

Article

Testing Landscape, Climate and Lithology Impact on Carbon, Major and Trace Elements of the Lena River and Its Tributaries during a Spring Flood Period

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Abstract: Transport of carbon, major and trace elements by rivers in permafrost-affected regions is one of the key factors in circumpolar aquatic ecosystem response to climate warming and permafrost thaw. A snap-shot study of major and trace element concentration in the Lena River basin during the peak of spring flood revealed a specific group of solutes according to their spatial pattern across the river main stem and tributaries and allowed the establishment of a link to certain landscape parameters. We demonstrate a systematic decrease of labile major and trace anion, alkali and alkaline-earth metal concentration downstream of the main stem of the Lena River, linked to change in dominant rocks from carbonate to silicate, and a northward decreasing influence of the groundwater. In contrast, dissolved organic carbon (DOC) and a number of low-soluble elements exhibited an increase in concentration from the SW to the NE part of the river. We tentatively link this to an increase in soil organic carbon stock and silicate rocks in the Lena River watershed in this direction. Among all the landscape parameters, the proportion of sporadic permafrost on the watershed strongly influenced concentrations of soluble highly mobile elements (Cl, B, DIC, Li, Na, K, Mg, Ca, Sr, Mo, As and U). Another important factor of element concentration control in the Lena River tributaries was the coverage of the watershed by light (for B, Cl, Na, K, U) and deciduous (for Fe, Ni, Zn, Ge, Rb, Zr, La, Th) needle-leaf forest (pine and larch). Our results also suggest a DOC-enhanced transport of low-soluble trace elements in the NW part of the basin. This part of the basin is dominated by silicate rocks and continuous permafrost, as compared to the carbonate rock-dominated and groundwater-affected SW part of the Lena River basin. Overall, the impact of rock lithology and permafrost on major and trace solutes of the Lena River basin during the peak of spring flood was mostly detected at the scale of the main stem. Such an impact for tributaries was much less pronounced, because of the dominance of surface flow and lower hydrological connectivity with deep groundwater in the latter. Future changes in the river water chemistry linked to climate warming and permafrost thaw at the scale of the whole river basin are likely to stem from changes in the spatial pattern of dominant vegetation as well as the permafrost regime. We argue that comparable studies of large, permafrost-affected rivers during contrasting seasons, including winter baseflow, should allow efficient prediction of future changes in riverine ‘inorganic’ hydrochemistry induced by permafrost thaw.

Keywords: river; hydrochemistry; permafrost; forest; landscape; lithology; carbonate rocks; trace element; major element

1. Introduction

The climate warming, permafrost thaw, change of hydrological connectivity and northward shift of tree line currently observed in northern Eurasia and throughout the Arctic and subarctic regions [1,2] are expected to result in massive carbon (C), nutrients, major and trace elements mobilization from permafrost soils and groundwaters to the rivers, and further to the Arctic Ocean [3,4]. Large Arctic rivers are the main players in element delivery from the land to the ocean, which becomes especially important during climate warming and permafrost thaw because such rivers integrate large areas of essentially pristine permafrost and forested regions [5]. As a result, assessment of lateral riverine export fluxes of organic and inorganic solutes in permafrost-affected regions is needed for defining adequate models of ecosystem functioning under various climate change scenarios [6].

The Lena River of Central and Eastern Siberia is located almost entirely within a permafrost zone; it exhibits the highest seasonal variation in water flow, and demonstrates an annual discharge increase over recent decades [7–15]. Among all the solutes transported by the Lena River water, organic carbon has received most attention [16–22] although information on general hydrochemistry is also available [23–29]. Most recently, novel isotopic approaches were applied for nutrients [30] and trace metals such as Li [31] and Fe [32]. However, the majority of these studies were performed during summer-autumn baseflow or the end of spring flood (July–September) whereas the peak of spring flood, when the main part of annual riverine transport of solutes in high latitude occurs [33–36], has not been sufficiently studied. The exception is regular (monthly to weekly) monitoring of the Lena River terminal gauging station at Kysyr, performed by the Russian Hydrological Survey and within the PARTNERS/ARCTIC GRO projects [34,37]. Furthermore, in contrast to this extensive research on carbon and major element transport by the Lena River main stem, its tributaries remain very poorly known. Thus, no detailed hydro-chemical studies at the peak of spring flood have been performed and the understanding of various contrasting tributaries of the Lena River remains quite poor. Taken together, our knowledge of environmental factors controlling the major and trace element concentration in the Lena River basin during the most crucial hydrological period of the year remains limited and thus deserves special attention. In particular, distinguishing the role of groundwater feeding and surface influx (vegetation, organic topsoil and mineral soil leaching) to the river remains one of the main challenges in understanding the mechanisms of solute flux formation in high latitude rivers. Here we suggest a landscape approach to unravel the role of different environmental factors for the Lena River basin, taking advantage of recent progress in GIS-based mapping of Siberian territory [38,39]. We anticipate that this information should allow, for the first time, testing the impact of main physio-geographical factors (vegetation, soil, lithology, climate and permafrost coverage) on the spatial pattern of major and minor solutes at the scale of a large Siberian river.

Based on the bulk of information acquired by previous chemical and isotopic work on major and trace elements in boreal and permafrost-affected rivers [40–47], we hypothesize that, during spring flood, the impact of lithology (which is reflected via deep subsoil waters and groundwater feeding) will be quite low and the river water chemical composition will be dominated by surficial flow originating from water leaching of organic topsoil and vegetation litter. In order to test this hypothesis, we sampled the main stem of the Lena River and its tributaries at the peak of the spring flood and we analyzed dissolved (<0.45 µm) major and trace components of the river water. We aimed at identifying environmental factors controlling element transport in the Lena River basin in order to use this information to foresee future changes in elemental export from the land to the Arctic Ocean.

2. Study Site, Materials and Methods

2.1. The Lena River and Its Tributaries

The sampled Lena River main stem and its 20 tributaries are located along a 2400 km latitudinal transect from SW to NE and includes watersheds of distinct sizes, geomorphol-

ogy, permafrost extent, lithology, climate and vegetation (Figure 1 and Figure S1; Table S1). The total watershed area of the rivers sampled in this work is about 1.66 million km², representing 66% of the entire Lena River basin. Permafrost is mostly continuous except for some discontinuous and sporadic patches in the southern and south-western parts of the Lena basin [48]. The mean annual air temperatures (MAAT) along the transect range from $-5\text{ }^{\circ}\text{C}$ in the southern part of the Lena basin to $-9\text{ }^{\circ}\text{C}$ in the central part of the basin. For the studied part of the main stem, the MAAT is $-8.76 \pm 2.95\text{ }^{\circ}\text{C}$, whereas the range of MAAT for the tributaries is from -4.7 to $-15.9\text{ }^{\circ}\text{C}$. The mean annual precipitation ranges from $350\text{--}500\text{ mm y}^{-1}$ in the southern and south-western part of the basin to $200\text{--}250\text{ mm y}^{-1}$ in the central and northern parts [48]. The mean precipitation of the studied Lena River basin and its 20 tributaries is $418 \pm 77\text{ mm y}^{-1}$. The lithology of the Siberian Platform which is drained by the Lena River is highly diverse and includes Archean and Proterozoic magmatic and metamorphic rocks, late Proterozoic, Cambrian and Ordovician dolostones and limestones, volcanic rocks of Permo-Triassic age and essentially terrigenous silicate sedimentary rocks of the Phanerozoic. Note that salt deposits are abundant in the SW part of the basin, where the carbonate rocks dominate the lithology of the watersheds. Further description of the Lena River basin landscapes, vegetation and lithology can be found in numerous works [18,20,23–25,29,49].

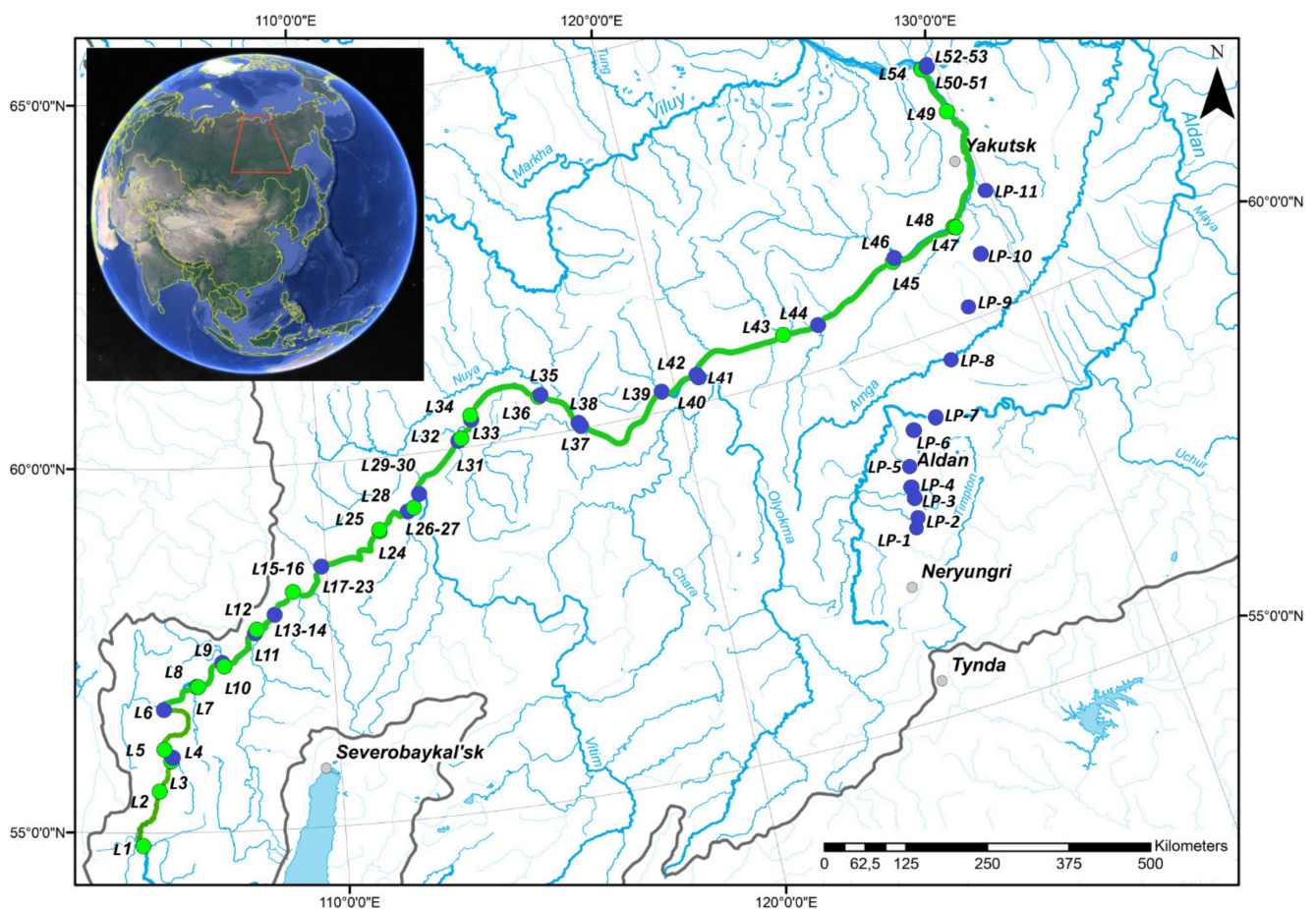


Figure 1. Map of the studied part of the Lena River basin with sampling points of the main stem (green circles) and tributaries (blue circles). The positions of tributaries are shown in Figure S1. See Table S1 for tributaries and river watersheds (LP) parameters.

The peak of annual discharge depends on the latitude and occurs in May in the south (Ust-Kut) and in June in the middle and low reaches of the Lena River (Yakutsk, Kuysyr). The peak of discharge at the Kuysur station is $140,000\text{--}160,000\text{ m}^3/\text{s}$, the winter baseflow dis-

charge is 2000–3000 m³/s, and the summer baseflow discharge is 20,000–40,000 m³/s [7–15]. From 29 May to 17 June 2016, we moved downstream the Lena River with an average speed of 30 km h⁻¹ [50]. As such, we followed the progression of spring and moved from the southwest (Zhigalovo) to the northeast (Yakutsk), thus collecting river water at approximately the same stage of maximal discharge. Note that route sampling is a common way to assess river water chemistry in extreme environments [23,51], and generally a single sampling during high flow season provides the best agreement with time-series estimates [52]. Regular stops each 80–100 km at the middle of the river allowed sampling of major hydro-chemical parameters of the main stem. We also moved 500–1500 m upstream of selected tributaries where we sampled the tributary for hydrochemistry.

In addition to 20 tributaries, evenly distributed over the boat route on the main stem, between 29–31 May 2016, we sampled 10 rivers belonging to the Lena River watershed (mostly the middle part and upper reaches of Aldan). The choice of these 10 rivers of the Lena watershed was restricted by the possibility of ground access. For this, we used road transportation and we moved at least 500 m upstream of each river where it crossed the bridge to grab a water sample 2 m offshore (Figure 1).

2.2. Hydrochemical Measurements

The water temperature, pH, dissolved oxygen, and electric conductivity in the main stem and tributaries were measured directly in the field using Hanna and WTW portable instruments. The water was sampled in pre-cleaned polypropylene bottle from 20–30 cm depth in the middle of the river and immediately filtered through disposable single-use sterile Sartorius filter units (0.45 µm pore size). The first 50 mL of the filtrate was discarded. Filtered river waters were processed using the analytical approaches employed by the GET Laboratory (Toulouse) to analyze DOM-rich waters from boreal and permafrost-bearing settings [53,54]. Filtered solutions for cations and trace element analyses were acidified (pH = 2) with ultrapure double-distilled HNO₃ and stored in HDPE bottles previously washed with 1 M HCl and rinsed with MilliQ deionized water. Filtered water samples for anions were not acidified and were stored in HDPE bottles previously washed according to the above-described procedure for cations. The major anion concentrations (Cl⁻ and SO₄²⁻) were analyzed by ion chromatography (Dionex 2000i), with an uncertainty of 2%. The DOC and Dissolved Inorganic Carbon (DIC) were determined by a Shimadzu TOC-VSCN Analyzer with an uncertainty of 3% and a detection limit of 0.1 mg/L. The major and trace elements were measured by quadrupole ICP-MS (7500ce, Agilent Technologies, Santa Clara, California, USA). Indium and rhenium were used as internal standards. The international geo-standard SLRS-5 (Riverine Water Reference Material for Trace Metals, certified by the National Research Council of Canada) was used to check the validity and reproducibility of analyses. Good agreement existed between our replicated measurements of SLRS-5 and the certified values (relative difference < 15%).

2.3. Landscape Parameters of the Lena River Basin and Data Treatment

The physio-geographical characteristics of the 20 Lena tributaries and the other 10 rivers of the Lena River basin sampled in this study and the two points of the Lena main stem (upstream and downstream r. Aldan Table S1 of the Supplementary Materials) were determined by digitalizing available soil, vegetation, lithological, and geocryological maps. The landscape parameters were typified using the TerraNorte Database of Land Cover of Russia ([38], <http://smiswww.iki.rssi.ru/default.aspx?page=356>, assessed on 29 July 2021) with original resolution of 230 × 230 m pixel size. This included various types of forest (evergreen, deciduous, needle-leaf/broadleaf), grassland, tundra, wetlands, water bodies and urban area. The climate and permafrost parameters of watershed were obtained from CRU grids data (1950–2016) and NCSCD data, respectively, whereas the biomass and soil organic carbon content was obtained from BIOMASAR2 and NCSCD databases. The permafrost extent type layer was taken from NCSCDv2 (The Northern Circumpolar Soil Carbon Database, ref. link: <http://su.diva-portal.org/smash/record.jsf?pid=diva2%3A637770&dswid=1526>,

assessed on 29 July 2021) in vector GIS format with a scale of 1:1,000,000 (which is about 1×1 km pixel resolution in rasterized format). The lithology layer was taken from the GIS version of the Geological map of the Russian Federation (scale 1:5,000,000 in vector format which is about 5×5 km pixel resolution in rasterized format). To test the effect of carbonate rocks on dissolved C parameters, we distinguished felsic plutonic, terrigenous silicate rocks (sedimentary siliciclastic of Archean, early Proterozoic and Cainozoic age) and dolostones and limestones of upper Proterozoic, Cambrian and Ordovician age.

The Pearson rank order correlation coefficient (R_s) ($p < 0.05$) was used to determine the relationship between each major and trace element concentration and climatic, lithological and landscape parameters of the Lena River tributaries. Further statistical treatment of element concentration drivers in river waters included a Principal Component Analysis using a variance estimation method, which allowed test of the effect of various environmental factors of the watershed on behavior of riverine solutes in both the Lena River main stem and its tributaries. All graphics and figures were created using MS Excel 2010, MS Visio Professional 2016 and GS Grapher 11 package. Statistical treatment was performed using STATISTICA-7 (<http://www.statsoft.com>, assessed on 29 July 2021).

3. Results

3.1. Element Concentration in the Main Stem of the Lena River

All measured hydro-chemical parameters of the Lena River and tributaries are available from the Mendeley database repository [55]. The concentrations of major and trace elements in the main stem averaged over 2600 km distance are listed in Table 1. For a number of elements, the greatest changes occurred between first 0–800 (± 200) km (upstream of Kirenga/Chaika) and the remaining 800–2600 km downstream to the Aldan River. These two parts of the river transect reflect sizable change in the lithology of rocks, landscape and climate and distinguish upper reaches and the middle course of the Lena River.

Table 1. Major and trace element concentration (average \pm s.d.) in the Lena River main stem. The distances are along the river, starting from Zhigalovo (the Lena River headwaters).

	Upper Reaches, 0–804 km	Middle Course, 804–2600 km
$T_{\text{air}}, ^\circ\text{C}$	21.9 ± 1.3	19.6 ± 0.65
$T_{\text{water}}, ^\circ\text{C}$	11.9 ± 0.4	9.6 ± 0.3
$\text{O}_2, \text{mg L}^{-1}$	6.1 ± 0.1	6.3 ± 0.05
pH	8.0 ± 0.1	7.64 ± 0.03
S.C., $\mu\text{S cm}^{-1}$	226 ± 17	99.7 ± 5.9
Depth, m	3.8 ± 0.554	7.5 ± 0.63
Cl mg L^{-1}	13.7 ± 0.89	9.2 ± 1.1
$\text{SO}_4 \text{mg L}^{-1}$	17.9 ± 2.0	6.42 ± 0.36
DOC, mg L^{-1}	11.0 ± 1.0	9.36 ± 0.34
DIC, mg L^{-1}	15.3 ± 1.8	5.3 ± 0.19
Li, $\mu\text{g L}^{-1}$	2.87 ± 0.32	1.08 ± 0.07
B, $\mu\text{g L}^{-1}$	8.9 ± 0.93	3.2 ± 0.39
Na, $\mu\text{g L}^{-1}$	$10,400 \pm 595$	6770 ± 738
Mg, $\mu\text{g L}^{-1}$	7203 ± 858	2331 ± 109
Al, $\mu\text{g L}^{-1}$	69.3 ± 8.6	117 ± 5.8
Si, $\mu\text{g L}^{-1}$	1970 ± 40	1804 ± 18.5
P, $\mu\text{g L}^{-1}$	11.6 ± 2.2	6.38 ± 0.43
K, $\mu\text{g L}^{-1}$	651 ± 46	483 ± 8.6

Table 1. Cont.

	Upper Reaches, 0–804 km	Middle Course, 804–2600 km
Ca, $\mu\text{g L}^{-1}$	24,800 \pm 3090	8440 \pm 264
Ti, $\mu\text{g L}^{-1}$	7.95 \pm 0.97	10.2 \pm 0.67
V, $\mu\text{g L}^{-1}$	1.17 \pm 0.10	0.689 \pm 0.06
Cr, $\mu\text{g L}^{-1}$	0.33 \pm 0.075	0.45 \pm 0.05
Mn, $\mu\text{g L}^{-1}$	8.54 \pm 1.2	4.79 \pm 0.23
Fe, $\mu\text{g L}^{-1}$	80.0 \pm 7.6	85.7 \pm 3.8
Co, $\mu\text{g L}^{-1}$	0.059 \pm 0.004	0.058 \pm 0.003
Ni, $\mu\text{g L}^{-1}$	0.41 \pm 0.08	0.54 \pm 0.05
Cu, $\mu\text{g L}^{-1}$	1.2 \pm 0.13	1.1 \pm 0.05
Zn, $\mu\text{g L}^{-1}$	3.38 \pm 0.36	4.6 \pm 0.5
Ga, $\mu\text{g L}^{-1}$	0.012 \pm 0.0016	0.0164 \pm 0.0009
Ge, $\mu\text{g L}^{-1}$	0.0073 \pm 0.0005	0.0076 \pm 0.0003
As, $\mu\text{g L}^{-1}$	0.338 \pm 0.03	0.171 \pm 0.005
Rb, $\mu\text{g L}^{-1}$	0.35 \pm 0.058	0.66 \pm 0.019
Sr, $\mu\text{g L}^{-1}$	254 \pm 39	66.8 \pm 3.6
Y, $\mu\text{g L}^{-1}$	0.372 \pm 0.038	0.422 \pm 0.005
Zr, $\mu\text{g L}^{-1}$	0.189 \pm 0.02	0.167 \pm 0.007
Nb, $\mu\text{g L}^{-1}$	0.022 \pm 0.003	0.038 \pm 0.0026
Mo, $\mu\text{g L}^{-1}$	0.416 \pm 0.02	0.251 \pm 0.018
Cd, $\mu\text{g L}^{-1}$	0.0093 \pm 0.0008	0.0099 \pm 0.001
Sb, $\mu\text{g L}^{-1}$	0.0242 \pm 0.0014	0.0155 \pm 0.0007
Cs, $\mu\text{g L}^{-1}$	0.0019 \pm 0.0003	0.003 \pm 0.0003
Ba, $\mu\text{g L}^{-1}$	33.68 \pm 3.906	10.29 \pm 0.488
La, $\mu\text{g L}^{-1}$	0.402 \pm 0.085	1.02 \pm 0.07
Ce, $\mu\text{g L}^{-1}$	0.39 \pm 0.07	1.02 \pm 0.04
Pr, $\mu\text{g L}^{-1}$	0.09 \pm 0.02	0.17 \pm 0.003
Nd, $\mu\text{g L}^{-1}$	0.36 \pm 0.06	0.629 \pm 0.01
Sm, $\mu\text{g L}^{-1}$	0.0867 \pm 0.01	0.119 \pm 0.002
Eu, $\mu\text{g L}^{-1}$	0.018 \pm 0.002	0.019 \pm 0.0004
Gd, $\mu\text{g L}^{-1}$	0.0763 \pm 0.0099	0.105 \pm 0.0012
Tb, $\mu\text{g L}^{-1}$	0.0115 \pm 0.0014	0.014 \pm 0.00016
Dy, $\mu\text{g L}^{-1}$	0.0662 \pm 0.0075	0.0785 \pm 0.001
Er, $\mu\text{g L}^{-1}$	0.0361 \pm 0.0041	0.0414 \pm 0.00049
Tm, $\mu\text{g L}^{-1}$	0.00474 \pm 0.00056	0.00575 \pm 0.0001
Yb, $\mu\text{g L}^{-1}$	0.0312 \pm 0.0035	0.0374 \pm 0.00063
Lu, $\mu\text{g L}^{-1}$	0.00446 \pm 0.00049	0.00537 \pm 0.00010
Hf, $\mu\text{g L}^{-1}$	0.0326 \pm 0.0047	0.0259 \pm 0.0009
Pb, $\mu\text{g L}^{-1}$	0.065 \pm 0.011	0.0807 \pm 0.0066
Th, $\mu\text{g L}^{-1}$	0.0243 \pm 0.004	0.059 \pm 0.0043
U, $\mu\text{g L}^{-1}$	0.310 \pm 0.02	0.256 \pm 0.004

According to element behavior along the Lena River main stem, from Zhigalovo to Aldan (2600 km downstream), three groups of solutes could be distinguished: (i) Cl, SO₄, DIC, Li, B, Na, Mg, K, Ca, As, Sr, Mo, Sb, Ba and U, decreasing the concentration from SW to NE (Figure 2); (ii) Al, Ti, Cr, Fe, Ga, Rb, Y, Zr, Nb, Cs, REEs, Ce, Hf, Th, increasing their concentration from SW to NE (Figure 3); and finally (iii) DOC, Si, P, V, Mn, Co, Ni, Cu, Zn, Ge, Cd, Hf and Pb, which did not exhibit any statistically significant dependence ($r < 0.3$, $p < 0.05$) on the river distance (Figure 4). The Mann-Whitney test demonstrated significant ($p < 0.001$) difference in most element concentration between the SW part of the Lena main stem (upper reaches, 0–800 km) and its middle course (800 km—Aldan River), as listed in Table S2 of the Supplementary Materials. The exceptions are DOC, P, Cr, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Cd, heavy REE, Hf and Pb which did not show statistically significant differences.

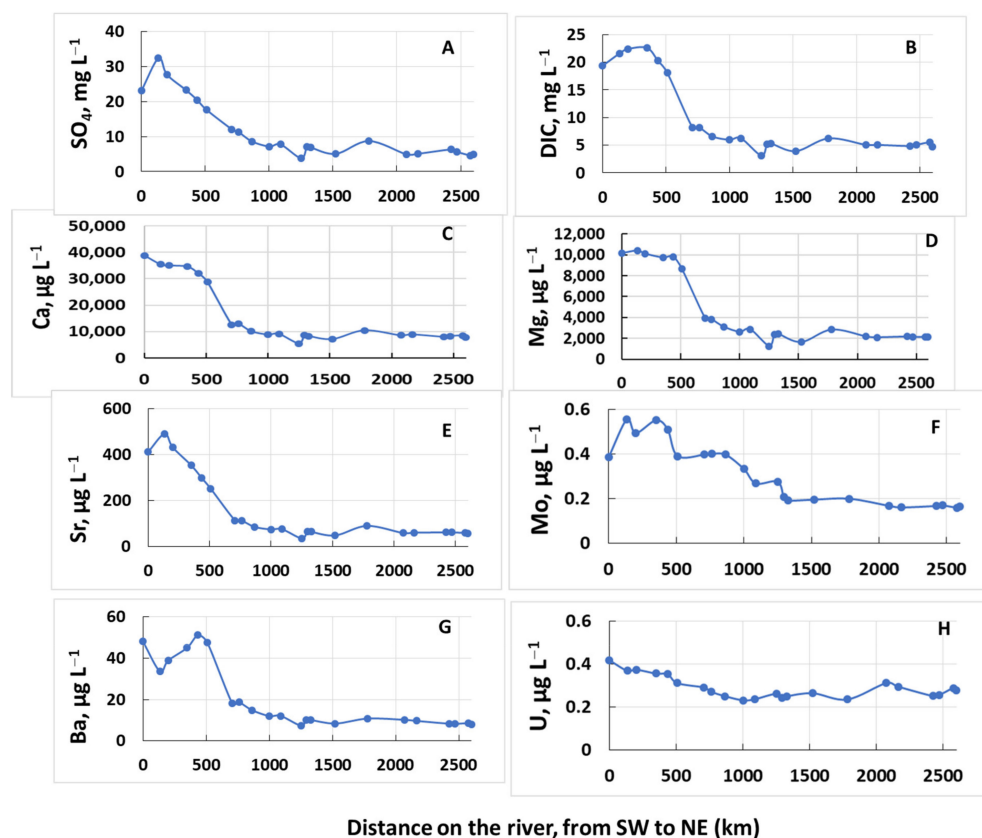


Figure 2. Examples of elements decreasing their concentration in the main stem of the Lena River from SW to NE: SO₄ (A), DIC (B), Mg (C), Ca (D), Sr (E), Mo (F) Ba (G) and U (H) The distance is km of river from Zhigalovo (0 km, upper reaches) to the Aldan River (~2600 km).

A linear (Pearson) pairwise correlation between solutes in the main stem demonstrated three potential interlinked carriers and sources of dissolved elements in the river water (Table S3 of the Supplementary File). Firstly, this is DOC, which positively correlated with B, Mg, P, K, Ca, V, Ni, Cu, As, Zr, Sb, Ba, Hf and U. The second potential carrier and source tracer is Fe which correlated with the largest number of trace elements (Si, P, Ti, V, Mn, Co, Ga, Y, Zr, Nb, Cs, REEs, Hf and Th). Only a few elements were significantly ($p < 0.05$) linked to both DOC and Fe (P, V, Zr, Hf). Aluminum most strongly correlated with Ti, Ga, Rb, Y, Nb, Cs, all REE, and Th.

3.2. Dissolved Elementary Composition of Tributaries of the Lena Basin: Impact of Permafrost, Climate, Vegetation, Soil and Landscape on Major and Trace Element Concentration

The Lena River tributaries exhibited strong variability of dissolved elementary composition, independent of river size and location within the main river basin. A Pearson

correlation of solutes in the tributaries demonstrated three groups of elements depending on their link to potential carriers (or common source) in the river water (Table S3 of the Supplementary Materials). Similar to the main stem, DOC positively correlated ($R_{\text{Pearson}} > 0.5$) with Si, P, K, V, Cr, Ni, Cu, As, Y, Zr, Sb, HREE, Hf, and Th. Dissolved Fe strongly correlated with Si, P, Ti, Cr, Co, Ni, Cu, Ge, As, Rb, Y, Zr, Cd, Sb, La, heavy REE, Hf and Th, but preferentially (higher than DOC) correlated with P, Ti, Cr, Ni, Ge, Th. Finally, Al most strongly correlated with Ti, Cr, Ga, Nb, Cs, REE, (from Ce to Er) and Th. Similarly in the main stem, a number of elements were significantly ($p < 0.05$) linked to both DOC and Fe (Si, P, Ti, Cr, Cu, As, Y, Zr, Sb, HREE, and Th).

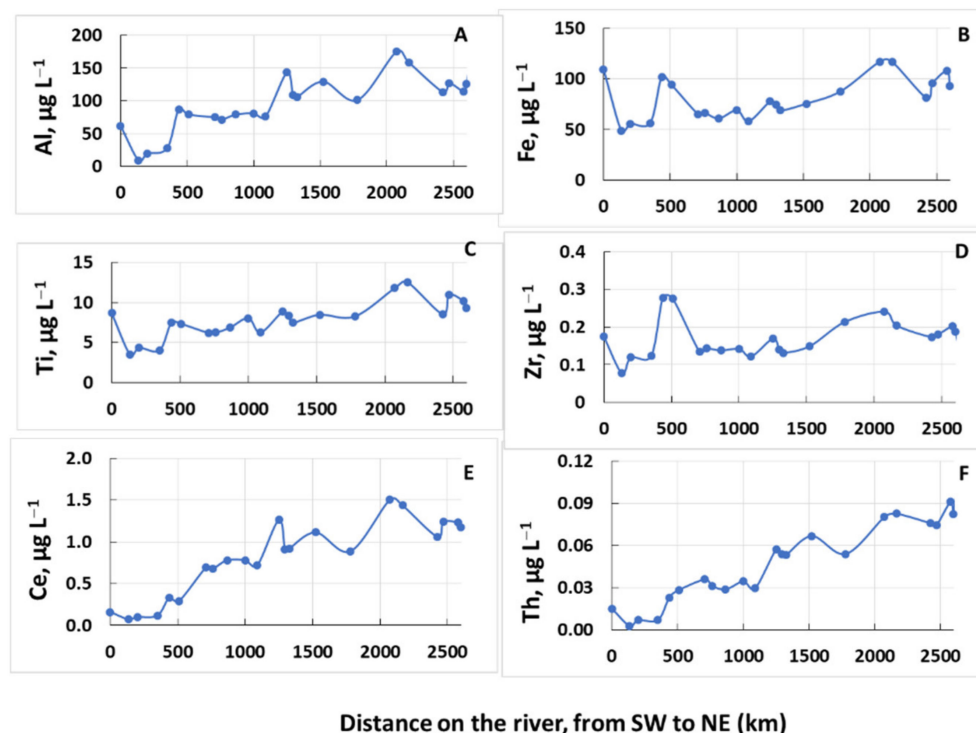


Figure 3. Examples of elements increasing their concentration in the main stem of the Lena River from SW to NE: Al (A), Fe (B), Ti (C), Zr (D), Ce (E) and Th (F). The distance is km of river from Zhigalovo (0 km, upper reaches) to the Aldan River (2600 km).

To test the impact of physio-geographical parameters on the hydrochemistry of the Lena River tributaries, a correlation matrix of element concentration with climate, permafrost, vegetation coverage and lithology was constructed (Table S4). These correlations revealed several environmental factors that are likely to control the elemental composition of various rivers of the Lena Basin. The first important factor was the vegetation, namely the coverage of watershed by light (Li, B, Cl, SO₄, Na, V, Sr, U) and deciduous (Si, Ni, Ge, Zr, Hf, Th) needle-leaf forest and broadleaf forest (DOC, Cl, SO₄, Li, Na, Si, Ca, Ti, V, Co, Ge, Sr, Cd, some heavy REE (Er, Yb), Hf and U) as illustrated in Figure 5. The humid grassland coverage of the watershed increased the concentrations of low-mobile elements such as Al, Ga, light REE, and also relatively labile Cs, Ba, Pb, U. Among other environmental variables, the proportion of sporadic permafrost strongly controlled the concentration of soluble highly mobile elements such as Cl, B, Na, Sr, Mo, and U, whereas the presence of carbonate rocks of the watershed provided elevated concentration of DIC, Mo, Ba and U (Figure 6). It is important to note that other potentially important landscape factors of the river watershed (riparian vegetation, tundra, water bodies, peatlands, recent burns, proportion of peatland and bogs, tundra coverage, total aboveground phyto-mass, OC stock in the upper 0–100 cm of soil, mean annual temperature and precipitation) did

not significantly correlate with major and trace element concentration in the Lena River tributaries (Table S4).

The relationships between river water chemistry and landscape parameters of the watersheds were further examined using multi-parametric statistics. The PCA demonstrated the presence of two factors capable of explaining only 32% of total variability in element concentration and landscape parameters of the watersheds (Figure S2). The first factor was positively linked to broadleaf forest and humid grassland coverage of the watershed and included Al, Fe, Ti, Cr, Ni, Ga, Y, Zr, Nb, Zr, REEs, Hf and Th. As for the second factor, the presence of light needle-leaf, mixed forest, percentage of sporadic permafrost coverage and carbonate rock on the watershed controlled the distribution of mobile elements such as Li, B, Si, Na, Mg, Ca, K, V, Sr, Ba, Mo, As, Sb and U.

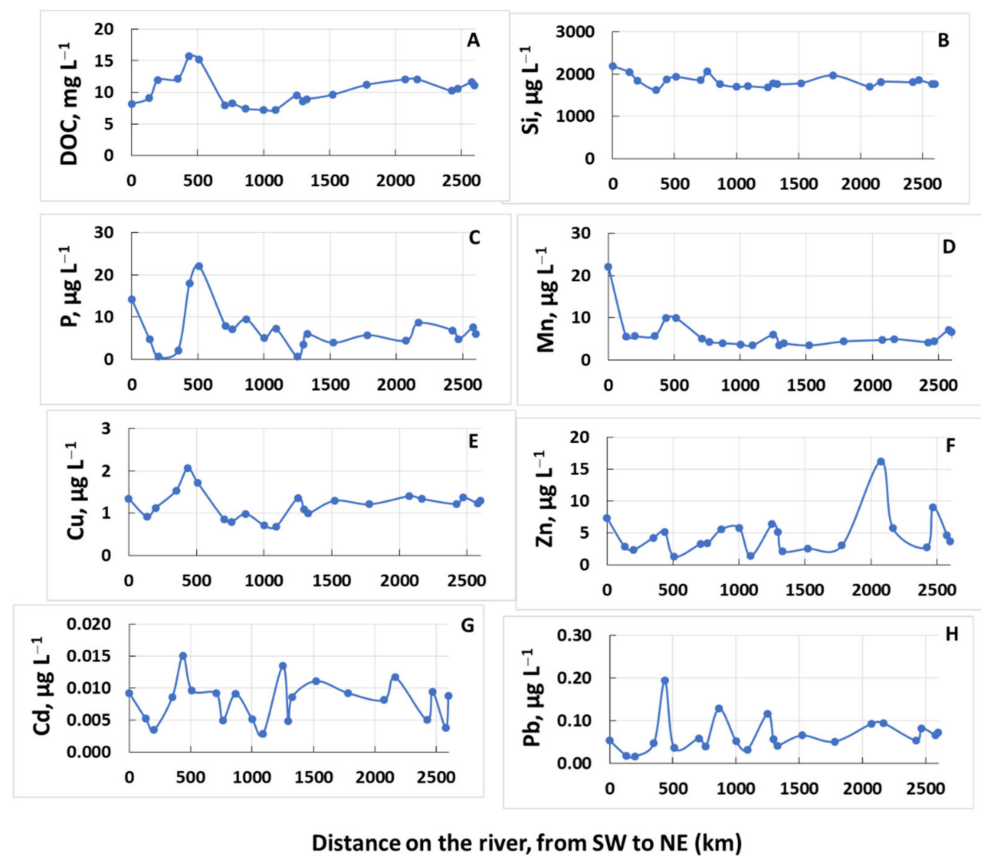


Figure 4. Examples of elements not exhibiting any concentration trend in the main stem of the Lena River from SW to NE: DOC (A), Si (B), P (C), Mn (D), Cu (E), Zn (F), Cd (G) and Pb (H). The distance is measured in km of river from Zhigalovo (0 km, upper reaches) to the Aldan River (2600 km).

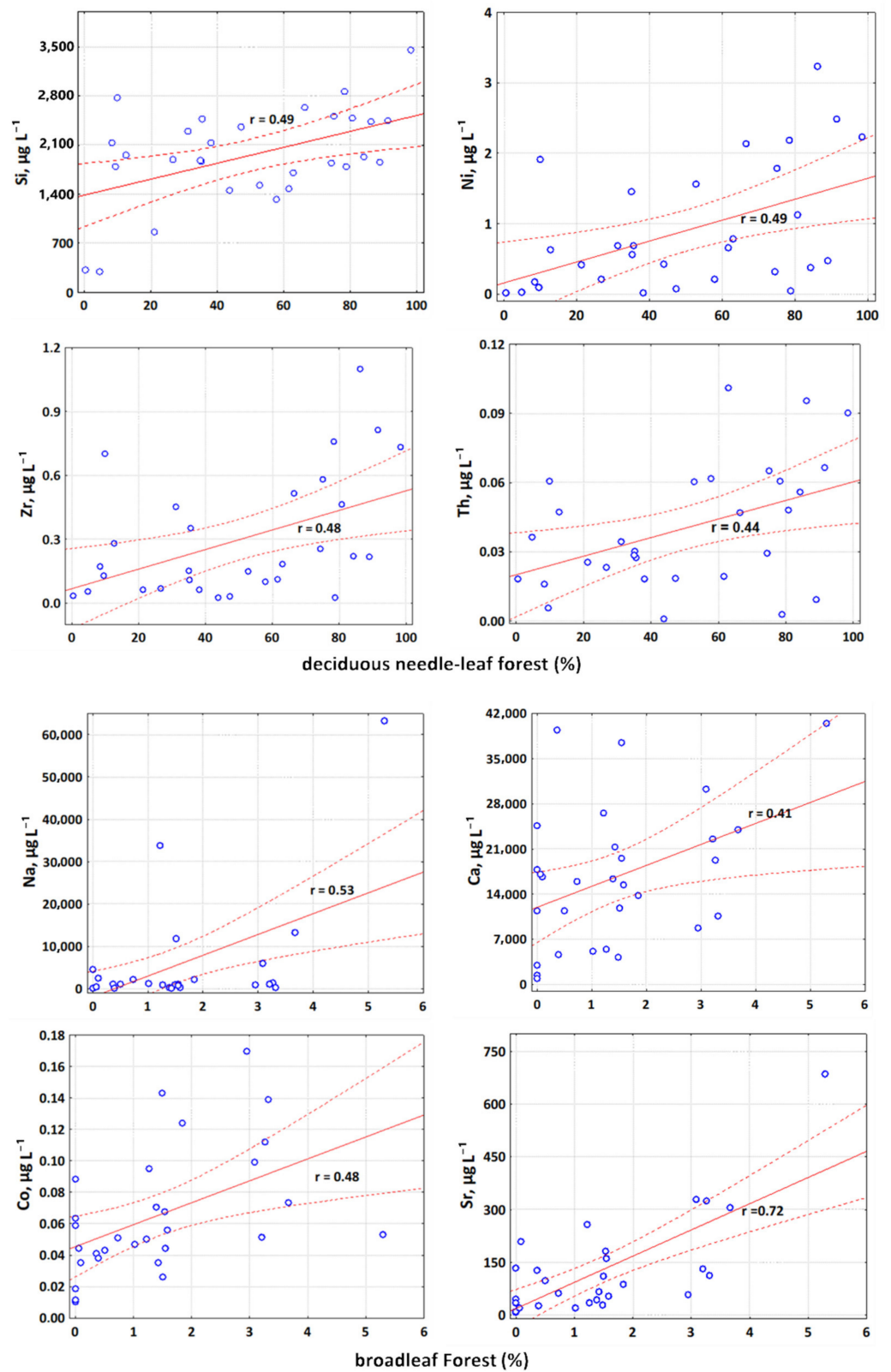


Figure 5. Significant ($p < 0.05$) positive control of landscape parameters—percentage of deciduous needle-leaf forest (Si, Ni, Zr, Th) and broadleaf forest (Na, Ca, Co, Sr) on element concentration in the Lena River tributaries.

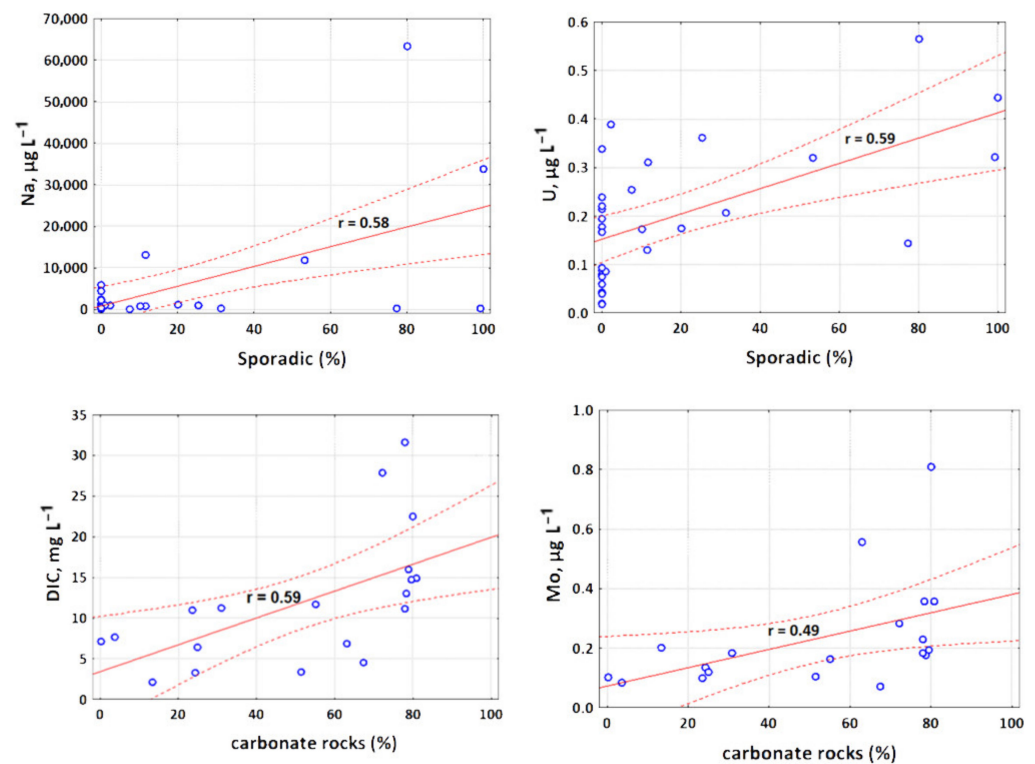


Figure 6. Significant ($p < 0.05$) positive control of permafrost distribution—percentage of sporadic permafrost coverage (Na and U) and lithology of rocks—percentage of carbonate rocks (DIC, Mo) on element concentration in the Lena River tributaries.

4. Discussion

4.1. Comparison with Other Data on Element Concentration in the Lena River and Its Tributaries

As for the Lena River main stem, there are several occasional measurements of the major river solutes in the middle course obtained during summer baseflow. During spring flood in June, we observed generally lower concentrations of Si (less than a factor of 2) compared to the July–August period [26], and also lower (less than $\times 2$) concentrations of Ca, Mg, Sr, SO_4 but comparable concentrations of Na and Cl to those reported in the Yakutsk-Kyusur region [28]. The Kyusur gauging state average Ba concentration $18 \mu\text{g L}^{-1}$, [56]) is comparable with our data for the Lena main stem in the Yakutsk region. However, in general, the regular monitoring of the Lena River hydrochemistry at its terminal gauging station of Kyusur by Russian Hydrological Survey [57,58], and more recently, via PARTNERS and ARCTIC GRO projects [34,37], cannot be directly compared with our most northern sampling point (Yakutsk and the vicinity of the Aldan River), because there are substantial changes in the Lena River flow and landscape context over its last 800 km, from Yakutsk to the Lena delta. The most recent and complete data set on the upper and middle course of the Lena River, southwest of Aldan, is provided by the work of the group of Porcelli and Andersson [30–32]. There was full consistency in Li, Na, K, Si, Al and Fe dissolved concentrations measured in this study in June and those reported by these authors in July–August (range of 0.5–2, 10 to 1000, 500 to 900, 1700 to 2300, 70 to 140, and 50 to $130 \mu\text{g L}^{-1}$, respectively). Overall, this comparison demonstrates rather stable concentrations over a large spatial and temporal range, with maximal variability of a factor of 2 to 3. Such a similarity of hydro-chemical composition of the main stream during quite contrasting seasons (spring flood and summer baseflow) is noteworthy, given the five-fold variation in the discharge. A likely cause of elevated Al, Fe and insoluble trace element concentration during high flow period is that these elements transport in the form of organic and organo-mineral colloids as is known for other permafrost regions [41]. The availability of DOM which stabilizes these Al, Fe-rich colloids and relevant trace elements

is the highest during the high flow period, because mobilization of soil OM to the river is most efficient during freshet [36]. As such, despite sizable dilution during the high flow period, the concentration of these elements remains comparable with that during the baseflow. It thus can be concluded that such a transport enhancement of insoluble elements compensates for their source limitation due to dilution. Given that the first principal component acting on insoluble elements was linked to broadleaf forest and humid grassland vegetation, an empirical conclusion is that this type of vegetation is most efficient for mobilization of Fe and Al from the topsoil and forest litter to the river at the scale of the Lena Basin.

For the Lena river tributaries, the most comprehensive data set on major ions, Si and Sr was acquired in July–August of 1991–1996 by Huh and Edmond's group [23–25]. The following rivers could be quantitatively compared with those sampled in this work: Buotama (No 18), Tuolba (No 16), Siniaya (No 17), Olekma (No 14), Chuya (No 7), Orlinga (No 1), Tayura (No 3), Nuya (No 11), Vitim (No 8), Bolshoi Patom (No 12), Bolshoi Nimnyr (LP 3), and Amga (LP 8). For most of these rivers, the concentrations of Ca, Mg, and DIC were a factor of 3 to 15 lower during spring flood compared to summer baseflow. The concentrations of Na, Cl and SO₄ were typically 3 to 10 times lower, especially in the upper reaches (SW part) of the Lena basin, where the underground waters can bear the signature of Cambrian and Ordovician salt deposits. These waters are mostly pronounced in summer baseflow and only partially during spring flood, for example, Ichera, exhibiting 10 times higher NaCl concentration compared to other rivers (see database [55]). The impact of salty springs on the river water chemistry in SW part of the Lena basin (the Northern Baikal region) is fairly well known [58,59]. Noteworthy rather similar (<30% difference) concentration of K in all rivers sampled during spring flood (this study) and summer baseflow [23–25], despite significant dilution. A likely cause could be K leaching from terrestrial vegetation and silicate river suspended matter; both sources are most pronounced during spring flood, as is known from other permafrost Siberian rivers [41,60,61]. Enhanced coastal abrasion and extensive surface flux of melted snow are both responsible for efficient mobilization of K to the river during this period.

Another interesting observation is much higher (a factor of 3 to 20) Si concentrations during spring flood compared to summer baseflow. This is observed for a number of small rivers in the upper reaches of the Lena basin (Nuya, Tayura, Bolshaya Tira, Siniya and Buotama) as follows from the comparison of the data collected by Huh and Edmond group [23–25] and the results of the present study. It may reflect an uptake of this essential nutrient by diatomous periphyton growing in clearwater rivers which drain crystalline rocks of the Siberian Platform. Such an uptake during summer baseflow is known for many Arctic settings [40,62,63]. Another possible cause could be the fact that the mobilization of Si from subsurface soil is lower in summer compared to spring when the water mainly passes through the topsoil. Note that such a difference in Si concentration between two seasons is not observed for the main stem, presumably due to lower transparency of the water column and lower availability of solid surfaces, required for siliceous plankton and periphyton development in the summer. A nutrient limitation of the big river relatively to headwater streams may also contribute to lower uptake of Si in the main stem during the baseflow [16,28,30]. Additional sources of dissolved Si in the main stem could be dissolution of river suspended matter, which is highest during the high flow, as is known from other permafrost settings [41].

4.2. Possible Carriers of Trace Elements in the Lena River Basin Based on Elementary Correlations and PCA

In boreal and permafrost-affected aquatic environments, the most important colloidal carriers of trace elements are dissolved organic matter (DOM) and Fe/Al hydroxides stabilized by DOM, as follows from ex-situ and in-situ fractionation results [53,60,64–68]. Based on correlations between element concentration in both the main stem and Lena's tributaries (Table S3), three main group of trace solutes were distinguished. First, these correlations revealed possible control of organic matter on transport of V, Ni, Cu, As and

heavy REE. Note that strong complexation of DOM with divalent transition metals, notably Cu and Ni and HREE, is fairly well known ([53,68]). The second major carrier of trace metals in boreal waters is high molecular weight Fe oxy-(hydr)oxide colloids stabilized by organic matter. By virtue of their dual organic and mineral nature, these colloids are responsible for transport of the largest number of elements such as P, Cr, Ni, Zn, Ge, Sb, Y, Zr, La, Hf. Finally, Al-rich colloids and sub-colloidal particles are likely to have controlled typically lithogenic trace elements (Ti, Cr, Ga, Nb, Cs, REE, Th) and could be produced during riverine DOM leaching of aluminosilicate river suspended matter (i.e., Ref. [61]). Intensive mobilization of lithogenic elements via desorption from aluminosilicate material of the river suspended matter into soluble ($<0.45 \mu\text{m}$) form is consistent with strong correlations of these elements with Al, in both main stem and the tributaries (Table S3).

The PCA generally confirmed the presence of the group of low-soluble elements (Al, trivalent and tetravalent trace elements, Nb), which were affected by the first factor, and the group of labile elements—alkalis, alkaline earth metals (Li, Na, Mg, K, Ca, Sr), anions or neutral molecules (B, Si, V, Mo, As, Sb) and uranyl ion—which were controlled by the second factor (Figure S2 of the Supplementary Materials). The first factor was presumably linked to organic and organo-ferric colloids which usually carry low-mobile elements originating from silicate minerals. The second factor reflected migration of elements in truly dissolved (ionic or molecular) forms, not linked to any chemical carrier and originating from water–carbonate rock interaction in deep underground reservoirs.

4.3. Landscape Factors Controlling Spatial Pattern of Elementary Composition of Riverwater in the Lena Basin (Main Stem and Tributaries)

A decrease in concentrations of soluble highly mobile elements such as alkali and alkaline-earth metals, Cl, SO_4 , B, Mo, As, Sb and U between the upper reaches of the Lena River (first 0–800 km of the transect) and the middle course of the main stem (second part, 800 km—Aldan) may reflect a decrease of connectivity between the river water and the deep underground waters. The latter are located within carbonate rocks and affected by salt deposits in the SW part of the Lena Basin compared to its NE part. We hypothesize that sporadic and isolated permafrost, frequently occurring in the SW part of the basin, facilitates the exchange between groundwater reservoirs and surface waters. In contrast, in the rest of the Lena Basin, essentially continuous permafrost prevents any impact of underground waters on river water chemistry, especially during the high flood period sampled in this work.

Another group of elements whose concentration systematically evolved over the river transect is the that of the lithogenic low-soluble elements (essentially trivalent and tetravalent hydrolyses). The concentration of these elements increased from the SW to the NE. On the one hand, this may reflect a change in dominant rocks: from carbonates and evaporites in the upper reaches of the Lena River basin to metamorphic and igneous silicates and Phanerozoic (silicate) sedimentary rocks in the middle course of the river. On the other hand, there is a general increase in soil OC stock from the SW to the NE part of the Lena River as follows from GIS assessment of the Lena basin parameters. We hypothesize that a coupled ‘source’ (abundance of silicate rocks) and ‘transport’ (organic colloids, stabilizing insoluble TE in solution) enhancement mechanisms are responsible for elevated concentrations of lithogenic insoluble elements in the NE part of the Lena River main stem relative to its SW part.

To sum up, in the Lena River basin, there are three major types of rock capable of affecting river water hydrochemistry: sedimentary carbonates (limestones and dolostones), Precambrian igneous and Phanerozoic sedimentary silicates, and salt deposits (evaporates) of early Phanerozoic age, distributed in the upper reaches of the Lena basin. The carbonate rocks play a visible role in the upper reaches of the Lena River and head waters. Enhanced connectivity between surface waters and deep groundwaters in the SW part of the basin, where the evaporate deposits are present, can provide highly mobile soluble elements (alkalis, alkaline-earth metals, oxyanions) to the river water. Silicate rocks which dominate the middle course of the Lena River act as an important source of lithogenic elements

(trivalent, tetravalent hydrolysates), whose export from the soil to the river is facilitated by abundant DOM from coniferous vegetation.

The impact of environmental factors on major and trace element spatial pattern was further tested based on GIS-based landscape parameters of the Lena River tributaries. The proportion of sporadic and isolated permafrost strongly controlled concentrations of soluble highly mobile elements (Cl, B, DIC, Na, K, Mg, Ca, Mo, Ba and U). At the same time, the proportion of carbonate rocks at the watershed (per se) impacted only a very limited number of elements (Mg and Mo). A lack of direct impact of the rock lithology is consistent with low connectivity of deep groundwaters to the rivers during the high flow spring flood period. Another reason could be the rather small size (relative to the Lena River main stem) of the studied rivers and streams, so that the link between the river hyporheic zone and the underground reservoirs, especially under permafrost conditions, is not pronounced.

Another important landscape parameter controlling surficial and shallow subsurface flux to the river, as is known from adjacent permafrost territories covered by larch forest [41,42,69], is ground vegetation. Specifically, an important factor of element concentration control in the Lena River tributaries was the coverage of river watershed by light (Cl, SO₄, Na, Li, B, V, Sr, U) and deciduous (Si, Ni, Ge, Zr, Hf, Th) needle-leaf forest (dominance of *Pinus sylvestris* and *Larix*, respectively). The first group of elements may reflect their intense recycling with pine, which grow on carbonate-rich rocks of the SW part of the basin. In contrast, Si (and presumably Ge) are known to be concentrated in larch [40,69] and can be massively leached from their needles during the spring. A part of the second group of elements (usually low mobile tetravalent hydrolysates) could be affected by the DOC-mediated transport in the NW part of the basin. The NW part is dominated by silicate rocks and continuous permafrost, compared to carbonate rock-dominated and groundwater-affected SW part of the Lena basin. Enhanced mobility of Zr, Hf and Th in forested soils developed on silicate rocks is known in various boreal settings [68,69].

The PCA generally confirmed the linear correlations between the landscape parameters and the solute concentrations, although the explanation capacity of the two potential factors was rather low, at 21% and 11% of overall variability. This could be linked to relatively weak landscape control on elementary composition in the river water during the spring high flow season. Furthermore, the response of the hydrochemistry of small rivers of the Lena basin to key environmental parameters of the watersheds such as permafrost coverage and underground rock lithology was less pronounced than that of the main stem. A likely reason for this is weaker connectivity of small rivers with deep underground and subsurface waters during the studied period of high-flow spring flood. In contrast, given that the main input to small and medium size rivers in permafrost regions occurs via surface and shallow subsurface flow in June, essentially through plant litter and topsoil [42], the vegetation of the watershed exhibited discernable control on elementary composition of river waters.

Summarizing the analysis of the spatial pattern of solutes in the Lena River basin, we conclude that the working hypothesis of this study, regarding the low impact of rock lithology on elementary composition of the river water during spring flood, is verified only in the case of the Lena tributaries. The hydrochemistry of the main stem of the Lena clearly reflected the control of carbonate rocks and the impact of groundwater via isolated/sporadic permafrost in the southwestern part, contrasting with a lack of groundwater connection and dominance of silicate rocks in the northeastern part. However, another important factor increasing mobility of low soluble trivalent and tetravalent trace metals from SW to NE is dissolved organic carbon which, in turn, depends on the soil organic pool and the presence of various forests. At the same time, we do not exclude that the resolution of our GIS mapping resolution and spatial sampling are not sufficiently fine, so they cannot catch fine-scale landscape patches that are known to drive solute generation in small Arctic rivers ([70]).

Within a climate warming and permafrost thaw scenario, the main source of elements during spring flood will remain the surface flow, given that, for the majority of the Lena River basin, the permafrost is continuous and unlikely to become isolated or sporadic. This strongly contrasts with the scenario of permafrost thaw in other Siberian regions such as the Western Siberia Lowland (WSL), where the permafrost is mostly discontinuous to sporadic, and, instead of silicate crystalline and carbonate sedimentary rocks as mineral substrates in Eastern Siberia, the rivers of the WSL drain through thick, partially frozen peat deposits (i.e., Ref. [54,71,72]). During spring flood, surface flow rather than underground input regulates the pattern of riverine solutes in the Lena River basin. As such, the change in dominant forest species and the forestation of tundra [73,74], which typically requires several decades [75], rather than an increase in active layer depth, will determine the overall pattern of river water chemistry during high water flow. At the same time, the response of the Lena River main stem to the thawing of permafrost (leading to enrichment of the river water in soluble, highly mobile elements) might be more significant than that of its tributaries and other small rivers of the basin. The main reason is that the hydrological connectivity between river water and shallow subsurface or deep underground water is sizably higher in a large river compared to small tributaries. In this regard, comparable studies of large, permafrost-affected rivers of Eastern Siberia during most contrasting seasons, including notably winter baseflow, when the connection of the groundwater with surface waters is at its maximum, should allow efficient prediction of future changes in riverine 'inorganic' hydrochemistry induced by changes in the permafrost regime.

5. Conclusions

While seasonal and annual export fluxes (yields) of carbon (C) and inorganic solutes are fairly well known for all large Arctic rivers, spatial variations in elementary concentration along the river length and among its tributaries remain poorly understood. Moreover, the landscape factors controlling riverine element concentration in permafrost-affected regions are still poorly constrained. This is especially true for the largest river of Eastern Siberia, the Lena River, which drains through continuous permafrost zones with highly variable lithology and vegetation. In this work we measured dissolved carbon, major and trace elements over a 2600-km transect of the Lena River main stem (upper and middle reaches) including its 30 tributaries and watershed rivers, at the peak of the spring flood. There were two main groups of solutes in the main stem depending on their spatial pattern: (i) elements that decreased their concentrations downstream, from SW to NE (Cl, SO₄, DIC, Li, B, Na, Mg, K, Ca, As, Sr, Mo, Sb, Ba and U), which reflected a decrease in the proportion of carbonate rocks in the watershed and the degree of groundwater feeding, and (ii) elements that increased their concentrations downstream (Al, Ti, Cr, Fe, Ga, Rb, Y, Zr, Nb, Cs, REEs, Hf and Th), which was tentatively linked to an increase in organic C stock in soils, larch forest coverage and enhanced mobilization of lithogenic elements from silicate minerals.

In contrast to the main stem, the chemical composition of the tributaries was only partially controlled by soils, rock lithology and permafrost. In particular, the type of permafrost distribution impacted mostly labile elements, whereas the role of carbonate rocks in the watersheds of the Lena River tributaries has not been explicitly pronounced. Furthermore, the watershed coverage by needle-leaf, broadleaf forest and humid grassland exhibited positive correlation with concentration of labile elements (Cl, SO₄, Li, B, Na, Si, Ca, V, Sr, U), but also some low-soluble traces (Al, Ga, REEs, Nb, Zr, Hf, Th). In accord with previous observations in permafrost-affected forested regions of Siberia, we believe that, during the high flow period of the spring flood, the main control on river water chemistry is exerted by surface flow. The latter often occurs over still frozen ground and thus primarily depends on the type of forest. As such, within the climate warming scenario, future changes in dominant ground vegetation and greening of tundra will mostly impact the river water chemistry, whereas the thawing of continuous permafrost and increase in the active layer depth might have a subordinate influence.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/w13152093/s1>, Figure S1: Landscape map of the Lena River and tributaries (RLC based); Figure S2: Results of PCA treatment of the Lena River tributaries chemical composition, including landscape parameters. Table S1: Physico–geographical parameters of the studied Lena River tributaries; Table S2: Mann–Whitney test of the difference in element concentration in the upper (0–800 km) and middle (800–2600 km) course of the Lena River main stem; Table S3: Pearson correlation coefficients ($p < 0.05$) of major and trace elements with three main potential carriers—DOC, Fe and Al in the main stem of the Lena River and its tributaries; Table S4: Pearson correlation matrix of landscape parameters and river water chemistry.

Author Contributions: S.N.V. and O.S.P. designed the study and wrote the paper; Y.K. performed sampling of 10 tributaries and mapping; S.N.V. and O.S.P. performed sampling, analysis and their interpretation; M.A.K. provided landscape estimation of the Lena River tributaries. Each co-author has seen and approved the final paper and contributed to writing the manuscript. All authors have read and agreed to the published version of the manuscript.

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