different levels of concentration, the proportion between them is the same, as shown in Fig. 9a.

Graphs in Fig. 9a. show that a vast number of metals occur at the highest levels (B, Mn, Cu, Ni, Ba, Sr, Cr, Rb, Al) or are only present in Recherchebreen (Cd, U). Similarities in values of B, Mn, Cu, Ni, Ba and Sr on the surface of four glaciers suggest a correlation between them. The relatively high concentrations of B, Ba and Sr suggest the marine origin. Elements such as Fe, Mn, Al, Zn and Rb can be derived from the leaching of dust accumulated on the glacier of local origin and long transport of anthropogenic origin. Recherchebreen, as a tidewater glacier without significant slope of the glacial tongue, has a huge predisposition to accumulate much more atmospheric contaminants (e.g. metals) than other glaciers studied in this article. However, the presence of cadmium and uranium, not detected on any other of the glaciers, is most probably related to the geological conditions of the surroundings of the glacier. Also significant amounts of selenium (typical of samples of ice collected on Scottbreen), iron and aluminium are visible in Fig. 9a, b. Graphs in Fig. 9b, however, show that metals such as Fe, Se or Pb were not detected or are present on the Recherche glacier in very low concentrations in comparison to their presence on Scottbreen (Fe, Se) and Renardbreen and Blomlibreen (Pb). A map of geological conditions of the studied glaciers in Wedel Jarlsberg Land is described in details by Dallmann et al. (1990).



**Fig. 9** Occurrence of particular metals on the surface of the glaciers (← Blomlibreen; ↑ Scottbreen; → Recherchebreen; ↓ Renardbreen)

## Conclusions

Based on the results, levels of chemical compounds on glaciers are also frequently observed to be dependent on the height and slope of glaciers. Higher levels of chemical substances in the lower part of glaciers (Blomlibreen, Scottbreen, Renardbreen) are probably the result of their transport with melting waters of glaciers or their flush from the surface with precipitation waters.

Glaciers of the same morphological type (Blomlibreen, Scottbreen, Renardbreen) show similarities in the spatial distribution of chemical compounds of natural or anthropogenic origin. Recherchebreen representing tidewater glaciers is significantly different from the remaining studied glaciers. Both the spatial distribution of chemical substances and their levels are significantly higher on Recherchebreen than on ground-based type of glaciers (Figs. 6 and 7a, b). The factor significantly affecting the chemistry of the glacier surface is the development of the accumulation zone in the upper part of the glacier. This permits the accumulation of part of impurities deposited in the upper part of the glacier. As a consequence, higher amounts of the analysed compounds are observed both in the upper part of the glacier as in its lower part, where they are flushed out by precipitation waters (Fig. 6a). The presence of the analytes at various concentration levels on particular glaciers is strongly dependent on the exposure of the glaciers and their minimum elevation (Tables 4 and 5).

Dry and wet deposition of substances supplied with atmospheric precipitation is of basic importance in the development of the level of metal elements accumulated in ice on the glacier surface. Deposition of silts transported from local peaks is equally important. In contact with water, they are subject to dissolution processes. Intensive leaching particularly occurs in the summer season. Higher concentrations of the elements in the upper part of the glacier may be caused by the meteorological conditions and the related process of intensive melting/washing out of substances accumulated on its surface.

The research showed that despite the presence of metals in precipitation, their spatial distribution on glaciers with a significantly developed ablation area is strongly related to the geological bed of the glaciers. The spatial distribution of metal concentrations on the studied glaciers reflects the geochemical environment of their bedrock. This conclusion is confirmed by very weak correlations between morphological parameters and levels of metals determined on the glaciers (Tables 4 and 5).

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