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# Headwater chemistry in subarctic areas with different plant communities (Finnish Lapland)

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*The study determines the differences in the chemistry of small headwater streams located in areas with different plant communities in Finnish Lapland. Water samples from 76 catchments with four different plant communities were collected and analyzed. The statistical analyses of water temperature, water specific electric conductivity and the concentration of main ions, revealed the greatest variation in ion concentrations related to rock weathering:  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $HCO_3^-$  in the studied catchments. Enrichment of water with these ions occurred in catchments representing forest communities with thick soils, especially in the boreal forest community. This suggests that future changes in the northern treeline may affect the surface water chemistry depending on the direction of changes. In case of the expansion of the treeline to the north due to climate warming, an increase in water mineralization and a shift of hydrochemical facies towards a Ca-Mg- $HCO_3$ -type can be expected. On the other hand, the regression of the northern treeline could be expected to result in a reduction of nutrient pools and leaching them into streams. Eventually, it could result in the depletion of soils and the dominance of atmosphere-derived ions in waters, and the hydrochemical facies will shift towards Na-Cl-type.*

## Introduction

Headwater areas are known to be a significant source of water as well as mineral and organic matter for the downstream parts of catchments (Gomi et al., 2002). The chemistry of headwaters is a reflection of chemical weathering patterns in catchments and plays an important role in element cycling in the environment (Likens, 1999; Wohl et al., 2012). The water chemistry in catchments in general is the effect of an array of factors, among which lithology is the most

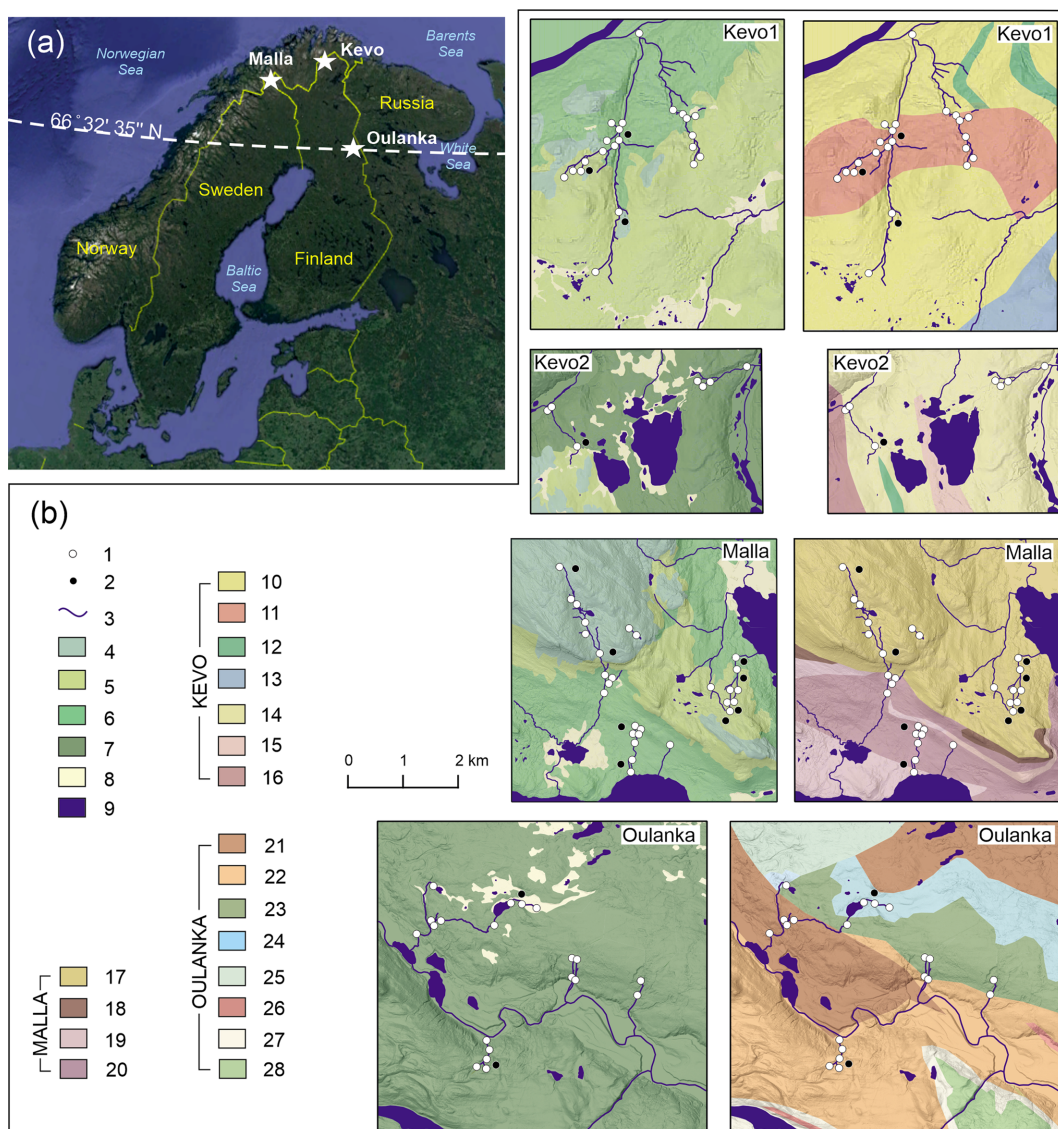
important because it determines the availability of key elements to the ecosystems. However, it can become strongly affected by other factors such as climate conditions, influx of sea salt, thickness of soil and regolith, relief, presence of permafrost, and the water runoff regime (McLean et al., 1999; Stutter and Billett, 2003; Beylich et al., 2004; Beylich and Laute, 2012; Żelazny et al., 2013). Plant community changes may contribute significantly to the chemistry of surface water as plants play an important role in the weathering processes and element cycling of the ecosystems (Wohl, 2017). As relationships between plant community changes and water chemistry are well-understood in the temperate climate zone (Flum and Nodvin, 1995; Likens, 1999; Nédeltcheva et al., 2006; Sajdak et al., 2021), they are relatively poorly understood in cold environments, as chemical weathering has been postulated to play a minor role for a long period of time (Peltier, 1950; Dixon and Thorn, 2005). However, Rapp (1960) was the first who noted the importance of chemical denudation in cold regions. This study sparked further research on this issue and indicated a high contribution of chemical weathering and denudation processes in subarctic environments, even in poorly soluble crystalline rocks (Dixon et al., 1984; Bartsch et al., 1994; Darmody et al., 2000; Beylich et al., 2004; Beylich and Laute, 2012; Stachnik et al., 2014).

The plant community changes have a significant effect on surface water chemistry of large catchments in subarctic areas (Zakharova et al., 2007). We expect, that such an effect can be distinct also in small headwater areas which are claimed to be susceptible to environmental disturbances (Wohl, 2017). The effect of vegetation cover on surface water chemistry can be different depending on the dominant recharge component (Duvert et al., 2018). Springs recharged mostly by interflow are expected to be more susceptible to water chemistry changes related to plant community changes than those recharged mostly by baseflow. As the surface water chemistry in Lapland is comparable to shallow groundwater chemistry within the moraine cover (Lahermo, 1971), the effect of plant community on water chemistry in the study area should be visible in both spring and stream water.

The climate warming and subsequent increase in the forested areas may increase chemical weathering intensity in small Lappish catchments. Recent studies do not show unambiguously that warming in recent years has changed forest areas or treelines in Lapland (Holtmeier et al., 2003; Holtmeier, 2005; Franke et al., 2015). However, dendrochronological studies by Kullman (2015) and Holtmeier (2005) showed that climate warming had favored the growth of young trees. Those studies suggest that current climate warming observed in Lapland (Luoto et al., 2017) could help increase forest surface area in the future. A reduction in reindeer herding that causes a reduction in the biting of young trees by animals may also cause an increase in forest area (Van Bogaert et al., 2011). On the other hand, some researchers emphasized that in some cases warming could cause a reduction of forest area in Lapland, e.g., due to summer drought or moth and fungi

invasion (Holtmeier, 2005; Franke et al., 2015; Gómez-Gener et al., 2020). Depending on the direction of forest area changes in the future, the consequence could be a significant increase or decrease in chemical weathering in catchments and changes in the stream water chemistry.

In the aspect of progressive climate changes and the related changes in the plant communities' ranges in subarctic areas, it is important to recognize the current hydrogeochemical conditions in the headwater catchments. Therefore, the aim of the study was to determine the differences in the chemistry of small headwater streams located in areas with different plant communities in Finnish Lapland. The results of these studies will constitute the background for further research carried out at the Kilpisjärvi Biological Station, Kevo Subarctic Research Institute and Oulanka Research Station, where the



**Figure 1.** (a) Location of the study areas (<https://earth.google.com/>), (b) plant communities and geological maps of the study areas (<https://kartta.paikkatietoikkuna.fi/>). 1) water measuring and sampling site, 2) soil sampling site, 3) streams, 4) grass heath, 5) heath tundra, 6) birch forest, 7) boreal forest, 8) wetlands, 9) water bodies, 10) quartz feldspar paragneiss of the Silisjoki Suite, 11) granodiorite, 12) amphibolite, 13) mica gneiss, 14) quartz feldspar paragneiss of the Kaamanen Complex, 15) diorite, 16) garnet-cordierite gneiss, 17) arkose quartzite, 18) dolomite, 19) silicate sandstone, 20) silicate claystone, 21) dolomite, 22) orthoquartzite, 23) mafic tuff, 24) biotite paraschist, 25) basaltic andesite, 26) dolerite (diabase), 27) sericite quartzite, 28) volcanic rock.

monitoring of the climatic conditions and their links with ecosystems is currently being carried out.

## Study Area

Three study sites were selected for research purposes, each representing a different form of environmental protection: 1) Malla area, which lies in Malla Nature Reserve, 2) Kevo area, which is located in Kevo Nature Reserve and Kaldoaivi Wilderness Area, 3) Oulanka area, which is found in Oulanka National Park (Fig. 1a). According to the Köppen-Geiger climate classification system (Peel et al., 2007), Kevo and Oulanka are located within the subarctic climate zone (Dfc)

and Malla in the tundra climate zone (ET). The Foehn wind effect, associated with the presence of the Scandinavian Mountains, causes the average annual precipitation totals to be rather low and reach a value of around 400 mm in Malla and Kevo and up to 518 mm in Oulanka (Autio and Heikkinen, 2002); half of the precipitation occurs in the form of snow (Kuusisto, 2004). The average annual temperature is  $-2.4^{\circ}\text{C}$  in the Malla and Kevo areas and  $0^{\circ}\text{C}$  in Oulanka.

The Malla area is located within the Caledonian thrust belt that contains Paleozoic arkose quartzite of the Nalganas Nappe underlain by Cambrian silicate claystone and dolomite of the parautochthonous Jerta Nappe and archean granodiorite and basic metavolcanic rock (Luukas et al., 2017). The Kevo area is mostly built of Paleoproterozoic quartz feldspar paragneiss of the Kaamanen Complex and Silis-

**Table 1. Characteristics of the study areas, spring and stream waters, and their catchments in the Malla (N=28), Kevo (N=29) and Oulanka (N=19) areas**

Parameters	Malla				Kevo				Oulanka			
	Mean	Min.	Max.	Std.Dev.	Mean	Min.	Max.	Std.Dev.	Mean	Min.	Max.	Std.Dev.
Area characteristics:												
Treeline height [m]	500				200				-			
Average distance to sea [km]	40				70				160			
Height differences [m]	460				320				240			
Catchment parameters:												
Hight [m a.s.l.]	621.93	475.27	910.15	119.40	229.13	67.31	328.07	63.85	222.24	163.94	253.71	27.97
Area [km <sup>2</sup> ]	0.34	0.002	1.99	0.54	0.75	0.01	4.82	1.25	0.72	0.002	3.37	0.90
Slope gradient [°]	11.47	6.45	17.75	2.63	5.54	1.32	8.40	1.73	5.46	0.93	9.33	2.46
Water properties:												
pH [-]	7.16	5.43	8.37	0.89	6.34	4.88	7.74	0.65	7.69	6.35	8.39	0.55
SEC [ $\mu\text{S cm}^{-1}$ ]	39.96	4.16	114.64	40.53	22.86	13.60	42.49	6.53	148.07	21.67	238.80	74.40
T [°C]	10.18	4.10	14.70	2.74	7.95	2.60	13.60	2.33	8.13	3.10	13.80	3.15
Q [ $\text{L s}^{-1}$ ]	3.10	0.02	20.00	4.99	2.55	0.01	12.00	3.26	3.23	0.01	15.00	4.14
Ion content [ $\text{mg L}^{-1}$ ]:												
Ca	5.26	0.37	15.56	5.42	1.85	0.27	3.53	0.77	21.31	2.64	36.46	10.92
Mg	1.40	0.06	5.47	1.87	0.70	0.17	1.48	0.32	6.08	1.10	10.87	2.87
Na	1.22	0.33	1.89	0.51	1.95	1.29	2.62	0.33	1.23	0.85	1.98	0.40
K	0.34	0.08	0.64	0.16	0.27	0.07	0.71	0.16	1.61	0.21	3.20	1.09
NH <sub>4</sub>	0.01	0.00	0.08	0.02	0.01	0.00	0.04	0.01	0.00	0.00	0.05	0.01
HCO <sub>3</sub>	22.86	1.18	78.05	27.48	7.26	0.84	17.41	3.98	97.04	9.26	150.40	49.12
SO <sub>4</sub>	1.49	0.22	7.28	1.46	1.64	0.48	3.41	0.68	3.57	0.51	13.85	3.72
Cl	0.92	0.43	1.86	0.49	1.62	0.99	2.62	0.34	0.73	0.38	2.10	0.52
NO <sub>3</sub>	0.28	0.00	2.87	0.57	0.10	0.00	1.94	0.36	0.11	0.00	0.66	0.15
F	0.01	0.00	0.02	0.01	0.02	0.00	0.06	0.01	0.02	0.01	0.05	0.01
Ion share [% meq L <sup>-1</sup> ]:												
Ca	55.21	38.63	72.32	8.68	36.82	12.48	49.36	6.44	61.27	47.90	69.98	6.92
Mg	18.23	8.49	36.99	8.57	22.63	13.02	32.17	4.51	30.97	25.11	36.24	2.65
Na	21.67	6.23	36.89	10.81	36.69	25.73	59.97	7.47	5.31	1.88	15.87	5.01
K	3.83	0.91	10.01	2.60	2.76	0.63	5.05	1.09	2.40	1.40	3.72	0.79
NH <sub>4</sub>	0.56	0.00	9.12	1.79	0.32	0.00	1.29	0.33	0.02	0.00	0.22	0.05
HCO <sub>3</sub>	72.75	42.13	94.12	14.63	55.20	18.34	76.51	13.40	93.08	86.18	98.00	4.43
SO <sub>4</sub>	11.78	2.30	34.68	7.42	18.29	5.07	32.11	6.45	4.52	0.71	10.98	2.95
Cl	13.01	2.62	30.21	8.38	25.42	15.39	57.18	9.19	2.18	0.53	6.71	2.24
NO <sub>3</sub>	2.27	0.00	15.28	3.72	0.48	0.00	8.02	1.51	0.09	0.00	0.42	0.11
F	0.16	0.00	0.54	0.15	0.55	0.00	1.34	0.27	0.10	0.03	0.27	0.09

joki Suite, which include granodiorite intrusions. The Oulanka area is primarily composed of Precambrian orthoquartzite and biotite parashist, accompanied by dolomitic carbonate rocks and mafic tuff (Fig. 1b; <https://kartta.paikkatietoikkuna.fi>). Bedrock is covered with glacial or glaciofluvial sediments. The thickness of moraine formations is 0–1.5 m at the foot of the fells plateau, 2–7 m in wide-bottom valleys and on flatlands, with a maximum of 22 m in depressions. Rock material of the moraine hills features various grain sizes and is often coarse, and in some places quite well-sorted (Lappalainen, 1970; Hirvas, 1991), which allows free flow of shallow subsurface water. The soil type in areas covered by moraine formations mainly consists of Podzols, while Leptosols have developed on bedrock polished by the local glacier (<https://kartta.paikkatietoikkuna.fi>). In the study areas there is an absence of continuous permafrost, while sporadic permafrost is connected with palsa mires. However, temperature in bedrock in the Malla and Kevo areas in barren fells above treeline remains below 0°C (King and Seppälä, 1987). All study areas feature mountainous landscapes defined by rather large differences in elevation (Table 1).

The bedrock in all study areas is impermeable and contains only 0.5–1.0% pore water, but groundwater may flow in numerous faults, fractures and fissures (Lahermo, 1970; Talvitie and Paarma, 1973). There are two main aquifers in the studied areas. One of them is associated with quaternary formations, primarily with glacial till, although glaciofluvial sediments are the most abundant with water. The other

one is a fractured “hard rock” aquifer (Lahermo et al., 1990). Groundwater flows out to the surface on hillslopes via springs and peat bog seeps. The highest water level in streams and discharge value for springs were recorded usually during the spring snowmelt season (May–June) but also in the summer or fall as a result of intense rainfall or during mild winters (Korhonen and Kuusisto, 2010).

Barren fell areas, found in the highest part of the Malla and Kevo areas, are covered with heath tundra vegetation and grass heath (Clark et al., 1985; Heikkinen et al., 2002). Downhill from the treeline (Table 1) occur subalpine birch forest (Holtmeier et al., 2003) in the Malla area and Kaldoaivi Wilderness Area, and birch and pine forest (Holtmeier, 2005) in the Kevo Nature Reserve. Boreal forest is found in the Oulanka area, which is dominated by spruce and pine (Suppl. mat. A; Söyrinki et al., 1977; Havas and Kubin, 1983).

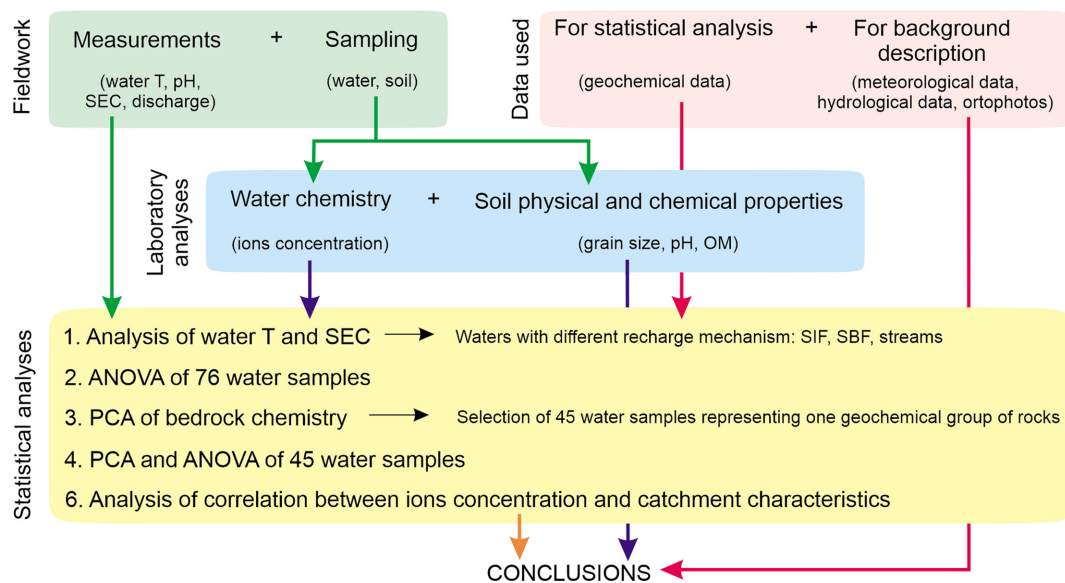
## Materials and Methods

### Materials

Table 2 presents all data and materials used in this study (Fig. 2) and their sources. Geochemical data originated from the closest available locations (0–10 km) to the respective study area. Meteorological and hydrological data in daily resolution were derived from the closest observation stations: Enontekiö Kilpisjärvi kyläkeskus and Kilpis-

**Table 2. Data and materials used in the study**

Data	Source
Cartographic and remote sensing materials: topographic maps, geologic maps, Digital Elevation Models (DEM) with a resolution of 2 m and 10 m, orthophotos and aerial photos	National Land Survey of Finland ( <a href="https://kartta.paikkatietoikkuna.fi">https://kartta.paikkatietoikkuna.fi</a> )
Geochemical data: chemical composition of bedrock	Geological Survey of Finland ( <a href="https://hakku.gtk.fi/fi/locations/search?location_id=4">https://hakku.gtk.fi/fi/locations/search?location_id=4</a> )
Meteorological data: daily average air temperature, daily precipitation totals	Finnish Meteorological Institute ( <a href="https://www.ilmatieteenlaitos.fi">https://www.ilmatieteenlaitos.fi</a> )
Hydrological data: average daily runoff in 2017, multiannual average, minimum and maximum runoff	Finnish Environment Institute ( <a href="http://www.ymparisto.fi">www.ymparisto.fi</a> )



**Figure 2. Flowchart of research methodology.**

järvi – luusua 2 km away from the Malla study area, Utsjoki Kevo and Utsjoki Patoniva 10–20 km away from the Kevo study area and Kuusamo Kiutaköngäs and Oulankajoki located in the vicinity of the studied catchments in the Oulanka study area. A total of 76 headwater catchments, with surface areas not exceeding 4 km<sup>2</sup> (Table 1), were selected based on orthophotos and topographic maps. Groundwater flowing out to the surface in the form of bog seeps was not considered in this work.

## Fieldwork

Measurements of the physical and chemical properties of water collected from springs and streams as well as all water sampling (Fig. 2) were performed in August 2017. Stream and spring discharge was measured using the volumetric method via a calibrated vessel. Specific electric conductivity (SEC), recalculated to represent its value at a temperature of 25°C, pH and water temperature (T) were measured *in situ* using the ELMETRON multifunctional meter CX-461. The accuracy of measurements was: ±0.1% SEC, ±0.002 pH, ±0.1°C. The pH sensor was calibrated with 4.01, 7.00 and 9.21 buffers. The water sample collection sites were located at elevations ranging from 67 to 910 m a.s.l. Two water samples were collected at each of 76 measurement points in 200 ml polyethylene bottles. Water samples were stored in a portable cooling box and filtered in the laboratory within a few hours after collection.

Soil pits were dug out in the studied areas under each type of plant community to expose soil profiles. Soil material was collected from 15 pits altogether. Soil pits were dug down to the lithic contact or >90% of stones and gravel content or groundwater level and described according to Schoeneberger et al. (2002). One representative bulk sample was collected from each studied genetic soil horizon, and then placed in a sterile polyethylene bag. The studied soils were classified according to the WRB system (IUSS Working Group WRB, 2015).

## Laboratory Work

Laboratory analyses of water samples were performed at the Institute of Geography and Spatial Management of Jagiellonian University in Krakow (Fig. 2). Fourteen ions (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Li<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, Cl<sup>-</sup>, F<sup>-</sup>, Br<sup>-</sup>) were determined in water samples using ion chromatography (DIONEX ICS 2000). Four of them (Li<sup>+</sup>, NO<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, Br<sup>-</sup>) were not subject to interpretation as their values were below the detection limit. The accuracy of the water chemistry data was verified using the certified reference material (CRM) Mississippi-14. Three tests with CRM were performed, which showed a strong consistency between the concentration of each tested ion and the CRM values and low values of the relative standard deviations calculated by the Chromeleon 6.7 Chromatography Data System (CDS; Suppl. Mat. B).

Laboratory work of soil samples was performed at the Institute of Geography and Spatial Organization of the Polish Academy of Sciences in Krakow. Bulk soil samples taken from mineral horizons were air-dried, gently crushed using a wooden rolling pin, and sieved using a 2 mm sieve. Live roots were removed. Soil samples from organic horizons were milled after the living parts of plants in the samples had been removed. Stone and gravel content (particles > 2 mm) and soil

colour in the moist state were determined visually according to Munsell Soil Colour Charts (Oyama and Takehara, 2002). Soil texture was determined using a Malvern Mastersizer 3,000 laser particle sizer (Malvern Instruments, Worcestershire, UK). The range of the laser particle sizer was from 0.01 to 3,500 µm. The concentration of organic matter (OM) was determined by loss of ignition at 650°C for 4 h after drying soil at 105°C (Hänninen et al., 1995). Each sample's pH was measured in 1M KCl (1:2.5 soil / KCl ratio; Thomas, 1996).

## Statistical Analyses

The equivalent weight of each ion in spring and stream water (*rX*) was calculated as:

$$rX = \frac{X \text{ concentration } \left(\frac{\text{mg}}{\text{L}}\right) * X \text{ valence}}{X \text{ atomic weight}} \left(\frac{\text{meq}}{\text{L}}\right) \quad (1)$$

The percentage share of each ion was calculated (%*rX*):

$$\%rX(\text{cation}) = \frac{rX(\text{cation}) * 100\%}{\Sigma r\text{Cations}} \quad \text{or} \\ \%rX(\text{anion}) = \frac{rX(\text{anion}) * 100\%}{\Sigma r\text{Anions}} \quad (2)$$

In statistical analyses, the concentration of main ions and their percentage share were included. All data used for statistical analyses were checked in terms of their distribution by computing coefficients of skewness and kurtosis for all variables. Nonlinear transformations – taking the log to the base 10 or the square root of the variable – were applied to the variables that showed large skewness and kurtosis coefficients. These transformations were selected for their typicality in the earth sciences. The application of nonlinear transformations to the selected variables resulted in a substantial decrease in the magnitude of skewness and kurtosis and maximized the value of the Kolmogorov-Smirnov test of normality (Suppl. mat. C-1). Although few variables were still significant ( $p \leq 0.05$ ), the nonlinear transformation of their distributions shifted them towards normality. All data were standardized.

Water temperature and SEC were used as indicators of water origin and recharge mechanism (Płaczowska et al., 2018; Toumi and Remini, 2021). The spring water temperature similar to the average daily air temperature and SEC similar to stream water indicated the interflow dominant recharge. Springs with a much lower temperature than the air temperature during sampling (<6°C) and higher SEC than stream water in the area, have been considered as the baseflow recharged. Three types of water were distinguished (Fig. 2): springs mostly recharged by baseflow (SBF), springs mostly recharged by shallow groundwater (SIF) and streams. Differences in the ion composition between these three water types (N=76) were checked using a one-way analysis of variance (ANOVA; 3 groups). The significance of differences between particular groups was determined using Tukey's test for post-hoc analysis ( $p \leq 0.05$ ). For all catchments (N=76) an analysis of the Pearson correlation coefficients between equivalent weight of cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>) and equivalent weight of anions (HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>) was performed ( $p \leq 0.05$ ). The analysis of the Pearson correlation coefficients between ions was also performed for water samples representing each rock type separately. Mass ratios of Na<sup>+</sup> and Cl<sup>-</sup> ions were calculated for each water sample.

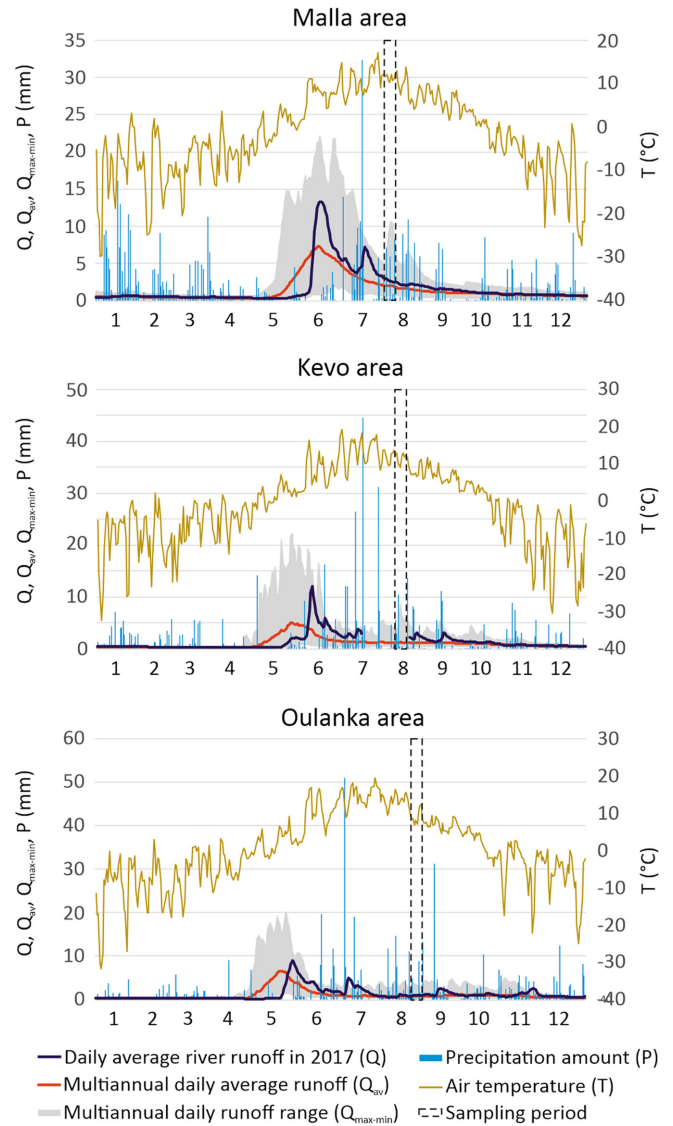
In the next step, a principal component analysis (PCA) was used to identify rocks (N=9) with a similar chemical composition in the studied catchments (Fig. 1). The following variables were considered in the study: Al, Ca, Cl, Fe, K, Mg, Na, P, S. Variables represented concentrations of particulate main chemical elements (ppm). According to the results of the PCA, four groups of rocks different in terms of chemical composition were distinguished. In all performed PCAs the two first factors, distinguished according to the Kaiser criterion, and only component loadings greater or equal to the absolute value of 0.5 were subject to interpretation.

For further analysis, 45 catchments were selected that represented one recharge mechanism (interflow) and one geochemical group of bedrock. The selected catchments were located in areas with igneous felsic rocks and metamorphic rocks rich in quartz and plagioclase due to the fact that these catchments were abundant compared to catchments located in areas with other rock types. The selected catchments represent four types of plant communities: grass heath, heath tundra, birch forest, and boreal forest (Suppl. mat. A). In addition, springs recharged mainly by baseflow were excluded from further analyses. For the selected 45 catchments, a PCA was employed to identify other factors besides lithology, controlling water chemistry in the studied catchments. The following water variables were considered in the analysis: pH, SEC, concentrations of main ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ) and percentage share of ions. Water temperature was not included in this analysis as the chosen 45 catchments were recharged mostly by shallow groundwater which was strongly affected by the air temperature. In this analysis, the percentage share of main ions was also considered. Moreover, for the selected 45 catchments, one-way ANOVA was used in order to show any differences in the chemistry of water samples representing different plant communities (four groups) as well as to show differences in the chemistry of water samples representing different geographic locations (three groups). The significance of differences between particular groups was determined using Tukey's test for post-hoc analysis ( $p \leq 0.05$ ). An analysis of the Pearson correlation coefficients between equivalent weight of ions and catchment parameters was performed for the selected 45 catchments ( $p \leq 0.05$ ).

### Hydro-meteorological Conditions During Fieldwork

2017 was characterized by higher river runoffs in Lapland compared to the average multiannual runoff (Fig. 3; [www.ymparisto.fi](http://www.ymparisto.fi)). High runoff related to the spring thaw began about a month later than usual. However, during the fieldwork, river runoffs were close to the average multiannual runoff (Oulanka area) or slightly higher (Malla area).

Precipitation totals in Lapland are high in August (<https://www.ilmatieteenlaitos.fi>), but this does not necessarily lead to high river runoffs (Fig. 3; Hyvärinen, 1998; Korhonen and Kuusisto, 2010). A lowering of runoff in August was observed in Lappish catchments in Sweden and Russia (Beylich et al., 2005; Zakharova et al., 2007). During fieldwork the precipitation in the Malla study area was 17.7 mm, in the Kevo study area – 16.2 mm and in the Oulanka study area – 29.6 mm. Hydro-meteorological conditions in the fieldwork period were characterized as medium wet.



**Figure 3. Hydro-meteorological conditions in the study areas in 2017.** Daily precipitation totals and average daily air temperature data derived from the Enontekiö Kilpisjärvi kyläkeskus observation station for the Malla area, from the Utsjoki Kevo observation station for the Kevo area, and from the Kuusamo Kiutaköngäs observation station for the Oulanka area. River discharge data for the Malla area derived from the Kilpisjärvi – luusua observation station (multiannual data for 1952-2011), for the Kevo area from the Utsjoki Patoniva observation station (multiannual data for 1962-2011), and for the Oulanka area from the Oulankajoki observation station (multiannual data for 1966-2011). For data sources see Table 2.

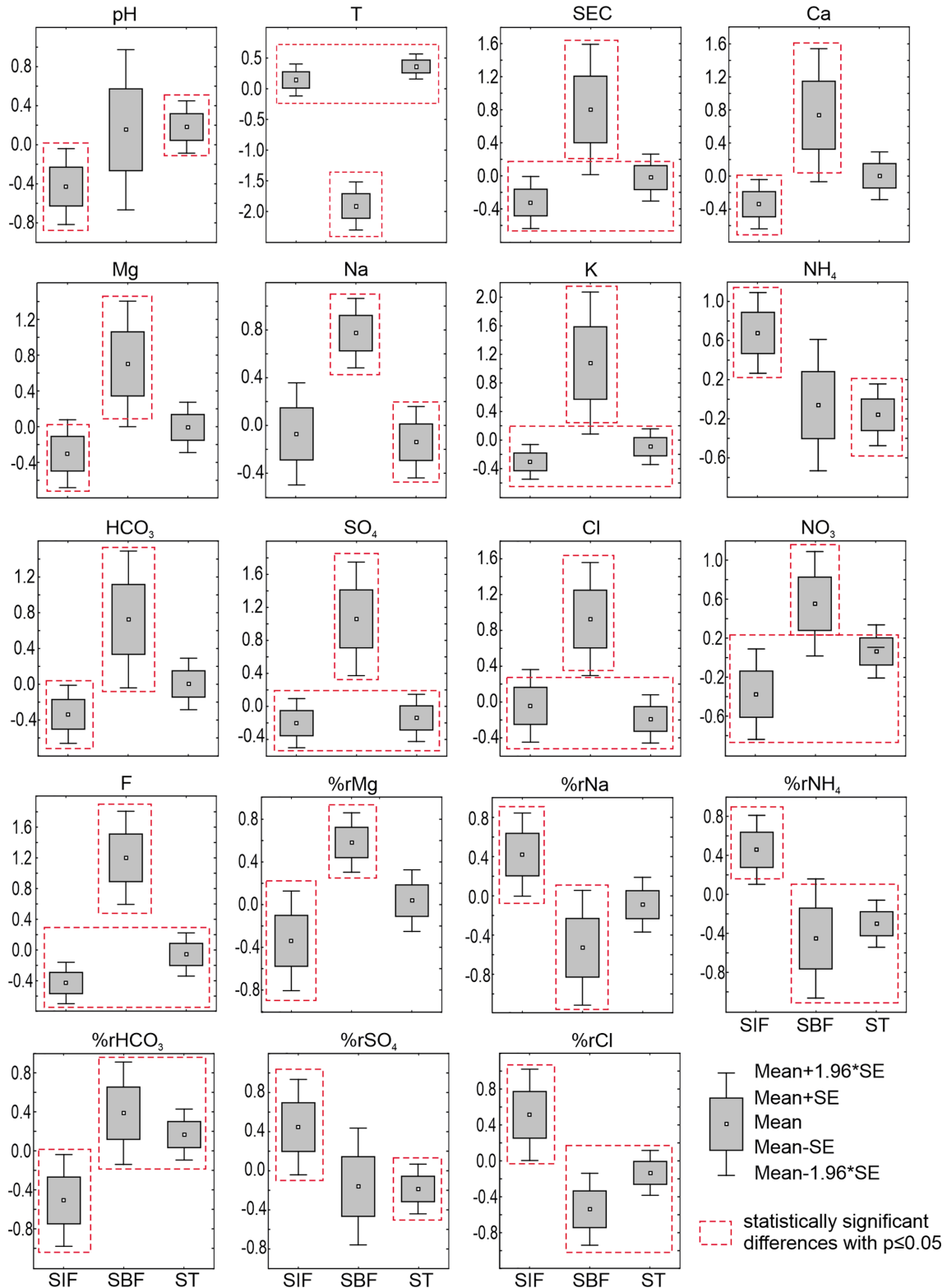
## Results

### Characteristics of Springs, Streams and Their Contributing Areas

Water in the studied areas had low mineral content and its specific electric conductivity (SEC) was, on average,  $60 \mu\text{S cm}^{-1}$  and usually did not exceed  $100 \mu\text{S cm}^{-1}$  (Table 1). This only occurred in areas formed of rocks vulnerable to weathering such as dolomite, mafic tuff

and biotite parschist, where it reached up to  $238 \mu\text{S cm}^{-1}$ . The sequence of average cation concentrations in the Malla and Kevo areas was:  $\text{Ca} > \text{Na} > \text{Mg} \gg \text{K}$ , and in the Oulanka area:  $\text{Ca} > \text{Mg} \gg \text{Na} > \text{K}$ . The sequence of average anion concentrations in the Malla and Kevo areas was:  $\text{HCO}_3 \gg \text{Cl} > \text{SO}_4$ , while in the Oulanka area it was:  $\text{HCO}_3 \gg \text{SO}_4 > \text{Cl}$ .

Both springs and streams were characterized by a wide range of temperatures, i.e.  $2.6\text{--}13.6^\circ\text{C}$  and  $4.0\text{--}14.7^\circ\text{C}$ , respectively (Table 1). However, most spring waters had a temperature similar to the average daily air temperature, which ranged from  $10.3$  to  $12.2^\circ\text{C}$  in the Malla area, from  $9.0$  to  $12.9^\circ\text{C}$  in the Kevo area and from  $6.9$  to  $12.0^\circ\text{C}$  in



**Figure 4.** Differences in physical and chemical properties of water between springs recharged by shallow groundwater (SIF), springs recharged by baseflow (SBF), and streams (ST) determined using Tukey's test;  $N=76$ . Only statistically significant differences ( $p \leq 0.05$ ) are shown.

the Oulanka area. The SEC of these springs was similar to stream water SEC which may indicate the interflow dominant recharge. Only few springs were characterized by a temperature that was much lower than the average daily air temperature during fieldwork (between 2 and 5°C) and a significantly higher SEC than stream water and other springs (Fig. 4) which may indicate the baseflow dominant recharge.

The one-way ANOVA exhibited significant differences in physical and chemical properties between springs recharged mainly by baseflow (SBF), springs recharged by shallow groundwater (interflow; SIF), and streams. SBF that remain in contact with the bedrock for longer periods of time were characterized by lower temperatures, higher SEC, and higher concentrations of most main ions than SIF (Fig. 4). The  $\text{NH}_4^+$  ion was an exception, as the concentration of this ion as well as its share was higher in SIF than in streams and SBF. SIF and streams were not significantly different with respect to the concentrations of main ions. In terms of the percentage share of ions in the chemical composition of water, SIF stood out, as they were characterized by larger %rNa, %r $\text{SO}_4$ , %rCl and smaller %rMg and %r $\text{HCO}_3$  than SBF and streams.

The bedrock lithology varied in the study areas (Fig. 2). However, the analysis of the chemical composition of rocks (Suppl. mat. C-2) indicates the existence of four different geochemically groups of rocks: 1) igneous mafic rocks and metamorphic rocks rich in Fe, K and Mg, represented in the study area by biotite paraschist and mafic tuff, farther referred to as “igneous mafic/metamorphic” rocks; 2) igneous felsic rocks and metamorphic rocks containing primarily quartz and sodium feldspar, represented in the study area by arkose quartzite, quartz feld-

spar paragneiss from the Silisjoki Suite, quartz feldspar paragneiss from the Kaamanen Complex, granodiorite and orthoquartzite, farther referred to as “igneous felsic/metamorphic” rocks; 3) sedimentary carbonate rocks rich in Ca, Mg and total C, represented in the study area by dolomite; 4) sedimentary clastic rocks containing primarily quartz, represented in the study area by silicate claystone.

Waters in the Oulanka area represent similar hydrochemical types, independently from the geochemical group of rock in the catchment, dominated by  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$  ions (Fig. 5). The rest of waters connected with igneous felsic/metamorphic rocks represent mixed type between Ca-Mg- $\text{HCO}_3$ -type and Na-Cl-type, with the latter dominating in the Kevo area. Part of waters connected with silicate claystone in the Malla area was hydrochemically similar to waters in the Oulanka area and the other part to waters of the igneous felsic/metamorphic bedrock catchments.

The waters of hydrochemical Na-Cl-type dominated in the areas which are located closest to the sea. A strong positive correlation ( $r=0.89$ ) was found between the concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  ions (Table 3). All the investigated waters were relatively more enriched in  $\text{Na}^+$  than in  $\text{Cl}^-$  ions compared to seawater (Fig. 6). The Na:Cl ratio was closest to seawater in the case of water flowing out of perennial snow patches in the Malla area, while most water in the Oulanka area and some water in the Malla area was the least similar to seawater. Most water samples from the Malla and Kevo areas were characterized by an Na:Cl ratio typical of marine aerosols (Fig. 6).

When considering all water samples ( $N=76$ ), there was a significant positive correlation between base cations originating mostly

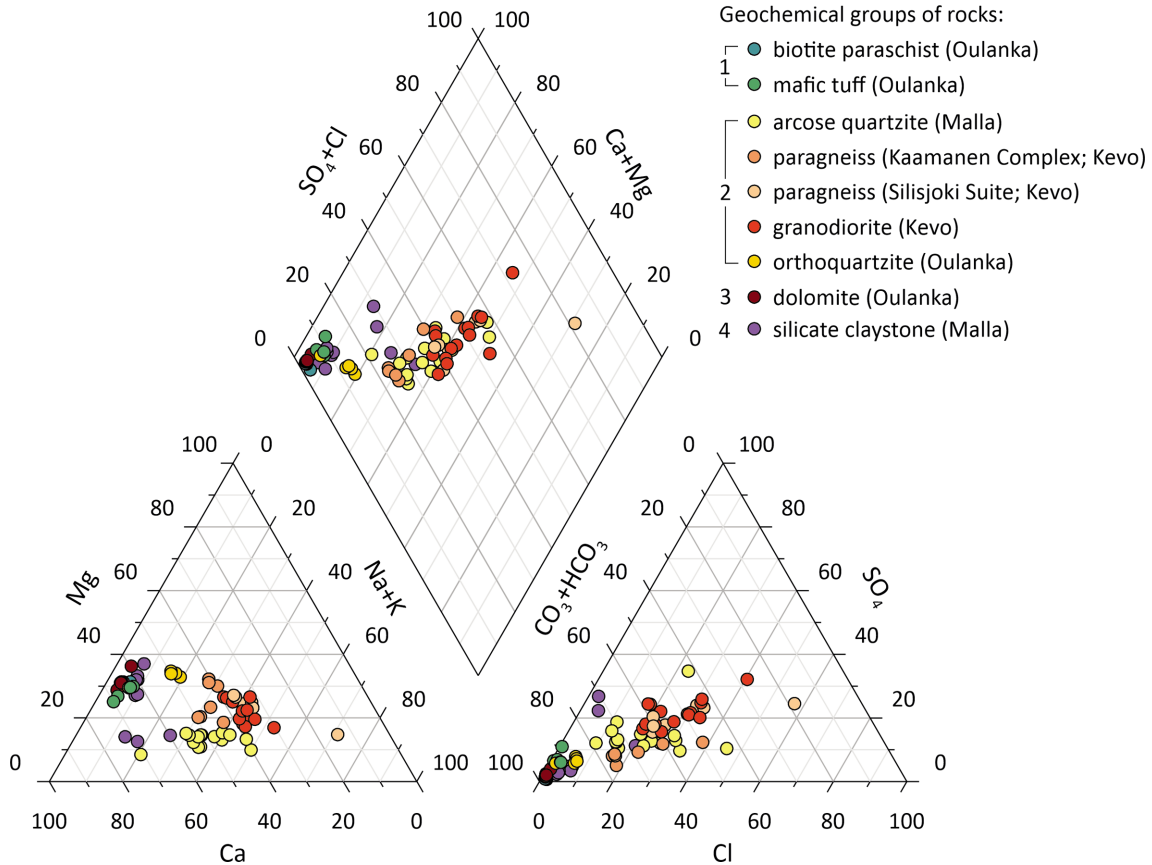
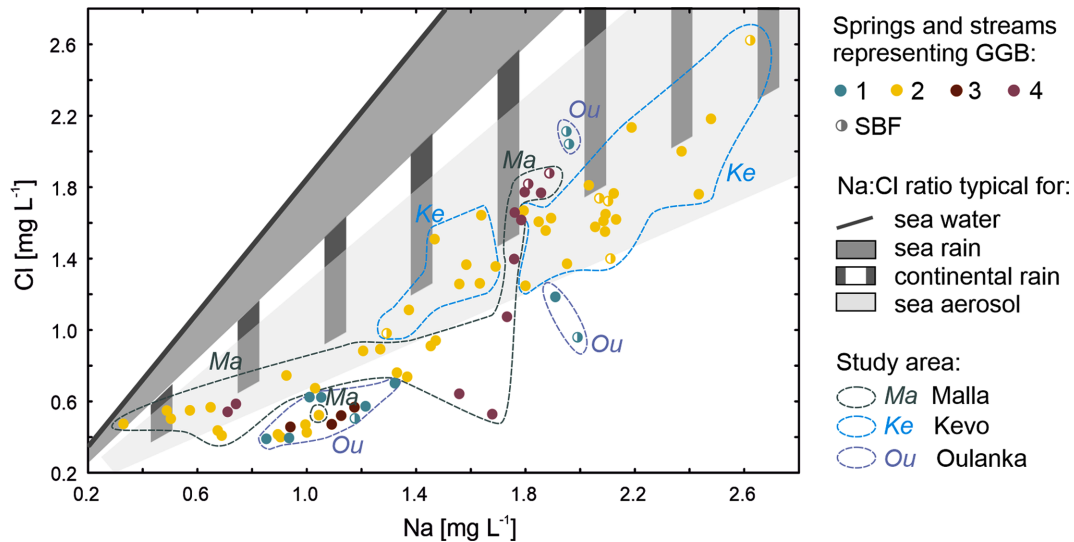


Figure 5. Spring and stream water samples representing catchments with different rock types plotted in the Piper tri-linear diagram.



**Figure 6.** Na:Cl ion ratios in springs and streams representing geochemical groups of bedrock in different study areas in relation to Na:Cl ion ratios in the seawater, sea rain, continental rain and sea aerosols according to Möller (1990). Geochemical group of bedrock (GGB): 1 – igneous mafic/metamorphic rocks; 2 – igneous felsic/metamorphic rocks; 3 – dolomite; 4 – silicate claystone.

**Table 3.** Matrix of Pearson correlation coefficients between cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ) and anions ( $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ) in all studied catchments ( $N=76$ ). Correlations bolded are significant at  $p \leq 0.05$ .  $r$  – equivalent weight of ion concentration in water

Variable	$r\text{HCO}_3^-$	$r\text{SO}_4^{2-}$	$r\text{Cl}^-$	$r\text{NO}_3^-$
$r\text{Ca}^{2+}$	<b>0.99</b>	<b>0.59</b>	-0.15	<b>0.28</b>
$r\text{Mg}^{2+}$	<b>0.99</b>	<b>0.56</b>	-0.10	<b>0.31</b>
$r\text{Na}^+$	-0.05	<b>0.55</b>	<b>0.89</b>	-0.08
$r\text{K}^+$	<b>0.87</b>	<b>0.64</b>	-0.05	<b>0.33</b>
$r\text{NH}_4^+$	-0.10	0.08	0.16	<b>-0.35</b>

from the terrestrial environment ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$ ) and the  $\text{HCO}_3^-$  anion (Table 3). This correlation was genuine for all rock groups separately (not shown). The positive correlation between  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and the  $\text{SO}_4^{2-}$  anion is weaker, but still significant (Table 3). This correlation was found only for certain rock groups: arkose quartzite in the Malla area and igneous mafic/metamorphic rocks in the Oulanka area (not shown). The positive correlation between  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and the  $\text{NO}_3^-$  anion is weaker than for both  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  anions.

### Morphology and Chemistry of Soils in Particular Plant Communities

All studied soils were characterized by small thickness, significant share of rock fragments (such as fine gravel, gravel and cobble), very low content of clay (<4%) and a very low pH ( $\text{pH}_{\text{KCl}}$  3.4 to 4.5; Table 4). Soils with distinct morphologies occurred under the grass heath in the Malla area. Very shallow Leptosols with no regular soil horizons have developed at higher elevations. Gleysols, which have developed in nivation hollows are deeper soils with sandy loam texture and a small share of rock fragments. Shallow Podzol soils were found under heath tundra in the Malla and Kevo areas; these Podzols had a high content of rock fragments and a sandy loam and loamy sand texture.

Soils under birch and boreal forests in the Malla, Kevo and Oulanka areas were deeper Podzols (>50 cm), with a sandy loam texture.

### Spring and Stream Water Chemistry in Catchments with Similar Bedrock Lithology

The F1 factor of the PCA ( $N=45$ ) explained 45.4% of variance in the water chemistry data and exhibited a positive relationship between SEC, concentrations of  $\text{Na}^+$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{Ca}^{2+}$ , and  $\text{K}^+$  (Fig. 7a, Suppl. mat. C-3). This factor could be called “geogenic”, as it involves ions that originated from the weathering of rocks occurring *in situ* or which entered as a result of transport and atmospheric deposition. The F2 factor explained 22.5% of variance in the water chemistry and referred to a negative relationship: the higher water pH and concentrations of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ ; the lower concentrations of  $\text{NH}_4^+$  and  $\text{Cl}^-$ .

The PCA concerning the concentration of ions identified four groups of water that represent certain defined ecosystems (plant communities and soils; Fig. 7a). The first group includes water from streams that drain grass heaths atop Leptosol and Gleysol soils found in the Malla area. The studied waters were characterized by low SEC, low concentrations of most ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{F}^-$ ). The second group included waters from heath tundra that grows atop Podzols in the Malla and Kevo areas. These water samples were characterized by a low SEC and low concentrations of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ , such as waters from the first group, however, also by a lower pH and higher concentrations of  $\text{NH}_4^+$  and  $\text{Cl}^-$ . The third group included primarily water samples from birch forests in the Kevo and Malla areas that grow atop deeper Podzol soils. In contrast to waters from the first and second groups, the water samples were characterized by a higher SEC and higher concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{HCO}_3^-$ , and similar to the second group by a low pH and high concentrations of  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ . The fourth group included water samples from a boreal forest in the Kevo and Oulanka areas that grows atop Podzol soils. The water samples in this group were char-

**Table 4. Physical and chemical properties of selected soils**

Soil horizon	Depth [cm]	Particles >2 mm [% vol]	Sand [%]	Silt [%]	Clay [%]	Texture	pH <sub>KCl</sub>	OM [%]
Grass heath, Malla area								
Dystic Oxygleyic Stagnic Gleysol (Loamic, Umbric)								
AE	0-5	0	54.7	42.2	3.1	sandy loam	3.5	12.60
Bg1	5-10	5	49.1	48.3	2.6	sandy loam	4.1	2.56
Bg2	10-35	10	n.a	n.a	n.a	n.a.	4.4	2.12
Dystric Hyperskeletic Lithic Leptosol								
O	0-5		n.a	n.a	n.a	n.a.	3.9	82.87
C	>5	>95	n.a	n.a	n.a	n.a.	n.a.	n.a.
Heath tundra, Kevo area								
Hyperskeletic Albic Podzol (Loamic)								
OF	0-5	0					3.5	48.62
OH	5-8	0					3.3	65.77
E	8-10	0	30.4	66.5	3.1	silt loam	3.9	5.72
Bhs	10-12	15	43.0	53.4	3.6	sandy loam	4.0	13.14
Bs1	12-15	50	63.0	35.6	1.4	sandy loam	4.2	6.82
Bs2	15-25	70	62.2	36.6	1.3	sandy loam	4.4	1.48
C	25-30	>90	60.1	38.3	1.6	sandy loam	4.3	1.14
Birch forest, Malla area								
Skeletic Albic Podzol (Loamic)								
OL	0-1						4.4	95.73
OH	1-6						3.6	43.60
A	6-8	0	61.0	37.1	1.9	sandy loam	3.6	21.98
E	8-10	5	54.0	44.1	1.9	sandy loam	3.4	3.17
Bhs1	10-30	25	67.7	30.5	1.8	sandy loam	4.0	1.83
Bhs2	30-(50)	50	67.4	31.2	1.3	sandy loam	4.4	4.10
Boreal forest, Kevo area								
Skeletic Albic Podzol (Loamic)								
OF	0-3						3.2	75.36
AE	3-5	10	60.9	36.4	2.7	sandy loam	3.6	4.50
Bhs1	5-10	10	63.2	34.8	2.0	sandy loam	4.0	2.36
Bhs2	10-20	15	59.2	38.7	2.1	sandy loam	4.4	2.95
C	20-30	40	63.1	34.1	2.8	sandy loam	4.5	1.38

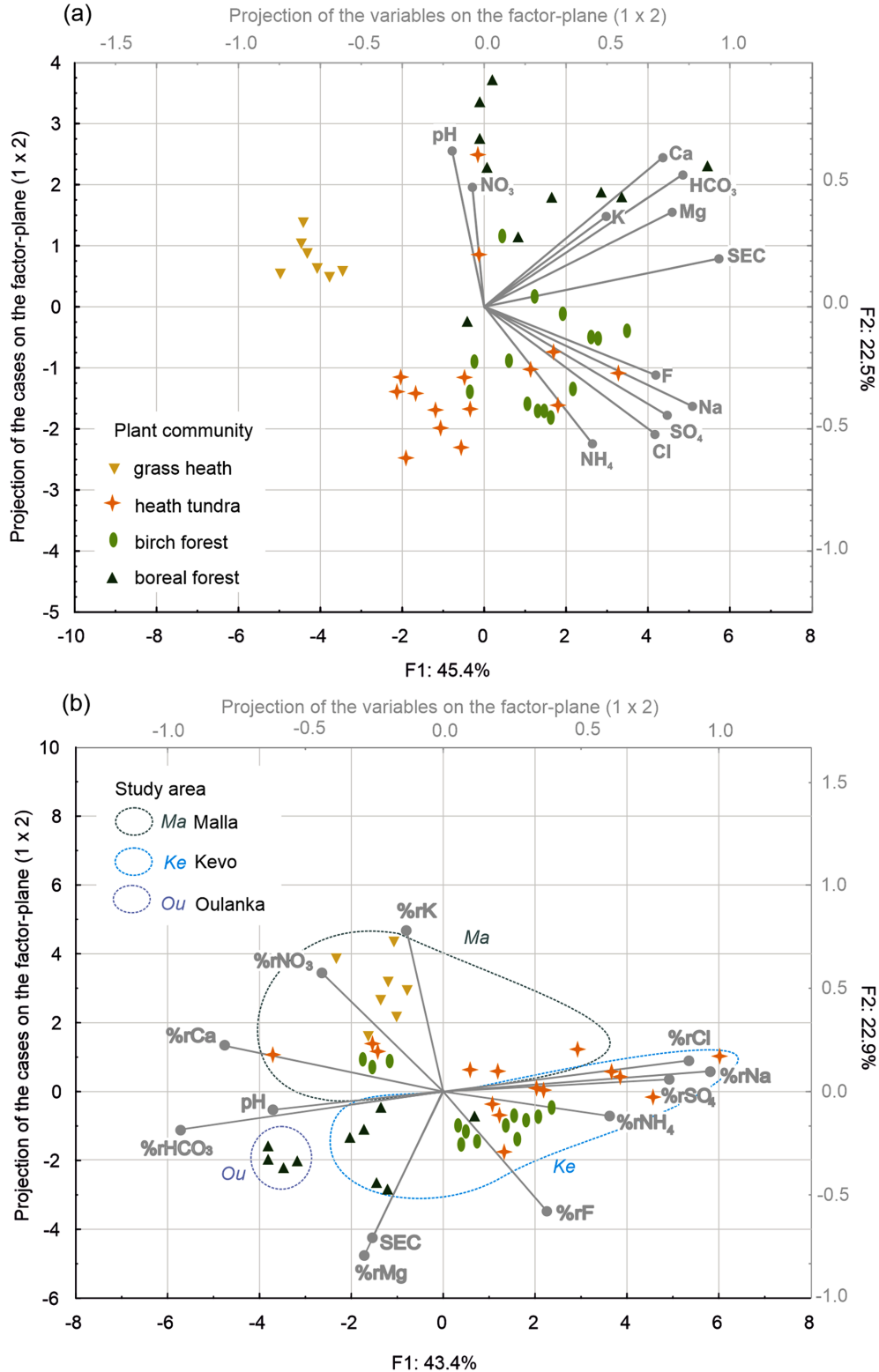
acterized by high SEC and pH and high concentrations of most ions, especially Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> and HCO<sub>3</sub><sup>-</sup>.

Regarding the percentage share of ions, the F1 factor explained 43.4% of variance in the water chemistry data and referred to a negative relationship: the higher shares of Na<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> originating mostly from atmospheric deposition and NH<sub>4</sub><sup>+</sup>, the lower shares of HCO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup>, originating from the weathering of rock *in situ* and lower water pH (Fig. 7b, Suppl. mat. C-4). This factor, therefore, strongly emphasizes the contribution of atmospheric deposition. The F2 factor explained 22.9% of variance and referred to a negative relationship: the higher shares of biogenic ions (NO<sub>3</sub><sup>-</sup>, K<sup>+</sup>), the lower SEC and shares of Mg<sup>2+</sup> and F<sup>-</sup>.

The PCA with regard to percentage share of ions allowed classifying the studied water samples into three principal groups (Fig. 7b). The largest group included water found in the Kevo area, representing the plant communities of heath tundra and birch forest. These waters were characterized by a high percentage share of ions originating

from atmospheric deposition (%rNa, %rSO<sub>4</sub> and %rCl) as well as NH<sub>4</sub><sup>+</sup>, at the same time by a lower percentage share of ions derived from weathering *in situ* (%rCa and %rHCO<sub>3</sub>), and biogenic ions (%rK, and %rNO<sub>3</sub>). The next group consisted of water samples collected in a boreal forest in the Kevo and Oulanka areas and were characterized by a lower %rNa, %rSO<sub>4</sub> and %rCl and a higher percentage share of ions derived from the weathering of rocks *in situ* (i.e. %rCa, %rMg and %rHCO<sub>3</sub>). The third group were samples from the grass heath plant community in the Malla area which were characterized by a higher share of %rCa and %rHCO<sub>3</sub> than those originating from atmospheric deposition and also by a high %rK and %rNO<sub>3</sub>.

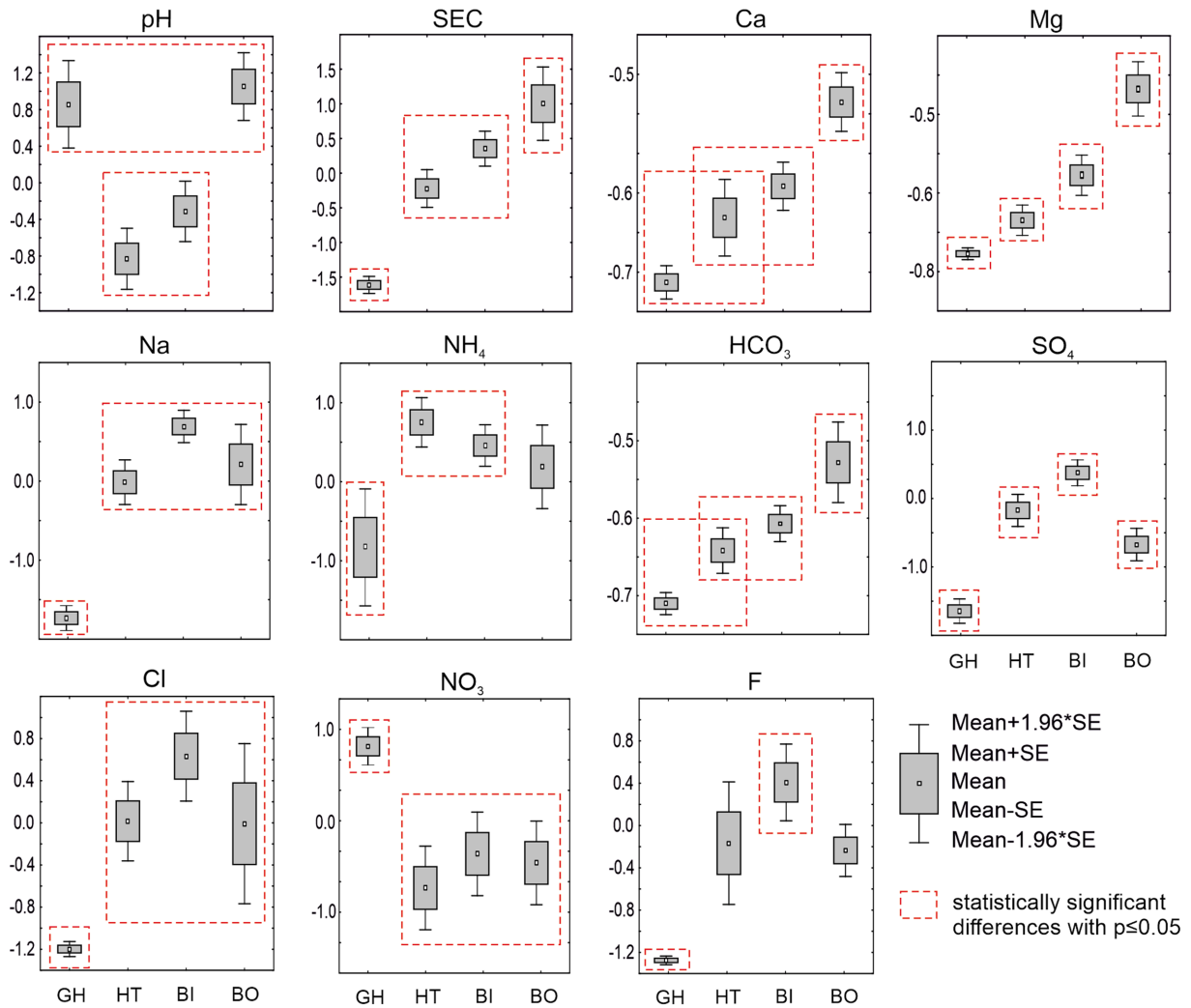
Statistically significant differences between catchments covered with different plant communities occurred in water pH, SEC and concentrations of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> (Fig. 8). Statistically significant differences between study areas occurred in the case of concentrations of ions supplied by atmospheric deposition (Na<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>; Fig. 9).



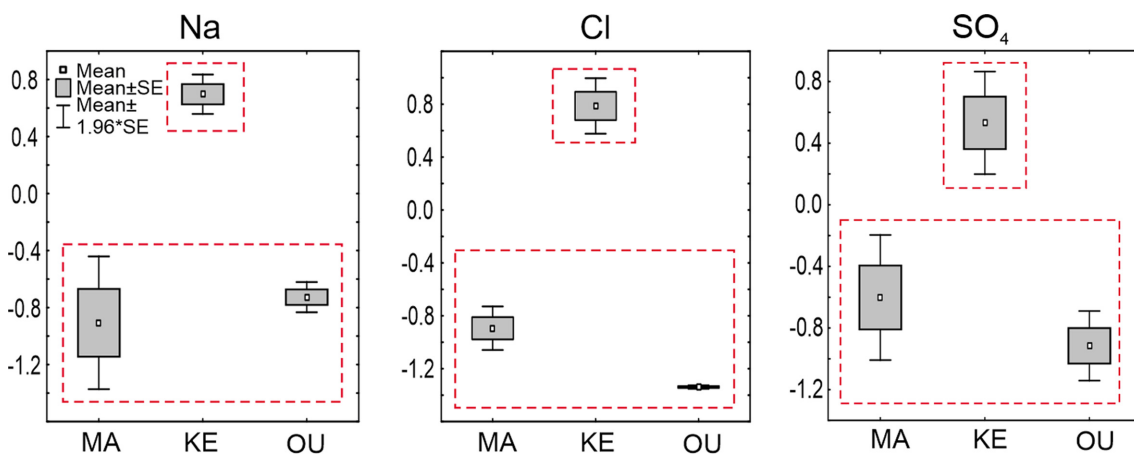
**Figure 7.** PCA of chemical properties of SIF and streams representing igneous felsic/metamorphic rocks of (a) ion concentrations, (b) percentage share of ions. Black axis describes the projection of cases (water representing four plant communities; N=45) on the factor-plane. The Grey axis describes the projection of variables on the factor-plane: water pH, conductivity (SEC), and concentrations of ions or percentage share of ions.

Water chemistry was strongly correlated with some characteristics of the catchment (Table 5). Elevation was an important factor controlling SEC and the concentrations of most ions – the higher the ele-

vation, the lower the SEC and concentrations of most ions coming from weathering processes and atmospheric deposition (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, F<sup>-</sup>) and the higher the concentration of NO<sub>3</sub><sup>-</sup>. Hillslope



**Figure 8.** Differences in chemical properties of SIF and streams in igneous felsic/metamorphic catchments ( $N=45$ ) represent four plant communities: GH - grass heath, HT - heath tundra, BI - birch forest, and BO - boreal forest; determined using Tukey's test. Only statistically significant differences ( $p \leq 0.05$ ) are shown.



**Figure 9.** Differences in concentration of Na<sup>+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions in waters located in different study areas: MA – Malla, KE – Kevo, OU – Oulanka; determined using Tukey's test. Dashed rectangles indicate statistically significant differences with  $p \leq 0.05$ .

gradient was an important factor controlling SEC and concentrations of some ions. The higher the hillslope gradient, the lower SEC and

concentrations of Mg<sup>2+</sup>, Na<sup>+</sup>, Cl<sup>-</sup>, and F<sup>-</sup>. Catchment area was positively correlated with Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, and F<sup>-</sup> concentration and negatively cor-

**Table 5. Matrix of Pearson correlation coefficients of catchment characteristics and water properties (N=45). Correlations bolded are significant at  $p \leq 0.05$ . Variables: H – elevation of the sampling point, A – catchment surface area, Sp – catchment average slope gradient, Q – spring or stream discharge, pH – spring and stream water pH, SEC – spring and stream water electric conductivity, rCa-rF - equivalent weight of ion concentration in spring and stream water**

Variable	pH	SEC	rCa	rMg	rNa	rK	rNH <sub>4</sub>	rHCO <sub>3</sub>	rSO <sub>4</sub>	rCl	rNO <sub>3</sub>	rF
H	0.07	<b>-0.75</b>	<b>-0.41</b>	<b>-0.75</b>	<b>-0.79</b>	-0.02	0.18	<b>-0.47</b>	<b>-0.56</b>	<b>-0.70</b>	<b>0.72</b>	<b>-0.57</b>
A	0.17	0.23	0.19	<b>0.48</b>	0.27	-0.05	<b>-0.44</b>	<b>0.30</b>	0.19	0.17	-0.08	<b>0.47</b>
Sp	0.04	<b>-0.42</b>	-0.01	<b>-0.40</b>	<b>-0.61</b>	0.24	-0.06	-0.13	-0.29	<b>-0.67</b>	0.26	<b>-0.44</b>
Q	0.13	-0.05	-0.07	-0.05	-0.12	-0.07	<b>-0.33</b>	-0.02	0.14	0.13	0.23	<b>0.35</b>

related with NH<sub>4</sub><sup>+</sup>. There was a negative correlation between discharge and NH<sub>4</sub><sup>+</sup> and a positive correlation between discharge and F<sup>-</sup>.

## Discussion

In most cases, spring water temperature in the studied areas was similar to the average daily temperature during fieldwork indicating the recharge by interflow. Water temperature together with SEC are claimed to be good indicators of water origin (Toumi and Remini, 2021) and recharge mechanism (James et al., 2000; Płaczkowska et al., 2018). Our results showed the lack of significant differences between chemistry of spring recharged by interflow (SIF) and streams (Fig. 4). Moreover, a group of water samples representing different geochemical group of rocks i.e. dolomite, igneous mafic/metamorphic rocks, silicate claystone and orthoquartzite, were located close to one another in the Piper diagram (Fig. 5) which indicates similar water chemistry. All these waters were strongly dominated by bicarbonates (>85 meq%). Probably, these sites are recharged mainly by shallow groundwater within glacial till or weathered soil cover. All of them are located in the Oulanka area or in the lower part of the Malla area (silicate claystones) where rather thick moraine covers or fluvioglacial formations are found, reaching more than 10 m in thickness (Hirvas, 1991). These sediments contain diverse rock material with only about 50% of till stones of local origin. The subsequent 50% could be transported from a few kilometers to more than 10 km (Virkkala, 1956). This lithologically diverse material in moraines (e.g. dolomites, igneous and metamorphic rocks in the Malla and Oulanka areas), as well as aeolian transport of carbonate dust of local and further origin (Raidla et al., 2015) may cause averaging of the water chemistry (Ca-Mg-HCO<sub>3</sub>-type; Fig. 5). This implies that the contact between groundwater and bedrock at these sites was likely limited and that areas of sedimentary deposits represented the primary source of main ions (Ca<sup>2+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>). This finding is in the line with other studies made in the Central Finnish Lapland that confirm the shallow groundwater in the moraine cover is characterized by similar chemistry dominated by Ca<sup>2+</sup>, Mg<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup>, regardless of the lithology of the bedrock (Lahermo, 1971). Therefore, in most of the studied streams, rather long headwaters were supposedly recharged by shallow groundwater within the sedimentary deposits that flowed directly into stream channels, thus unifying the water chemistry in streams and springs.

However, few springs were characterized by temperatures lower than the average daily temperatures during fieldwork (Table 1, Fig. 3). In one spring in the Malla area a low water temperature was accompa-

nied by a very low SEC, which was a result of being recharged by melting perennial snow patches. Some springs in all study areas had a relatively high SEC compared to other springs in the vicinity. It may point to recharge by groundwater from a deep, hard rock aquifer with a long residence time (Płaczkowska et al., 2018).

The waters found in igneous mafic/metamorphic and dolomitic catchments had several times higher concentrations of Ca<sup>2+</sup>, Mg<sup>2+</sup> and K<sup>+</sup> cations, HCO<sub>3</sub><sup>-</sup> anion and SEC than the waters found in catchments formed of igneous felsic/metamorphic rocks not vulnerable to weathering. The most important sources of Ca<sup>2+</sup>, Mg<sup>2+</sup> and K<sup>+</sup> ions are rock weathering and leaching from soil exchange sites because of soil acidification (Legout et al., 2009; Raidla et al., 2019; Wasak-Søk et al., 2021). Some bedrock found in the study areas might be a rich source of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions, such as dolomites and mafic tuffs in the Oulanka area. In case of K<sup>+</sup> ions, their cycling is strongly connected with biological cycling and soil processes (Binkley, 1986). In the environments rich in calcium and magnesium, K<sup>+</sup> cations can be released from the soil exchange sites and transported to soil water because the charge on divalent ions allows them to be retained more strongly by the soil exchange sites than monovalent K<sup>+</sup> ions. It seems to be in line with field and laboratory experiments that showed a high susceptibility of K<sup>+</sup> to leaching from the soil (Dahlgren and Driscoll, 1994; Wasak-Søk et al., 2021).

The important process enhancing mineral weathering in Lapland in silicate rocks can be the oxidation of sulphide and sulphuric acid formation (Thorn et al., 2001; Darmody et al., 2007; Raidla et al., 2019). According to Raidla et al. (2019) such processes can occur in arcose quartzite and silicate claystone in the vicinity of the Malla area (Lake Saana catchment), because arcose quartzite rich in pyrite is the source of sulphuric acid percolating with water through both types of rocks. We found a significant positive correlation between all basic cations and SO<sub>4</sub><sup>2-</sup> in waters flowing out from arcose quartzite catchments, but not from silicate claystone catchments (not shown). It suggests, the process described by Raidla et al. (2019) can be an important trigger of rock weathering as well as water chemistry in the catchments with arcose quartzite bedrock.

The same mechanism can be responsible for weathering processes taking part in mafic tuffs in the Oulanka area. Significant correlations between SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup>, Mg<sup>2+</sup> and K<sup>+</sup> cations in surface water (not shown) seem to confirm such phenomena. Springs with lower temperature and higher SEC, which are likely recharged by deep groundwater from igneous mafic/metamorphic aquifers with a long residence time, had higher SO<sub>4</sub><sup>2-</sup> content than those supposed to be recharged mostly by interflow in this group of rocks. The same waters were also enriched in base cations: Ca<sup>2+</sup>, Mg<sup>2+</sup> and K<sup>+</sup>.

Strong positive correlations between three base cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$ ) and  $\text{HCO}_3^-$  observed in all studied waters (Table 3) as well as in every geochemical group of rocks separately (not shown) suggest, that the dissolution and leaching processes connected with  $\text{HCO}_3^-$  have greater importance in the area studied.  $\text{HCO}_3^-$  ion is one of the most important factors controlling rock weathering because of its ubiquity in the environment (Egli et al., 2008; Andrews and Slesinger, 2001). It is the presence of this ion that probably regulates the variation in the concentrations of “geogenic” ions in water between different environments.

Considering only waters flowing from igneous felsic/metamorphic catchments (excluding baseflow recharged springs), the concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$  ions differed significantly between catchments with different plant communities (Fig. 8). We assume that the highest potential of the boreal forest to accelerate chemical weathering (Zakharova et al., 2007; Balogh-Brunstad et al., 2008) is a result of an array of factors. First of all, boreal forests in the study areas are located on the lowest altitudes with the warmest conditions. Higher temperatures accelerate soil microbial activity and in consequence higher  $\text{CO}_2$  production, which is a source of bicarbonate favouring chemical weathering. This effect was observed by Egli et al. (2008) in carbonate Alps. They found that limestone weathering was more intense in coniferous forests than in higher montane belts, which was accompanied with more intense soil respiration. In a field experiment conducted in soils developed on igneous bedrock (granodiorites and diorites), Andrews and Slesinger (2001) observed that the sum of base cations in soil waters was significantly higher under elevated  $\text{CO}_2$  concentration. They concluded that base cations resulted mostly from increased soil acidification rather than weathering of primary minerals, because changes in Si concentrations were negligible. Despite the fact that biological analyses were not carried out in our study, this pattern was indirectly demonstrated by a significant negative correlation between elevation and the concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$  and SEC (Table 5). Cation leaching to the soil water and in consequence to surface water in the forested catchments in comparison to tundra areas can be facilitated also due to a lower position on the slope, where moraine and fluvio-glacial deposits are usually thicker. It facilitates water percolating and, thus, both soil acidification and rock weathering, as the shallow groundwater can be an additional source of  $\text{CO}_2$  (Duvert et al., 2018). In addition, deep root systems of trees in comparison to tundra plants (Reiman et al., 2001) can facilitate chemical weathering because of enhanced biological activity and the triggering of physical rock weathering (Brantley et al., 2017).

Our results showed a higher concentration of base cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) in waters flowing from catchments covered with coniferous boreal forests than from catchments covered with birch forests (Fig. 8), suggesting higher intensity of weathering processes or higher soil acidification under coniferous trees. These results are in line with observations from temperate mountainous areas (Rothe et al., 2002; Drewnik et al., 2016; Wasak-Sęk et al., 2021). In addition to the lowest elevations and the highest biological activity, it may be the result of coniferous trees producing greater amounts of organic acids and dissolved organic carbon, accelerating soil acidification and weathering (Likens et al., 1998). Another explanation may be the unique cycling pattern of elements in coniferous trees, promoting the production of protons and, consequently, soil acidification, as well as the leaching of

base cations (Berger, 2006). In the studied areas, both birch and boreal forests had a thick forest floor mostly consisting of heath (Suppl. mat. A), which itself acidified the soil. However, the birch itself and willow shrubs, which are often admixed in birch forests, can suppress this effect, because the fallen leaves of both species could be a source of base cations in the soil (Reimann et al., 2001; Darmody et al., 2004; Zakharova et al., 2007).

In waters flowing from catchments covered with birch forest, exceptionally high concentrations of  $\text{SO}_4^{2-}$  were found. This could be an effect of the unique sulphur cycle, which is strongly associated with biological processes. Forests have a high potential of  $\text{SO}_4^{2-}$  uptake due to high canopy deposition (Hultberg and Grenfeld, 1992). Birch forest soils feature higher amounts of organic matter than tundra soils (Table 4), thus, they can potentially sequester more  $\text{SO}_4^{2-}$ , as soil organic matter is an important sulphur sink in the environment (Hultberg and Grenfeld, 1992; Reimann et al., 2001). Additionally, Reimann et al. (2001) found that birch trees and willow shrubs were much more effective at taking up  $\text{SO}_4^{2-}$  ions from the atmosphere and collecting in their leaves than coniferous trees, tundra species or grass.

In contrast to waters flowing from forest catchments, the lowest concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$  ions were found in spring and stream waters in catchments covered with grass heath and heath tundra, which occurred in the Malla and Kevo areas. Sparse vegetation, thin soil and regolith cover, and permafrost in the ground on barren fells above the treeline can prevent water from deep percolation (Sverdrupp and Warfvinge, 1988; Beylich et al., 2004) and reduce soil acidification and weathering. This is especially noticeable in grass heath areas. The retardation of weathering processes in these areas was also confirmed by lack of Podzols despite the fact that soils were very acidic (Table 4). Furthermore, the highest located streams in the Malla area were recharged by perennial snow patches which are cation-poor (especially in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ; Beylich et al., 2005; Raidla et al., 2015). The lowest SEC and concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$  in waters in catchments covered with grass heath and heath tundra could also be the result of reindeer herding. In both the Malla and Kevo areas reindeer herding can take an intense form, e.g. there is 1200–2000 reindeers in the Malla area grazing for 3–4 months every summer (unpublished information from the Kilpisjärvi Biological Station). The most significant effects of reindeer grazing are destruction of vegetation cover (Kitti et al., 2009) and increased soil erosion (Uhlir et al., 2002), which in turn leads to the reduction of nutrient pools in the soil (Väre et al., 1995; Peth and Horn, 2006) and may also reduce nutrient leaching by interflow to streams.

In contrast to  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  anions, the  $\text{NO}_3^-$  anion, which is often claimed to be an important factor enhancing soil acidification and weathering (Legout et al., 2009; Tremblay et al., 2009), seems to play a less significant role in the study areas. The correlations between  $\text{NO}_3^-$  and base cations were much weaker in comparison to  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  (Table 3) and the concentration of  $\text{NO}_3^-$  was rather low. It might be the result of strong N limitation in subarctic soils (Liu et al., 2018). Higher concentrations of  $\text{NO}_3^-$  were only noted in the spring and stream water flowing from catchments covered with grass heath in the Malla area, recharged by perennial snow patches. It might be the result of suppressed plant uptake of  $\text{NO}_3^-$  in a harsh environment (Kamenik et al., 2001; Wolanin et al., 2015). A significant positive correlation between the  $\text{NO}_3^-$  concentrations and elevation (Table 5) seems to confirm this.

Melting snow is also an important source of  $\text{NO}_3^-$  ions for surface waters in mountain and subalpine catchments, causing acidification of river waters (Murdoch and Stoddard, 1992; Casson et al., 2013).  $\text{NO}_3^-$  ions may result from nitrification of  $\text{NH}_4^+$  ions, occurring in the snowpack (Raidla et al., 2015). Also, reindeer grazing could be an additional source of  $\text{NH}_4^+$ , as Väre et al. (1995) reported elevated N concentrations at grazed sites compared to ungrazed sites. Both, recharging by perennial snow patches and reindeer grazing may be the reasons for elevated concentrations of  $\text{NH}_4^+$  in spring recharged mainly by interflow (SIF; Fig. 4). Significantly lower concentrations of  $\text{NH}_4^+$  in streams in comparison to SIF water were likely an effect of the uptake of  $\text{NH}_4^+$  by microorganisms and plants living in water with N limitation. These processes caused a clear decrease in the  $\text{NH}_4^+$  concentrations, which occurred over a short segment of a stream in the order of several tens to several hundreds of meters in catchments located in the Alaska (Webster et al., 2003) and Rocky Mountains (Day and Hall, 2017).

Zakharova et al. (2007) showed that the effect of plant community on surface water chemistry was observed in large catchments in the Russian Lapland and was mostly noticeable during periods of the year with high discharge. As we demonstrated, the effect of plant community on spring and stream water chemistry, especially the concentrations of “geogenic ions”  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$ , could be observed also in small headwater catchments (<4 km<sup>2</sup>). This effect was observable at the end of the summer season (Figs. 7, 8) when discharge was similar to the multiannual average and soils were wet. This statement emphasizes the importance of headwater catchments as the “hotspots” of matter and energy in subarctic environments. Wohl et al. (2012) and Duvert et al. (2018) claim, that headwater catchments are important sources of soil organic carbon and  $\text{CO}_2$  in subarctic ecosystems. This in turn can accelerate chemical weathering and denudation processes shaping water chemistry in larger catchments.

Significant negative correlations between slope gradient and SEC and concentrations of some ions (Table 5) suggest that the time of contact of water with soil cover and regolith is an important factor controlling water chemistry. Elevated ions concentration in catchments of lower slope steepness can be the result of weathering or soil exchange processes, as postulated by Beylich and Laute (2012), or atmospheric deposition. However, high correlations of slope gradients with ions deriving mostly from the atmosphere ( $\text{Cl}^-$ ,  $\text{Na}^+$ ) and lack of correlation with  $\text{Ca}^{2+}$  ions being considered an indicator of the terrestrial environment (Raidla et al., 2015), suggest that the observed phenomenon was a result of a longer time interval for the possible deposition of atmospheric-derived ions in catchments.

A strong positive correlation between  $\text{Na}^+$  and  $\text{Cl}^-$  occurred in all studied waters irrespective of geological factors. This, together with the lack of correlations between  $\text{Na}^+$  and  $\text{HCO}_3^-$  (Table 3), responsible for weathering processes, and between other base cations (not shown) suggests that  $\text{Na}^+$  and  $\text{Cl}^-$  ions were to a large extent atmosphere-derived. The chemistry of waters representing the Na-Cl-type or mixed type between Ca-Mg- $\text{HCO}_3^-$  and Na-Cl, mainly waters in the Kevo and Malla areas, were apparently affected by atmospheric deposition. They are located close to the hydrochemical facies of ocean and brine waters in the Piper diagram (Piper, 1944). The highest concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$ , observed in the Kevo area, were most likely due to the geographic location as Kevo is located closer to the sea than Oulanka (Table 1) and, in contrast to Malla, is not located in the shadow of the

Scandes. The result of such a location is one of the highest sea-borne ion deposition rates in all of Finland (Ruoho-Airola et al., 2003).

However, the Na:Cl ratio varied for different water samples. The deviation of water samples from the sealine (according to Möller, 1990; Fig. 6), which indicates enrichment in  $\text{Na}^+$ , may be a result of Na-bearing mineral dissolution from local rocks (Stachnik et al., 2014; Raidla et al., 2015). It can be also the result of wet deposition of sea-salt aerosols, which are enriched in  $\text{Na}^+$  due to the chemical reaction between sulphuric acid and sea-salt (Möller, 1990; Raidla et al., 2015). In northern Scandinavia dry deposition is a more important source of sea-derived ions than precipitation (Hultberg and Grenfeld, 1992; Ruoho-Airola et al., 2003). The lowest concentrations of  $\text{Na}^+$  ions in water flowing from catchments covered with grass heath were therefore most likely the result of both: retarded silicates weathering or reduced sea-salt deposition with increasing altitude, as sea salt deposition in cold environments decreased rapidly as a function of elevation (Suzuki et al., 2002).

Waters in Kevo were also more enriched in  $\text{SO}_4^{2-}$  compared to other areas (Fig. 9). We suppose that in this case  $\text{SO}_4^{2-}$  ions had rather an atmospheric origin. There was a significant positive correlation between  $\text{SO}_4^{2-}$  and both  $\text{Na}^+$  and  $\text{Cl}^-$  ions (partly shown in Table 3). The effect of pollutants from the Kola Peninsula cannot be excluded (Hultberg and Grenfeld, 1992; Pacyna, 1995; Kähkönen, 1996).

## Conclusions

The pilot studies let us demonstrate the significant differences in surface water chemistry in headwater areas with different plant communities in Finnish Lapland. These differences were most of all expressed in the diversification of concentrations of ions linked with rock weathering:  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ . Enrichment of water with these ions occurred in catchments representing forest communities with thick soils, especially in the boreal forest community. This probably resulted both from the properties of coniferous trees, which enhance acidification of the soil and intensify the weathering process, as well as increased biological activity at lower elevations. The waters of grass heath were poorest in  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$  ions. This probably results not only from the plant community, but also was associated with the way these waters were recharged (from snow patches) and with very shallow weathering covers found in the area.

Using the indirect tracers of the water recharge component (water temperature and SEC), we showed that in most cases springs and streams were recharged by shallow groundwater. This can imply certain environmental consequences. One can assume that small catchments mostly recharged by interflow can be more susceptible to environmental factors than those recharged by baseflow, especially in terms of progressive climate and vegetation changes in Finnish Lapland. Changes in the location of the northern treeline in the future will result in the greatest changes in the chemistry of surface waters. This means that in the case of the expansion of the treeline to the north due to climate warming, it can be expected that the surface water will be enriched with basic cations and  $\text{HCO}_3^-$ . This will likely lead to an increase in water mineralization and a shift of hydrochemical facies towards Ca-Mg- $\text{HCO}_3^-$ -type. On the other hand, the regression of the northern treeline, related to, e.g., the emergence of new insect species, will probably

result in a reduction of nutrient pools and leaching them into streams. It can be expected that there will be a temporary increase in the mineralization of surface waters, but eventually the lack of forest will result in the depletion of soils and the dominance of atmosphere-derived ions in waters and the hydrochemical facies will shift towards Na-Cl-type. However, in order to fully recognize the problem, further research and recognition of the chemistry of surface waters under different wetness conditions of the catchment area are necessary.

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