

Chemical composition of groundwaters in the Horsund region, southern Spitsbergen

Tomasz Olichwer, Robert Tarka and Magdalena Modelska

ABSTRACT

Chemical composition of groundwaters was investigated in the region of the Hornsund fjord (southern Spitsbergen). The investigations were conducted during polar expeditions organized by the University of Wrocław in two summer seasons of 2003 and 2006. Three zones of groundwater circulation: suprapermafrost, intrapermafrost and subpermafrost, were identified in areas of perennial permafrost in the region of Hornsund. The zone of shallow circulation occurs in non-glaciated (suprapermafrost) and subglacial areas. In this zone, the chemical composition of groundwater originates from initial chemical composition of precipitation, mineralogical composition of bedrock, oxidation of sulphides and dissolution of carbonates. The intermediate system of circulation is connected with water flow inside and below perennial permafrost (intrapermafrost and subpermafrost). In this zone, the chemical composition of groundwater is mainly controlled by dissolution of carbonates, ion exchange processes involving Ca^{2+} substitution by Na^+ , and oxidation of sulphides under oxygen-depleted conditions. The subpermafrost zone (deep groundwater circulation) occurs in deep-tectonic fractures, which are likely conduits for the descent of shallow groundwater to deeper depths. In this zone, the groundwater shows lower mineralization comparing to intrapermafrost zone and has a multi-ion nature $\text{Cl-HCO}_3\text{-Na-Ca-Mg}$.

Key words | chemical composition, groundwaters, Hornsund region

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INTRODUCTION

This article presents the research review of the chemical composition of groundwaters circulating in different hydrogeological systems in southern Spitsbergen, based on the example of the Horsund region. Water samples were collected during the 16th (2003) and 19th (2006) scientific expeditions of the Wrocław University to Horsund, Spitsbergen and were summarized with a large number of previous hydrogeological investigations which have been conducted in this region since the 1970s.

In polar areas, most of water occurs in the form of ice covers, glaciers and permafrost. In these regions, an active hydrological cycle relates to short summer periods when intensive melting of snow and glaciers, as well as of the top layer of perennial permafrost, takes place.

Therefore, melting and freezing of water influences surface and subsurface water circulation (van Everdingen 1990).

In the Hornsund region, various occurrences of groundwater have been observed such as ephemeral springs related to snow melt and water outflows from perennial permafrost in glacier marginal zone (Krawczyk 1992), karst springs (Pulina 1977; Leszkiewicz 1982), and long-term thermal springs (Orvin 1934, 1944; Krawczyk 1990; Pociask-Karteczka 1990). The diversity of chemical composition in individual outflows encourages determination of the regularity of the occurrence of groundwater flows and the origin of their chemical composition. Additionally, previous observations reported for other regions of Spitsbergen give

detailed characterization of the occurrence and interpretation of origin of chemical composition of the groundwater in Polar Region (Haldorsen & Lauritzen 1993; Banks *et al.* 1998; Wadham *et al.* 1998, 2000; Haldorsen *et al.* 1996; Cooper *et al.* 2002).

Observations in the Hornsund region during the period 1972–2006 allow investigation of the temporal variability of groundwater chemical composition in relation to observed changes of climate in that region (Marsz & Styszyńska 2007; Haldorsen *et al.* 2009).

STUDY AREA

The study area is located in the region of Hornsund fjord (76°57'–77°12' N), which is the farthest southern fjord of Spitsbergen separating Sørkappland (the Land of Southern Cape) in the south from the Wedel Jarlsbergland in the north (Figure 1). The fjord landscape is dominated by several mountain ranges arranged in the form of meridional chains and by coastal lowlands originated from the uplifted sea terraces. The highest peak of

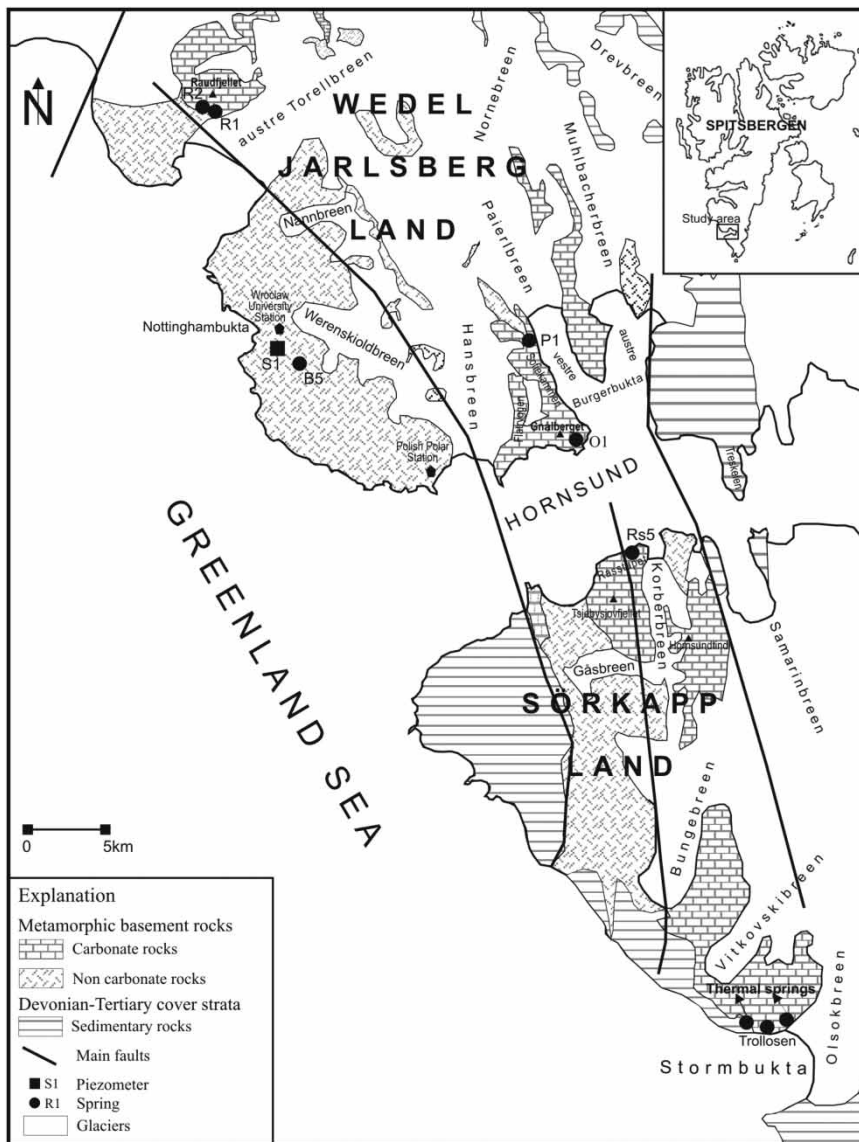


Figure 1 | A simplified geological map of Hornsund region and location of water sampling points in 2003 and 2006.

the southern Spitsbergen is Hornsundtind, rising to 1,431 m a.s.l.

Svalbard has a long geological history reflected in four major geologic units: Tertiary basin sediments, Carboniferous through Cretaceous platform cover sequence, Devonian basin sediments, and metamorphic basement rocks.

The oldest formations, so-called basement, consist of Precambrian, Cambrian and Ordovician rocks (Figure 1). The study area comprises strongly metamorphosed Proterozoic rocks being part of the Hecla Hoek Succession. This lithostratigraphic complex is represented by paragneisses, mica-schists with marbles, quartzites, schists, amphibolites, greenschists, gneisses, conglomerates and limestones (Birkenmajer 1990).

The Devonian succession at Hornsund begins with fluvial red conglomerates, sedimentary breccias and sandstones, limestones and schists with limestones. Beginning with the Lower Carboniferous, the study area became part of the continental platform and is dominated by conglomerates, sandstones, shales, mudstones, limestones, and dolomites. Triassic and Jurassic rocks are represented by conglomerates, shales, mudstones, sandstone and limestones.

The Mesozoic magmatism is mainly represented by basalts (sills and dikes). The Tertiary formations overlie the Mesozoic magmatic rocks and are represented by sandstones, shales and conglomerates. During the Tertiary period, the western part of Spitsbergen was subject to strong tectonic deformations. The Late Pleistocene and Holocene were dominated by glacial activity and deposition. Since Holocene, the marine beaches, terraces and cliffs are characteristic coastal features of the Hornsund fjord (Birkenmajer 1990). The youngest Quaternary sediments are mainly represented by unconsolidated moraine, fluvial, beach, talus and scree deposits formed during and after the last Ice Age.

Tectonism has been common since pre-Cambrian and led to formation of a great number of faults and discontinuities, with large lateral extent. Tectonic fractures greatly influence circulation of groundwater in the Hornsund region and are important conduits for groundwater in the subpermafrost zones and thermal waters originated from deep circulation.

Zonation of groundwater circulation in the region of Spitsbergen

In areas of continuous perennial permafrost, the occurrence of groundwater is usually related to three zones (Williams & van Everdingen 1973): (1) above the perennial permafrost (suprapermafrost); (2) inside the perennial permafrost (intra-permafrost), and (3) below perennial permafrost (subpermafrost). Flow of groundwater above the perennial permafrost occurs in active, de-freezing layer during the spring and early summer (Figure 2(c)) and is linked to non-glaciated areas of Spitsbergen (Pociask-Karteczka 1989; van Everdingen 1990; Gascoyne 2000). Precipitation and de-freezing perennial permafrost are the main source of water for the suprapermafrost zone. However, the outflows of subglacial water discharging from the glacier (Figures 2(a) and 2(b)) may also contribute some portions of water in this zone. Temperature of groundwater in the perennial permafrost is near 0 °C.

The groundwater from inside the perennial permafrost occurs in zones of unfrozen area (taliks). Taliks are created in places of higher heat flow coming from rivers, lakes (Figure 2(c)) and stable sources or they form in places where discharging water shows high salt concentration.

Water recharging under perennial permafrost is related to open taliks and glaciers. The larger Svalbard glaciers tend to be polythermal. They have warm-based accumulation areas, while the glacier tongue is cold based (Figure 2(a)). Melt water present in the warm-based part of these glacier systems may penetrate pores or fissure within the bedrock, thus, recharging the circulation system under the perennial permafrost (Haldorsen & Lauritzen 1993).

Groundwater circulating below perennial permafrost is under constant hydrostatic pressure. A line of piezometric pressures in a valley system may be formed above the morphological surface (Haldorsen *et al.* 1996). This likely involves groundwater to rise to the surface; particularly, in karst system (Figure 2(b)), or in tectonically fractured terrains (Figure 2(c)). Groundwater outflow in the form of springs is characterized by considerable discharge and in the case of small outflows the pingo-like features may be created (Banks *et al.* 1998). The circulation depth of groundwater under perennial permafrost is within 100–400 m, which represents the average thickness of

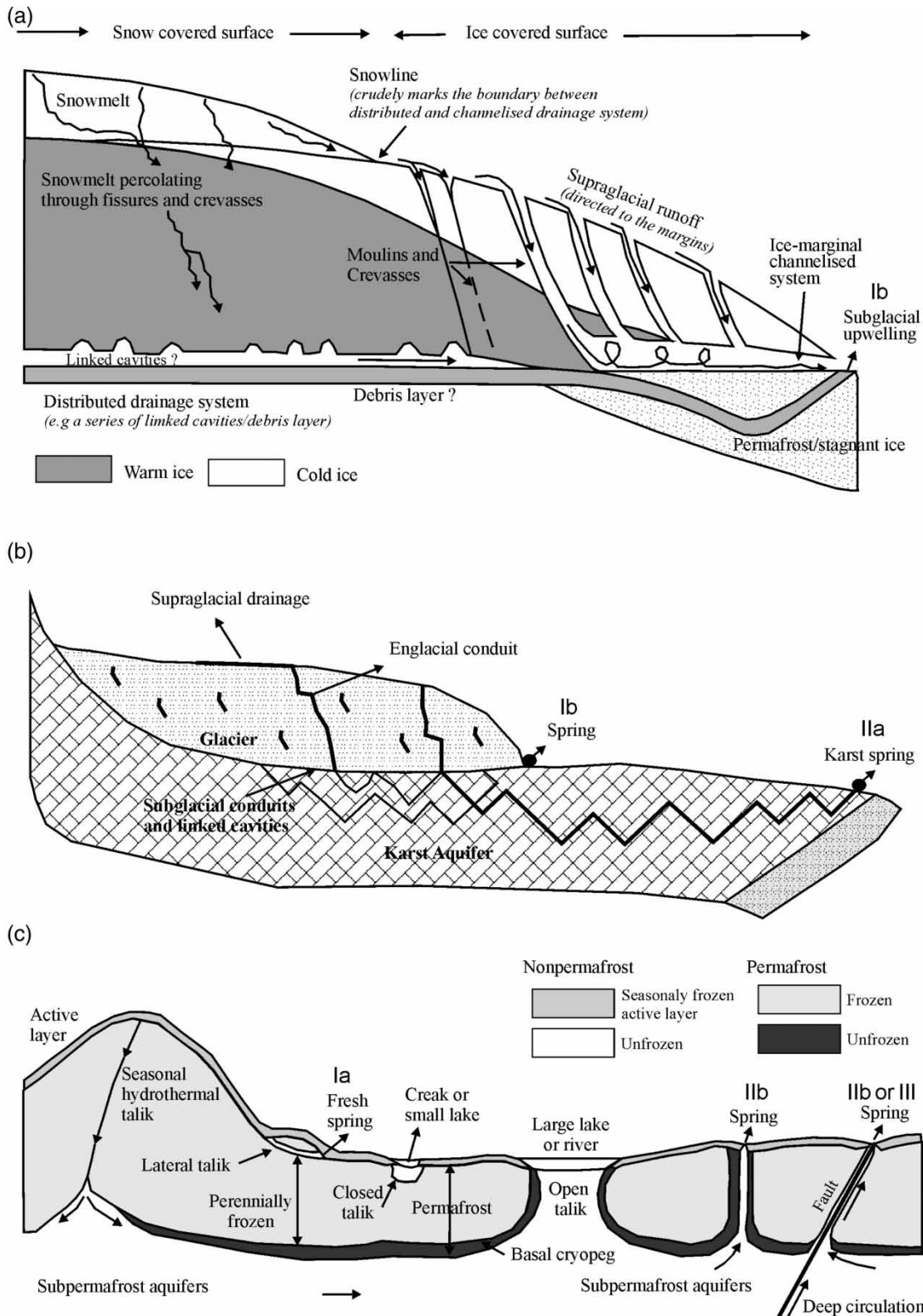


Figure 2 | Simplified models of groundwater occurrence and circulation in Spitsbergen. (a) – water circulation on not karst glacial areas (Wadham *et al.* 1998); (b) – water circulation on glaciated karst areas (Lauritzen 2006); (c) – circulation of groundwaters on non-glacial areas (modified from van Everdingen 1990). Ia, Ib – outflows from suprapermafrost zone; Ila, Ilb – outflows from intrapermafrost zone; III – outflows from subpermafrost zone.

perennial permafrost in Spitsbergen. The temperature of waters at outflow point is $\sim 4^\circ\text{C}$.

In this study, the groundwater circulation system above the perennial permafrost is understood as a suprapermafrost zone, while groundwater circulation system inside and under the permafrost are understood as intrapermafrost and subpermafrost zones, which are hydrogeologically isolated from surface reservoirs. In addition, a zone of deep circulation in Spitsbergen is also recognized. This zone refers to tectonic discontinuities where waters from shallow and intermediate depth may infiltrate to much deeper depths ($>1,500\text{ m}$), and ascend from them onto the surface. Numerous springs of thermal and thermo-mineral waters, with outflow temperatures from $10\text{--}14^\circ\text{C}$ to over 25°C , are usually related with deep groundwater circulation.

Groundwater occurrence in the Horsund region

In the Horsund region (Figure 1), groundwater of the suprapermafrost zone occurs in the Quaternary glacial, fluvial and marine deposits and in shallow bedrock fissures. During summer the active zone de-freezes to depths of $1\text{--}1.5\text{ m}$ and the water layer of $0.3\text{--}0.5\text{ m}$ thickness is formed in the shallow subsurface of the perennial permafrost (tundra area). The main source of water in this system comes from snow melt and precipitation. Groundwater usually discharges onto the surface in the form of periodical springs, which were numerous at the base of mountain slopes.

Outflows of subglacial water exist in front of glaciers in many locations such as in Nanbreen, Werenskioldbreen or Gasbreen Glaciers. During spring and summer, the subglacial waters form efficient springs which represent the mixture of waters from subglacial and supraglacial systems. In autumn and winter, this type of groundwater forms naled-like features. Groundwater circulating in carbonate rocks of the Horsund region is related to the zone of intermediate circulation. They discharge onto the surface in the form of springs under the Rasstupet wall. Waters of this type are also known from southern Spitsbergen, where they discharge in the Strombukta area in the form of spring with the greatest discharge observed in Svalbard ($10\text{--}18\text{ m}^3\text{ s}^{-1}$) so far (Figure 1). Numerous springs of this type and characterized by increased mineralization are assumed to originate

from the intermediate circulation (Bieroński 1977; Postnov 1983).

Various springs of thermal waters are indications of a subpermafrost zone in the Horsund region (Krawczyk 1990; Pociask-Karteczka 1990). These thermal springs occur under the Raudfjellet and the Gnalberget summits and also further to the south in the Strombukta area (Figure 1). The temperature of these waters at the discharge point ranges from 12 to 14°C .

REVIEW OF THE CHEMICAL COMPOSITION OF WATERS FROM THE HORSUND REGION

Detailed studies of chemical composition of the waters from the Horsund region (Figure 1) began at the beginning of the 1970s. A map of hydrochemical types of waters from the Horsund area (Bieroński 1977) was made based on 261 analyses done in years 1972–1974. This article showed the types of surface water differentiation depending on the bedrocks. The additional class of waters was created by connecting with end moraines of Nannbreen, Werenskioldbreen and Hansbreen glaciers and with the lateral moraine of the Hynbreen glacier. This type of water was characterized by increased mineralization (an average of $400\text{--}500\text{ mg L}^{-1}$ and with the increased content of sulphates). In the above-quoted article, the origin of the waters which flow out from six karst springs located under the Rasstupet wall was explained. These springs were also analysed in the years 1978–1979 (Wach 1980; Leszkiewicz 1982; Leszkiewicz *et al.* 1982). Karst springs and streams supplied by the melting of water in permafrost within a low terrace were observed. Measurements were carried out in the following periods: from 6th June to 11th September 1978, and from 19th July to 7th September 1979. Nine points were explored and every point was analysed about 12 times during each season. Findings were presented in tabular form to document the material. Findings of daily changes of chemical composition from each point were also presented. These results indicate that there was a large variability of mineralization of karst spring waters ($111\text{--}725\text{ mg L}^{-1}$) and the ionic composition during the season. For example, chloride fluctuated from 91.6 to 433.8 mg L^{-1} , and sulphate from 15.4 to 75.8 mg L^{-1} . On

the basis of scientific research it was ascertained that the water in these outflows stayed in contact with the seawater of the fjord in proportion to the size of the pressure in channels formed by the column of water delivered in sinkhole zones (Leszkiewicz 1982; Leszkiewicz *et al.* 1982).

Detailed hydrochemical analysis of waters from the unglaciated area of the Horsund region was the subject of the studies conducted by Krawczyk & Pulina (1982). These studies, located in Fugleberget river basin (Table 1), were started on 23th July 1979 and finished on 4th September 1980, and presented results of the analyses of the chemical composition of the waters, which were analysed in one day, two or a few days intervals (depending on level of the surface water) in three stable river sections.

The results showed that the chemical composition of the waters in this area was determined by the dissolution of carbonate rocks; mineral salts as a result of precipitation and biochemical processes. In spring and late autumnal period an increase in the solute content of waters, originating from the cryochemical effect, was also indicated (Pulina 1984). Groundwater in the basin was $\text{HCO}_3\text{-Cl-Ca}$, $\text{HCO}_3\text{-Ca-Na-K}$, Cl-Na-K-Ca hydrochemical types.

In turn the detailed hydrochemical characteristics of the waters on the foreground of the glacier, taken from the Werenskiold glacier basin, were a main goal of the Krawczyk studies (1992). From the end of the first half of July 1986 to the beginning of October 1986 changes in the chemical composition of the waters at six points were analysed. The authors showed the existence of two largely

independent drainage systems in the glacier. The summer system was connected with an overflow of the englacial reservoirs. The mineralization of waters ranged 40 mg L^{-1} and type of water $\text{HCO}_3\text{-Ca}$ was dominated. The winter system was characterized by significantly less volume of water and a higher mineralization (about 200 mg L^{-1}). After the middle of August the amount of magnesium ions and sulphate ions increased significantly (Krawczyk 1992). Also after this time other ion concentrations changed too, some by several times (HCO_3^- from 27 to 100 mg L^{-1}). Water type $\text{HCO}_3\text{-SO}_4\text{-Ca-Mg}$ was dominant.

The thermal springs of the Horsund region were also the object of much research (Krawczyk 1990; Pociask-Karteczka 1990). This research suggested that the Orvin spring and the Raudfjellet springs belong to the same hydrogeological zone. The summaries of these studies together with the list of chemical analyses of the waters from the thermal springs of this region have been presented by Krawczyk (1996).

METHODS

During investigations in July 2003 and 2006 (the half of the polar summer), samples representing several of the zones of circulation discussed in the article were taken (Table 2). Water samples were collected once, because of logistical difficulties. Interpretations were relied on data from 2006. Results from 2003 were used to assess temporal changes.

Water electrical conductivity (EC), temperature, pH and redox potential (Eh) were measured in situ during the field work using an Elmetron CX401 multiparametric meter that was one-point calibrated with a solution of $141 \mu\text{S cm}^{-1}$, two-points calibrated with 4 and 7 pH buffers at temperature of 10°C , using combined electrode ERPt-13 for Eh determination (not calibratable). Measurement precision was 0.05 for pH, $1 \mu\text{S cm}^{-1}$ for EC, and about 5 mV for Eh determination.

Colorimetric titration with an indicator of $\text{pH} = 4.3$ was utilized to determine alkalinity. The mean value of three titrations was determined in order to characterize alkalinity. The overall analytical precision of this analysis was better than 1%. Water samples ($2 \times 100 \text{ mL}$) collected in polyethylene bottles were taken from each sampling point. Before collecting the water, the bottle was rinsed with water from

Table 1 | Selected values of total mineralization of surface water from the Fugleberget basin from 1979–1980 (Krawczyk & Pulina 1982)

Date	Profile 1 – Fugleberget stream Mineralization [mg L^{-1}]	Profile 2 – stream at the Klipes	Profile 3 – outflow from the lake
23.07.79	66.6	75	64.9
24.08.79	80.6	80.6	85.6
24.09.79	92.4	81.2	114.7
12.09.79	119.1	80	86.8
23.06.80	27.9	38.4	22.3
24.07.80	76.9	78.1	76.3
24.08.80	80.6	81.9	93
01.09.80	80.0	80.6	96.1

Table 2 | Samples representing various zones of groundwaters circulation

Sample symbol (according to Figure 1)	Date of water sampling July 2003	Date of water sampling July 2006	Zone of Circulation	Point description
B5	13.07	25.07	Suprapermafrost	Underslope spring (brattegvelva river basin)
S1		01.08	Suprapermafrost	Piezometer, sample from melt water, screening depth at 1.5 m
P1		10.07	Suprapermafrost	Karst spring
R2		21.07	Intrapermafrost	Spring near raudfjellet
Rs5	19.07	10.07	Intrapermafrost	Karst spring (rasstupet),
R1	01.08	21.07	Subpermafrost	Spring near raudfjellet, thermal spring
O1	19.07	19.07	Subpermafrost	Orvin spring, thermal spring

the testing location and was twice rinsed with filtrated water from the spring. The samples were filtered through a nitrocellulose membrane of 0.45 μm diameter. Then one of the samples was acidified with the use of 0.5 mL HNO_3 per 100 mL H_2O . Chemical composition of waters was determined by Elan 6100 ICP-MS one month after the time of sampling. Until delivery to the laboratory (1 week to 2 months after sampling) the samples were stored in a frozen state. Ion balance errors were less than 5% for all analyses. Chemical analysis were expanded and included 29 cations (Na^+ , K^+ , Li^+ , Be^{2+} , Ca^{2+} , Mg^{2+} , Ba^{2+} , Sr^{2+} , Fe^{3+} , Mn^{2+} , Ag^+ , Zn^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Pb^{2+} , Hg^{2+} , Cd^{2+} , Se^{2+} , Sb^{3+} , Al^{3+} , Cr^{3+} , Mo^{6+} , V^{5+} , Zr^{4+} , Ti^{4+} , As^{3+} , Tl^{4+} , W^{6+}) and 9 anions (Cl^- , Br^- , I^- , SO_4^{2-} , HCO_3^{2-} , CO_3^{2-} , NO_3^- , PO_4^{3-} , BO_3^{3-}). Content of H_2SiO_3 , pH, Eh, electrical conductivity were also determined. Major ion concentrations only were used for the purpose of interpretation together with physical-chemical data recorded during field work.

RESULTS

In all sampling points chemical differences between water circulation systems were noted. For suprapermafrost zone (samples B5, S1, P1), lower mineralization, pH and temperature were observed compared to considerably higher values of these indicators for intrapermafrost (Rs5, R2) and subpermafrost (R1, O1) zones (Tables 3 and 4). For the suprapermafrost zone low concentrations of Cl^- (5.5–10.8 mg L^{-1}), SO_4^{2-} (1.0–15.1 mg L^{-1}), Ca^{2+} (2.3–25.3 mg

L^{-1}), Mg^{2+} (0.7–14.4 mg L^{-1}) and Na^+ (1.7–6.0 mg L^{-1}) were observed (Table 3). For intrapermafrost and subpermafrost sampling points concentration of those ions were significantly higher: 41.5–140.4 $\text{mg Cl}^- \text{L}^{-1}$, 19.8–200 $\text{mg SO}_4^{2-} \text{L}^{-1}$, 14.4–84.7 $\text{mg Ca}^{2+} \text{L}^{-1}$, 7.5–39.9 $\text{mg Mg}^{2+} \text{L}^{-1}$, 30.3–110.3 $\text{mg Na}^+ \text{L}^{-1}$. Only the K^+ ion concentration showed no significant difference across all zones (Table 3). In all sampling points oxidizing conditions were observed (Table 4). More detailed results are discussed in the next section.

DISCUSSION

The suprapermafrost zone

The main factor affecting the chemical composition of shallow groundwaters is the chemical composition of precipitation and bedrock lithology. In the case of precipitation, dissolution of salts present on the surface of airborne dust is assumed to be most important in the increase of salt content of rain water. Furthermore, oxidation of sulphides and dissolution of carbonates by rain and snow melt water controls chemical composition of groundwater in shallow environments (Cooper *et al.* 2002; Wadham *et al.* 2007). However, locally, chemical composition of shallow groundwater may be controlled by various biochemical processes such as supply of nitrogen and phosphorus from organic components near the colony of birds (Bieroński 1977).

In summer of 2000, the conductivity values of precipitation in the nearby area of the Polish Polar Station in

Table 3 | Chemical composition of groundwaters in the Hornsund region in July 2006 and July 2003

Sample	Year of water sampling	Balance error %	Mineralization ueq L ⁻¹		Cl ⁻ mg L ⁻¹	HCO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
B5	2006	0.85	86.9	30.5	5.5	14.0	1.14	4.41	1.39	1.69	1.07
B5	2003	1.39	78.2	27.0	6.2	11.6	1.00	2.30	0.67	5.04	0.20
S1	2006	0.88	175.3	67.6	9.0	31.0	4.21	7.06	2.64	3.87	4.70
P1	2006	0.85	381.0	142.4	10.8	77.8	15.10	25.30	4.10	6.03	0.90
Rs5	2006	2.92	1,368	468.0	108.8	180.0	27.21	18.29	14.41	110.30	5.37
Rs5	2003	0.30	1,328	429.5	140.4	137.3	19.8	15.53	22.42	89.93	4.10
R2	2006	1.99	1748	599.2	41.5	195.2	200.0	84.72	39.93	30.28	2.80
R1	2006	0.6	666	228.3	49.2	79.3	30.62	14.14	10.15	35.75	2.17
R1	2003	0.38	560	187.1	46.1	62.2	22.60	15.03	7.54	31.95	1.60
O1	2006	0.7	1,147.6	378.2	107.6	105.0	47.48	29.91	16.13	64.25	2.87
O1	2003	0.7	978	316.7	95.3	84.2	41.28	23.87	14.21	56.21	1.65
O1 ^a	2006	<i>x</i>	<i>x</i>	<i>x</i>	49.57	104.57	39.38	28.66	12.25	31.99	1.70

^aexcluding 0.3% portion of sea waters.

B5, S1, P1 – supraperafrost waters; R2, Rs5 – intrapermafrost waters; R1, O1 – subpermafrost waters.

Table 4 | Physicochemical data of groundwaters on the basis of field measurements in July 2006 and July 2003

Sample	Year of water sampling	Temperature (°C)	EC [$\mu\text{S cm}^{-1}$]	pH [–]	Eh (mV)
B5	2006	2.5	42.6	7.10	465
B5	2003	<i>x</i>	25	6.89	<i>x</i>
S1	2006	0.1	78.3	6.82	484
P1	2006	2.2	143.7	6.76	468
Rs5	2006	2.7	800	7.96	414
Rs5	2003	<i>x</i>	513	7.75	<i>x</i>
R2	2006	6.9	776	7.66	444
R1	2006	11.9	336	8.03	365
R1	2003	<i>x</i>	286	7.65	<i>x</i>
O1	2006	13.0	661	7.51	391
O1	2003	<i>x</i>	550	7.65	<i>x</i>

x – no data.

Hornsund, varied in a wide range from 9.5 to 58.5 $\mu\text{S cm}^{-1}$ (Krawczyk *et al.* 2002). Rain water showed a Cl–HCO₃–Na water type in respect to ions. Na⁺ and Cl⁻ made over 70% of cations and over 50% of anions, respectively, and hydrogen carbonates less than 30%. The chemical composition of the snow cover was similar (Głowacki & Pulina 2000). Generally, greater concentration of chlorides and

sodium was observed only in the near coastal zone, thus, it was related to deposition of sea aerosols on the snow cover.

The mineralization of groundwaters from the supraperafrost zone usually ranged from 20 to 100–150 mg L⁻¹, rarely above 200 mg L⁻¹. Mineralization of groundwaters on non-carbonate areas were in the range 40–50 mg L⁻¹ and increased to 80–90 mg L⁻¹ in more calcareous areas. HCO₃–Cl–Ca and Cl–HCO₃–Ca types of water were dominant (Bieroński 1977). In the areas of carbonate rocks the average mineralization of groundwaters was in the range 100–150 mg L⁻¹ and the main types of water were HCO₃–Cl–Ca, HCO₃–SO₄–Ca and HCO₃–Cl–Ca.

In this study an example of the outflow of groundwaters from carbonate deposits was represented by the spring P1 (Panorama) (Tables 3 and 4) discovered on 12th July 2006 in Vestre Burgerbukta, at the foot of the vertical wall of the Sofiekammen (mountain range). Temperature at the point of water discharge was 2.2 °C with mineralization of 142.4 mg L⁻¹ (381 ueq L⁻¹) in the period of sampling. HCO₃⁻ ion made up almost 70% of anions and Ca²⁺ 67% of cations (Tables 3 and 4). In contrast, the ion composition of springs in non-carbonate bedrock was dominated by the HCO₃–Cl–Ca–Mg (Figure 3). Mineralization of groundwaters occurring above perennial permafrost (S1 – piezometer) as a

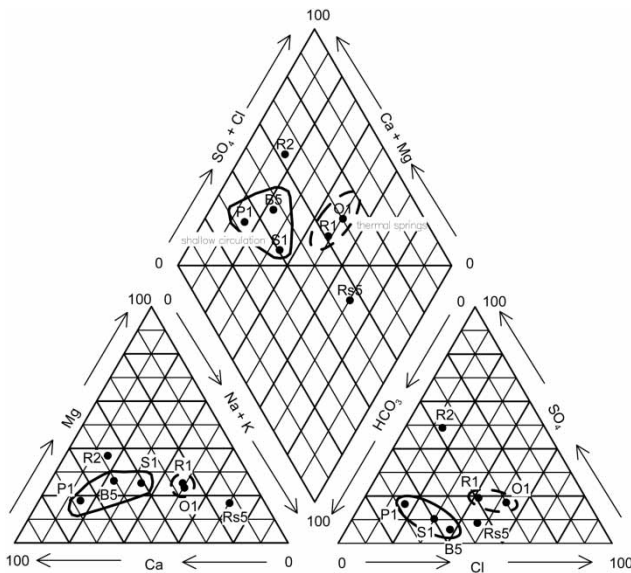


Figure 3 | Piper diagram showing the major-ion composition of groundwater from Hornsund area in July of 2006.

layer of water was significantly higher than mineralization of springs occurring under the slopes (B5 – spring) which are largely fed by snow melt water in higher portions of the slopes (Tables 3 and 4).

The increase in mineralization of some of the shallow groundwater occurred during the spring and late autumn (Figure 4) as a result of leaching of various salts deposited in the tundra by freezing water during the autumn and winter seasons. These effects haven't changed the percentage share of ions dissolved in water but have increased

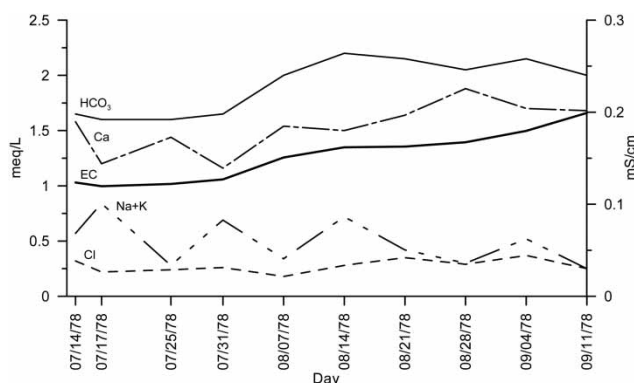


Figure 4 | Content changes of major cations and anions of water from suprapermafrost zone (in August 1978) near Russtupet karst springs (based on data from Leszkiewicz *et al.* 1982, point z1).

their overall mineralization (Krawczyk & Pulina 1982; Pulina 1984).

The processes controlling the chemical composition of groundwater and their annual variability in subglacial systems were widely discussed for the Finsterwalderbreen Glacier in papers by Wadham *et al.* (1998, 2000). The work of Krawczyk (1992) described the chemical composition of groundwater discharging from the glacier in the Hornsund region. In the period of July and August waters flowing out from the springs in front of the glacier Werenskioldbreen originated to a large extent from the supra-glacial system. In most cases, their mineralization does not exceed 75 mg L^{-1} . Water in the subglacial system began to appear in the second half of September after a period of intensive melting of the glacier from the surface. At this time the mineralization of the water increased to over 200 mg L^{-1} and sulphate and magnesium, apart from bicarbonate, began to appear more abundantly in the ion composition. Concentrations of sulfates were rising along with the transition from the summer to autumn and winter, and range from $0\text{--}40 \text{ mg L}^{-1}$ (Krawczyk 1992). The source of sulphates was the oxidation of sulphide minerals, while dissolution of carbonates contributes the Mg^{2+} (Wadham *et al.* 2000). This is the main process controlling chemical composition of subglacial waters and waters in the proglacial zone (Wadham *et al.* 2000; Cooper *et al.* 2002).

The intrapermafrost zone

The intrapermafrost zone mainly occurs in the karst areas. The main process controlling chemical composition of waters is dissolution of carbonates. However, it is difficult to determine directly the chemical composition of waters circulating in this system in the Hornsund region because it is believed that the waters flowing out of both the Russtupet (Rs5 in this study) and Trollosen springs (karst spring of Sorkapland, located between two thermal outflows; Figure 1) are a mixture of groundwaters and sea water (Leszkiewicz 1982; Leszkiewicz *et al.* 1982). The sea water is siphoned to the karst systems. Lauritzen & Bottrell (1994) suggest that in Trollosen the salinity has a different origin to the present seawater, because the $[\text{Cl}^-]/[\text{Na}^+]$ ratio is much lower than in seawater. The Russtupet springs $[\text{Cl}^-]/[\text{Na}^+]$ ratio had low value, 0.64 (calculated for our

data), that indicates ion exchange reactions where Na^+ is substituted by Mg^{2+} and Ca^{2+} .

The hydrochemical investigations of Rasstupet (Leszkiewicz *et al.* 1982) showed great variability of water mineralization from 110 to over 700 mg L^{-1} . Simultaneously they indicated a great stability of temperature during the summer season within the range of 2.2–2.8 °C (Table 5). Only during the period of rapid snow and ice melting when there was an increased inflow of waters into the suprapermafrost zone, the temperature of these waters

decreased to about 2.2 °C. The lowest mineralization of water was also observed in this period (Figures 5 and 6).

A great inertia of ionic composition and lack of daily variability, which would indicate the outflow of ablation water, suggest a relatively long time of groundwater flow and common ion exchange processes in the studied karst system (Leszkiewicz 1982).

A different type of groundwater has been reported for springs discharging in frontal moraines of the Nannbreen, Werenskioldbreen, Hansbreen Glaciers located on eastern

Table 5 | The main statistical parameters of chemical composition of Rasstupet karst spring (Rs5) (based on data from Leszkiewicz *et al.* 1982 and own data)

Component	Unit	Population	Min	Max	Arithmetic average	Geometrical average	Standard deviation
HCO_3^-	mg/L	17	49	180	71.68	66.82	33.37
Cl^-	mg/L	17	45	436.7	229.14	198.54	110.2
SO_4^{2-}	mg/L	16	5.8	73.9	41.02	34.58	20.71
Ca^{2+}	mg/L	17	12.8	28.8	21.4	20.83	4.72
Mg^{2+}	mg/L	17	7.7	37.9	22.42	21.07	7.54
Na^+	mg/L	2	89.93	110.3	100.12	99.6	10.18
K^+	mg/L	2	4.1	5.37	4.74	4.69	0.64
EC	mS/cm	17	0.155	1.002	0.63	0.567	0.249
pH		17	7.4	7.96	7.6	7.6	0.16
Temp.	°C	17	2.2	2.8	2.6	2.6	0.2

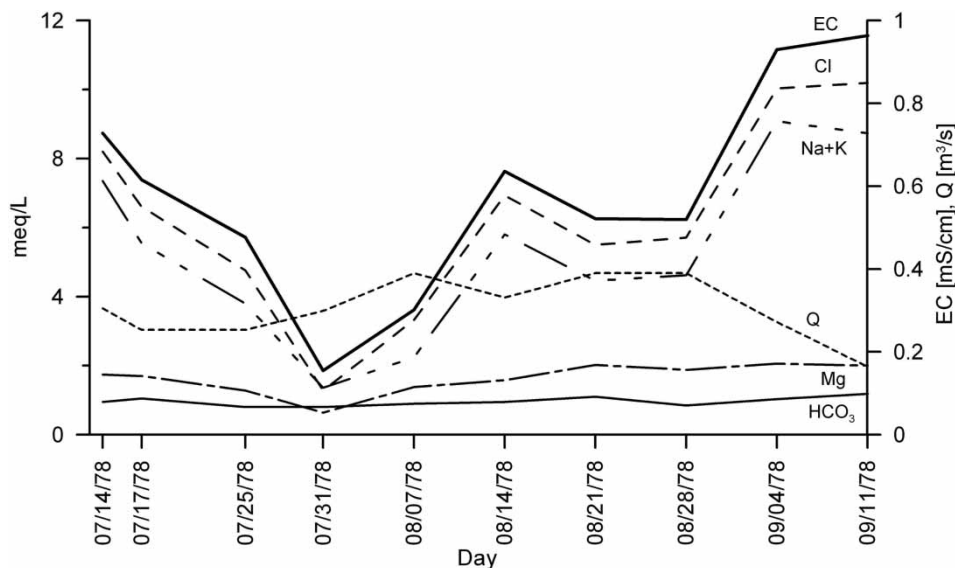


Figure 5 | Content changes of major cations and anions of water from Russtupet karst springs (based on data from Leszkiewicz *et al.* 1982, point z4).

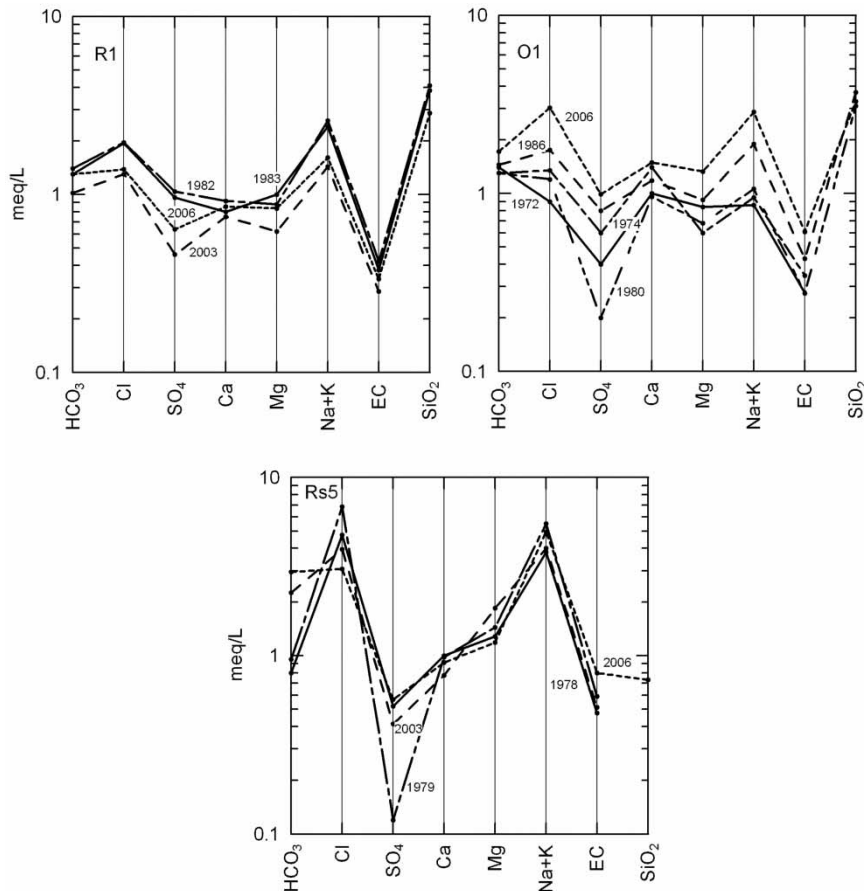


Figure 6 | Physico-chemical property changes of water in years 1972–2006 (based on data from Krawczyk 1996 and own data). R1,O1 – thermal waters, subpermafrost zone; Rs5 – karst water, intrapermafrost zone.

slopes of Flatryggen and the Treskellen peninsula (Bieroński 1977; Krawczyk 1990), and also under Raudfjellet. The observed temperature of the water in the spring R2 (6.9 °C) was higher than assumed for this circulation zone (Table 4). This is probably the impact of air temperature in summer, with a small spring discharge ($0.18 \text{ dm}^3 \text{ s}^{-1}$). The corresponding temperatures were also listed in springs of the suprapermafrost zone (Krawczyk & Pulina 1982; Pociask-Karteczka 1989). Waters from frontal moraines are characterized by high percentage and weight content of sulphates (up to 200 mg L^{-1}) which probably were the result of complicated processes connected with sulfide oxidation and sulfate second salts dissolution due to a lack of primary gypsum in the bedrock (ex. Moses *et al.* 1987; Birkenmajer 1990; Dallmann *et al.* 1990; Wadham *et al.* 1998, 2000, 2010; Cooper *et al.* 2002). Waters of this type

were characterized by increased mineralization in relation to waters of suprapermafrost zone, up to $600\text{--}700 \text{ mg L}^{-1}$. Analysis of water collected under the Raudfjellet (R2) showed the concentration of sulphates higher in relation to bicarbonate compared to Rs5 spring (Tables 3 and 4). The ratio $\text{SO}_4^{2-}/(\text{SO}_4^{2-} + \text{HCO}_3^-)$ is approximately 0.5, which suggest that oxidation of sulphide minerals and dissolution of carbonates occurs in an environment cut off from contact with atmospheric pressure during which the ratio of formed sulphates and hydrogen carbonates is equal to 1:1 (Wadham *et al.* 1998). These waters were $\text{HCO}_3\text{--SO}_4\text{--Ca--Mg}$ type. Additionally, in water of spring R2 compared with Rs5, lower concentrations of sodium and chloride were noted, which may indicate that there is no addition of marine waters and intensive ion exchange reactions may occur, which are associated with chemical

weathering of limestone rocks with metal sulfides in an absence of CO₂. Currently, there is no data discussion on stability of groundwater circulation of this type during winter periods. However waters of similar type were reported for the Kongress spring (Postnov 1983) (opposite the Russian estate of Barentsburg). Near the shore of the Kongressvatnet there is a group of springs of 25 dm³ s⁻¹ discharge. Outflows were characterized by mineralization of 1,660 mg L⁻¹ and the contribution of sulphates was 92% for SO₄-Ca-Mg type of waters. The Kongress springs are active during the summer and winter period, and the outflow of water occurs through underground channels directly to the Kongressvatnet.

The subpermafrost zone

Thermal waters of the Hornsund region were characterized by mineralization from about 200 to 350 mg L⁻¹. Small fluctuations of water temperature discharging in thermal springs during the summer season (Pociask-Karteczka 1990; Krawczyk 1996) suggest that inflows of waters from the suprapermafrost zone controlled by snow melt and precipitation is small.

The chemical composition of thermal springs was different and resulted from variable contribution of sea water in particular springs (Pociask-Karteczka 1990; Krawczyk 1996). For example the Orvin spring (O1) showed the Cl-Na type. However after taking into account the inflow

of 0.17–0.40% seawater in waters of subpermafrost zone (Krawczyk 1996) the concentration of bicarbonate among anions began to be comparable with chlorides and the concentration of sodium began to be comparable with calcium. After taking into account the inflow of water in the Orvin spring its chemical composition was similar to the springs of Raudfjellet (R1) (Table 3). Waters circulating in this system were of multi-ion nature Cl-HCO₃-Na-Ca-Mg where the content of the first four elements were similar to each other (Table 6).

Observations of the chemical composition of groundwaters in the Hornsund region from the last 30 years allow us to observe temporary variability. This has meaning in connection with observed changes of climate in that region (Marsz & Styszyńska 2007).

In periods of climate warming a decreased volume of warm-based ice causes a decrease of recharge and discharge of groundwaters in deep aquifers (Haldorsen *et al.* 2009). These changes should also be reflected in the chemical composition of outflowing waters from springs. In Figure 6, ion content of waters in three springs in different periods of time are represented. The greatest changes of the chemical composition were observed in the Orvin spring (O1). There, one notices the steady increase of the concentration of all main ions during last 30 years. In Rasstupet (Rs5) and Raudfjellet (R1) springs, the variability of the chemical constitution was not large and significant changes in ion composition have not been observed.

Table 6 | The main statistical parameters of chemical composition of Orvin thermal spring (O1) (based on data from Krawczyk 1996 and own data)

	Unit	Population	Min	Max	Arithmetic average	Geometrical average	Standard deviation
HCO ₃ ⁻	mg L ⁻¹	15	18.31	109.84	77.99	73.13	22.18
Cl ⁻	mg L ⁻¹	15	31.91	107.6	55.65	52.89	18.87
SO ₄ ²⁻	mg L ⁻¹	15	0.5	48.03	25.42	18.42	14.67
Ca ²⁺	mg L ⁻¹	15	13.43	32.06	22.46	21.78	5.52
Mg ²⁺	mg L ⁻¹	15	2.8	17.02	10.11	9.29	3.75
Na ⁺	mg L ⁻¹	2	1.3	2.79	2.05	1.91	0.75
K ⁺	mg L ⁻¹	2	0.06	0.07	0.07	0.07	0.01
EC	mS cm ⁻¹	14	0.253	0.61	0.37	0.36	0.1
SiO ₂	mg L ⁻¹	5	3.1	3.7	3.44	3.43	0.24
pH		13	6.9	8.6	7.62	7.6	0.47
Temp.	°C	12	12	13	12.41	12.41	0.25

The difference in ion composition between waters circulating in subpermafrost zone and waters of the intrapermafrost zone, especially their lower mineralization, indicates that these groundwaters originate from the surface/subsurface environment of the suprapermafrost zone, descending to deeper depths to tectonic fractures.

SUMMARY

Three zones of groundwater circulation: suprapermafrost, intrapermafrost and subpermafrost have been determined in the Hornsund region. Water in the suprapermafrost zone may originate from the melting of ice in perennial permafrost (in non-glaciated areas) and subglacial waters (in glaciated areas; Figures 2(a) and 2(c), outflows Ia and Ib). In non-glaciated areas, the main factors controlling chemical composition of groundwaters are considered likely to be the initial chemical composition of precipitation and mineralogical composition of bedrock. Therefore, the HCO₃-Ca type of water has dominated in karst areas and HCO₃-Cl-Ca-Mg type in other terrains where carbonates are less common. Chemical composition of sub-glacial waters was mainly controlled by oxidation of sulphides and dissolution of carbonates. However, at the end of the summer, when the discharge supra-glacial water is limited, the groundwater more resembled the HCO₃-SO₄-Ca-Mg type composition.

The zone of intermediate system (intrapermafrost and subpermafrost zone) was most likely dominated by groundwater flows below perennial permafrost. This circulation has taken place both in karst areas and in fractured terrains with tectonic discontinuities. In Rasstupet springs flowing out from the carbonate massive, the main processes forming the chemical compositions of waters were dissolution of carbonates and ion exchanges where Ca²⁺ ions were substituted by Na⁺ ions. The water in this system had the composition of Cl-HCO₃-Na, and after taking into account the possible influence of sea water it had the composition of HCO₃-Na-Ca. Waters of the intermediate zone occurring in the areas of tectonic discontinuities were characterized by higher content of SO₄²⁻ where their concentration has been similar to the concentration of HCO₃⁻. The SO₄²⁻ / (SO₄²⁻ + HCO₃⁻) ratio of 1:1 indicates that oxidation of

sulphides and dissolution of carbonates under oxygen-limited condition has been a major process accounting for chemical composition of SO₄-HCO₃-Ca-Mg type waters occurring in the intrapermafrost and shallow subpermafrost zone. The subpermafrost zone related to tectonic fractures, which serve as conduits for shallow circulation groundwater to greater depths. Usually, this groundwater has showed mineralization from 200 to 350 mg L⁻¹ and multi-ion nature of the Cl-HCO₃-Na-Ca-Mg type. Springs related with the subpermafrost zone were characterized by outflow temperatures from 10–14 °C to over 25 °C.

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