

## Article

# The Origin of the Natural Water Chemical Composition in the Permafrost Region of the Eastern Slope of the Polar Urals

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**Abstract:** This article presents the results of the study of water chemical composition and formation processes in the eastern slope of the Polar Ural where permafrost is widely spread. To date, this region has not been studied in detail. However, it is very important to have information on the natural waters in this region because they play a significant role in all geochemical processes, including climate formation. For this study, 107 water samples were collected from lakes, rivers and active layer waters. The studied waters are ultrafresh; total dissolved solids vary from 14 to 438 mg/L. pH ranges from 3.5 to 9.0. The chemical type of the studied waters is mostly  $\text{HCO}_3\text{--Ca--Mg}$ . The geochemical environment of the studied waters contributes to the accumulation of such trace elements as Fe, Mn, Al, Ni, Au, Co, Li, Sc, Ti, Cr, Sr, Nb, Mo, Cs, La, Eu, Lu, Hg, and Se. The chemical composition peculiarities of active layer waters, rivers, lakes and waters of stone pits and exploration trenches and the description of their chemical composition formation processes are given in the present study. The water–rock interaction is a dominant process of water chemical composition formation in the studied region. The obtained results have both potential theoretical and practical applications.

**Keywords:** water chemical composition; hydrogeochemical processes; the eastern slope of the Polar Urals; permafrost; water–rock interaction; organic matter

## 1. Introduction

The Polar Urals is a region of northern Russia on which great hopes are pinned for the development and renewal of the mineral resource base of the Russian Federation [1–3]. This remote region has not been studied well, particularly with respect to hydrogeochemical aspects. The specific feature of this region is widespread permafrost, as in other northern regions including Canada and the USA.

The formation of the natural water composition in the northern regions, where permafrost is widely spread, occurs under specific conditions. The natural waters of this region are in close contact with the atmosphere; they undergo seasonal phase changes and they are in solid phase most of the year. These and other factors determine the peculiarities of water composition formation processes in the permafrost region. The problems of water geochemistry in regions with a cold climate and permafrost have been well studied.

The geochemical processes occurring in the temperate region also operate in the permafrost region [4]. Cationic denudation in the permafrost regions is substantially higher than the world average [5] indicating the intensity of chemical weathering in such an environment [6–9]. Evidently the low average temperatures do not inhibit chemical weathering reactions.

According to [10–13] the main geochemical processes that control both surface water and groundwater chemistry in the studied regions are silicate weathering: the dissolution of freshly weathered, easily soluble rocks (mainly gypsum, anhydrite, calcite, dolomite, halite and limestone) sometimes combined with sulfide oxidation [14]. Moreover, the weathering rate is determined by the permafrost degradation factor [15,16]. Soluble cations in permafrost and the active layer of static cryosols at recently disturbed sites were two orders of magnitude higher than in the active layer at undisturbed sites [16].

The detailed analysis [17] of Sr isotopic composition and river chemical composition shows that silicate weathering reactions are not the only mechanisms that control solute concentrations. An atmospheric component, constituted by the dissolution of evaporate and carbonate aerosols, is necessary to explain the dispersion of chemical ratios such as Ca/Na, Mg/Na, Sr/Na and Cl/Na. These aerosols are probably of local origin.

Different aspects of hydrogeochemistry of permafrost regions are described in these works including specificity of water–rock (sulphate, carbonate, aluminosilicates) interaction and water chemical composition formation during phase transformations etc. The study of water chemical composition formation based on the research of water–rock interaction is up-to-date. Not enough attention has been paid to the role of dissolved organic matter in the processes of water chemical composition formation in the permafrost regions. Data on water enrichment in dissolved organic matter in the arctic regions are given in some articles [18–25]. Most of them focus on studying river water composition, while less attention is paid to groundwater research, and lake water chemical composition formation has not been studied at all. The lakes of the arctic zone are unique objects worth studying and there are some publications on lake water balance characteristics and their influence on permafrost [26,27].

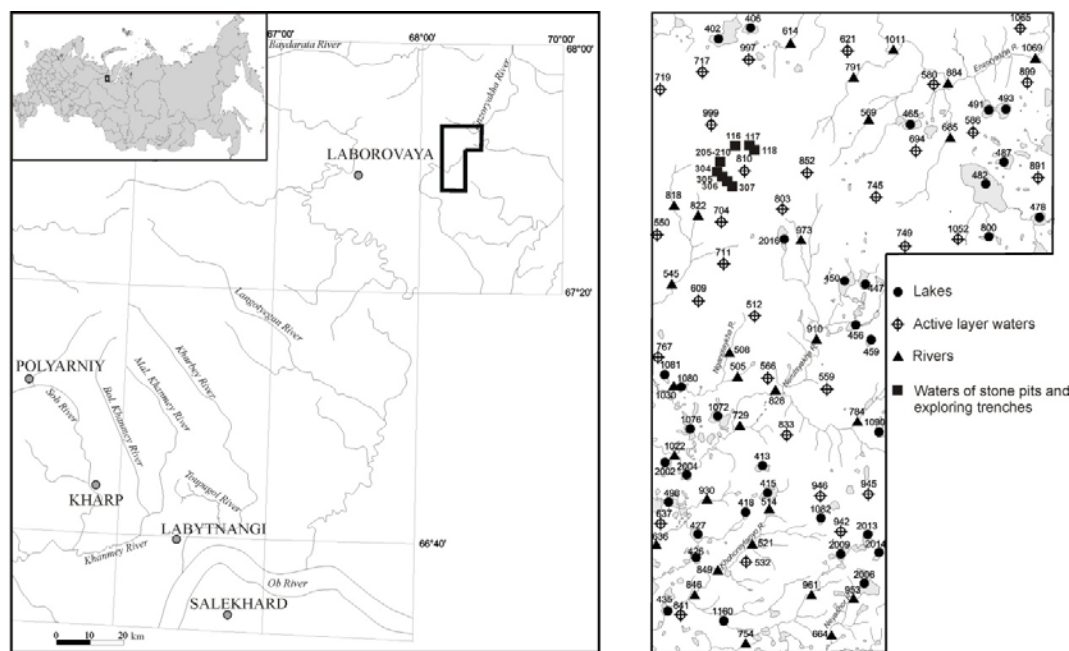
Little work has been done on the geochemistry of water of the Polar Urals. Previous studies on lake waters circulating in this area have been carried out [28] and aimed at investigating the distribution and size of lakes on the eastern slope of the Polar Urals, but there is no information on the origin of lake water chemical composition. Nevertheless, the lake, river and groundwater geochemistry of the arctic regions has not been well studied yet.

The purpose of this work is to study the geochemical characteristics of water in order to identify the main hydrogeochemical processes controlling the chemical composition based on major ion chemistry. Another aim of the study is to assess the concentration of trace elements in lakes, rivers and groundwater on the eastern slope of the Polar Urals in order to evaluate the regional geochemical background. This study would be useful for conducting hydrogeochemical prospecting for ore deposits on the eastern slope of the Polar Urals, and for investigating sources of drinking-water.

## 2. Site Description and Methods

### 2.1. Study Area

The study site covers an area of approximately 170 km<sup>2</sup> on the eastern slope of the Polar Urals, between latitudes 67°36'29'' N and 67°46'48'' N and longitudes 68°08'50'' E and 68°25'58'' E (Figure 1). The morphology status of the region is a denudation plain; the elevation range is from 55 m to 202 m. The studied area covers the watershed of the rivers Enzoryakha and Yunyakha. The climate of the studied area is subarctic. The mean annual air temperature is about −5 °C. The annual precipitation is 400–600 mm. In the region, the continuous permafrost thickness varies between 100 and 320 m [29]. The thickness of the active layer, the layer of soil above the permafrost thawing out during the summer, reaches a maximum 2.5 m.



**Figure 1.** Sketch map of the studied area showing the sampling sites. Inset shows location of the study area in the Russian Federation.

The groundwater stratification is not so much determined by geological structure and water bearing rocks as by permafrost thickness and framework and its temperature regime [30]. According to the groundwater localization in relation to permafrost in the studied area, the following types of groundwater can be distinguished: supraperafrost (water saturated part of the active layer), intra- and subpermafrost waters. In the present study only supraperafrost waters are described, which refer to the active layer waters in the present research.

Several large rivers flow in the studied area, such as the Nganotaykha, Nerutsyakh, Khohoreytanyo and Neyashor; all of these are within the Ob basin. These rivers are fed by snowmelt waters, precipitation and permafrost thawing. Besides these rivers, about 140 lakes are situated here. They are located in clusters having different sizes. The water surface of the largest lake is 0.87 km<sup>2</sup>, other lakes have smaller water surfaces which are less than 0.25 km<sup>2</sup>. The depth of the lakes is not more than 2–3 m, while the depth of a few shallow lakes is less than 1 m. Only few lakes are connected to rivers.

From the geological point of view, the studied area consists of two structure levels such as the Paleozoic and the Mesozoic (Figure 2). The Paleozoic structural level is represented by three structural stages such as the Lodlow-lower Eifelian, the upper Eifelian-Givetian and the Givetian-mid-Carboniferous. The Lodlow-lower Eifelian stage is composed of the rhyolite-andesit-basaltic unit intruded by gabbroid. The upper Eifelian-Givetian stage lies unconformably and is represented by bituminous limestones intruded by gabbro-diorite unit. The Givetian-mid-Carboniferous stage is represented by terrigenous rocks. The Mesozoic stratified rocks are represented by the Carnian-Norian stage of the Triassic period [31].

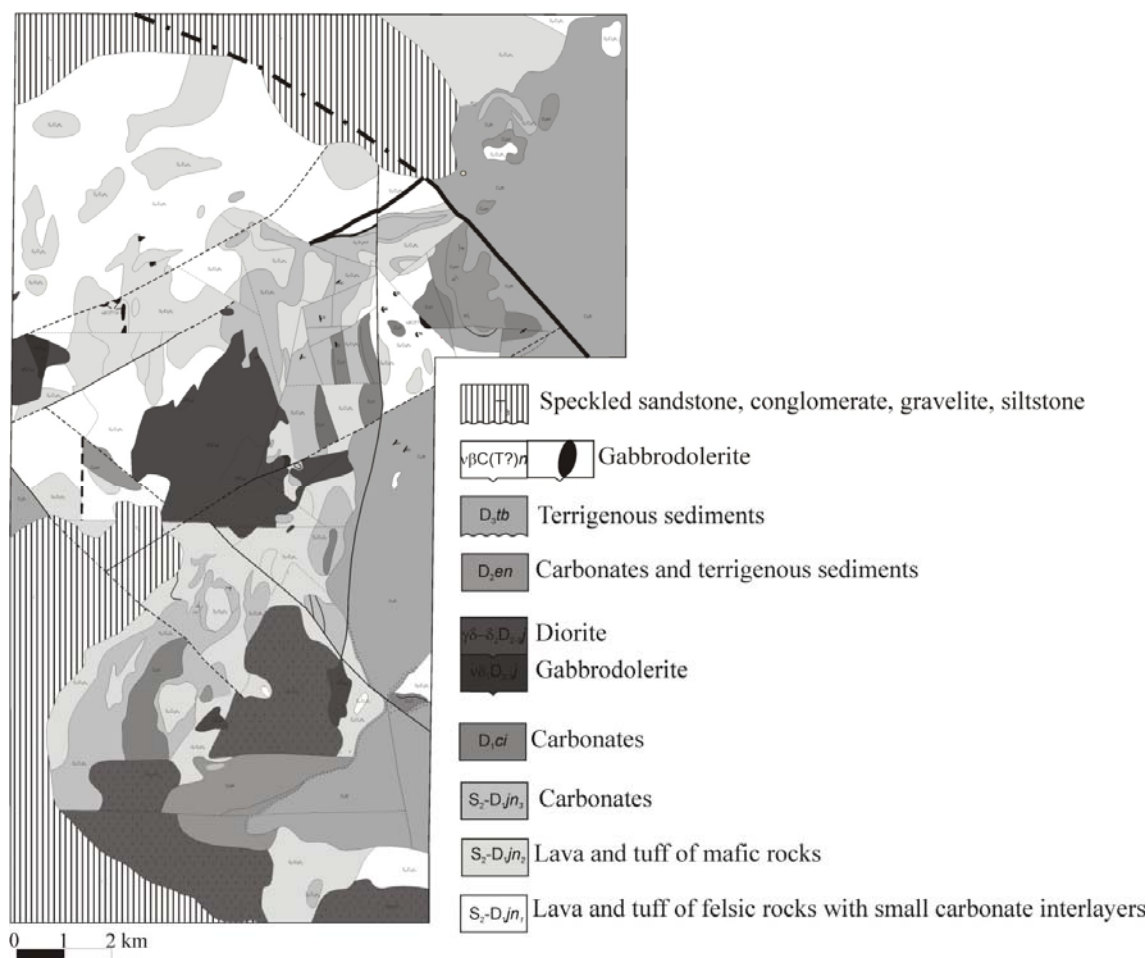


Figure 2. Lithology sketch-map of the studied area.

## 2.2. Sampling and Analysis

The waters were sampled for chemical characterization during the summer period with 107 samples collected from active layer waters (32 samples), rivers (29 samples), lakes (34 samples) and waters of stone pits and exploration trenches (12 samples). The locations of the water sampling points are shown in Figure 1. At each point, two water samples were collected. The samples for ionic analyses were stored in 500 mL clean polyethylene bottles which were rinsed twice by the sampled water. The samples for trace elements analyses were stored in 50 mL clean polyethylene bottles. Each sample was filtered in situ through a 0.45  $\mu$ m acetate cellulose membrane filter of 30 mm in diameter using a pre-cleaned syringe. First, 5 mL of the filtered water was eliminated at the beginning of filtration. The samples were immediately acidified with concentrated  $\text{HNO}_3$  in order to prevent metal precipitation.

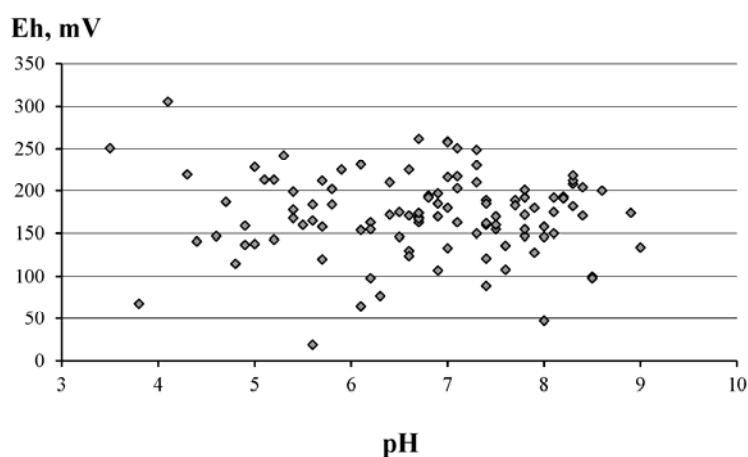
The field measurements including the water temperature, pH and redox potential (Eh) were carried out using a portable device Water Test (Hanna Instruments, Cluj-Napoca, Romania). The pH measurements were performed after calibration with pH 4.01 (HI 7004) and 7.01 (HI 7007) buffer solutions. The accuracy of the instrument is  $\pm 0.2$  pH and  $\pm 5$  mV. The concentration of  $\text{HCO}_3^-$  was determined by titration with 0.01 N solution of HCl against methyl orange indicator. The titration method was used for the determination of the fulvic and humic acid concentration. Cations and anions, including  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  were analyzed by Dionex 1000 and 2000 ion chromatographs. Dissolved trace elements were determined by inductively coupled mass spectrometry (ICP-MS, ELAN-DRC-e, Perkin Elmer, Shelton, CT, USA). All the standard solutions for it were prepared with ultra-pure deionized water and Perkin Elmer Multi Element Standard Solutions.

The physico-chemical modelling program HydroGeo [32] was used for calculation of the ion activities in the studied waters. To show the water saturation state with respect to key mineral phases, the diagrams of some secondary and primary mineral stability fields were used. Statistica, version 8.0, was used to perform statistical analyses. Correlation was estimated using the Pearson correlation coefficient ( $R$ -coefficient) with statistical significance  $p = 0.05$ . The mean content of chemical elements was determined according to their distribution laws with the use of excess and asymmetry coefficients.

### 3. Results and Discussion

#### 3.1. General Characteristics of Waters

The results of the chemical composition analysis and field measurement are given in Appendix A. Total dissolved solids (TDS) range from 14 to 438 mg/L. Most waters (at 94 points) of the studied area are fresh and have TDS of less than 200 mg/L. pH values are from 3.5 to 9.0 (Figure 3). Most waters in the region have pH 6.5–7.5. The lowest pH values 3.5–4.9 were obtained in a wetland area. Lake waters are mostly alkaline with pH ranging from 8.5 to 9.2.



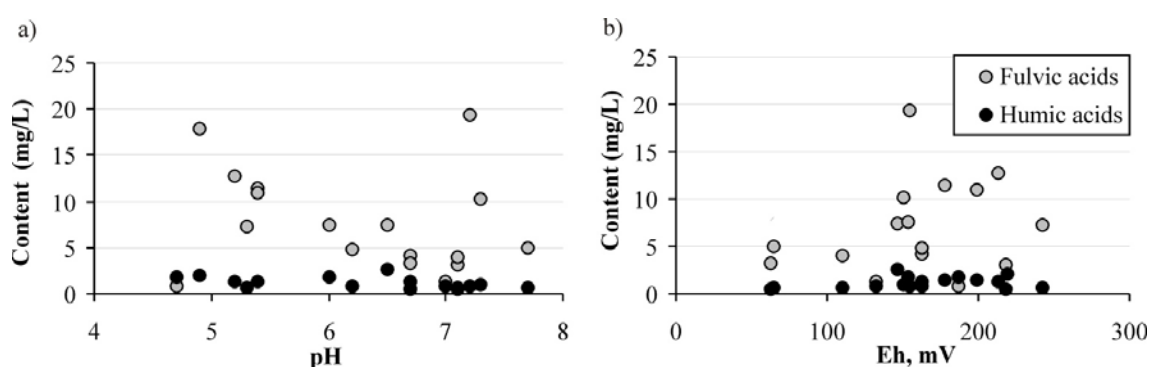
**Figure 3.** pH vs. redox potential (Eh) plot for the studied area.

The redox conditions are characterized by values Eh  $-68$  to  $347$  mV. There is a weakly positive relationship between Eh and pH ( $R^2 = 0.0032$ ) (Figure 3) in the studied waters. This pH and Eh relationship is not typical for the natural water; it is caused by the wide variety of the chemical composition of the studied waters. The most common waters in the studied area have the values of redox potential of  $150$ – $200$  mV. More oxygenated environments (where Eh is greater than  $200$  mV) are formed mainly in acidic and neutral waters in watershed areas and upstreams, where water exchange is more active. More reducing conditions (where Eh is below  $200$  mV) are formed in water with low water exchange intensity. The enrichment processes of organic substances in water play a significant role in the formation of the reduction environment [33].

The concentrations of fulvic and humic acids at a number of points are shown in Table 1. The fulvic acid concentrations in waters vary from  $1.3$  to  $19.4$  mg/L and humic acid concentrations vary from  $0.5$  to  $2.8$  mg/L. The highest fulvic acid concentrations are found in waters with a reducing environment where Eh value is less than  $200$  mV (Figure 4). The maximum concentrations of fulvic acid are noted in the most acidic waters with a pH less than  $5.5$ . The fulvic acid concentrations decrease with an increase in pH. The behavior of soluble humic acid is practically independent of geochemical parameters of the aquatic environment [33,34].

**Table 1.** The physico-chemical parameters and fulvic and humic acid contents in several water points in the studied area.

Water Type	Eh	pH	Fulvic Acids (mg/L)	Humic Acids (mg/L)
river	150	7.3	10.2	0.9
river	155	7.2	19.4	0.7
river	133	7.00	1.3	0.8
river	111	7.10	4.0	0.6
river	64	7.70	5.0	0.7
waters of active layer	125	6.50	7.4	2.7
waters of active layer	163	6.7	4.2	1.3
waters of active layer	178	5.4	11.5	1.3
waters of active layer	199	5.4	10.90	1.4
waters of active layer	213	5.2	12.8	1.3
waters of active layer	163	6.2	4.8	0.8
waters of active layer	219	4.9	17.8	2.0
waters of active layer	242	5.3	7.2	0.6
waters of active layer	218	7.1	3.1	0.5
waters of active layer	153	6.0	7.5	1.8
waters of active layer	62	6.70	3.3	0.5
Average for waters of the Vasugan swamp [33]			25.1	7.06

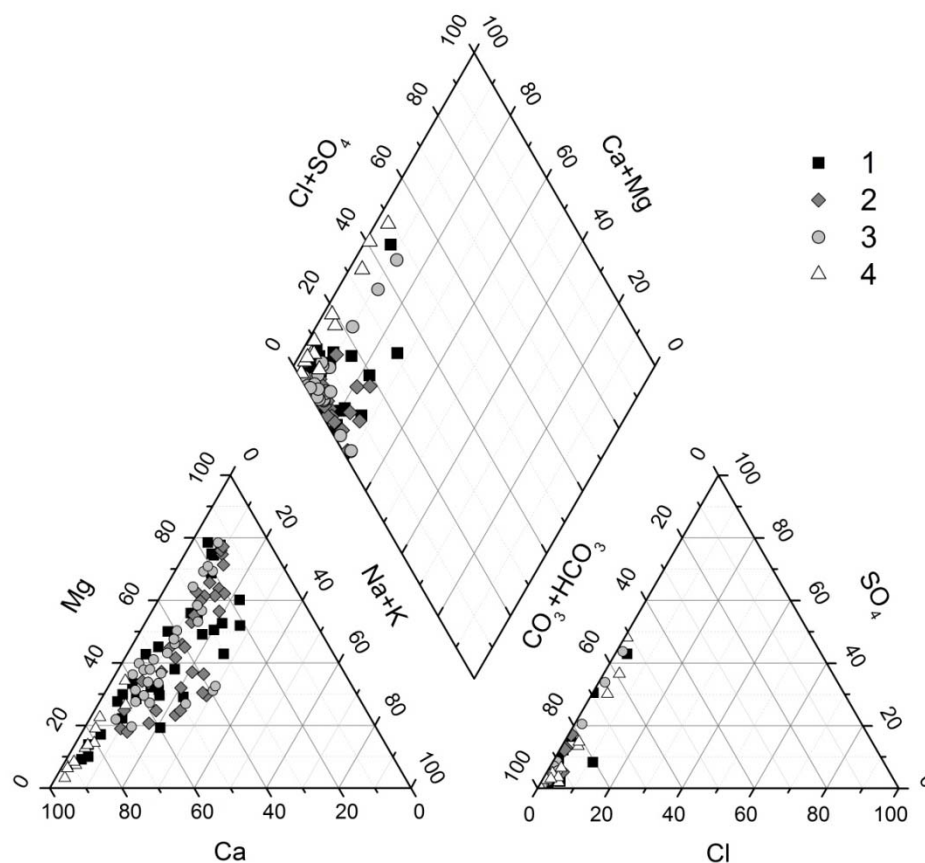
**Figure 4.** Relationship of organic acid content vs. pH (a); organic acid content vs. Eh (b) for same water points from the studied area

Among inorganic anions bicarbonate is predominant, the concentrations of which range from 2.6 to 325 mg/L. Waters with  $\text{HCO}_3^-$  concentrations less than 150 mg/L are widely spread. The second most abundant anion is  $\text{SO}_4$ , ranging from 0.5 to 50 mg/L. The Cl content is low (less than 0.3–0.5 mg/L). Ca and Mg are the most abundant cations with concentrations of 1.6–91.7 mg/L and 0.7–21.2 mg/L, respectively (Appendix A). The concentrations of Na range from 0.4 to 15.9 mg/L. K is the least abundant major cation with a content of 0.01–7.1 mg/L.

Hydrogeochemical types of the studied waters are shown in Figure 5. Thus, the  $\text{HCO}_3^-$  contents are mostly more than 70% of the total anion, except for a few data points (50%–70%). At these points, the  $\text{SO}_4$  concentration (30%–50%) increases and these waters belong to  $\text{HCO}_3^-$ – $\text{SO}_4$  type. The waters with a higher concentration of  $\text{SO}_4$  (10%–50%) are widely spread in the north-western part of the studied area. The Cl content increase in waters in the north-western part of the study area.

The cation composition mostly varies between Ca, Ca–Mg, Mg–Ca and Ca types. A significant feature of cation composition of the studied waters is largely a function of rock composition. Mostly magnesium waters (with Mg of more than 50%) are located in the area with widely spread granite and gabbro. Calcium waters (with Ca of more than 50%) are widely spread in the area with carbonates. Na concentration is generally less than 10% in the studied waters. The waters with Na concentration of more than 10% have low TDS and they are located in the northern part of the studied area.





**Figure 5.** Piper diagram showing anion and cation compositions of the studied waters. 1—waters of active layer; 2—lakes; 3—rivers; 4—waters of stone pits and exploration trenches.

The silicon concentrations vary from 0.16 to 28.75 mg/L. A significant feature of these waters is hydrolysable cation accumulation such as Al, Fe, and Mn. Their mean concentrations are high for waters with such low TDS and reach 0.03, 0.25, and 0.01 mg/L respectively.

The average concentrations of trace elements in the studied waters correspond to both the average of world rivers and mean contents in groundwaters of tundra landscapes [33]. The average concentrations of Sc, Eu, Fe, Ho, Dy, Tb, Gd, Pr, Er, Yb, Sm, Se, Nd, Lu, Nb, Tm, Ce, Mn, La, and Ni in the studied waters exceed the average of world rivers by 1.5–10 times (Table 2).

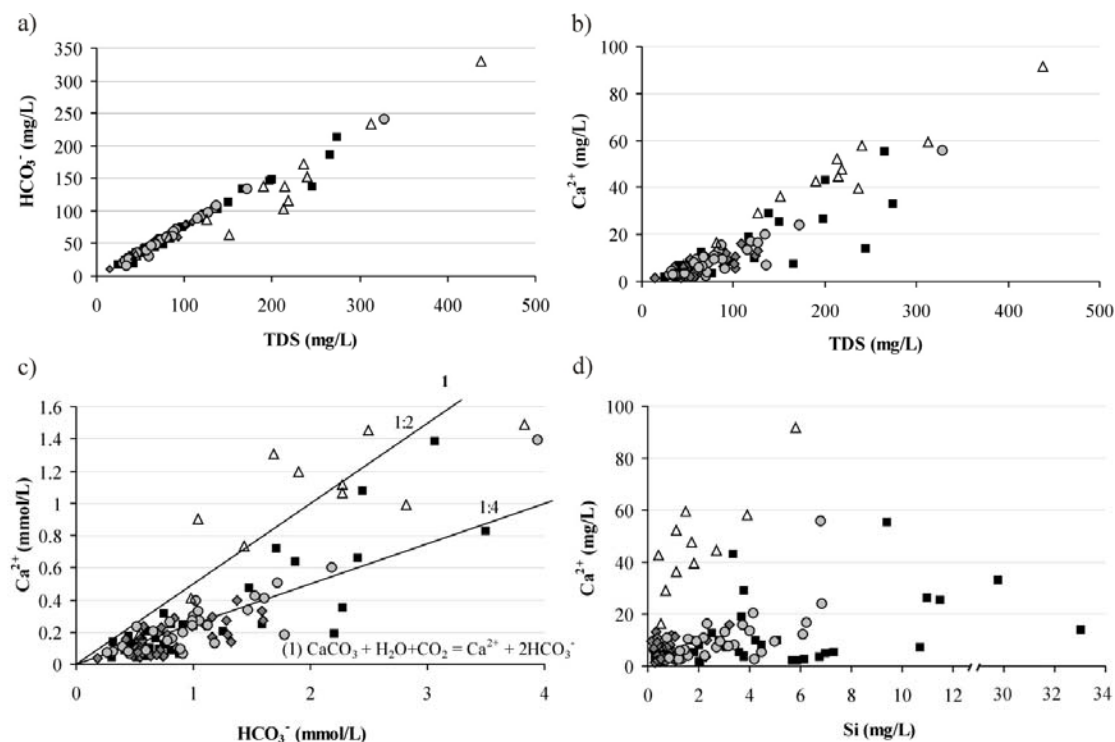
The trace element concentrations in the studied waters are lower than those in waters of tundra landscape; exceptions are Sc, Fe, Mn, and Ni concentrations. The Cu, V, As, Sr, I, and Ba concentrations in the studied waters are close to those in waters of tundra landscape. Moreover, new information about Bi, Cd, Pt, B, Ge, Se, Br, Y, Rh, Pd, Te, Cs, TR, Hf, Ta, W, Re, Ir, Hg, Tl, and Th distribution in the natural waters in the eastern slope of the Polar Urals was found (see Table 2).

Figure 6a,b show the concentration of the main ions plotted against TDS. On the whole, the data show a strong positive linear correlation pointing to the significant dependence of  $\text{HCO}_3$  and Ca on TDS ( $R = 0.97$  and  $R = 0.90$ ,  $p = 0.05$  respectively).

**Table 2.** Trace elements content in the studied waters, µg/L ( $\frac{\text{min-max}}{\text{average}}$ ).

Elements	Waters of Active Layer	Rivers	Lakes	Waters of Stone Pits and Exploring Trenches	Average of World Rivers [33]	Elements	Waters of Active Layer	Rivers	Lakes	Waters of Stone Pits and Exploring Trenches	Average of World Rivers [33]
Li	$\frac{0.13-54.17}{2.07}$	$\frac{0.07-25.67}{1.6}$	$\frac{0.14-20.61}{2.6}$	$\frac{0.06-6.81}{0.5}$	2.5	Br	$\frac{0.1-31.9}{8.30}$	$\frac{0.1-84.47}{6.61}$	$\frac{0.1-28.97}{6.62}$	$\frac{0.2-151.53}{57.68}$	20.0
Be	$\frac{0.002-2.72}{0.024}$	$\frac{0.0016-0.54}{0.010}$	$\frac{0.002-0.21}{0.013}$	$\frac{0.0002-0.25}{0.004}$	-	Rb	$\frac{0.03-56.1}{0.75}$	$\frac{0.003-6.1}{0.30}$	$\frac{0.008-2.4}{0.30}$	$\frac{0.04-2.9}{0.20}$	2.0
B	$\frac{0.04-270.81}{5.40}$	$\frac{1.18-146.72}{6.59}$	$\frac{1.39-45.57}{9.55}$	-	20	Sr	$\frac{3.4-366.9}{30.8}$	$\frac{6.84-113.93}{22.90}$	$\frac{3.93-69.84}{13.40}$	$\frac{12.02-378.32}{75.0}$	50.0
Sc	$\frac{0.18-28.12}{1.92}$	$\frac{0.09-10.38}{1.19}$	$\frac{0.03-2.43}{0.41}$	$\frac{0.2-4.91}{0.78}$	0.004	Y	$\frac{0.009-26.9}{0.36}$	$\frac{0.008-5.02}{0.10}$	$\frac{0.0063-0.69}{0.09}$	$\frac{0.001-2.42}{0.02}$	0.7
Ti	$\frac{0.43-155.70}{3.13}$	$\frac{0.21-117.71}{1.9}$	$\frac{0.40-13.71}{2.0}$	$\frac{0.17-249.02}{60.4}$	3.0	Zr	$\frac{0.1-6.2}{0.2}$	$\frac{0.012-1.13}{0.14}$	$\frac{0.006-0.62}{0.07}$	$\frac{0.0065-3.49}{0.19}$	2.6
V	$\frac{0.0003-4.35}{0.21}$	$\frac{0.0003-2.28}{0.18}$	$\frac{0.0003-2.04}{0.05}$	$\frac{0.001-6.35}{0.28}$	1.0	Nb	$\frac{0.002-0.47}{0.01}$	$\frac{0.0007-0.081}{0.007}$	$\frac{0.0005-0.16}{0.005}$	$\frac{0.0009-0.26}{0.005}$	0.001
Cr	$\frac{0.01-66.96}{1.42}$	$\frac{0.01-18.96}{1.2}$	$\frac{0.01-8.09}{0.5}$	$\frac{0.84-11.64}{3.1}$	1.0	Mo	$\frac{0.001-2.5}{0.06}$	$\frac{0.1-31.9}{8.30}$	$\frac{0.1-31.9}{8.30}$	$\frac{0.1-31.9}{8.30}$	1.0
Co	$\frac{0.07-363.39}{2.13}$	$\frac{0.03-23.53}{0.21}$	$\frac{0.05-1.35}{0.20}$	$\frac{0.01-1.03}{0.08}$	0.3	Ru	$\frac{0.003-0.02}{0.0006}$	$\frac{0.0001-0.04}{0.0005}$	$\frac{0.0003-0.005}{0.0004}$	$\frac{0.0001-0.0059}{0.001}$	-
Ni	$\frac{0.003-219.19}{1.3}$	$\frac{0.003-22.42}{0.8}$	$\frac{0.003-13.23}{2.4}$	$\frac{0.52-6.69}{1.4}$	2.5	Rh	$\frac{0.0003-0.0289}{0.002}$	$\frac{0.0002-0.01}{0.0013}$	$\frac{0.0003-0.0079}{0.001}$	$\frac{0.0007-0.014}{0.003}$	-
Cu	$\frac{0.30-80.04}{3.0}$	$\frac{0.34-34.69}{1.5}$	$\frac{0.26-4.66}{1.4}$	$\frac{0.34-21.48}{1.7}$	7.0	Pd	$\frac{0.002-0.08}{0.007}$	$\frac{0.002-0.03}{0.005}$	$\frac{0.002-0.03}{0.005}$	$\frac{0.002-0.27}{0.003}$	-
Zn	$\frac{0.66-410.90}{18.9}$	$\frac{0.55-205.00}{4.8}$	$\frac{0.16-326.40}{4.6}$	$\frac{0.43-51.88}{2.5}$	20.0	Ag	$\frac{0.0003-0.6}{0.01}$	$\frac{0.0003-0.099}{0.003}$	$\frac{0.0003-0.05}{0.002}$	$\frac{0.0013-0.11}{0.007}$	0.2
Ga	$\frac{0.00005-0.21}{0.006}$	$\frac{0.00005-0.045}{0.0028}$	$\frac{0.00005-0.066}{0.003}$	-	0.1	Cd	$\frac{0.002-3.51}{0.06}$	$\frac{0.002-0.37}{0.01}$	$\frac{0.002-0.16}{0.01}$	$\frac{0.0013-0.21}{0.005}$	0.2
Ge	$\frac{0.00005-0.042}{0.0016}$	$\frac{0.00005-0.037}{0.0013}$	$\frac{0.00005-0.018}{0.0007}$	-	0.07	Sn	$\frac{0.00005-0.37}{0.01}$	$\frac{0.00005-0.14}{0.005}$	$\frac{0.00005-0.04}{0.005}$	$\frac{0.0007-0.09}{0.004}$	0.04
As	$\frac{0.19-4.31}{0.53}$	$\frac{0.007-2.08}{0.37}$	$\frac{0.12-2.86}{0.44}$	$\frac{0.23-9.50}{1.03}$	2.0	Sb	$\frac{0.03-2.3}{0.20}$	$\frac{0.031-1.26}{0.19}$	$\frac{0.02-0.52}{0.15}$	$\frac{0.084-4.7}{0.37}$	1.0
Se	$\frac{0.001-13.91}{0.50}$	$\frac{0.001-11.36}{0.45}$	$\frac{0.001-9.88}{0.35}$	$\frac{0.16-7.38}{0.80}$	0.2	Te	$\frac{0.0004-0.17}{0.002}$	$\frac{0.0001-0.03}{0.0009}$	$\frac{0.0004-0.038}{0.001}$	$\frac{0.0001-0.048}{0.0004}$	-
Cs	$\frac{0.0006-0.64}{0.009}$	$\frac{0.0003-0.36}{0.002}$	$\frac{0.0003-0.068}{0.003}$	$\frac{0.0003-0.31}{0.00078}$	0.03	Pt	$\frac{0.0001-0.004}{0.0002}$	$\frac{0.00008-0.02}{0.0002}$	$\frac{0.0001-0.001}{0.0002}$	$\frac{0.0004-0.06}{0.005}$	-
Ba	$\frac{1.35-44.3}{7.6}$	$\frac{1.15-10.13}{5.51}$	$\frac{0.90-9.72}{5.82}$	$\frac{1.24-16.31}{7.36}$	30.0	Au	$\frac{0.00005-0.007}{0.0004}$	$\frac{0.00005-0.03}{0.0007}$	$\frac{0.00005-0.007}{0.0006}$	$\frac{0.0008-1.13}{0.004}$	0.002
La	$\frac{0.006-34.28}{0.3}$	$\frac{0.002-5.99}{0.059}$	$\frac{0.008-0.98}{0.087}$	$\frac{0.0008-0.82}{0.005}$	0.05	Hg	$\frac{0.002-0.85}{0.03}$	$\frac{0.002-0.75}{0.02}$	$\frac{0.002-0.26}{0.03}$	$\frac{0.002-3.91}{0.02}$	0.07
Eu	$\frac{0.0004-1.82}{0.02}$	$\frac{0.0004-0.43}{0.005}$	$\frac{0.0004-0.064}{0.007}$	$\frac{0.00035-0.036}{0.002}$	0.001	Tl	$\frac{0.0003-0.21}{0.002}$	$\frac{0.0002-0.05}{0.0007}$	$\frac{0.0002-0.007}{0.0007}$	$\frac{0.0002-0.02}{0.0009}$	1.0
Lu	$\frac{0.0003-0.47}{0.008}$	$\frac{0.0002-0.89}{0.0024}$	$\frac{0.0003-0.013}{0.0003}$	$\frac{0.0002-0.013}{0.0003}$	0.001	Pb	$\frac{0.01-39.6}{0.8}$	$\frac{0.001-4.3}{0.17}$	$\frac{0.042-2.19}{0.31}$	$\frac{0.002-2.05}{0.04}$	1.0
Hf	$\frac{0.0003-0.21}{0.007}$	$\frac{0.0003-0.032}{0.004}$	$\frac{0.0003-0.022}{0.003}$	$\frac{0.0003-0.083}{0.003}$	-	Bi	$\frac{0.0003-0.19}{0.004}$	$\frac{0.00002-0.03}{0.001}$	$\frac{0.0003-0.01}{0.0009}$	$\frac{0.000015-0.03}{0.0013}$	-
Ta	$\frac{0.0001-0.02}{0.0006}$	$\frac{0.0001-0.0084}{0.0006}$	$\frac{0.0001-0.0051}{0.0004}$	-	-	Th	$\frac{0.0004-2.17}{0.04}$	$\frac{0.0005-0.22}{0.03}$	$\frac{0.003-0.23}{0.02}$	$\frac{0.0002-0.63}{0.002}$	0.1
W	$\frac{0.001-0.07}{0.005}$	$\frac{0.001-0.03}{0.003}$	$\frac{0.001-0.44}{0.002}$	$\frac{0.0009-66.85}{0.014}$	0.03	U	$\frac{0.0005-6.39}{0.01}$	$\frac{0.0005-2.18}{0.02}$	$\frac{0.0006-0.11}{0.01}$	$\frac{0.00005-18.06}{0.04}$	0.5
Re	$\frac{0.0003-0.009}{0.0005}$	$\frac{0.0003-0.054}{0.0005}$	$\frac{0.00025-0.0015}{0.0003}$	$\frac{0.0006-0.21}{0.008}$	-	-	-	-	-	-	-





**Figure 6.** Relationships  $\text{HCO}_3^-$  vs. TDS (a); Ca vs. TDS (b); Ca vs.  $\text{HCO}_3^-$  (c); Ca vs. Si (d) for waters from the studied area. Symbols as in Figure 5. TDS—total dissolved solids

The dependence of the calcium concentration on the bicarbonate concentration, with a positive connection ( $R = 0.87$ ,  $p = 0.05$ ), is shown in Figure 6c. However, water enrichment in these ions is not determined only by simple calcite dissolution but it is controlled by the processes of aluminosilicates hydrolyses because this type of rock is widely spread in the studied area (Figure 6d). The exception is waters in stone pits and exploration trenches. Calcium entering in these waters occurs primarily due to the calcium dissolution processes.

No strong dependence of other ions on TDS was found (Table 3). However, there are positive correlations between K and Al, K and Si, demonstrating likely their common source.

**Table 3.** Correlation matrix for water chemical composition in the study area ( $n = 107$ ,  $p = 0.05$ ,  $R = 0.5$ ).

Element	$\text{HCO}_3^-$	$\text{Cl}^-$	$\text{SO}_4^{2-}$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{Na}^+$	$\text{K}^+$	TDS	Si	Al	Mn	Fe
$\text{HCO}_3^-$	1											
$\text{Cl}^-$	0.15	1										
$\text{SO}_4^{2-}$	0.16	0.01	1									
$\text{Ca}^{2+}$	0.87	0.16	0.35	1								
$\text{Mg}^{2+}$	0.56	0.11	0.22	0.18	1							
$\text{Na}^+$	0.54	−0.05	0.39	0.45	0.24	1						
$\text{K}^+$	0.23	0.13	0.29	0.15	0.28	0.24	1					
TDS	0.97	0.15	0.39	0.90	0.55	0.60	0.28	1				
Si	0.43	0.12	0.26	0.30	0.47	0.24	0.58	0.45	1			
Al	0.19	0.0003	0.26	0.14	0.27	0.14	0.61	0.24	0.85	1		
Mn	0.15	0.20	0.10	0.10	0.19	0.03	0.40	0.16	0.32	0.30	1	
Fe	0.08	0.01	0.08	0.08	0.08	−0.0004	0.27	0.09	0.30	0.33	0.39	1

In Table 3, a positive correlation between Al and Si ( $R = 0.85$ ,  $p = 0.05$ ) is observed in the study waters: concentrations of Al increase with the growth of Si.

### 3.2. Chemical Composition of Water Types

Chemical composition variety of the studied waters is determined by various existence factors and processes in the study area. The chemical compositions of rivers, lakes and groundwaters (waters of active layer) form in natural conditions of landscape. At the same time, chemical composition of waters in stone pits and exploration trenches form in other hydrodynamic and physico-chemical conditions, which are mostly the result of anthropogenic activity. Meanwhile, the specific feature of the study area is the absence of a great anthropogenic influence. Therefore, it is necessary to describe each type of the studied waters separately.

Waters of the active layer are presented by small swampy land sometimes with water table, but more often by water-bearing peat soils. These waters have a color similar to “strong tea”, which is conditioned by high concentrations of organic matter. Active layer waters are mostly weak-acid or neutral, pH values range from 3.5 to 7.5. Their TDS vary from 24.1 to 273.0 mg/L, average TDS is 96.2 mg/L (Appendix A). On average, the chemical composition of active layer waters is close to that in river waters. The values of TDS were estimated using only main inorganic ions, but for this type of water, organic matter plays a significant part in chemical composition. In this manner, values of TDS can be increased more than 10%. The studied waters are characterized by  $\text{HCO}_3$  type with various ratios of Ca and Mg.

The high concentrations of such elements as Si, Ag, Bi, Cu, Cd, Pb, Be, Sc, Rb, Y, Nb, Te, Cs, Eu, Lu, Hf, Ta, W, Th, V, Ga, Ge, As, I, and Ba are observed in this type of water (Table 2).

It should be noted that the concentrations of Mn, Co, Zn, Pd, La, Tl, Sn, Fe, and Ir are significantly higher in active layer waters than those in rivers and lakes.

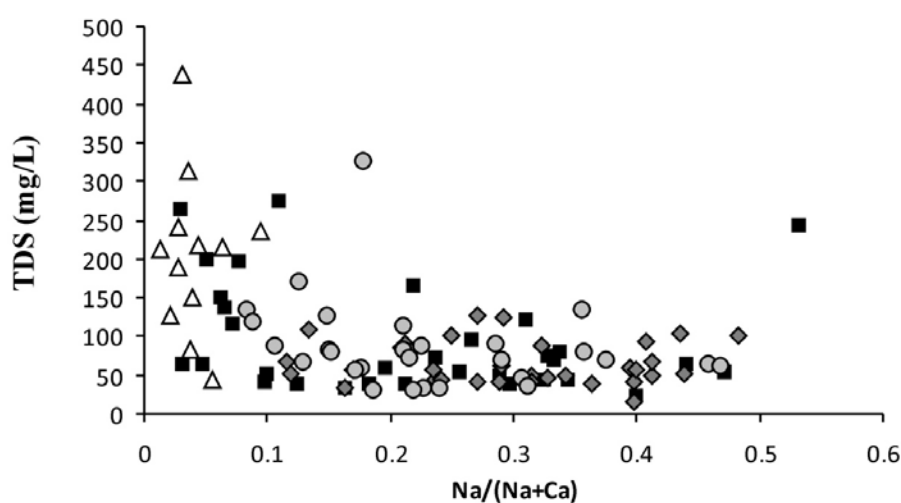
The lake waters are ultrafresh; the maximum value of TDS is less than 200 mg/L. Geochemical environment of lake waters is characterized by pH from 5.3 to 9.2 with an average value of 7.3, and Eh from 47 to 341 mV with an average value of 175 mV. The values of these parameters are very close to those in rivers in the studied area. Calcium and magnesium are the dominant cations in lake waters; together they account for 72%–92% of the cations measured (Figure 5). Anion chemistry is dominated by  $\text{HCO}_3$  constituting from 80% to 99% of the major anions. Higher concentrations are characteristic of some trace elements in lake waters among which are lithophilous elements—Li, Be, B, Ti, Cs, La, Eu, I, Ba and chalkophilous elements—Pb, Rb, Pd, Te, Hg, Tl, and As (Table 2). For siderophilous elements, only Ni reveals a higher content. The high concentration of Ni in the waters is a one of the specific features of the studied area [35].

The river waters are characterized by values of Eh from 65 to 225 mV. Measured pH values range from 4.8 to 8.2. The average value of TDS is 80 mg/L, which is equal that of active layer waters. The maximum value of TDS is 319.2 mg/L. River waters belong to  $\text{HCO}_3$ -Ca hydrogeochemical type. Geochemical conditions in river waters are appropriate for enrichment in lithophilous elements—Si, Al, Mn, Sc, Cr, Y, Zr, Nb, Hf, Ta, W, and U, chalkophilous elements—Au, Zn, Cu, Cd, Sb, V, and Se, and siderophilous elements—Co, Pt, Mo, Ru, Rh, Ir, Re, and Ge (Table 2).

Waters in stone pits and exploration trenches are characterized by different chemical composition in all studied water types. The measured pH values are neutral to alkaline, ranging from 7.4 to 8.9. The water exhibit redox potential characteristic of a more oxygenated environment; measured values of Eh vary from 121 to 218 mV. On the whole, TDS ( $45 < \text{TDS} < 438$  mg/L; average 218 mg/L) levels are greater than those of all studied water types. As in the previous water type, bicarbonate is the most abundant major anion; its values range from 32.9 to 330.4 mg/L. However, the highest contents of sulfate are observed in waters in stone pits and exploring trenches for all studied water types; their content ranges from 1.0 to 50.0 mg/L. The dominant cations are calcium and magnesium. Therefore, these waters belong to the  $\text{HCO}_3$ - $\text{SO}_4$ -Ca-Mg type. The highest concentrations of Cl and K (up to 6.3 and up to 5.7 mg/L respectively) were found in this type of water. Also among all the studied water types, the maximum concentrations of such elements as Al, Fe, Au, Pt, Ti, Ni, Cr, Sr, Mo, Ru, Rh, Sb, Re, Ir, and U were detected in the waters of stone pits and exploring trenches.

### 3.3. Water-Rock Interaction

According to the dependence of TDS on  $\text{Na}/(\text{Ca} + \text{Na})$  [36] (Figure 7), study waters are characterized by low values of  $\text{Na}/(\text{Na} + \text{Ca})$  at less than 0.5, with moderate TDS values of less than 250 mg/L, typical of rock-dominated waters. Several regularities can be identified in Figure 5. On one hand, values of  $\text{Na}/(\text{Na} + \text{Ca})$  decrease with TDS growth in active layer waters. On the other hand, a  $\text{Na}/(\text{Na} + \text{Ca})$  value decrease does not lead to TDS increase in river and lake waters. It may be conditioned by dilution waters with precipitation. Moreover, waters in stone pits and exploration trenches with minimum values of  $\text{Na}/(\text{Na} + \text{Ca})$  are characterized by maximum values of TDS. Therefore, in the studied area, water chemical composition formation is mostly dominated by rock weathering processes. The point positions in Figure 7 confirm this fact.

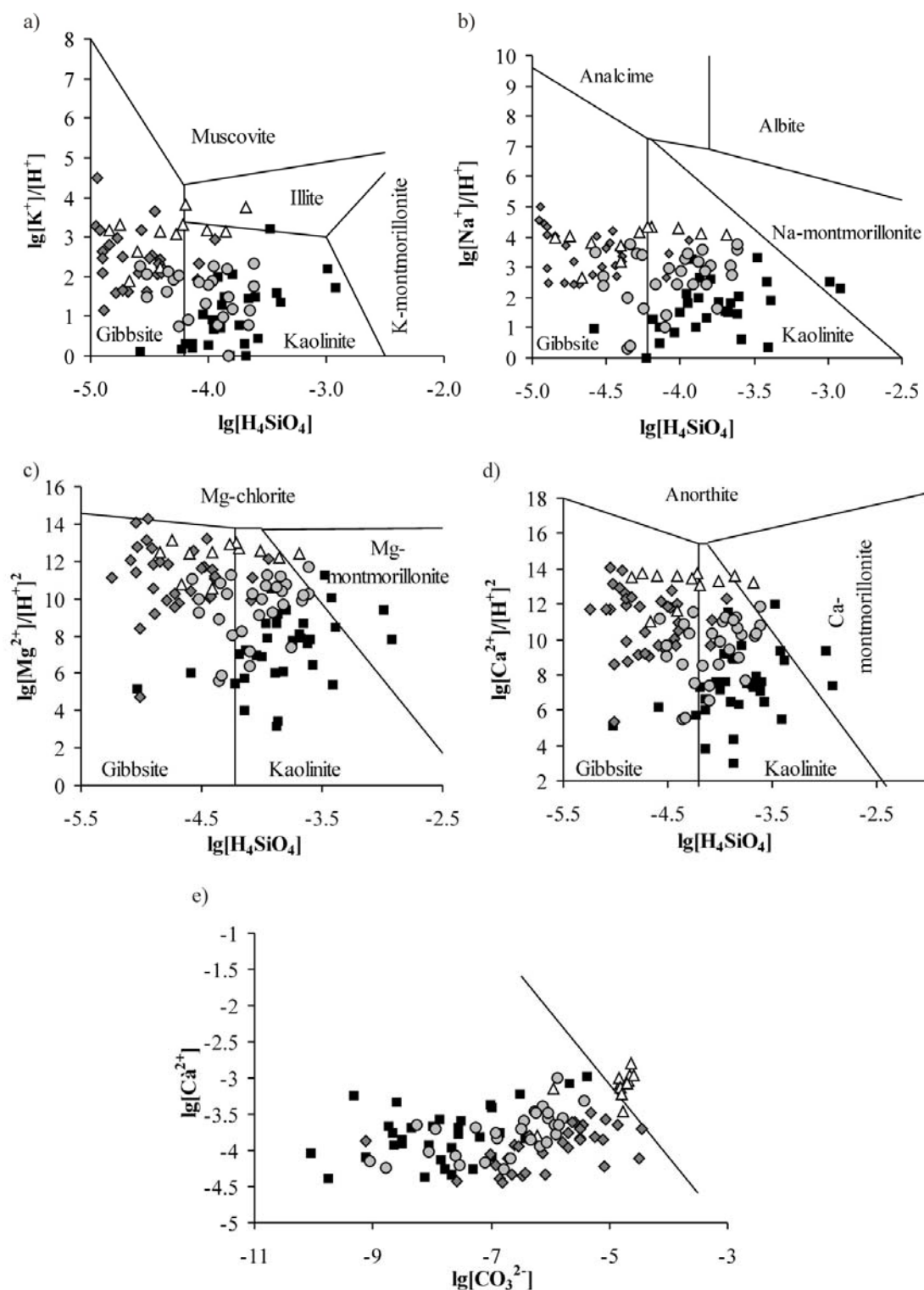


**Figure 7.** Gibbs plots indicating the mechanisms that determine major-ion composition of the studied waters. Symbols as in Figure 5.

In the studied area, aluminosilicate rocks are mostly predominant, whereas carbonate rocks are less common. Thus, the main process of water chemical composition formation is hydrolysis of aluminosilicate minerals and less the dissolution of carbonates. These processes lead to the release of chemical elements in solution and secondary mineral precipitation. For the study of these processes, the major component activities of the water samples were plotted on diagrams of some secondary and primary mineral stability fields (Figure 8).

The point positions outside the anorthite, albite, Mg-chlorite, analcim, and muscovite stability fields (Figure 8) indicate that all the analyzed waters are not in equilibrium with these minerals of primary rocks. Therefore, the studied waters are likely to promote dissolution of primary aluminosilicate minerals and constantly dissolve them. Weathering of aluminosilicate minerals is a slow process [37], releasing chemical elements in solution from primary rocks and also producing secondary minerals; removing chemical elements from solution. As previously reported [33], the processes of water–rock interaction have a stage character, one of the main factors in which is water–rock interaction time, determined by water exchange intensity.

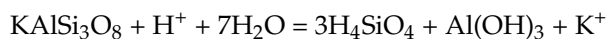
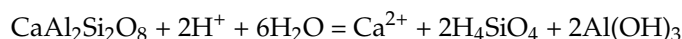
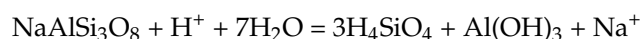
The chemical composition formation of the studied waters occurs under different conditions of water–rock interaction. Active layer waters, rivers, lakes and waters of stone pits and exploration trenches are characterized by different time of interaction with rocks and therefore they reach different water–rock interaction stages. In Figure 8, the point positions in the gibbsite, kaolinite, montmorillonites, calcite stability fields demonstrate that the studied waters are in equilibrium with the products of primary rock weathering. Each point position in the secondary mineral stability fields shows that the studied waters reach four stages of water–rock interaction [38].



**Figure 8.** Selected activity diagram in  $K_2O-SiO_2-Al_2O_3-H_2O$  (a);  $Na_2O-SiO_2-Al_2O_3-H_2O$  (b);  $CaO-SiO_2-Al_2O_3-H_2O$  (c);  $MgO-SiO_2-Al_2O_3-H_2O$  (d) systems and calcite equilibrium diagram (e) at 25 °C and 1 bar. Symbols as in Figure 5.

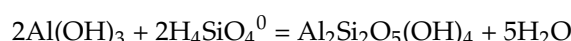
The relatively short time of interaction between waters and rocks defines the development of water-rock system until the first stage, namely water equilibrium with mineral groups of oxides,

hydroxides. At this stage of water–rock interaction, the aluminosilicates hydrolyses processes can be described by following reactions:

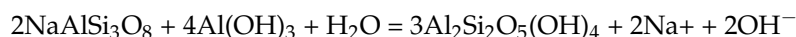
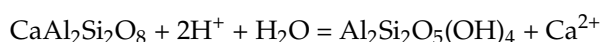


In the first stage of water–rock interaction, the primary aluminosilicates of various compositions actively dissolve by water. This leads to the release of a great quantity of chemical elements in solution. The accumulation of Al, Si and other chemical elements in waters occurs until saturation with respect to the least soluble secondary mineral—gibbsite, ferrihydrite, goethite and other minerals of the oxides, hydroxides group. According to the diagram in Figure 8, the large part of samples is located in the gibbsite stability field. This is characteristic, especially in acid lake waters and rivers and partly for active layer waters. In addition, studied waters are in equilibrium with goethite; the average value of SI is 32.

In the state of saturation with respect to gibbsite, the Al content growth slows down because of its removal from solution with the formation of secondary phase but it does continue. Accumulation of Si in solution occurs during the continued aluminosilicate hydrolyses. When the appropriate ion activity product is gained, waters reach the state of saturation with respect to kaolinite, the second stage of water–rock interaction. It can be shown by following reactions:



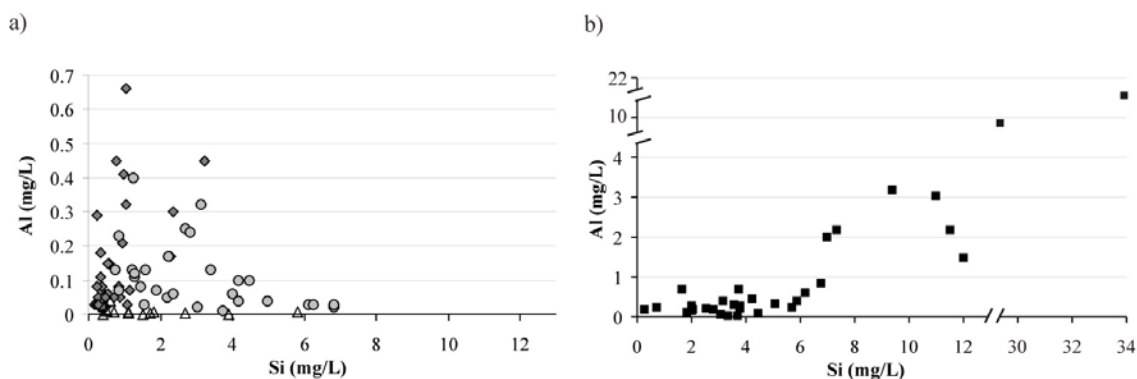
or



This stage is mostly reached by active layer waters and rivers at the floodplain areas.

With the Si accumulation in solution, the degree of water saturation with respect to clay minerals grows and the water–rock system can reach the next stage—saturation with respect to montmorillonites. However, the waters are oversaturated with respect to montmorillonites only in single points among all the studied water samples (Figure 8).

The behavioral peculiarity of Al and Si during the process of interaction between studied waters and rocks is plotted on Figure 9. The expected rise of Al concentration in solution occurs with the Si content growth and therefore with the increase of interaction time between water and aluminosilicate minerals (Figure 9). The intensive growth of the Al content with the Si content growth is observed for the active layer waters, the water chemistry of which is mostly determined by the water–rock interaction processes. Meanwhile, the staging of Al removal from solution during the formation of secondary mineral phase is shown in Figure 9. In the first stage of water–rock interaction there are at least three limitations for Al accumulation in the studied waters: water saturation with respect to gibbsite, kaolinite and montmorillonites. In Figure 9a, the points of the Al content or accumulation rate decreases can be noted at the Si concentrations of 2.5 and 6–15 mg/L, which correspond to the points of saturation with respect to kaolinite and montmorillonites [37]. This dependence is characteristic, mostly for active layer waters. However, it should be noted that the Al accumulation rate decreases with Si content increase in river waters. In addition, there is no dependence of Al content on Si concentration in waters of stone pits and exploring trenches, because their water chemistry is dominated by mostly carbonate rock dissolution processes. The expected Si decrease in solution during secondary mineral precipitation in all mentioned stages of water–rock interaction does not occur; this is because silica concentration in primary minerals is higher than that in clay minerals [39].



**Figure 9.** Relationships Al vs. Si for lakes, rivers, waters of stone pits and exploration trenches (a) and for waters of active layer (b). Symbols as in Figure 5.

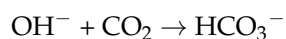
The point position in Figure 8 shows that the studied waters are mostly undersaturated with respect to calcite, but the saturation is indicated in the single points, corresponding mainly to waters of stone pits and exploring trenches. In addition, alkaline lake waters are oversaturated with respect to calcite, or in a state close to saturation. The state of water saturation with respect to calcite is not typical for natural waters in the permafrost regions [33]. The state of studied waters is conditioned by the influence of local factors such as interaction between water and carbonates and weak water exchange. Weak water exchange is caused by flat land surface and presence permafrost layer, which do not assist to precipitation infiltration. Active layer waters and rivers are far from saturation with respect to calcite.

The presented results of the thermodynamic calculations of water–rock interaction are proven by field observations of precipitation of the secondary minerals in the studied permafrost region or under similar conditions, presented in publications. Thus, under similar conditions in the Bolshezemelskaya tundra, the presence of highly dispersed clay minerals, aluminium and iron colloids in large amounts were found in the active layer rocks [40,41]. These published data, our thermodynamic calculations and field observations show the ability of mentioned secondary mineral formation in permafrost regions.

### 3.4. Mechanisms of Water Chemical Composition Formation

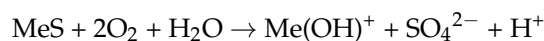
According to our investigation, the main process of water chemical composition formation is the interaction between water and rocks.

As it was shown in the present study, the main anion in the studied water is  $\text{HCO}_3^-$ . Water enrichment in  $\text{HCO}_3^-$  results the neutralization of alkalinity, forming as a result of aluminosilicates hydrolysis, by the products of organic matter mineralization [42].



The neutralization reaction may also occur in the presence of organic acids existing in essential amounts in waters.

The main source of  $\text{SO}_4$  in the studied waters is the oxidation processes. It is the result of oxidation processes of sulfide ores, which are in contact with the atmosphere, especially in stone pits and exploring trenches.



The formation of active layer water chemical composition occurs under the influence of different factors and processes, with differing results. On one hand there is weak water exchange because of flat



ground surface on the studied area. On the other hand, there is a process of seasonal freezing–melting of water-bearing rocks. This determines the water existence in the solid state for the most part of the year. For that reason, water–rock interaction time decreases and water enrichment in chemical elements is low.

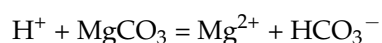
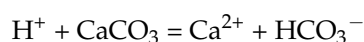
However, in the waters of active layer there are favorable conditions for chemical element accumulation, such as acid conditions and high concentrations of organic matter. Acidic environment of the studied waters defines the water aggressivity on water-bearing rocks and organic acids contribute to formation of organic species of chemical elements.

Various chemical compositions of the studied waters predefine the peculiarity of water–rock interaction. Those active layer waters are oversaturated with respect to gibbsite and kaolinite. The degree of saturation with respect to these minerals increases with a water exchange intensity decrease—from watershed to river floodplain. Waters in watershed areas are characterized by low TDS and pH values, because the water–rock interaction time is very short. Waters on river floodplain areas have higher pH values, which is defined by water enrichment in  $\text{OH}^-$  and chemical elements, forming as a result of water–rock interaction.

The lake water chemistry is mostly dominated by dissolution of carbonates. This process defines the geochemical peculiarities of lake waters such as the highest values of pH and the lowest values of TDS among all the studied waters. Moreover, more alkaline lakes with pH 7.3–9.2 are located at the upper main river parts where carbonates are widely spread. These lake waters are very close to saturation with respect to calcite. This is one of the main peculiarities of lake waters. Among alkaline lakes, there are lakes with low pH (4.6–7.0). These lakes are located at the floodplain of main rivers, where lake waters enrich in organic matter, resulting in the decrease of pH. At the same time, the lowest values of TDS may be conditioned by dilution waters with precipitation. Thus, the main factors and processes of lake water chemical composition formation are carbonate dissolution, morphology position, scant quantity of organic matter, and short time of water–rock interaction.

As for waters in stone pits and exploring trenches, the main processes and factors of water chemical composition formation are weak water exchange, scant quantity of organic matter and active oxidation processes. According to the lithology of the studied area, marble rocks with sulfide inclusions are widely spread.

Oxidation of sulfide minerals causes water enrichment with the sulfate ion. The result of this process is a pH decrease [43], whereas the studied waters are characterized by high pH values. This is due to the neutralization processes accompanying water interaction with carbonated rocks according to following reactions.



It should be noted that waters of stone pits and exploration trenches are oversaturated with respect to calcite. This is due to the weak intensity of water exchange, assisted to reach this stage of water–rock interaction.

Thus, chemical composition of waters in stone pits and exploration trenches is mostly conditioned by natural factors which were intensified by negligible exploration activity in the studied area.

#### 4. Conclusions

The present investigation shows that the studied waters are ultrafresh with TDS from 14 to 438 mg/L. Geochemical environment is characterized as typical for swamp and groundwaters. The pH values range from 3.5 to 9.0, Eh values vary from −68 to 347 mV. The fulvic acid concentrations in waters vary from 1.3 to 19.4 mg/L and humic acids from 0.5 to 2.8 mg/L. The studied waters mostly belong to  $\text{HCO}_3\text{--Ca--Mg}$  or  $\text{HCO}_3\text{--Mg--Ca}$  chemical water types, rarely do waters have  $\text{SO}_4\text{--HCO}_3\text{--Ca}$  composition.

The studied water types are namely active layer waters; rivers, lakes and waters of stone pits and exploration trenches have their own chemical composition peculiarities caused by the different conditions of chemical composition formation. For example, active layer waters are enriched with organic matter more strongly than other water types in the studied area. However, lakes and waters of stone pits and exploration trenches are more alkaline.

The geochemical environment of studied waters assists in the accumulation of such trace elements as Fe, Mn, Al, Ni, Au, Co, Li, Sc, Ti, Cr, Sr, Nb, Mo, Cs, La, Eu, Lu, Hg, and Se, with concentrations much higher than the average for rivers around the world.

The chemical composition of the studied waters is the result of chemical element enrichment mainly during the processes of aluminosilicate hydrolysis and carbonate dissolution. The presented thermodynamic calculations of water equilibrium with rocks show that the studied waters are undersaturated with respect to primary minerals and oversaturated with respect to secondary minerals such as Al, Mn, Fe oxides, hydroxides, kaolinite, rarely montmorillonites and calcite.

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**Conflicts of Interest:** The author declares no conflict of interest.

## Appendix A

**Table A1.** Analytical Data on Water Samples: Physico-Chemical Parameters and Major Components. Redox Potential (Eh, mV), Total Dissolved Solids (TDS) and Ionic Concentration in mg/L.

Type	Sample	pH	Eh	HCO <sub>3</sub>	Cl	SO <sub>4</sub>	Ca	Mg	Na	K	TDS	Si	Al	Mn	Fe
Active layer waters	512	5.8	202	35.4	0.2	0.5	2.5	5.0	1.2	0.4	44	5.88	0.39	0.06	0.60
	532	6.3	77	213.4	0.3	0.5	33.2	19.3	4.1	3.4	274	28.75	9.52	0.26	17.45
	550	5.6	184	49.4	4.0	4.0	3.5	7.4	1.7	6.0	76	6.76	0.85	2.40	3.80
	559	7.5	155	186.7	1.9	12.0	55.4	5.7	1.7	2.1	266	9.38	3.19	1.20	2.75
	566	6.6	130	134.2	0.6	0.5	7.5	21.2	2.1	0.4	166	12.0	1.50	0.08	0.91
	580	3.5	251	38.2	0.3	0.5	4.2	3.8	1.7	1.5	50	3.75	0.69	0.71	6.21
	586	4.3	219	49.3	0.3	1.0	10.1	3.4	0.5	1.2	66	1.66	0.70	0.11	9.79
	609	6.1	231	53.3	1.5	1.0	2.6	8.9	1.3	0.9	69	6.16	0.62	1.56	3.20
	621	4.1	306	18.4	0.3	0.5	1.8	1.9	1.2	0.4	24	2.01	0.26	0.15	3.49
	637	6.2	163	89.7	0.3	0.5	19.2	5.4	1.5	0.5	117	3.68	0.04	1.39	6.88
	694	7.3	249	148.9	0.3	2.0	43.2	2.8	2.3	0.2	200	3.34	0.04	0.03	0.33
	704	6.7	262	38.0	0.3	6.0	8.2	2.9	2.0	0.9	58	4.46	0.08	0.19	0.14
	711	5.9	225	36.2	0.3	0.5	2.1	5.5	1.1	0.1	45	5.69	0.25	0.05	0.42
	717	5.4	199	45.8	0.3	4.0	5.1	4.4	4.0	2.0	66	6.99	1.99	0.24	1.88
	719	5.3	242	138.5	0.3	48.0	14.0	20.8	15.9	7.3	245	33.83	21.21	6.95	23.37
	745	5.2	143	27.1	0.9	0.5	5.6	1.1	1.5	1.3	38	3.57	0.29	1.77	6.02
	749	4.9	137	36.4	0.3	3.0	8.2	2.3	0.9	1.0	52	2.02	0.16	0.52	1.30
	767	5.5	160	31.9	0.4	0.5	1.9	4.9	0.8	0.2	40	2.05	0.19	0.05	0.35
	803	6.5	146	27.2	0.2	3.0	7.1	1.4	1.0	0.1	40	3.06	0.06	0.27	1.74
	810	5.2	213	19.1	0.7	12.0	5.5	3.2	0.6	0.7	42	7.32	2.17	0.34	5.09
	833	4.4	141	146.4	0.3	7.0	26.5	13.3	2.2	1.5	197	10.97	3.04	11.34	108.64
	841	6.1	154	113.8	0.3	1.0	25.6	6.4	1.7	0.8	150	11.50	2.17	2.78	218.26
	852	5.4	178	45.6	0.3	3.0	12.6	1.7	0.4	1.1	65	2.53	0.20	1.69	8.61
	891	5.0	228	41.5	0.3	0.5	6.4	3.2	2.2	0.5	54	0.73	0.24	0.37	0.77
	899	5.4	168	55.2	0.3	0.5	10.0	3.3	3.1	0.3	72	2.79	0.18	0.69	1.92
	942	6.7	163	43.3	0.3	0.5	3.7	4.6	3.3	0.4	56	3.79	0.26	0.30	1.51
	945	5.7	120	76.3	0.3	0.5	8.3	8.6	3.0	0.4	97	3.14	0.39	0.86	12.70
	946	5.6	19	96.6	0.3	0.5	10.0	10.8	4.5	0.6	123	5.05	0.34	0.72	1.71
	997	4.7	187	25.3	0.3	0.5	3.6	2.6	0.7	0.1	33	0.26	0.19	0.10	2.22
	999	5.6	165	29.2	0.3	0.5	5.4	1.9	1.2	0.2	38	1.81	0.12	0.26	0.58
	1052	3.8	68	104.2	0.3	0.5	28.9	2.1	2.0	0.4	138	3.76	0.22	2.56	15.19
	1065	5.0	138	61.3	0.3	0.5	9.8	3.6	5.0	0.4	80	4.21	0.45	0.18	8.36
Mean		6.0	173	57.5	0.4	1.5	8.6	4.5	1.9	0.4	80.0	3.69	0.19	0.26	1.58

Table A1. Cont.

Type	Sample	pH	Eh	HCO <sub>3</sub>	Cl	SO <sub>4</sub>	Ca	Mg	Na	K	TDS	Si	Al	Mn	Fe
Lakes	402	7.0	216	33.6	0.3	4.0	5.4	2.9	2.8	0.5	50	1.03	0.66	0.04	0.64
	406	8.9	174	60.5	0.3	10.0	9.5	5.4	6.5	0.5	93	0.25	0.29	0.06	1.08
	413	8.3	208	97.5	0.3	0.5	10.9	10.4	4.5	0.4	124	0.31	0.02	0.03	0.20
	415	7.7	189	71.0	0.3	0.5	11.8	5.3	3.2	0.3	92	0.93	0.21	0.02	0.50
	418	8.1	175	96.9	0.3	2.0	13.2	9.2	4.9	0.5	127	0.34	0.04	0.02	0.32
	426	7.9	180	33.7	0.3	0.5	4.9	2.9	1.5	0.5	44	0.47	0.02	0.01	0.09
	427	7.8	192	78.2	0.3	0.5	10.8	4.7	8.3	0.3	103	0.35	0.07	0.01	0.30
	435	7.4	160	67.2	0.3	0.5	9.8	6.1	2.6	0.3	86	2.34	0.30	0.03	0.66
	447	7.8	172	51.0	0.3	0.5	11.3	2.6	1.5	0.2	67	1.08	0.03	0.01	0.20
	450	7.8	147	42.9	0.3	0.5	7.9	2.9	1.6	0.2	56	0.88	0.05	0.01	0.21
	456	7.5	170	31.7	0.3	0.5	4.2	2.9	1.7	0.2	41	1.13	0.07	0.03	0.47
	459	7.4	162	45.1	0.3	2.0	2.2	7.5	1.4	0.3	59	1.13	0.07	0.01	0.35
	465	7.7	183	35.4	0.3	4.0	9.5	1.6	1.3	0.5	53	0.16	0.03	0.01	0.14
	478	8.0	146	44.1	0.3	0.5	9.1	1.9	2.8	0.1	58	0.35	0.02	0.04	0.21
	482	8.1	150	33.8	0.3	0.5	6.6	1.7	2.1	0.2	45	0.40	0.02	0.04	0.17
	487	6.5	175	10.9	0.3	0.5	1.6	0.7	1.1	0.2	15	0.27	0.05	0.02	0.23
	491	8.5	100	34.0	0.3	2.0	6.5	1.7	2.9	0.5	48	0.26	0.03	0.05	0.25
	493	7.8	201	34.4	0.30	0.5	5.9	1.7	2.9	0.5	46	0.25	0.03	0.05	0.30
	498	7.0	259	29.6	0.3	0.5	2.1	3.8	1.2	0.9	38	1.05	0.32	0.06	0.69
	800	4.6	147	25.9	0.3	0.5	6.0	0.9	1.2	0.1	34	0.27	0.03	0.04	0.10
	1072	9.0	134	43.8	0.3	0.5	3.6	5.0	2.4	1.2	56	0.32	0.11	0.11	0.62
	1076	7.1	203	47.3	0.3	0.5	7.5	3.1	3.1	1.0	62	0.53	0.06	0.08	0.14
	1080	6.7	169	80.6	0.3	0.5	5.5	10.1	5.1	0.3	102	0.83	0.08	0.02	0.47
	1081	6.7	167	38.7	0.3	0.5	1.9	5.9	1.3	0.3	48	0.58	0.15	0.01	0.50
	1082	6.4	172	52.3	0.3	0.5	4.1	6.5	2.9	0.2	66	0.36	0.08	0.03	0.31
	1090	6.8	194	33.0	0.3	1.0	1.7	5.30	1.1	0.2	43	0.46	0.05	0.02	0.35
	1160	6.9	197	32.9	0.3	0.5	3.5	3.69	1.3	0.4	42	2.27	0.17	0.05	0.62
	2002	7.0	258	45.7	0.3	0.5	2.0	7.14	1.4	0.5	57	0.72	0.05	0.05	0.27
	2004	7.1	251	41.7	0.3	0.5	2.2	6.02	1.8	0.4	52	0.35	0.18	0.05	0.51
	2006	8.5	98	34.4	0.3	1.0	2.7	4.75	1.2	0.6	45	0.98	0.41	0.20	1.22
	2009	6.7	174	32.1	0.3	0.5	2.8	4.00	1.3	0.4	41	0.53	0.15	0.01	0.31
	2013	8.0	47	79.0	0.3	1.0	7.4	10.14	2.5	0.6	101	0.76	0.45	0.09	1.80
	2014	7.8	155	70.7	0.3	0.5	6.6	8.52	3.1	0.1	89	0.23	0.08	0.03	0.29
	2016	7.9	128	84.0	0.3	0.5	15.9	5.78	2.4	0.5	109	3.21	0.45	0.08	0.81
	<b>Mean</b>	<b>7.3</b>	<b>175</b>	<b>47.0</b>	<b>0.3</b>	<b>0.2</b>	<b>5.4</b>	<b>3.7</b>	<b>2.0</b>	<b>0.3</b>	<b>57</b>	<b>0.67</b>	<b>0.08</b>	<b>0.03</b>	<b>0.40</b>
Rivers	505	6.6	225	55.5	0.2	1.0	2.6	8.9	1.6	0.01	70	4.18	0.10	0.01	0.25
	508	7.1	217	72.2	0.2	0.5	5.4	10.0	2.2	0.1	90	4.48	0.10	0.00	0.18
	569	7.0	133	60.8	0.3	1.0	12.1	3.42	3.3	0.03	81	6.10	0.03	0.02	0.22
	614	7.3	210	63.2	0.3	1.0	13.3	3.6	2.3	0.2	84	3.01	0.02	0.02	0.26
	636	6.9	185	36.1	0.3	0.5	3.5	4.2	1.6	0.6	46	0.85	0.23	0.10	0.78
	685	6.9	107	240.3	0.3	9.0	55.9	9.9	12.0	0.3	328	6.81	0.02	0.20	1.08
	754	4.8	115	19.1	0.3	4.0	3.2	2.5	0.7	0.4	30	1.22	0.13	0.10	0.82
	784	4.9	159	27.4	0.2	0.5	2.6	3.6	0.8	0.1	35	1.29	0.11	0.03	0.55
	791	5.7	212	24.2	0.3	0.5	4.3	1.7	1.2	0.1	32	2.23	0.17	0.01	0.71
	822	5.7	158	31.4	0.5	13.0	9.5	2.9	2.0	0.1	59	4.96	0.04	0.00	0.08
	930	7.0	180	104.5	0.3	0.5	20.3	7.6	1.8	0.1	135	4.16	0.04	0.04	0.25
	961	6.6	171	27.3	0.3	1.0	3.1	3.1	1.4	0.3	37	0.85	0.07	0.04	0.67
	1030	6.2	98	108.4	0.3	0.5	7.2	15.1	3.9	0.5	136	2.69	0.25	0.09	0.88
	729	6.9	170	92.8	0.3	0.5	16.9	7.4	1.6	0.1	119	6.25	0.03	0.01	0.10
	514	7.4	185	64.2	0.3	0.5	10.8	4.8	2.9	0.3	83	0.74	0.13	0.06	0.54
	521	7.4	89	89.3	0.3	0.5	13.5	7.8	3.6	0.3	115	3.99	0.06	0.07	0.34
	545	7.6	108	133.4	0.2	0.5	24.2	10.1	3.5	0.2	172	6.82	0.03	0.01	0.09
	664	5.8	184	54.3	0.3	2.0	3.9	8.1	1.6	0.4	71	1.59	0.13	0.06	1.49
	818	6.6	124	40.1	0.3	3.0	8.1	3.0	1.7	0.1	56	3.40	0.13	0.02	0.13
	828	5.1	213	60.2	0.3	1.0	10.8	4.7	1.9	0.2	79	2.20	0.05	0.01	0.18
	846	6.8	192	68.3	0.3	0.5	9.6	6.4	2.8	0.4	88	2.82	0.24	0.03	0.49
	849	7.5	160	55.4	0.3	1.0	7.8	5.5	2.1	0.2	72	3.14	0.32	0.03	0.54
	884	7.1	163	50.1	0.3	0.5	6.5	3.2	5.5	0.3	66	1.43	0.08	0.04	0.64
	910	7.6	136	48.8	0.3	3.0	10.6	3.3	1.6	0.1	68	1.56	0.03	0.04	0.26
	953	6.4	210	15.9	0.3	10.0	2.9	3.4	0.9	0.7	34	1.23	0.40	0.17	1.41
	973	7.3	230	62.2	1.1	3.0	15.7	2.9	1.9	0.02	87	3.73	0.01	0.01	0.25
	1011	7.3	150	47.3	0.3	0.5	5.9	3.1	5.2	0.2	62	1.27	0.12	0.05	0.85
	1022	6.2	155	98.1	0.3	0.5	16.4	8.1	2.8	0.4	126	2.34	0.06	0.04	0.31
	1069	6.1	65	60.3	0.3	0.5	9.7	3.3	5.4	0.3	79	1.89	0.07	0.03	0.50
	<b>Mean</b>	<b>6.9</b>	<b>170</b>	<b>64.8</b>	<b>0.3</b>	<b>1.8</b>	<b>10.9</b>	<b>4.2</b>	<b>1.9</b>	<b>0.2</b>	<b>80</b>	<b>2.32</b>	<b>0.13</b>	<b>0.026</b>	<b>0.4</b>

Table A1. Cont.

Type	Sample	pH	Eh	HCO <sub>3</sub>	Cl	SO <sub>4</sub>	Ca	Mg	Na	K	TDS	Si	Al	Mn	Fe
Waters of stone pits and exploration trenches	116	8.2	193	138.6	4.4	18.0	44.6	4.9	3.0	0.4	214	2.7	0.003	0.00003	0.56
	117	7.4	121	63.4	0.6	47.0	36.2	1.8	1.5	0.3	151	1.1	0.006	0.0004	0.41
	118	8.0	158	330.4	1.9	1.0	91.7	8.5	2.9	2.3	438	5.8	0.007	0.258	1.09
	205	8.3	212	102.8	4.4	50.0	52.3	2.4	0.7	0.3	213	1.1	0.002	0.003	0.60
	206	8.6	200	59.8	1.9	1.0	16.4	2.4	0.7	0.2	82	0.5	0.011	0.004	0.22
	207	8.1	192	172.0	1.9	7.0	39.6	9.8	4.1	2.1	236	1.8	0.008	0.106	0.88
	208	8.4	204	116.1	4.4	42.0	47.9	4.9	2.2	0.3	218	1.7	0.003	0.002	0.60
	209	8.3	218	152.4	4.4	22.0	58.0	1.2	1.6	0.3	240	3.9	0.001	0.002	0.80
	304	8.2	191	233.3	1.9	5.0	59.5	10.9	2.2	0.3	313	1.5	0.001	0.004	0.12
	305	7.4	189	32.9	0.8	1.0	7.2	2.4	0.4	0.1	45	0.6	0.039	0.012	0.65
	306	8.3	182	138.4	1.9	3.5	42.6	2.4	1.2	0.3	190	0.4	0.001	0.012	0.21
	307	8.4	171	87.6	1.9	5.0	29.3	1.2	0.6	0.1	126	0.7	0.007	0.006	0.05
Mean		8.1	186	135.6	2.5	16.8	43.8	4.4	1.8	0.6	206	1.8	0.007	0.034	0.52

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