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Dissolved Major and Trace Elements in the Largest Eurasian Arctic Rivers: Ob, Yenisey, Lena, and Kolyma

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Abstract: In contrast to fairly good knowledge of dissolved carbon and major elements in great Arctic rivers, seasonally resolved concentrations of many trace elements remain poorly characterized, hindering assessment of the current status and possible future changes in the hydrochemistry of the Eurasian Arctic. To fill this gap, here we present results for a broad suite of trace elements in the largest rivers of the Russian Arctic (Ob, Yenisey, Lena, and Kolyma). For context, we also present results for major elements that are more routinely measured in these rivers. Water samples for this study were collected during an international campaign called PARTNERS from 2004 through 2006. A comparison of element concentrations obtained for Arctic rivers in this study with average concentrations in the world's rivers shows that most elements in the Arctic rivers are similar to or significantly lower than the world average. The mineral content of the three greatest rivers (Ob, Yenisey, and Lena) varies within a narrow range (from 107 mg/L for Yenisey to 123 mg/L for Ob). The Kolyma's mineral content is significantly lower (52.4 mg/L). Fluxes of all major and trace elements were calculated using average concentrations and average water discharge for the 2004–2006 period. Based on these flux estimates, specific export (i.e., t/km^2/y) for most of the elements was greatest for the Lena, followed by the Yenisey, Ob, and Kolyma in decreasing order. Element pairwise correlation analysis identified several distinct groups of elements depending on their sources and relative mobility in the river water. There was a negative correlation between Fe and DOC concentration in the Ob River, which could be linked to different sources of these components in this river. The annual yields of major and trace elements calculated for each river were generally consistent with values assessed for other mid-size and small rivers of the Eurasian subarctic.

Keywords: Arctic; rivers; major and trace elements; fluxes; sources; transport; organic matter

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1. Introduction

Rivers are the main source of fresh water and water-borne materials from continents to the world's oceans. Among all regions, river discharge exerts a particularly strong influence on the Arctic Ocean. The river water supply to the Arctic Ocean is near 4300 km^3/year [1].

The ratio of freshwater volume to the volume of this ocean is about nine times higher than the value for the World Ocean. Furthermore, the ratio of the annual river water supply to the volume of the Kara Sea is 1.46×10^{-2}, which is 60 times higher than the ratio for the Arctic Ocean and 560 (!) times higher than that for the World Ocean. These numbers clearly demonstrate the influence of river discharge on the Arctic Ocean and especially on the Kara Sea—which receives the discharges of the two largest Arctic rivers, Ob and Yenisey—in comparison with the World Ocean. Obviously, the transport of huge masses of dissolved and suspended materials including organic matter, nutrients, and trace elements impacts all processes in the Arctic seas and their environmental status.

Early estimates of dissolved and particulate element fluxes from rivers to the Arctic Ocean and surrounding seas, including the Russian Arctic, were published toward the end of the 1940s [2,3]. The results of these and more recent works of different authors have been considered in a number of reviews [4,5]. The concentrations and fluxes of trace elements in both forms were investigated from the beginning of the 1950s, within the framework of the USSR Hydrometeorological Survey [6,7] and research programs of the USSR Academy of Sciences [8–10]. However, adequate methods of sampling, treatment, and analysis of water and suspended particulate matter (SPM) were not available at that time. The use of metal-made water samplers, paper filters, and analytical spectral methods of low sensitivity did produce reliable data, especially for dissolved heavy metals (HM). In the words of J.M. Edmond, the Scotland marine geochemist: "The experience gained in sea-water analyses where the criterion of 'oceanographic consistency' can be applied shows that trace metal data reported before 1973 are almost entirely invalid. It is reasonable to expect that a similar situation holds for fresh waters" [11]. This situation was improved through efforts of the Working Group N46 RIOS (River Inputs to Ocean Systems) (1973–1981). Then, at the end of the 1980s, the French–Russian–Netherlands Program SPASIBA (Scientific Program on Arctic and Siberian Aquatorium) was initiated by former members of the WG46 RIOS (J.-M. Martin, D. Eisma, V. Gordeev). Within the framework of this program, two expeditions were carried out to the estuaries of the Ob and Yenisey Rivers and to the delta of the Lena River. Modern methods of sampling and analyses were applied in these expeditions and reliable data for a number of trace elements (Fe, Cu, Zn, Ni, Pb, Cd, Hg, As) in river and estuarine waters were obtained for the first time [12–18]. The results of these expeditions have demonstrated that the previous numbers for trace element concentrations in the waters of the Ob, Yenisey, and Lena Rivers were indeed overestimated.

At the end of the 1990s–beginning of the 2000s, under the aegis of the Siberian Branch of the Russian Academy of Sciences, a complex ecological research program in the Ob basin called "Ecology of the Poymas of Siberian rivers and Arctic" was conducted. The investigations were organized in the middle reach of the Ob River, its great tributary Irtysh, the Tom' River, and some other rivers as reported in a number of publications [19–22]. In the middle of the 1990s, complex geochemical investigations of water, suspended matter, and bottom sediments in the Yenisey, Khatanga, Lena, and Yana Rivers were carried out within the frameworks of several Russian–German projects such as "The Laptev Sea System", "Siberian river-Runoff (SIRRO)", and others [23–31]. Scientific groups from the USA have also paid significant attention to the rivers of the Russian Arctic [32–35]. During the last 15–20 years, a series of publications on geochemistry and biogeochemistry of the great rivers of the Russian Arctic have appeared. Detailed studies have been performed for the Severnaya Dvina River of the White Sea basin. Reliable data were obtained for discharge-weighted concentrations of more than 50 elements in water and suspended matter and their fluxes based on sampling during 3–5 years at least once a month ([36–39] and references in these papers). High-frequency data have also been published recently for rivers of the Barents Sea basin such as Pechora [40]. A sizable amount of new information has become available for the largest Arctic rivers, Ob and Yenisey, and the catchments of Pur and Taz Rivers as well [41–44]. These include detailed reviews of data on the dissolved forms of elements in waters of the Ob, Yenisey, their tributaries, and many small rivers of the White Sea basin [45]. Much less information on the chemical composition of the Lena River is available, and most publications deal with organic matter [46] with occasional data on trace elements [47]. In work [48], seasonal variations in the suspended organic carbon degradation in the Kolyma River water are discussed. The first publication of data on the composition of trace elements in the water of this river appeared only recently [49].

A new international project called PARTNERS (Pan-Arctic River Transport of Nutrients, Organic Matter, and Suspended Sediments) was initiated in 2002 to improve the seasonal coverage of water sampling efforts in the six largest Arctic rivers (Ob, Yenisey, Lena, Kolyma, Yukon, and Mackenzie). This project, which included scientists from the USA, Russia, and Canada, aimed to better constrain estimates of material export from the major Arctic rivers and establish a baseline for detecting future changes [50]. The results presented in this paper come from samples collected by the PARTNERS team from 2004 to 2006. In 2009, the sampling program was revised and extended as the Arctic Great Rivers Observatory (ArcticGRO; www.arcticgreatrivers.org, accessed on 16 January 2024), and this program has continued until the present. The main results of both projects have been extensively disseminated (i.e., Ref. [51]).

Earlier review papers with data on average concentrations of trace elements in global rivers [52,53] were later improved and broadened [54,55]. At present, the most up-to-date and comprehensive review of trace element concentrations in river water is that of Gaillardet et al. [56]. In 2014, the chapter was reproduced practically without any changes. The authors have noted that their review was based on the most reliable data of filtered river water because they have used the most reliable ICP MS method of determination. At the same time, they noted that results from rivers in the tropical zone are disproportionally represented in their review and, as a result, the concentrations of several elements (such as Sc, W, REE) might be overestimated. It is worth noting here that similar reviews for the suspended forms of elements in global rivers are provided in the works of Savenko, Gordeev, and Viers [57–59].

Based on the above-presented information, the aims of the present work are to (1) report data on dissolved concentrations and fluxes of a large number of major and trace elements in the four largest rivers of the Russian Arctic during 2004–2006, (2) compare these concentrations with average values of world rivers, (3) establish the relationships between different elements, and (4) characterize possible mechanisms of element mobilization from the watershed to the river.

2. Sampling and Analytical Methods

2.1. Description of the Rivers Investigated and the Methods of Sampling

The Ob, Yenisey, Lena, and Kolyma are among the largest rivers of the Arctic Ocean basin. The main physico-geographical parameters of these rivers are provided in Table 1. According to the volumes of water discharges, the rivers take the following places in the World classification [60]—5, 8, 13, and 29 with total discharge of 1830 km^3/year [50], or 42.6% of total freshwater discharge to the Arctic Ocean and 59.1% of the discharge from Northern Eurasia.

The Ob River basin takes up nearly 81% of the West Siberian Plane territory. Elevations in this territory are relatively low (150–170 m above sea level) with a slight slope to the north. Excessive precipitation and weak drainage of surface waters give rise to heavy bogging and abundant wetlands. The world's largest mire (the Great Vasyugan Mire) is located between the main tributary of the Ob River Irtysh and the Ob itself and occupies nearly 800 $\times$ 350 km with wetland coverage up to 70%. This mire system is known to exert strong influence on the geochemistry of waters of the Irtysh and Ob Rivers [22,41]. In 1961, the Novosibirsk Dam was constructed. This created a huge reservoir in the upper reaches of the Ob River. The West Siberian Plane is covered by quaternary marine and continental sedimentary deposits with thicknesses up to 50–100 m. Neogene rocks under sedimentary cover appear locally only in the river's valleys. In the north of the basin, there are Sayan–Altay mountains (up to 2200 m elevation) with prevailing granites, basalts, and diabases. On the Salair Ridge, the limestones, sandstones, granites, and other rocks are distributed. Significant part of the Ob basin lay in highly productive zone of boreal taiga that is replaced in the northern part by tundra. The average air temperature ranges from +3.6 °C in the southwestern part of basin to −60 °C–−70 °C in the northeastern part.

Table 1. River discharges, PARTNERS sampling locations, and watershed characteristics ([50] with additions).

River/Watershed	Ob	Yenisey	Lena	Kolyma
Discharge gauging station	Salekhard	Igarka	Kyusyur	Kolymskoe
Water chemistry stations	Salekhard	Dudinka	Zhigansk	Chersky
Watershed area (10^6 km^2) at gauging station	2.99	2.40	2.43	0.53
Watershed area total (10^6 km^2)	2.99	2.54	2.46	0.65
River length (km)	3650	3490	4294	2129
Discharge (km^3/year) at gauging station	427	636	581	111
Discharge total (km^3/year)	427	673	588	136
Average air temperature (°C)	−3.8 Salekhard	−3.2 Igarka	−9.0 Tiksi	−13.0 Nijnekolymsk
% continuous permafrost	1	31	77	99
% continuous + discontinuous permafrost	4	43	90	100

The Yenisey River basin divides the western and eastern parts of Siberia. The basin is highly asymmetric with its western part almost 6 times smaller than its eastern (right) part. The eastern part belongs to the mountain country—Central Siberian plateau, accounting for 82% of the total basin area. The late Proterozoic Sayan–Yenisey folded zone is divided into 4 parts. (1) The East Sayan in the south, which consists of folded gneisses and schists, intruded by granite massifs. (2) Northward follows the Angara–Kansk fold system, which is mainly built up of Archean gneisses, and (3) the Angara Tungus fold system composed of folded carbonates, terrigenous series, mafic rocks, and gneisses. (4) Sand and mudstones, as well as carbonate layers characterize the Northernmost Turukhansk fold system. The northern edge of the Mid-Siberian platform, presented by the Putorana mountains (1400–1700 m asl), comes abruptly to the North Siberian (Taimyr) lowland limited by the Byrranga mountains in the north. Magmatic rocks—basalts, dolerites, and diabases—dominate the Putorana Plateau, with some number of shales, limestone, sandstones, and other sedimentary rocks.

The Lena River takes first place among the four rivers in this study in terms of length (4400 km), and its water discharge is only a little less than that of the Yenisey. Its watershed area, on the other hand, is in third place after the Ob and Yenisey (Table 1). The river flows along the eastern part of the Middle Siberian plateau. Its valley has asymmetrical form—the left shore is gently sloping, whereas the right one is steeper, and mountain ridges (Cherskiy, Verkhoyanskiy, and Suntar-Khayatskiy) are disposed on the eastern part. About 90% of the territory is covered by permafrost. Talics (small areas without permafrost) occupy no more than 10–15% of the watershed area. Some parts of the basin are covered by pine and larch forests, but for the most part, tundra dominates. The main sources of water to the river are thawing snow and rain. Groundwater contributions are very low (1–2%) due to prevailing of permafrost. The lithology of the Siberian platform, which is drained by the Lean River, is highly diverse. There are magmatic and metamorphic ores of Archean and Proterozoic ages, late Proterozoic Cambrian and Ordovician dolomites and limestones, volcanic and terrigenous silicate sedimentary rocks of the Phanerozoic. The carbonate rocks dominate in the southwestern part of the basin where salt deposits are also distributed. The Lena River is notable for its extraordinary delta, with an area of 32,000 km^2 that extends from the sea edge to over 150 km [61]. Twelve reservoirs were constructed in the basin, the greatest among them is Vilyuiskoe (35.9 km^3).

The Kolyma River, the main river of the East Siberian Sea basin, drains a much smaller area and has substantially lower discharge in comparison with the other three rivers (Table 1). The source of the river is situated at 1500 m altitude, via the confluence of two streams—Ain-Yuriakh and Kulu—on the eastern extremity of the Cherskiy Ridge. After confluence, the width of the river reaches 150–200 m. The slope of the river is quite significant—0.7046 m/km. In the middle part of the basin, near Srednekolymsk town (641 km from mouth), the river comes to plain marsh-ridden tundra and only the right shore remains hilly (the spurs of the Kolymskoe Upland). The mouth area consists of the delta (3000 km^2 area and 110 km length). The climate is strongly continental and cold, with strong seasonality. The river water comes from ~47% snow, ~42% rain, and ~11% groundwater despite 100% permafrost coverage of the basin. In the middle part of the basin, there is the Kolymskoe "sea", a reservoir with a dam with 110 m in height, 148 km in length, 441 km^2, and 15.6 km^3 in volume, which started to fill up in 1980. The Kolyma River basin is famous for containing a large deposit of dispersed gold that has become actively exploited at the end of 19th century despite extremely cold (−70 °C) winter temperatures.

2.2. Sampling

Water samples were collected from the Ob at Salekhard, Yenisey at Dudinka, Lena at Zhigansk, and Kolyma at Cherskiy Kolyma (Figure 1). These sites were chosen as the closest practical options for sampling in relation to terminal gauging stations on the four rivers. Open water sampling was conducted using a D-96 depth-integrating sampler [62] equipped with a Teflon nozzle and Teflon sample collection bag, which enabled depth-integrated and flow-weighted samples. Samples were collected at five roughly equal increments across the river channel and combined in a 14 L Teflon churn, resulting in a Watersingle composite sample. Wintertime (under ice) samples were collected by drilling a hole at the river's mid-point and collecting a sample from below the ice surface. Details of the PARTNERS sampling protocol have been described elsewhere [50]. For the analyses described herein, unfiltered samples were transferred to 0.5 L bottles from the sampling churn and were immediately frozen. The frozen samples were transported in coolers to Moscow by aircraft and stored in a freezer (−18 °C) at the Institute of Oceanology Russian Academy of Sciences until analysis. In the present work, we processed 61 water samples from all 4 rivers (14 samples from the Ob, 15 from the Yenisey, and 16 each from Lena and Kolyma). Seven samples were collected in winter (December–April), 23 in spring (May–June), 22 in summer (July–September), and 9 in autumn (October–November).

2.3. Analytical Methods

At the beginning of 2007, the samples were defrosted for 4 days at room temperature and immediately filtered through Nuclepore filters (with diameter of 47 mm, and pore size of 0.45 μm) on a Sartorius filter system under vacuum. The first 30–40 mL of the filtrate was discarded. Fifty-milliliter aliquots of filtrate were poured into plastic bottles and acidified with high-purity HNO_3 to pH = 2. These filtrates were transported to Toulouse (France) for analytical procedure. Blanks Milli-Q water from the clean room were processed parallel to river water samples.

All major and trace elements in river water were determined with an Agilent 7500ce ICP-MS (Agilent Technologies, Santa Clara, CA, USA) with In and Re as internal standards and three external concentrations as in-house standards. Concentrations of elements in processed blanks were below analytical detection limits, which was defined as ×3 machine blank signal. Analytical uncertainties on major element concentrations are in the range of 2 to 5%, for trace elements with relatively high concentrations (≥0.1 μg/L) 10—15%, and for ultra-trace elements with very low concentrations (<0.1 μg/L), they range from 20 to 30%. The uncertainties on calculated fluxes are between 30 (major elements) and 50% (trace and ultra-trace elements). SLRS-5 (Riverine Water Reference Material for Trace Metals certified by the NRC of Canada) was used to check the accuracy and reproducibility of analyses.

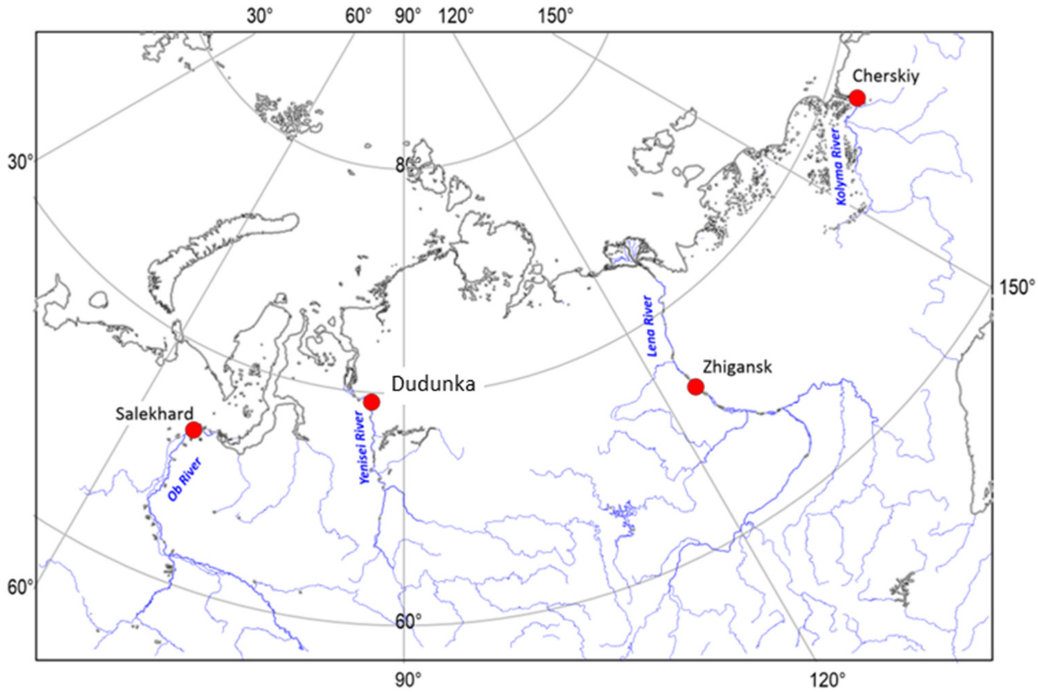

Figure 1. The schematic map of the watersheds of Ob, Yenisey, Lena, and Kolyma and the places of sampling.

A possible artifact could be introduced during freezing and thawing of river waters. However, in methodological works devoted to freezing and thawing (including multiple cycles) of organic and Fe-rich waters, we demonstrated high stability of filtrates under even several cycles of river, soil, and lake water freezing and thawing, for water samples collected in forest and bog settings of permafrost regions. Mean concentrations for Ca, K, Mg, Na, Ba, Rb, Sr, and U from long-term sampling of the Ob, Yenisey, Lena, and Kolyma (calculated from the data used in Tank et al. [51]) are higher than the values calculated herein. This may be partially attributed to methodological differences in sample collection and processing, but the higher long-term averages are also qualitatively consistent with documented trends in many of these constituents over time. Note that, during the 17-year (2003–2019) timespan analyzed in [51], the concentrations of Ca, K, Mg, Na, Ba, Rb, Sr, and U increased by an average of 7.5% per decade in the four rivers, with a range of 0–12% increases per decade among constituents.

The results of determinations of suspended sediment concentrations, pH, Alk, and DOC values, the correlation relationships of which with the elements determined could be of significant importance, were adopted from the archive data of the PARTNERS project that were obtained on the same water samples as those used in this study (http://ecoststems.mbl.edu.partners, assessed 16 January 2024).

3. Results and Discussion

3.1. Dissolved Major Elements

The numbers of samples, conditions of sampling, suspended particulate concentrations, and values of pH, Alk, and DOC for each sampling date are presented in Table 2.

Annual average concentrations of major cations, DOC, and Si are presented alongside specific export estimates in Table 3.

Table 2. Sampling locations, dates, and basic hydrochemical parameters.

River	Date	Sample	Water Temperature, °C	SPM, mg/L	pH	Alkalinity, mg/L	DOC, mg/L
Ob (Salekhard)	05.04.04	04-1	−1.0	60.1	7.0	130.6	5.50
	15.06.04	04-2	10.5	97.4	7.7	32.9	8.70
	17.06.04	04-3	12.4	61.5	7.7	34.4	8.70
	11.10.04	04-6	5.2	41.4	7.7	60.8	8.60
	14.10.04	04-7	3.3	24.5	7.6	66.6	8.40
	15.03.05	05-1	3.6	12.7	6.6	103.0	7.40
	04.06.05	05-2	10.0	59.35	7.0	36.5	9.80
	06.06.05	05-3	11.0	52.0	6.7	27.2	10.20
	28.06.05	05-4	16.0	38.0	7.2	36.0	10.20
	14.07.05	05-5	17.5	74.0	7.2	45.9	11.00
	05.09.05	05-6	16.0	14.5	7.8	64.5	10.10
	17.09.05	05-7	10.6	20.5	8.3	58.4	10.30
	07.06.06	06-1	9.6	33.8	7.7	34.8	9.90
	23.10.06	06-2	−2.0	4.9	8.0	65.8	10.67
Yenisei (Dudinka)	19.03.04	04-1	−0.1	9.2	7.3	67.7	2.80
	14.06.04	04-2	3.8	26.1	7.5	19.6	12.60
	16.06.04	04-3	5.4	21.5	7.5	19.4	12.40
	18.06.04	04-4	8.0	11.9	7.6	19.1	11.40
	25.08.04	04-5	10.1	20.0	7.9	58.6	4.90
	01.10.04	04-6	6.1	14.5	7.6	44.4	6.90
	02.10.04	04-7	5.5	14.5	7.8	42.36	7.10
	26.03.05	05-1	−1.0	1.7	7.5	58.5	3.50
	11.06.05	05-2	8.1	12.5	7.8	20.9	9.40
	16.06.05	05-3	10.9	6.8	7.7	22.8	9.70
	17.06.05	05-4	11.3	6.8	7.9	17.0	9.20
	16.08.05	05-5	13.1	1.4	8.3	61.3	9.50
	21.08.05	05-6	15.0	1.7	8.3	52.9	6.20
	21.09.05	05-7	10.1	1.0	-	55.9	5.30
	17.06.06	06-1	8.6	26.1	7.3	14.9	12.95
Lena (Zhigansk)	09.04.04	04-1	−0.1	17.7	7.3	71.1	6.70
	05.06.04	04-2	4.8	221.0	7.8	36.1	14.80
	07.06.04	04-3	8.9	156.0	7.4	34.5	12.40
	19.08.04	04-4	14.4	27.5	7.4	38.0	6.70
	24.08.04	04-5	14.9	21.0	7.8	36.8	6.50
	07.10.04	04-6	1.5	17.8	8.1	40.7	6.60
	10.10.04	04-7	1.1	16.5	8.1	31.1	7.40
	24.03.05	05-1	0.3	2.4	7.7	49.9	8.40
	27.05.05	05-2	2.8	77.3	7.6	38.9	14.80
	04.06.05	05-3	10.0	42.8	7.6	36.1	14.50
	06.08.05	05-4	14.7	49.5	7.7	35.2	8.80
	14.08.05	05-5	15.3	22.0	7.9	37.0	8.20
	09.10.05	05-6	0.1	27.0	8.0	43.1	7.30
	10.10.05	05-7	0.3	19.0	8.2	43.4	7.00
	06.06.06	06-1	7.3	133.3	7.7	36.9	13.65
	14.11.06	06-2	-	2.7	7.8	65.7	8.75

Table 2. *Cont.*

River	Date	Sample	Water Temperature, °C	SPM, mg/L	pH	Alkalinity, mg/L	DOC, mg/L
Kolyma (Cherskiy)	11.06.04	04-1	10.9	162.7	6.7	16.7	10.30
	15.06.04	04-2	11.8	82.5	7.4	18.4	9.06
	25.06.04	04-3	12.3	68.1	7.2	14.7	6.40
	15.07.04	04-4	7.1	38.6	7.1	15.9	5.93
	10.08.04	04-5	12.4	30.3	7.9	22.8	3.90
	25.08.04	04-6	12.6	37.4	7.5	23.0	4.35
	23.09.04	04-7	7.0	37.1	7.8	38.6	3.90
	22.04.05	05-1	0.1	-	6.0	25.8	3.15
	30.06.05	05-2	14.6	37.5	7.4	22.0	5.70
	19.07.05	05-3	13.2	12.0	7.7	27.1	3.70
	14.08.05	05-4	13.7	55.3	7.5	26.6	6.15
	27.08.05	05-5	12.8	55.3	7.7	42.1	8.05
	12.09.05	05-6	8.9	20.0	7.4	27.4	5.50
	29.09.05	05-7	4.1	10.0	7.5	27.8	6.55
	24.07.06	06-1	12.1	11.1	6.9	23.2	8.65
	20.11.06	06-2	0.0	0.4	7.0	28.0	7.20

Table 3. Average annual concentrations and specific export of major dissolved solutes in the Arctic rivers for period 2004–2006. Alkalinity is mg HCO_3^- L^{-1}. The pH is in dimensionless units.

Constituent	Ob, 360 km^3/Year		Yenisey, 618 km^3/Year		Lena, 600 km^3/Year		Kolyma, 109 km^3/Year	
	C, mg/L	Specific Export, t/km^2/Year	C, mg/L	Specific Export, t/km^2/Year	C, mg/L	Specific Export, t/km^2/Year	C, mg/L	Specific Export, t/km^2/Year
Ca	15.94	1.92	13.34	3.39	14.14	3.45	9.69	1.56
Mg	4.57	0.55	3.26	0.79	4.07	0.99	2.4	0.35
Na	7.86	0.94	5.58	1.35	11.54	2.81	1.69	0.77
K	1.21	0.14	0.61	0.15	0.51	0.124	0.48	0.077
Si	3.81	0.46	2.88	0.35	2.53	0.62	2.64	0.42
SPM	45.9		10.9		53.3		43.9	
pH	7.95		7.71		7.82		7.28	
DOC	9.25	1.11	8.3	2.02	8.7	2.12	6.2	1.01
Alkalinity	57	8.05	38.7	9.2	41.2	10.0	25.0	4.1
TDS_{cat} *	29.6	3.55	22.2	5.4	28.8	7.09	14.0	2.25
TDS_{cat} **	32.1	3.75	26.5	6.44	32.1	7.83	13.8	2.22
TDS_{Σ} ***	123	14.8	107	26.0	114	27.0	54.2	8.7

Notes: * TDS_{cat} = (Ca + Mg + Na + K)—this work; ** TDS_{cat} = (Ca + Mg + Na + K); *** TDS_{Σ} = Sum of cations and anions.

Date-specific concentrations of major cations and Si are included in Table S1(1–4) of Supplementary Materials. It can be seen from Table 3 that the sum of the main cations is in agreement with previous data based on the multiannual monitoring materials of the Hydrometeorological State Committee of the former USSR and Russian Federation. A comparison shows that, for the Kolyma and Ob Rivers, the difference between this study and previous data on average main cation concentrations is less than 10%, for the Lena River it is 11%, and only for the Yenisey River it reaches 19%. This testifies acceptable reliability of the archive data of the Hydrometeorological State Committee (HSC) on the major ions composition of the river waters in the Russian Arctic [63] as it was also demonstrated in numerous comparisons of major element composition of river waters across various rivers and seasons [38]. To calculate the fluxes of major cations, Si, DOC, and Alk, we used daily discharge data for each river, summed to annual values in accordance with the data of the HSC for 2004, 2005, and 2006 as follows. The Ob River, 353.6, 363.7, 363.9 km^3/year, the Yenisey River, 632.9, 535.4, 585.6 km^3/year, the Lena River, 551.0, 617.8, 630.0 km^3/year, and the Kolyma River, 119.9, 86.8, 122.0 km^3/year. For flux estimates, the average of 3 years of discharges was used, equal to 360, 618, 600, and 109 km^3/year accordingly. To calculate elemental yield, these mean discharge values were multiplied by the mean (averaged over 3 years) concentrations of each element and divided by the watershed area of each river. A comparison shows that the fluxes of major ions are especially high for Lena and Yenisey, a little lower for the Ob River, and significantly lower for the Kolyma River, which is notable among four rivers with the Alpine watershed basin and 100% distribution of permafrost.

3.2. Dissolved Trace Element Concentrations

Date-specific concentrations of trace elements in the four rivers are given in Table S1(1–4) in Supplementary Materials, and season-averaged concentrations are presented in Tables 4–7 and illustrated in Figure 2a–d, where the average values of each river measured in this study are compared with global world river averages [56].

Table 4. Average concentrations of dissolved trace elements and their annual fluxes for the period of 2004–2006 in the Ob River.

Element	**Concentration, μg/L (REE ng/L)**		**Global Average, μg/L (REE ng/L) [56]**	**[44] Near Salemal μg/L**		**[45] μg/L**	**Flux, kg/km^2/Year (±30–50%)**
	Average	**3σ**		**Average**	**3σ**		
B	20.5	3.8	10.2	-	-	12.4	2.46
Al	8.3	10.8	32	13.3		-	1.00
Sc	0.49	0.34	1.2	-	-	-	0.059
Ti	0.27	0.20	0.489	-	-	-	0.032
V	0.54	0.24	0.71	0.8	0.1	-	0.065
Cr	0.08	0.07	0.70	-	-	0.34	0.010
Mn	61.7	119.03	34	0.5	0.38	15.1	7.41
Fe	90.7	101	66	16	12.3	175	10.9
Co	0.16	0.20	0.148	-	-	-	0.019
Ni	1.28	0.15	0.801	1.3	0.14	1.94	0.15
Cu	1.67	0.43	1.42	1.8	0.21	2.25	0.20
Zn	1.46	0.64	0.6	-	-	0.58	0.175
Ga	0.0051	0.005	0.030	-	-	-	0.0006
Ge	0.0093	0.005	0.0068	-	-	-	0.0011
As	0.74	0.21	0.62	1.1	0.06	0.45	0.089
Rb	0.47	0.15	1.63	0.75	0.19	-	0.056
Sr	102	32	60	101.3	10.7	66.5	12.2
Y	0.074	0.03	0.04	-	-	-	0.0084
Zr	0.085	0.03	0.039	0.06	0.02	-	0.0096

Table 4. *Cont.*

Element	Concentration, µg/L (REE ng/L)		Global Average, µg/L (REE ng/L) [56]	[44] Near Salemal µg/L		[45] µg/L	Flux, kg/km²/Year (±30–50%)
	Average	3σ		Average	3σ		
Mo	0.35	0.07	0.42	0.394	0.02	-	0.042
Cd	0.0046	0.005	0.08	0.019	0.011	0.0030	0.0005
Sb	0.088	0.02	0.07	0.193	0.05	-	0.011
Ba	14.9	4.9	23	13.4	2.3	48	1.8
La	37.6	20.3	120	8.3	5.4	145	0.0045
Ce	76.9	40.4	262	13.3	6.6	-	0.0092
Pr	10.6	4.9	40	1.8	0.9	-	0.0013
Nd	52.0	20.2	152	6.7	4.6	-	0.0062
Sm	12.5	4.4	36	1.8	0.8	-	0.0915
Eu	5.2	1.6	9.8	-	-	-	0.0006
Gd	16.0	5.5	40	1.9	0.8	-	0.0019
Tb	2.0	0.7	5.5	1.1	0.4	-	0.00024
Dy	13.5	4.5	30	2.4	1.1	-	0.0016
Ho	2.5	0.9	7.1	0.9	0.3	-	0.0003
Er	8.5	2.6	20	2.3	1	-	0.0010
Yb	7.9	2.3	17	1.8	0.8	-	0.0009
Lu	1.2	0.3	2.4	-	-	-	0.00014
Hf	0.0012	0.001	0.0059	-	-	-	0.00012
W	0.010	0.004	0.1	0.059	0.15	-	0.0012
Tl	0.003	0.001	-	-	-	-	0.0003
Bi	0.002	0.001	-	-	-	-	0.0002
Th	0.043	0.074	0.041	0.0018	0.0003	-	0.0052
U	0.36	0.23	0.372	0.277	0.03	-	0.043

Table 5. Average concentrations of dissolved trace elements and their annual fluxes for the period of 2004–2006 in the Yenisey River.

Element	Concentration, µg/L (REE ng/L)		Global Average, µg/L (REE ng/L) [56]	[45] µg/L	Flux, kg/km²/Year (±30–50%)
	Average	3σ			
B	8.8	2.64	10.2	10.0	2.13
Al	19.5	18.4	32	15.4	4.7
Sc	0.43	0.17	1.2	-	0.10
Ti	0.52	0.33	0.489	0.39	0.126
V	0.91	0.23	0.71	-	0.22
Cr	0.14	0.09	0.70	0.24	0.034
Mn	4.7	3.4	34	7.6	1.13
Fe	44.7	29.4	66	76	10.9
Co	0.040	0.03	0.148	-	0.010

Table 5. *Cont.*

Element	Concentration, μg/L (REE ng/L)		Global Average, μg/L (REE ng/L) [56]	[45] μg/L	Flux, kg/km^2/Year (±30–50%)
	Average	3σ			
Ni	0.71	0.30	0.801	0.50	0.17
Cu	2.00	0.76	1.42	1.60	0.486
Zn	0.40	0.24	0.6	1.30	0.097
Ga	0.0045	0.002	0.030	-	0.001
Ge	0.0092	0.005	0.0068	-	0.0022
As	0.36	0.07	0.62	0.64	0.087
Rb	0.37	0.10	1.63	0.64	0.090
Sr	109	49	60	260	2.65
Y	0.15	0.12	0.04	0.051	0.036
Zr	0.17	0.10	0.039	-	0.041
Mo	0.33	0.21	0.42	-	0.08
Cd	0.005	0.004	0.08	0.0015	0.0012
Sb	0.03	0.004	0.07	-	0.007
Ba	7.25	2.8	23	8.80	1.76
La	81.9	56	120	200	0.02
Ce	132	96	262	-	0.0032
Pr	23.6	17	40	-	0.0057
Nd	116	81	152	-	0.028
Sm	27.9	20.6	36	-	0.0068
Eu	8.0	4	9.8	-	0.0019
Gd	35.5	23.4	40	-	0.0086
Tb	4.8	3.2	5.5	-	0.0012
Dy	33.2	19.6	30	-	0.0081
Ho	6.1	3.9	7.1	-	0.0015
Er	20.3	12.6	20	-	0.0049
Yb	19.1	12.2	17	-	0.0046
Lu	2.85	1.8	2.4	-	0.0007
Hf	0.0042	0.002	0.0059	-	0.010
W	0.008	0.003	0.1	-	0.020
Tl	0.004	0.001	-	-	0.010
Bi	0.003	0.002	-	-	0.07
Th	0.022	0.02	0.041	-	0.049
U	0.18	0.12	0.372	0.30	0.44

Table 6. Average concentrations of dissolved trace elements and their annual fluxes for the period of 2004–2006 in the Lena River.

Element	Concentration, µg/L (REE ng/L)		Global Average, µg/L (REE ng/L) [56]	[47] µg/L		Flux, kg/km^2/Year (±30–50%)
	Average	3σ		Average	3σ	
B	5.9	3.3	10.2	3.2	0.39	1.44
Al	35.5	20.6	32	117	5.8	8.67
Sc	0.31	0.13	1.2	-	-	0.077
Ti	0.7	0.4	0.489	10.2	0.62	0.17
V	0.44	0.11	0.71	0.69	0.06	0.11
Cr	0.10	0.06	0.70	0.45	0.05	0.024
Mn	5.5	2.23	34	4.79	0.23	1.32
Fe	67	42	66	85.7	3.8	16.4
Co	0.061	0.03	0.148	0.058	0.003	0.015
Ni	0.64	0.19	0.801	0.54	0.05	0.154
Cu	1.29	0.4	1.42	1.1	0.05	0.315
Zn	1.74	0.85	0.6	4.6	0.5	0.425
Ga	0.010	0.006	0.030	0.0164	0.0009	0.0024
Ge	0.013	0.005	0.0068	0.0076	0.0009	0.0032
As	0.33	0.1	0.62	0.17	0.005	0.08
Rb	0.49	0.12	1.63	0.66	0.019	0.12
Sr	125	54	60	66.8	3.6	30.5
Y	0.21	0.15	0.04	0.42	0.005	0.051
Zr	0.21	0.08	0.039	0.17	0.007	0.051
Mo	0.27	0.06	0.42	0.25	0.018	0.066
Cd	0.005	0.006	0.08	0.0099	0.001	0.0012
Sb	0.021	0.005	0.07	0.0155	0.007	0.005
Ba	13.55	5.1	23	10.29	0.49	3.3
La	265	233	120	1020	70	0.065
Ce	422	403	262	1020	40	0.10
Pr	66.7	56.4	40	170	3	0.016
Nd	289	241	152	629	10	0.071
Sm	56.5	46.1	36	119	2	0.014
Eu	12.8	7.9	9.8	19	0.4	0.003
Gd	67.9	54.0	40	105	1.2	0.016
Tb	7.11	5.39	5.5	14	0.16	0.0017
Dy	43.7	32.6	30	78.5	1	0.011
Ho	9.45	6.27	7.1	-	-	0.0023
Er	25.2	17.2	20	41.4	0.49	0.006
Yb	22.5	15.0	17	37.4	0.63	0.0055
Lu	3.30	2.15	2.4	5.37	0.1	0.0008
Hf	0.0060	0.003	0.0059	0.026	0.0009	0.0015
W	0.0065	0.0031	0.1	-	-	0.0016
Tl	0.0053	0.0017	-	-	-	0.0013
Bi	0.0034	0.0032	-	-	-	0.0008
Th	0.125	0.15	0.041	0.059	0.0043	0.03
U	0.31	0.07	0.372	0.256	0.004	0.076

Table 7. Average concentrations of dissolved trace elements and their annual fluxes for the period of 2004–2006 in the Kolyma River.

Element	Concentration, µg/L (REE ng/L)		Global Average, µg/L (REE ng/L) [56]	[49] µg/L	Flux, kg/km^2/Year (±30–50%)
	Average	3σ			
B	1.94	0.35	10.2	3.98	0.32
Al	51.5	50.3	32	33.8	8.3
Sc	0.40	0.19	1.2	0.027	0.07
Ti	0.67	0.62	0.489	0.45	0.11
V	0.33	0.18	0.71	0.19	0.05
Cr	0.085	0.082	0.70	0.061	0.014
Mn	4.50	2.66	34	3.61	0.73
Fe	31.0	31.6	66	71.9	5.0
Co	0.041	0.02	0.148	0.050	0.007
Ni	1.15	2.55	0.801	0.67	0.19
Cu	1.45	0.55	1.42	0.76	0.24
Zn	0.33	0.19	0.6	1.52	0.05
Ga	0.0156	0.013	0.030	0.016	0.0025
Ge	0.0105	0.007	0.0068	0.014	0.002
As	0.58	0.17	0.62	0.44	0.10
Rb	0.19	0.045	1.63	0.28	0.03
Sr	54.9	9.43	60	85.6	9.06
Y	0.096	0.08	0.04	0.065	0.015
Zr	0.13	0.08	0.039	0.027	0.021
Mo	0.13	0.022	0.42	0.142	0.021
Cd	0.0056	0.005	0.08	0.004	0.0009
Sb	0.065	0.024	0.07	0.070	0.011
Ba	7.23	1.18	23	11.4	1.2
La	48.9	51.6	120	0.046	0.008
Ce	95.5	94	262	0.078	0.016
Pr	16	15	40	0.013	0.0026
Nd	77	70	152	0.055	0.013
Sm	21	18	36	0.018	0.0035
Eu	6.2	4.2	9.8	0.0043	0.001
Gd	27	22	40	0.016	0.005
Tb	3.3	2.6	5.5	0.0023	0.0005
Dy	21	17	30	0.013	0.0035
Ho	3.8	3.2	7.1	0.0024	0.0005
Er	12	10	20	0.0066	0.002
Yb	10	9.3	17	0.0056	0.002
Lu	1.5	1.4	2.4	0.0009	0.0003
Hf	0.0065	0.013	0.0059	0.0012	0.001
W	0.0048	0.001	0.1	0.0019	0.0008
Tl	0.003	0.0008	-	0.0011	0.0005
Bi	0.006	0.005	-	-	0.0008
Th	0.025	0.025	0.041	0.0030	0.004
U	0.050	0.015	0.372	0.0028	0.008

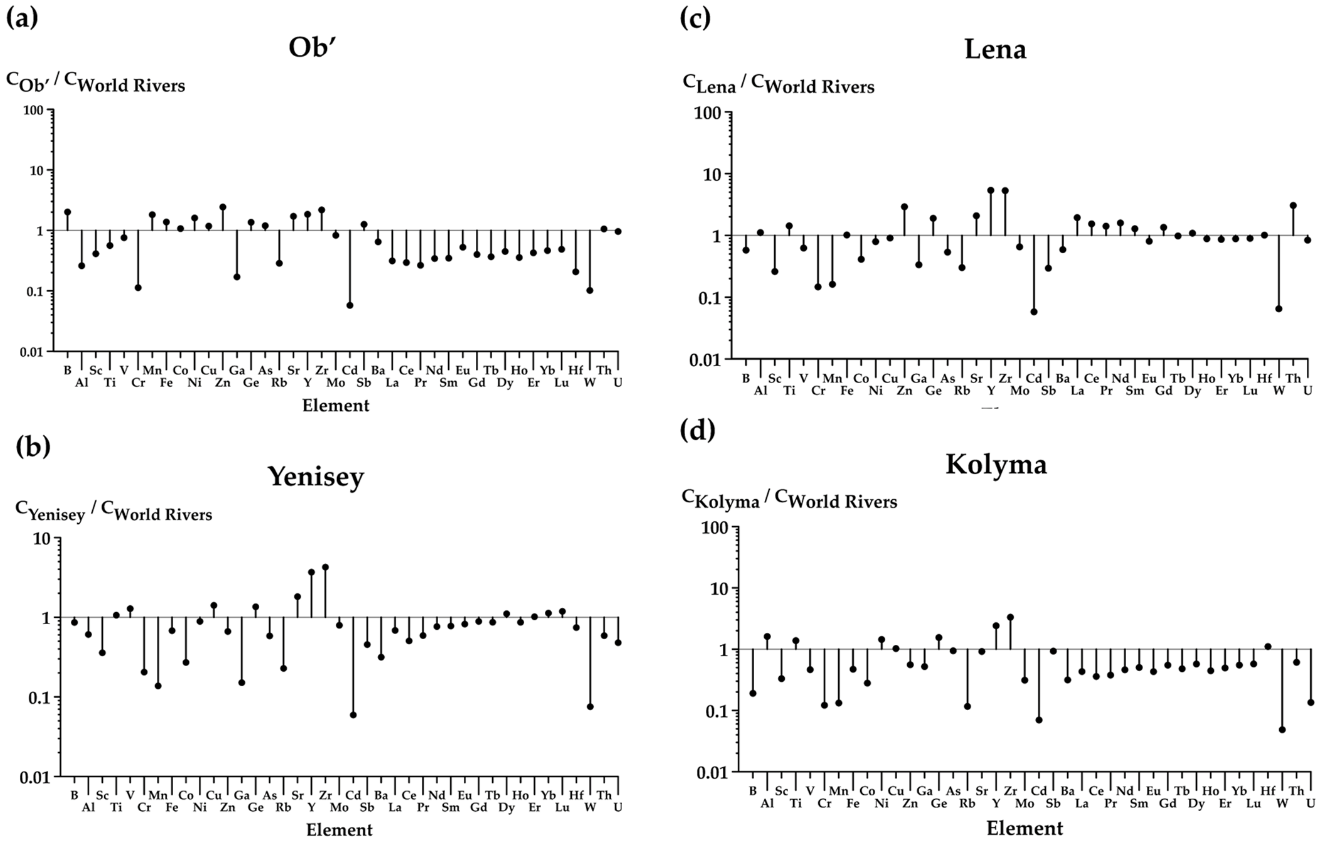

Figure 2. (**a**–**d**). Comparison of season-averaged trace element concentrations in waters of four Eurasian Arctic rivers ((**a**), Ob; (**b**), Yenisey; (**c**), Lena; and (**d**), Kolyma) assessed in this study with their average concentrations in the world rivers [56].

Ob River. A comparison of average concentrations in the Ob with the global average (Figure 2a) shows that none of the elements exceeds the world average more than two times. At the same time, several elements appeared to be significantly lower than the global value. These are Cr, Ga, Cd, and W. Their concentrations are 6 (Cr) to 20 (Cd) times lower than the global values. The concentration of Cd in the tributaries of the Ob, Pur, and Taz is equal to 0.003–0.0054 µg/L [56], which is quite similar to our results. A slightly higher average Cd concentration in the Ob River was reported in refs. [44] (0.019 µg/L). We believe that the average Cd concentration proposed in Ref. [56] is overestimated. These authors accepted high Cd concentration in the Amazon River waters (nearly 0.18 µg/L), and this, taking into account the huge discharge of this river, has resulted in a very high global average (0.08 µg/L). Note that other previous estimations were lower; for example, in Ref. [55], the value of 0.01 µg/L was reported. Our results for W seem to be very low due to the same reason—overestimated concentration of this element in the world rivers (0.1 µg/L). In Ref. [56], the estimation was based on a single datum from the Connecticut River with a range of W concentrations from 0.1 to 100 µg/L, which is obviously insufficient for such kinds of conclusions. We believe that it is not possible to consider as reliable the concentrations of Ga and Cd proposed for the world rivers in Ref. [56] due to very low levels of their concentrations in river waters and an insufficient number of measurements in different rivers. And only the Cr concentration measured in our work (av. 0.08 µg/L) looks too low compared to the global level (9 times lower) and the results of other authors (0.34 µg/L [45], 0.19 − 0.20 µg/L [46]. In this regard, we do not exclude some bias of Cr preservation prior to analyses in the present study—freezing and thawing, which could lead to the formation of some amount of Fe colloids/particles. These particles do not appreciably affect Fe concentration while impacting chromate ions, capable of coprecipitating with Fe hydroxide. Another reason could be a very low concentration of Cr in the Ob River during winter because this period has not been investigated in previous works.

Yenisey River. Average concentrations of trace elements in the Yenisey River waters are only slightly different from typical concentrations in the Ob River. For the major number of elements, their concentrations are practically at the level of the global river average within the natural range of variability. Only two metals—Y and Zr—exceed this level by a factor of 3 to 4. However, such differences are rather common and do not require specific explanations. Relative to what was observed for the Ob, a higher number of elements in the Yenisey demonstrated lower concentrations compared to the global average. This group included Rb, Cr, Mn, W, and Cd. Among them, the Rb concentration is 4.4 times lower while that of Cd is 17 times lower. The reasons for the possible underestimation of Cd, W, and Ga in Ref. [56] are practically the same as those proposed for the Ob River. Comparison of Cr, Mn, and Rb with the literature data [45] shows that the difference for these elements is less than a factor of two, which is comparable with natural seasonal and spatial variations in the river water and hence can be considered acceptable.

Lena River. In this river, the concentrations of a majority of elements are very similar to the global average. The same two metals—Y and Zr as in the Yenisey River exceed concentrations in the world rivers by a factor of 5.3–5.4. The same group of elements as in the Yenisey River—Cr, Mn, Cd, and W—appeared to be lower than the global concentrations. Our result for Mn (5.5 μg/L) is close to 13.2 μg/L reported in Ref. [47]. Chromium was determined only in Ref. [47]—0.45 μg/L—that is higher than our result—0.1 μg/L; with a global average of 0.7. Concentrations of Y and Zr in [47] (0.42 and 0.17 μg/L, respectively), are much closer to our values than to the global average (0.04 and 0.039, respectively). The situation with Cd and W is the same as in the Ob and Yenisey Rivers.

Kolyma River. In this river, the concentrations of all elements are at or below the global values. Noticeably lower is B concentration (5 times) and W (21 times). This group also includes Cr, Mn, Rb, Cd, and U. Almost all of them were also lower than the global average in three other Arctic rivers, and the reasons for these deviations from the global concentrations are probably the same.

3.3. Rare Earth Elements

For total concentrations of REE, the rivers follow the order: Lena River—1292 ng/L, Yenisey River—514 ng/L, Kolyma River—344 ng/L, and Ob River—247 ng/L. These values are generally comparable with the global river average (745 ng/L, Ref. [56]). However, the sum of REE in the Lena River water is 1.7 times higher than the global value, whereas, in waters of Yenisey, Kolyma, and Ob Rivers, it is 1.5, 2.2, and 3.0 times lower than the global. Generally, this order is similar to that of specific export of TDS, major ions, and DOC (Table 3). As such, taking into account the lithology of river watersheds, this similarity does not look unexpected, although the lowest REE concentrations in the Ob River require some explanations. The most probable reason is an absence of the crystalline granite and granitic gneiss rocks in the Ob River basin given that these rocks are the main source of REE in the river waters.

Shale-normalized REE concentrations (NASC) of all four rivers are shown in Figure 3. Fractionating between light (LREE) and heavy (HREE) REE is weak enough for all rivers. The negative Ce anomaly is typical for boreal waters due to high concentrations of dissolved and suspended particulate iron. According to previous observations [44], it is possible that DOC prevents Ce adsorption on the Fe colloids and its oxidation on the surface of colloidal oxy(hydro)oxides, especially during the period of spring flood, which provides more than 60–80% of REE annual export by the Arctic rivers. The weak maxima of Eu and Gd in the Arctic rivers were also observed previously [38,39,42,45].

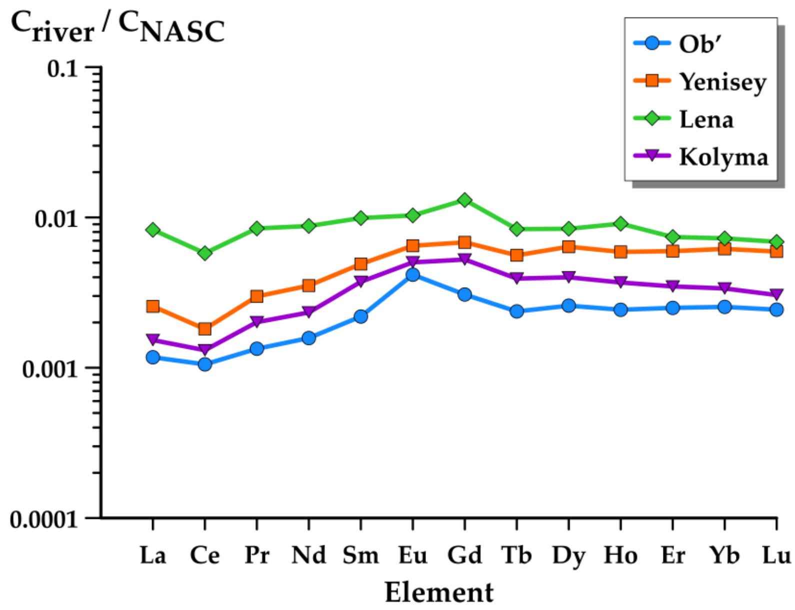

Figure 3. The shale-normalized REE patterns in the rivers of the Russian Arctic.

3.4. Relationship between Trace Element Composition and Total Dissolved Solids (TDS) of River Water

In recent work [49] on the chemical composition of trace elements in the water of the Kolyma River, the concentrations of almost all elements were reported to be quite close to our results, and at the same time, these concentrations were sizably lower than the typical the global river average (Table 7). The authors [49] noted that this could be due to the low intensity of trace element migration in the severe climate of the Arctic when the rates of chemical and biological weathering are reduced, and the relative role of sorption/desorption processes is increased. The main reason for the low mobility of trace elements in the Kolyma River compared to other Arctic rivers could be lower DOC concentration in the former, given that DOM is a main vector of trace element transfer in the river water. The authors of Ref. [49] demonstrated strong correlations between the mineralization of waters and concentrations of many trace elements. Figure 4 demonstrates such kinds of relations between the trace element concentrations in the world rivers and in the Arctic rivers in this study. The regression slopes are equal to 0.68, 0.73, 0.63, and 1.09 for Ob, Yenisey, Lena, and Kolyma, respectively.

The ratios between the average mineralization of global river waters (85.1 mg/L, [64]) and mineralization of our rivers (Table 3), are equal to 0.69, 0.73, 0.75, and 1.57 for Ob, Yenisey, Lena, and Kolyma, respectively. Considering analytical uncertainties and the natural range of variations in mean element concentrations in river waters, we can conclude that there is a definite link between the coefficients of regressions and the ratios of water mineralization. Furthermore, these ratios suggest that the chemical compositions of the three largest Arctic rivers (Ob, Yenisey, and Lena) are similar to each other while the waters of the Kolyma River are clearly different for the reasons mentioned earlier. Altogether, this corroborates the recent opinion [49] that water mineralization normalized trace element concentrations in all Eurasian Arctic river waters are similar within ca. 30%. This important result allows us to approximate, with reasonable uncertainty (±30%), the trace element composition of yet unknown rivers of the Russian Arctic, in which only major ions but not trace elements are available, using the data of already studied rivers.

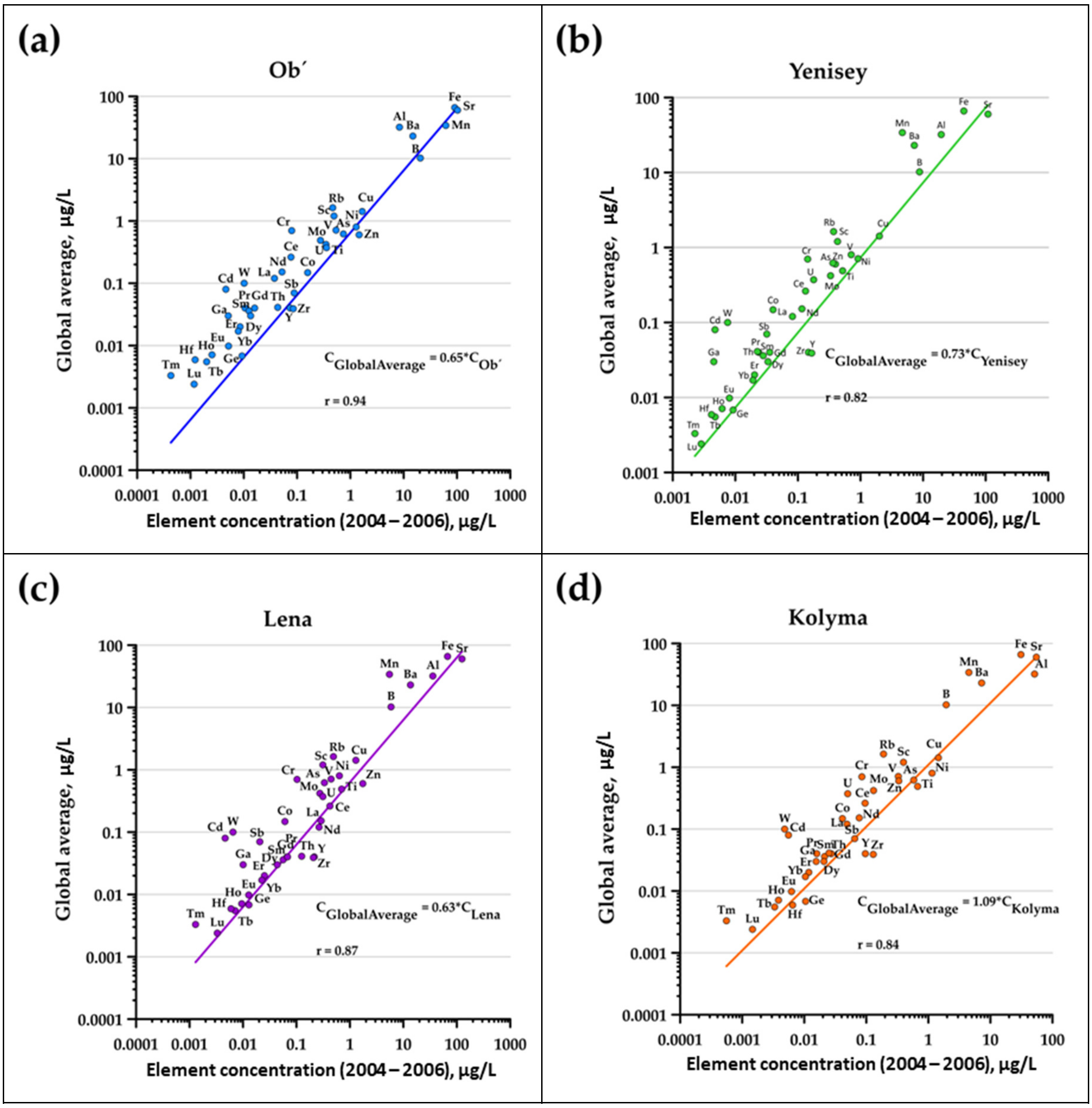

Figure 4. (**a**–**d**). Relationships between trace element concentrations in the rivers of the Russian Arctic and their global riverine average [56].

3.5. Annual Total Discharges of the Trace Elements

Estimates of trace element export by the rivers are presented in Tables 4–7. These data are related to the period 2004–2006 as in the case of major elements (Table 3). It is interesting to compare these data with more recent estimations for the period 2016–2021 available from the literature as detailed in Table 4. The recent studies on the changes in riverine water discharges with time [1,64,65] testify that in a majority of rivers of the Russian Arctic, especially in the basins with significant distribution of permafrost, increasing trends in water discharge are observed. Thus, the combined annual discharge of six Russian Arctic rivers (Severnaya Dvina, Pechora, Ob, Yenisey, Lena, and Kolyma), starting from the first year of observations in 1936 up to 1999 has increased with a rate of 2 ± 0.7 km^3/year. Using this conservative value for the period 2005 (average for 2004–2006) to 2019 (from 2016 to 2021), we calculate that during these 14 years, the rise of total discharge might be near 28 ± 10 km^3.

Contributions by the Severnaya Dvina and Pechora Rivers to this trend are rather small. Moreover, the Severnaya Dvina for the whole period of observations (1881–1999) demonstrated an insignificant stable decrease [39] while the discharge of Pechora increased from 1936 to 1979 to 2000 to 2015 from 107 to 111 km^3/year, i.e., 4 km^3/year only [1]. These changes are not important (<10%) at the scale of the total discharge of four large rivers (1687 km^3/year in 2005 against 1742 km^3/year in 2019, i.e., 55 km^3/year). Furthermore, the 3.1% increase in water discharge during the first decades of the 21st century is below the typical uncertainty of element flux estimations (≥30%) and hence can be neglected when analyzing possible trends in fluxes of riverine solutes.

A comparison of specific export fluxes of major elements and potential carriers of TE for each river (Table 4; Figure 5) demonstrates that the Lena River exhibits the highest fluxes of water mineralization, Alk, Ca, Mg, Na, DOC, Fe, and Al, and holds the second place for the fluxes of Si and Mn. The Yenisey River has the largest fluxes of K and Si and the second largest fluxes of Ca, Mg, Na, DOC, Alk, Fe, and water mineralization yields. The Ob River exhibits the highest Mn flux and occupies the second place for Fe and K fluxes. Finally, the Kolyma River exhibits the lowest fluxes of virtually all components, although it is worth noting that this river occupies the second place for Al flux, which is actually similar to that of Lena.

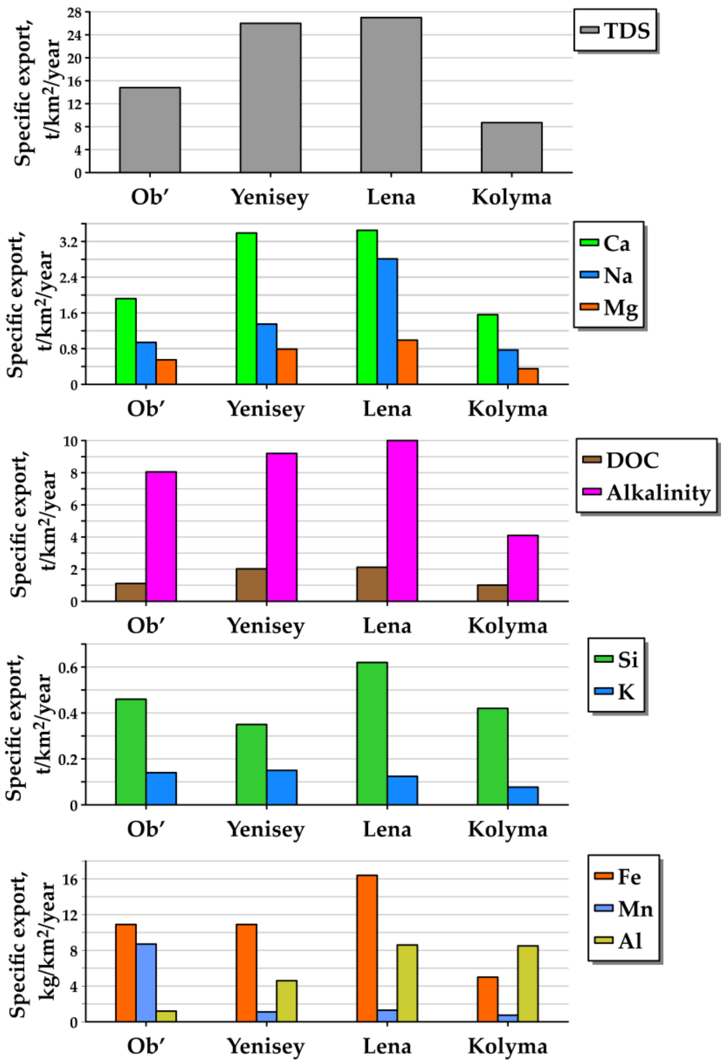

Figure 5. Specific export fluxes (yields) of TDS, Alk (HCO_3), DOC, major cations (t/km^2/year), and Fe, Al, Mn (kg/km^2/year) in the rivers of the Russian Arctic.

A comparison of element yields for the four Arctic rivers measured in this study with those available from recent high temporal resolution campaigns on the Severnaya Dvina, Pechora, and Taz [39,40,42] demonstrates general similarity, by the order of magnitude, for most major and minor solutes. The Ob River's fluxes are close to those of Taz, given a similarity in climatic, landscape, and lithological background, whereas Yenisey and Lena can be reasonably approximated by the fluxes measured in Severnaya Dvina and Pechora since the latter two have a combination of crystalline silicate and sedimentary (including carbonate) rocks on their watersheds. In addition to landscape, climate, and lithological conditions, the water runoff may be also a driving factor of element yields. Indeed, the coefficient Q/S (Q—water discharge, S—basin square) is practically the same for the Lena River and Yenisey River (2.43 and 2.44, respectively), which leads to very similar fluxes at similar element concentrations. The Q/S value of the Ob River is two times lower, and this can partially explain its lower export fluxes.

3.6. Correlation Dependencies between Major and Trace Elements and Mechanisms of Element Mobilization from the Watershed to the River

Correlations between major and trace element concentrations are helpful for distinguishing different groups of elements and identifying possible carriers of TE Table S2(1–4). It has been known for a long time that many trace elements are transported in the form of organic and organo-mineral colloids. The main components of colloids are DOC, Fe, Al, and probably Mn [38,41–43]. Calculations of pairwise correlation coefficients reveal significant relationships between these carriers and TE for each river.

In the Ob River, significant ($p < 0.05$) positive correlations were found between DOC and just a few other elements—Bi, W, Tl, and K. At the same time, the relationships were negative with Fe, Mn, Mg, Si, Cr, Co, Ga, Sr, Rb, Cd, Ba, and heavy REE. Note that two possible colloidal carriers, Fe and Mn, belonged to this second group with quite high coefficients (-0.63 and -0.70, respectively). It is thus possible that Fe, rather than DOC, is the main element carrier in this river since it had significant positive relationships with Al, Si, Ca, Ti, Sc, Cr, Co, Zn, Ga, Ge, Rb, and Cd while the negative links were only with DOC, K, Bi, and Sb. Aluminum had positive links with other lithogenic elements (Ti—0.95, Bi—0.95, Cr—0.90, Zn, Ga, Hf, Cd ≥ 0.75), likely reflecting their common origin from the dissolution of mineral silicate particles as invoked in previous studies of small rivers in Western Siberia [43]. Manganese was strongly correlated with Mg, Ca, Sr, Ba, Co, and U (all have coefficients more than 0.8), which could indicate the common origin of these elements from the groundwaters in this region [41].

In contrast to the Ob River, in the Yenisey River, a high correlation was observed between DOC and a large number of elements—REE, Th > 0.9, Zr, Y, Ni, Cu > 0.8, Hf, Al > 0.7, Fe—0.68, Mn—0.58, Cr, V, Co ≥ 0.55, Ti—0.46. Almost all these elements also correlated with Fe. These elements, with the addition of Ge and Zn, are also positively connected with Al giving us a possibility to consider that essentially colloidal fractions of DOC, Fe, and Al are the main carriers of these elements via shallow flow paths through organic-rich soils, which dominated under high flow conditions, as is known for permafrost regions. A strong negative correlation between DOC and elements of another group (in the order of decreasing of the coefficient correlation from -0.97 for Bi down to -0.4 for As)—Bi, Ba, Mo, Sr, U, B, W, Si, Se, and As) was observed. With the exception of W, Sc, and Sb the same elements correlate negatively with Fe. These labile elements likely originated from Fe and DOC-poor groundwater, hence reflecting deeper flow paths under baseflow conditions [66].

In the Lena River, an even higher number of elements exhibited positive correlations with DOC—K, Y, Zr, Cu, Ni, Co, Ge, Rb, As, Hf, Tl, REE, and Fe (+0.54). Most elements of this group were also positively associated with Fe—Cu, Ni, Co, Zn, Ti, V, Ge, Cr, As, Y, Zr, Hf, and REE, together with Al, Ga, Cd, and Bi. Similar to the Yenisey, such positive correlations likely reflect a crystalline rock source of low-mobile lithogenic elements, which are present in the river water in the form of organic and organo-ferric colloids, corresponding to their delivery from the watershed via surface and shallow subsurface water paths. The moderately positive correlation coefficients for the REE with C, Al, and Fe show that there is a sizable colloidal contribution to the "dissolved" load of the Lena River. Other trace elements (Ti, Cr, Ga, Ge, Y, Zr, Cd, and Bi) weakly correlate with Al and/or Fe and/or C, also reflecting organic colloidal material present. On the other hand, soluble and labile elements (Ca, Si, Na, Mg, B, Sr, Mo, Ba, and U) were also highly inter-correlated, suggesting their common underground water origin via taliks, especially in the southern part of the Lena basin [47] and dilution during high flow events.

In the most eastern Artic River (Kolyma), which has entirely continuous permafrost coverage and mountain relief in the main part of the basin, a noticeable number of elements are positively correlated with DOC, but the coefficient of these correlations was quite low. Only K, Y, and Zn exhibited $r \geq 0.6$, while V, REE, Bi −0.6–0.5, Mn, Fe, Cu, Zn, Ge, and Th had r between 0.5 and 0.4, and negative coefficient f was founded only for Si −0.64. In contrast, Fe strongly correlated with REE, K, Cr, Zn, (0.90–0.93), Al, Ti, Sc, V, Cu, Ga, Ge, Rb, Y, Zr, and Cd (0.89–080), and slightly lower with As, Bi, and Tl (0.78–0.76). Similarly good correlations with these elements were recorded for Al. Given that the average Al concentration in the Kolyma River is four times higher than that of Fe (on a molar scale), colloidal carriers of most trace elements could be of organo-aluminum rather than organo-ferric nature. Further, co-mobilization of Al and low-mobile trivalent and tetravalent hydrolysates from crystalline silicate rocks, highly abundant at the Kolyma River watershed, can be limited by their subsequent transport in the form of organic matter film that stabilized mineral micro and nanoparticles in the river water. In this regard, the Kolyma River, having a minimal connection between the river/tributaries hyporheic zone and underground Fe(II)-rich reservoirs and a relatively small number of bogs on its watershed, stands apart from other Arctic rivers as it could have the lowest impact of Fe-rich colloids. Unfortunately, any data on the colloidal forms of solutes in the waters of this river are still not available.

The role of the colloidal fraction in trace element transport has been extensively studied in the Severnaya Dvina River and the rivers of the Ob basin. The abundance of bogs and forest vegetation in the watershed of the Severnaya Dvina are the main reasons for strong water enrichment in DOC and dissolved Fe [38,39]. These authors demonstrated that high concentrations of DOC and Fe reflect their natural sources. Note that the high dissolved Fe concentration in this river is due to the colloidal form of transport, which is an important geochemical peculiarity. The major and trace elements in the waters of the Ob River and nearby Pur and Taz Rivers demonstrate similar behavior [41,42,44]. The geochemistry of the Ob River is in many aspects identical to that of the Severnaya Dvina River. Especially important for the Ob River is the Great Vasyugan Mire located between the main stream of the river and its greatest tributary Irtysh River. It was shown that low-mobile trivalent and tetravalent element hydrolysates (Al, Ti, Be, Ga, Y, REE, Hf, and Th), several trace elements (V, Cr, Nb, Cs) are leaching from soils with high organic matter content are transported into the sea mainly in the period of spring flood with DOC and Fe colloids. However, as was shown above, meaningful positive correlations with DOC in the Ob were detected only in a small group of elements (K, Bi, W, and Th). While for K, the reason for such correlation could be its mobilization from plant litter during the spring flood and high summer flow, the cause of such variations for trace elements remains elusive and could be biased due to analytical problems. It is therefore possible that in the Ob River, similar to that in the Taz [42], the behavior of these elements reflected a superposition of multiple source and transport factors. For example, Fe could exhibit two maxima—one in winter and another one during spring flood. This would diminish any positive relationship between Fe and DOC over the annual cycle. The winter maximum of Fe could be linked to the accumulation of Fe (II) from riparian sediments and within the river hyporheic zone under ice, at sites of local anoxia [66]. Such phenomena would be much less pronounced in other Arctic rivers that do not possess such a sizable floodplain. In contrast, the springtime maximum of Fe in the Ob River and other rivers is likely linked to its transport in the form of Fe(III)-OM colloids [41,43]. It is possible that the main reasons for the difference in DOC and other element behavior between the Ob and other rivers stem from (i) enhanced DOC export from wetlands and bogs to the Ob River tributaries and main stem, including during the winter period, given that this river drains through largest wetlands, developed in relatively "warm" (sporadic to discontinuous) permafrost zone, and (ii) a much more pronounced underground influx of Fe(II) and other elements in the Ob river, also due to essentially absent to discontinues permafrost on its watershed. It is fairly well known that the river size controls the degree of underground feeding via the discharge of underground anoxic Fe(II)-rich waters in the hyporheic zone (Shim et al., 2017 [67]), and generally, the permafrost prevents the hydrological connectivity between the groundwater and the river [68–74].

Note also that DOM in the Ob River exhibits a strong signal of wetlands and bogs (peat source [75], being more aromatic compared to other Arctic rivers [76]. We, therefore, suggest that the difference in DOM origin and transport capacity for trace elements may also be responsible for the different strengths of correlations between DOC and TE among different rivers. This is consistent with the fact that one of the most important factors controlling the association between DOM and dissolved trace metals is DOM molecular weight and aromaticity, which in turn can help to characterize the lability of DOM [77–88], and, presumably, DOM–TE complexes.

We found that the relative role of Al vs. Fe in TE transport in the rivers water systematically increases from the west to the east (Ob < Yenisey < Lena < Kolyma, as it is reflected in average Al:Fe concentration ratios, see Tables 4–7), following a decrease in the connection between the river and the groundwater reservoirs and bogs. The latter are capable of forming Fe-rich colloids with precipitated/adsorbed TE within oxygenated water bodies either in the riparian or hyporheic zone of the river. As the connection between these reservoirs loosens and Fe-rich sources decrease northeastward, Al colloids and particles, stabilized by OM, become more important for TE transport in the rivers.

Overall, the colloidal vector of DOC and trace metal transport in continental waters received sizable research efforts over the past decade [89–91]. Colloids, operationally defined as few nm (1 kDa)—0.45 µm, and truly dissolved or the low molecular weight (LMW < 1 nm) fraction of total dissolved (<0.45 µm) riverine load, are major forms of element migration from land to ocean [92–107]. The use of various size separation techniques in arctic and subarctic inland waters revealed the dominance of organic and organo-mineral (ferric and aluminous) colloids of low and high molecular weight (LMW and HMW), whose proportions vary strongly depending on the season and environmental context [98,100,104–106]. These colloids are subjected to various transformation processes, including bio-mineralization [108–111] and photodegradation [112–121]. Further, the coagulation of Fe hydroxide with DOM occurs at redox interfaces in peatlands [122] and at the surface of fens [123].

In addition to the clear control of trace element transport by carriers (DOM and colloid concentration and lability), another reason for stronger enrichment in lithogenic elements (including REE) of Yenisey, Lena, and Kolyma waters compared to Ob water is that the Ob does not include acidic crystalline magmatic and metamorphic rocks on its watershed. These rocks and products of their erosion, widely present on the Siberian Platform (Yenisey and Lena) and NE Siberian accretion zone (Lena and Kolyma), are strongly enriched in REE and other lithogenic elements and thus provide distinctly higher concentrations in river waters.

The global correlation matrix of all four river solutes (Table S2-5) demonstrates two main groups of elements, entirely consistent with the picture for individual rivers. The first group of elements (highlighted in yellow in Table S2-5), exhibit a maximum during winter reflecting the deep (underground) sources and labile elements DIC, B, Na, Mg, Si, K, Ca, Sc, Rb, Sr, Mo, Ba, and U, and possibly also SO_4 and Cl. Most likely, positive correlations of major cations and some trace elements (Sr, Mo, Ba, and U) with alkalinity reflect the weathering of carbonate rocks (limestones and dolomites) in the subsoil and groundwater reservoirs of the drainage basins.

The second group of inter-correlated elements (labeled in blue) originates from surface flow (shallow paths) and includes those carried by organo-Al colloids (with subordinary role of organo-ferric colloids): low mobile Ti, Cr, Ga, Y, Zr, and REEs, but also Ge, Cd, and

Bi. Finally, Fe, Mn, and Co constitute a separate group associated with labile elements (labeled in red). These elements have elevated concentrations in winter and are controlled by oxidation/reduction cycling and mobilization as has been reported for the permafrost-affected Taz River [42].

4. Conclusions

In this work, we assessed dissolved major and trace elements in the waters of four rivers of the Russian Arctic—Ob, Yenisey, Lena, and Kolyma. Water samples were collected within the framework of the international PARTNERS project during 2004–2006. In light of ongoing climate change and increasing anthropogenic pressure in the Arctic, the information on trace elements in Arctic rivers provides important insights into the level of water pollution by heavy metals and other elements. Comparison of average concentrations of all elements to those of the global river waters demonstrated a lack of any noticeable excess in the rivers of the Russian Arctic, hence indicating the absence of any significant anthropogenic pollution of these rivers by trace metals and metalloids.

Our comparison of area-normalized exports of major cations and DOC shows that the rivers follow a decreasing order—Lena, Yenisey, Ob, and Kolyma. According to the former multiannual observations by the State Hydrometeorological Committee combined with new data obtained in this study, the level of water mineralization is very similar in the three largest rivers—Ob—123 mg/L, Yenisey—107 mg/L, Lena—114 mg/L and significantly lower in Kolyma—54.2 mg/L.

Our results corroborated the recent finding [49] that water mineralization normalized trace element concentrations in all Eurasian Arctic river waters are similar within ca. 30%. This important result allows us to approximate, with reasonable uncertainty (±30%), the trace element composition of yet unknown rivers of the Russian Arctic using the data of already studied rivers.

Correlations between dissolved trace element concentrations and those of three main element carriers—DOC, Fe, and Al—demonstrated highly contrasting links in different rivers. A significant number of the elements that we analyzed were correlated with these major constituents of colloids in the Lena and Yenisey Rivers, while for the Kolyma River, a much lower number of trace elements exhibited significant correlations, and the coefficients of these correlations were lower. Al-rich organic matter-stabilized colloids are likely carriers of TE in the permafrost dominant rivers, whereas the Ob River exhibited negative coefficients of correlation between Fe and DOC, which could be due to different sources of element supply and different modes of element transport. Iron demonstrates in its annual cycle two maxima—in winter, at a low DOC level, and in spring, at a high DOC level in the river water. In winter, under ice, Fe^{2+} is accumulated in the areas of local anoxia, highly abundant within the flat watershed of the Ob River. A spring maximum is connected with the input of Fe^{3+} colloids that were observed earlier in the Ob River, and also in other Arctic rivers.

Compared to the Ob, the Lena, Yenisey, and especially Kolyma are strongly enriched in low-mobile element hydrolysates, including REE, which is likely to be associated with basin lithology. In the Obs basin, the acid crystalline magmatic and metamorphic rocks are absent while these rocks are abundant in the basins of the other three rivers.

Results of our study suggest a progressively increasing role of Al-rich colloid and sub-colloidal particles (stabilized by OM) in trace element transport, in the direction west–east, following the order "Ob' < Yenisey < Lena < Kolyma". This may stem from (1) a decreasing connection between deep groundwater and surface waters due to increasing permafrost coverage, (2) a decreasing bog influence on the river hydrochemistry, and (3) an increasing erosion of silicate crystalline rocks toward the northeastern direction. While the first and the second factors decrease the input of Fe-rich waters to the river main stem and tributaries, where organic ferric colloids are formed, the third factor provides abundant silicate material rich in low mobile lithogenic elements, those of disintegration and dispersion, followed by stabilization by OM, lead to enhanced export of Al-rich colloidal forms. However, further studies of colloidal transport of elements notably in the Lena and Kolyma River, are necessary to confirm these possibilities.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w16020316/s1, Table S1(1–4): Four tables contain the primary results of the determinations of major and trace dissolved elements in every river considered. Table S2(1–4): Four tables contain the reliable coefficients of correlation between all the elements in every river and Table S2-5 contains the coefficients of correlation between all the elements in four rivers all together with a total 61 water samples.

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