

Review

Trace Element Composition of the Dissolved Matter Runoff of the Russian Arctic Rivers

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Abstract: Data on the content of dissolved trace elements (P, Si, Li, Rb, Cs, Be, Sr, Ba, Mn, Fe, Co, Ni, Cu, Zn, Cd, Tl, Pb, Al, Ga, Y, Ti, Zr, Hf, Th, U, rare earth elements, F, B, Ge, V, As, Sb, Cr, Se, Mo, and W) in the river runoff from the Russian Arctic sea watersheds were systematized and generalized. There is a tendency for the decrease in the trace element concentrations in the direction from west to east for the considered Arctic watersheds (the White, Pechora, Kara, Laptev, and East Siberian seas). It was shown that the concentrations of dissolved trace elements in the river runoff from the Russian Arctic sea watersheds are in general consistent with modern estimates of the average composition of the global river runoff.

Keywords: trace elements; dissolved forms; river runoff; Russian Arctic



Citation: Savenko, A.V.; Savenko, V.S. Trace Element Composition of the Dissolved Matter Runoff of the Russian Arctic Rivers. *Water* **2024**, *16*, 565. <https://doi.org/10.3390/w16040565>

Academic Editor: Constantinos V. Chrysikopoulos

Received: 23 January 2024

Revised: 8 February 2024

Accepted: 12 February 2024

Published: 14 February 2024



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1. Introduction

The chemical composition of dissolved matter from river runoff, which is one of the main inputs that affects the ocean's geochemical balance, with the exception of cyclic salts, is formed as a result of the weathering of rocks in land catchment areas. Currently, an extensive database on the basic salt composition of the waters of the world's largest rivers was established, and fairly reliable estimates of the ion fluxes in the ocean were obtained [1–4]. Similar reports on dissolved trace elements [5,6] were compiled from a much smaller volume of factual material and should be considered as purely preliminary estimates.

It can be assumed that the petrographic differences in the lithogenic basis of watersheds decrease as their areas increase, due to which the specific chemical composition of river runoff from higher-order watersheds is formed to a greater extent under the influence of climatic factors. In this regard, it is important to expand the database based on the concentrations of dissolved trace elements in the river waters of various climatic zones.

For a long time, the authors systematically studied the abundance of dissolved trace elements in the waters of the outlet sections (mouth reaches) of large, medium, and small rivers of the Russian Arctic using modern, highly sensitive analytical methods. The objective of this work is to systematize and generalize the results of these studies [7–10] (including the unpublished data from A.V. Savenko) in conjunction with data from other literature sources [11–28] and to estimate the mean concentrations of dissolved trace elements in the river runoff from the White, Pechora, Kara, Laptev, and East Siberian sea watersheds.

2. Materials and Methods

Information about the location of the considered rivers, the long-term average water runoff in the outlet sections, observation periods, the phases of the hydrological regime during sampling, and the number of analyzed water samples are presented in Figure 1 and Table 1. The total number of river water samples was 217, 109, 535, 112, and 98 for the White, Pechora, Kara, Laptev, and East Siberian sea watersheds, respectively. At the same time, at least 5 water samples were collected in each river outlet section during

periodic hydrological and hydrochemical surveys, which covered different phases of the hydrological regime for the majority of rivers. The mean concentrations of dissolved trace elements in the outlets of large and medium rivers or a group of small rivers were calculated using all available information on these water bodies: research data from the authors and literature sources. The averaged composition of the runoff from the Arctic sea watersheds was obtained while taking into account the ratio of the volumes of the long-term average water runoff of the studied rivers. This ensured that the mean concentrations estimates are reasonably representative.

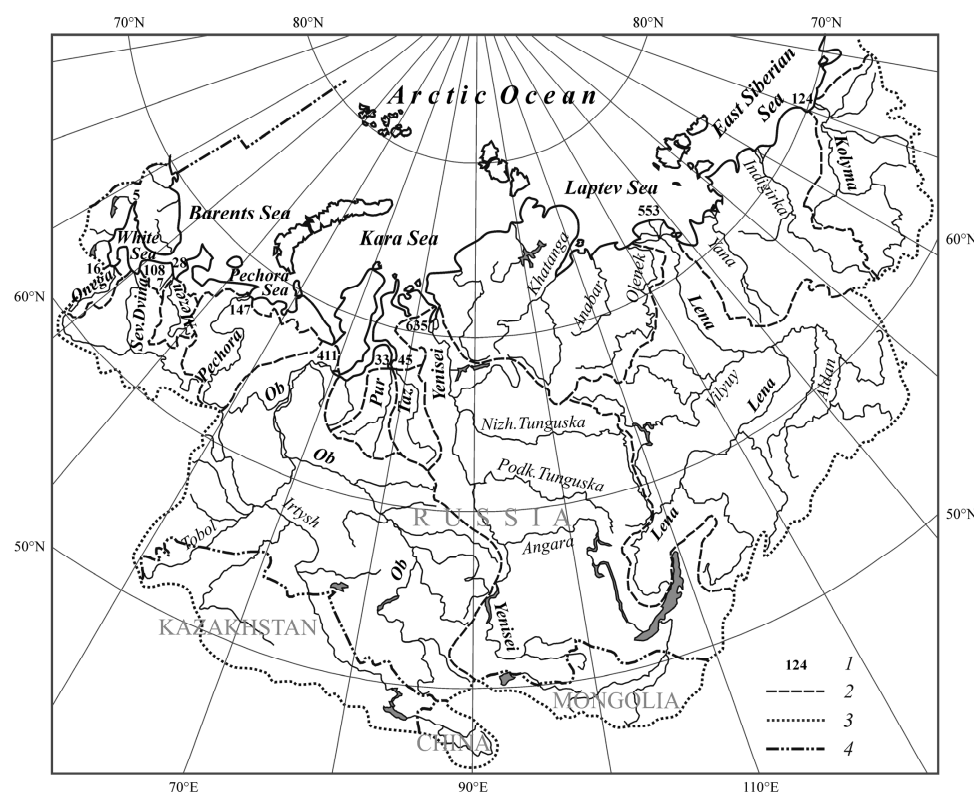


Figure 1. Map of the Russian Arctic sea watersheds: (1) volumes of the long-term average water runoff in the outlet sections of the considered Arctic rivers in km³/y according to [29,30] (with additions); (2) boundaries of the considered Arctic river basins; (3) boundary of the Russian part of the Arctic Ocean watershed; (4) state borders.

The authors carried out natural observations and an analysis of water samples as follows. Water samples were taken with a plastic bathometer and immediately after boarding, were filtered through an acetate–cellulose membrane filter with a pore diameter of 0.45 µm into 3 containers, hermetically sealed and placed in sealed plastic bags:

1. Plastic flasks measuring 100 mL with the addition of 1 mL of chloroform to determine the content of mineral phosphorus and silicon by standard colorimetric methods with ammonium molybdate;
2. Similar flasks measuring 30 mL without a preservative for measuring the fluoride content by direct potentiometry with a fluoride ion-selective electrode in the presence of acetate saline buffer;
3. Polypropylene tubes measuring 10 mL with 0.25 mL of 5 N nitric acid of ultrapure grade previously added under laboratory conditions to determine the concentrations of all other trace elements using inductively coupled plasma mass spectrometry (ICP-MS) on an Agilent 7500 ce instrument.

The relative measurement error was $\pm 3\%$. The accuracy of the analyses was assessed using the international river water standards SLRS-4 and SLRS-5, for which the discrepancy between the measured and certified concentrations of the studied elements did not exceed 20%.

Most of the literature data over the past 20–25 years were obtained using a similar sample preparation procedure and analytical measurements. In the 1990s, the most common method for the determination of heavy metals and other trace cations was atomic absorption with atomization in a graphite cuvette, the results of which showed close agreement with those of ICP-MS.

Table 1. Characteristic of water sampling in the mouth reaches of rivers of the Russian Arctic sea watersheds.

River (Number of Water Samples)	Observation Period	Phase of the Hydrological Regime	Reference
White Sea watershed			
Small rivers and streams of the Kandalaksha Bay ¹ (17)	July–September 2008, July–August 2010 February 2010 and 2020 June 2016	Summer–autumn low-water period Winter low-water period Spring–summer flood	Data from A.V. Savenko
Onega (16)	July 1998	Summer–autumn low-water period	[11]
	June 2011	Spring–summer flood	Data from A.V. Savenko
	January 2017	Winter low-water period	
	August 2017	Summer–autumn low-water period	
Kyanda (5)	August 2016	Summer–autumn low-water period	Data from A.V. Savenko
	February 2017	Winter low-water period	
Severnaya Dvina (149)	June 1998	Summer–autumn low-water period	[11]
	2007–2008	All phases	[12]
	2012–2014	All phases	[13]
	July 2016, August 2017	Summer–autumn low-water period	Data from A.V. Savenko
Kuloi (12)	August 2018, July 2022	Summer–autumn low-water period	Data from A.V. Savenko
	February 2019	Winter low-water period	
Mezen (13)	July 1998	Summer–autumn low-water period	[11]
	July 2009, August 2015	Summer–autumn low-water period	Data from A.V. Savenko
Semzha (5)	August 2018	Summer–autumn low-water period	Data from A.V. Savenko
Pechora Sea watershed			
Pechora (109)	2016–2019	All phases	[14]
Kara Sea watershed			
Ob (176)	1993–2001	Summer–autumn low-water period, Winter low-water period	[15]
	August 1998	Summer–autumn low-water period	[11]
	September 2007	Summer–autumn low-water period	[16]
	2004–2006	All phases	[17]
	2009–2021	All phases	[18]
	2018–2020	All phases	[8]
	July 2016	Spring–summer flood	[19]
	August 2020	Summer–autumn low-water period	[20]

Table 1. *Cont.*

River (Number of Water Samples)	Observation Period	Phase of the Hydrological Regime	Reference
Pur (5)	June 2013 and 2014	Spring–summer flood	[21]
	August 2013 and 2014	Summer–autumn low-water period	[21]
	February 2014	Winter low-water period	[21]
Taz (243)	June 2013 and 2014	Spring–summer flood	[21]
	August 2013 and 2014	Summer–autumn low-water period	[21]
	February 2014	Winter low-water period	[21]
	2015–2020	All phases	[22]
Yenisei (120)	1993–2001	Summer–autumn low-water period, Winter low-water period	[15]
	August 1998	Summer–autumn low-water period	[11]
	August 2009, September 2010	Summer–autumn low-water period	[7]
	March 2016	Winter low-water period	[7]
	2004–2006	All phases	[17]
	2009–2021	All phases	[18]
Laptev Sea watershed			
Lena (112)	September 1989	Summer–autumn low-water period	[23]
	September 1991	Summer–autumn low-water period	[24]
	October 1995	Winter low-water period	[25]
	June 1996	Spring–summer flood	[26]
	July 1995 and 2021	Spring–summer flood	[10]
	2004–2006	All phases	[17]
	2009–2021	All phases	[18]
	June 2016	Spring–summer flood	[27]
East Siberian Sea watershed			
Kolyma (98)	2004–2006	All phases	[17]
	2009–2021	All phases	[18]
	July 2020	Spring–summer flood	[9]
	July–August 2019, August 2021	Summer–autumn low-water period	[9]

¹ Luvenga River, Kolvitsa River, Porya River, Kostarikha Stream, stream in Dolgaya Bay of Porya Inlet, Umba River, Chernaya River, Kuzreka River, Indera River, Chavanga River, and Strelna River.

3. Results and Discussion

The results of the calculations of the mean concentrations of dissolved trace elements in the river waters of the Russian Arctic watersheds in comparison with estimates of the average composition of the global river runoff are given in Tables 2 and 3. Due to the rather strong spatial–temporal variability of dissolved trace element concentrations in the river waters and a relatively small number of measurements for most of them, discrepancies in the average values of 2–3 times are usually not taken into account, and only differences of more than half an order of magnitude (>5 times) are considered significant.

Table 2. The mean concentrations of dissolved trace elements in the waters of mouth reaches of rivers of the White and Pechora sea watersheds, µg/L.

Element	White Sea Watershed								Pechora Sea Watershed (C _{PS})	Mean for the Rivers of the White and Pechora Seas Watersheds (C _{WPS}) ⁴	Rivers World-wide ⁵ (C _{GR})	$\frac{C_{WS}}{C_{GR}}$	$\frac{C_{PS}}{C_{GR}}$	$\frac{C_{WPS}}{C_{GR}}$
	Kandalaksha Bay	Onega Bay		Dvina Bay		Mezen Bay		Mean for the Rivers of the White Sea Watershed (C _{WS}) ⁴						
	Small Rivers and Streams ¹ : 2008, 2010, 2016, 2020	Onega River: 1998 ² , 2011, 2017	Kyanda River: 2016, 2017	Severnaya Dvina River: 1998 ² , 2007–2008 ³ , 2012–2014 ³ , 2016, 2017	Kuloi River: 2018, 2019, 2022	Mezen River: 1998 ² , 2009, 2015	Semzha River: 2018							
									Pechora River: 2016–2019 [14]					
Nutrients														
P _{min} ⁶	5.0	5.6	16.0	21.6	6.6	26.3	9.1	19.7	14.0	17.0	38	0.52	0.37	0.45
Si ⁶	2400	1950	1420	2660	2730	3340	3320	2700	3400	3030	4070	0.66	0.84	0.74
Rare alkaline and alkaline earth elements														
Li	1.64	3.37	3.85	2.83	2.35	2.76	3.73	2.82	1.90	2.38	1.84	1.53	1.03	1.29
Rb	0.97	0.94	0.98	0.79	0.99	1.34	1.60	0.91	0.59	0.76	1.63	0.56	0.36	0.47
Cs	0.0082	0.0023	0.0037	0.0027	0.0057	0.0060	0.010	0.0035	0.0011	0.0024	0.011	0.32	0.10	0.22
Be	0.0080	–	–	–	0.0038	–	–	0.0057	0.0075	0.0074	0.0089	0.64	0.84	0.83
Sr	39.0	187	92.4	308	131	165	198	255	85.0	175	60	4.25	1.42	2.92
Ba	6.58	17.6	5.05	28.7	28.8	10.9	6.15	23.8	8.60	16.6	23	1.03	0.37	0.72
Heavy metals														
Mn	7.81	16.9	45.0	32.3	31.8	9.52	14.1	26.1	29.0	27.5	34	0.77	0.85	0.81
Fe	222	388	595	273	63.0	157	195	255	300	276	66	3.86	4.55	4.18
Co	0.035	0.077	0.095	0.078	0.074	0.065	0.080	0.074	0.057	0.066	0.148	0.50	0.39	0.45
Ni	0.66	0.78	0.62	1.28	0.57	0.82	1.12	1.10	0.94	1.03	0.80	1.38	1.18	1.29
Cu	1.28	0.62	0.85	1.71	1.40	1.29	1.50	1.50	1.40	1.45	1.48	1.01	0.95	0.98
Zn	9.10	1.27	1.98	4.61	1.17	3.54	5.15	4.11	11.5	7.59	0.60	6.85	19.2	12.7
Cd	0.015	0.0043	0.012	0.012	0.015	0.021	0.021	0.013	0.015	0.014	0.080	0.16	0.19	0.18
Tl	0.0025	–	0.0032	0.0040	0.0037	–	0.0040	0.0039	0.0015	0.0026	0.007	0.56	0.21	0.37
Pb	0.119	0.052	0.145	0.128	0.089	0.092	0.158	0.113	0.150	0.130	0.079	1.43	1.90	1.65
Hydrolysate elements														
Al	80.4	55.0	125	58.0	26.2	–	86.3	57.2	22.0	39.0	32	1.79	0.69	1.22
Ga	0.015	0.016	0.031	0.019	0.039	–	0.038	0.020	0.011	0.015	0.030	0.67	0.37	0.50
Y	0.112	0.190	0.227	0.200	0.142	0.133	0.202	0.182	0.150	0.167	0.040	4.55	3.75	4.18
Ti	1.39	1.22	1.70	1.26	0.64	–	1.00	1.23	0.44	0.82	0.49	2.51	0.90	1.67
Zr	0.105	0.191	0.197	0.215	0.132	–	0.210	0.204	0.075	0.137	0.039	5.23	1.92	3.51
Hf	0.019	0.0072	0.010	0.0075	0.012	–	0.014	0.0082	0.0034	0.0057	0.0059	1.39	0.58	0.97
Th	0.013	0.023	0.034	0.018	0.036	–	0.028	0.019	0.0084	0.014	0.041	0.46	0.20	0.34
U	0.088	0.205	0.094	0.208	0.270	0.146	0.155	0.195	0.084	0.143	0.372	0.52	0.23	0.38

Table 2. Cont.

Element	White Sea Watershed								Mean for the Rivers of the White Sea Watershed (C _{WS}) ⁴	Pechora Sea Watershed (C _{PS}) Pechora River: 2016–2019 [14]	Mean for the Rivers of the White and Pechora Seas Watersheds (C _{WPS}) ⁴	Rivers World-wide ⁵ (C _{GR})	C _{WS} C _{GR}	C _{PS} C _{GR}	C _{WPS} C _{GR}
	Kandalaksha Bay	Onega Bay		Dvina Bay		Mezen Bay									
	Small Rivers and Streams ¹ : 2008, 2010, 2016, 2020	Onega River: 1998 ² , 2011, 2017	Kyanda River: 2016, 2017	Severnaya Dvina River: 1998 ² , 2007–2008 ³ , 2012–2014 ³ , 2016, 2017	Kuloi River: 2018, 2019, 2022	Mezen River: 1998 ² , 2009, 2015	Semzha River: 2018								
Rare earth elements															
La	0.163	0.178	0.225	0.165	0.151	0.133	0.220	0.160	0.110	0.137	0.120	1.33	0.92	1.14	
Ce	0.254	0.330	0.452	0.300	0.259	0.234	0.458	0.289	0.170	0.233	0.262	1.10	0.65	0.89	
Pr	0.046	0.056	0.067	0.047	0.042	0.038	0.051	0.046	0.031	0.039	0.040	1.15	0.78	0.98	
Nd	0.160	0.241	0.280	0.235	0.162	0.165	0.272	0.218	0.130	0.177	0.152	1.43	0.86	1.16	
Sm	0.036	0.049	0.058	0.044	0.037	0.033	0.048	0.042	0.028	0.035	0.036	1.17	0.78	0.97	
Eu	0.0041	0.012	0.017	0.014	0.0084	0.0082	0.012	0.012	0.0076	0.010	0.0098	1.22	0.78	1.02	
Gd	0.020	0.048	0.057	0.048	0.039	0.034	0.056	0.044	0.031	0.038	0.040	1.10	0.78	0.95	
Tb	0.0025	0.0062	0.0079	0.0074	0.0055	0.0054	0.0077	0.0067	0.0046	0.0057	0.0055	1.22	0.84	1.04	
Dy	0.015	0.037	0.040	0.040	0.032	0.028	0.040	0.037	0.025	0.031	0.030	1.23	0.83	1.03	
Ho	0.0032	0.0069	0.0076	0.0070	0.0059	0.0052	0.0075	0.0065	0.0050	0.0058	0.0071	0.92	0.70	0.82	
Er	0.0079	0.019	0.025	0.019	0.017	0.014	0.025	0.018	0.014	0.016	0.020	0.90	0.70	0.80	
Tm	0.0017	0.0025	0.0032	0.0025	0.0024	0.0022	0.0030	0.0024	0.0019	0.0022	0.0033	0.73	0.58	0.67	
Yb	0.0075	0.017	0.021	0.017	0.016	0.013	0.021	0.016	0.012	0.014	0.017	0.94	0.71	0.82	
Lu	0.0015	0.0021	0.0027	0.0025	0.0020	0.0018	0.0029	0.0023	0.0018	0.0021	0.0024	0.96	0.75	0.88	
Anionogenic elements															
F	95.9	158	–	90.6	219	131	–	109	–	109	100	1.09	–	1.09	
B	26.1	19.7	12.0	18.2	32.2	24.1	80.0	20.3	19.0	19.7	10.2	1.99	1.86	1.93	
Ge	0.013	0.0098	0.0090	0.010	0.011	–	0.011	0.010	0.018	0.014	0.0068	1.47	2.65	2.06	
V	0.43	0.59	0.72	0.64	0.43	–	1.42	0.62	0.22	0.41	0.71	0.87	0.31	0.58	
As	0.19	0.50	0.65	0.73	0.53	1.47	1.16	0.81	0.57	0.70	0.62	1.31	0.92	1.13	
Sb	0.033	0.044	0.051	0.045	0.042	0.058	0.072	0.047	0.028	0.038	0.07	0.67	0.40	0.54	
Cr	0.35	0.69	0.65	0.34	0.15	–	0.37	0.37	0.17	0.27	0.70	0.53	0.24	0.39	
Se	0.049	–	–	–	0.062	–	–	0.056	0.045	0.046	0.07	0.80	0.64	0.66	
Mo	0.27	0.17	0.25	0.36	0.28	0.35	0.30	0.33	0.17	0.26	0.42	0.79	0.40	0.62	
W	0.018	–	0.0064	0.010	0.0078	–	0.012	0.010	0.0012	0.0053	0.10	0.10	0.01	0.05	

¹ Luvenga River, Kolvitsa River, Porya River, Kostarikha Stream, stream in Dolgaya Bay of Porya Inlet, Umba River, Chernaya River, Kuzreka River, Indera River, Chavanga River, and Strelna River. ² Data [11] on Cu, Zn, Cd, and Pb. ³ Weighted mean concentrations considering the river water runoff for hydrological year of 2007–2008 [12] and 2012–2014 [13]. ⁴ Taking into account the ratio of the volumes of the long-term average water runoff of rivers according to [29,30] (with additions). ⁵ P_{min} [31], Si [4], F [5], and other trace elements [6]. ⁶ The obtained data are of the same order with the estimates of the long-term average concentrations of P_{min} and Si, equal to 3.9 and 3450 µg/L for the Onega River, 11.1 and 2095 µg/L for the Severnaya Dvina River, and 7.2 and 2840 µg/L for the Mezen River, respectively, according to [32], and equal to 6.7 and 1990 µg/L for the Onega River, 13.0 and 2450 µg/L for the Severnaya Dvina River, and 40.2 and 2960 µg/L for the Pechora River, respectively, according to [28].

Table 3. The mean concentration of dissolved trace elements in the waters of mouth reaches of rivers of the Kara, Laptev, and East Siberian sea watersheds, µg/L.

Element	Kara Sea Watershed					Laptev Sea Watershed (C _{LS})	East Siberian Sea Watershed (C _{ESS})	Rivers Worldwide ⁴ (C _{GR})	C _{KS} C _{GR}	C _{LS} C _{GR}	C _{ESS} C _{GR}
	Ob Bay		Yenisei Bay		Mean for the Rivers of the Kara Sea Watershed (C _{KS}) ²						
	Ob River: 1993–2001 ¹ [15], 2007 [16], 2004–2006 [17], 2009–2021 [18], 2016 [19], 2020–2021 [20]	Pur River: 2013–2014 [21]	Taz River: 2013–2014 [21], 2015–2020 [22]	Yenisei River: 1993–2001 ¹ [15], 2009, 2010, 2016 [7], 2004–2006 [17], 2009–2021 [18]							
P _{min} ⁵	47.2	121	105	14.9	33.4	5.6	5.1	38	0.88	0.15	0.13
Si ⁵	2410	4800	4700	2910	2850	2330	2490	4070	0.70	0.57	0.61
Rare alkaline and alkaline earth elements											
Li	2.64	–	1.10	1.93	2.16	1.75	0.92	1.84	1.17	0.95	0.50
Rb	0.78	–	0.70	0.49	0.61	0.56	0.25	1.63	0.37	0.34	0.15
Cs	0.0019	–	0.0012	0.0022	0.0020	0.0018	0.0017	0.011	0.18	0.16	0.15
Be	–	–	0.0070	–	0.0070	–	0.0058	0.0089	0.79	–	0.65
Sr	99.0	17.4	41.0	161	129	124	76.5	60	2.15	2.07	1.28
Ba	16.4	17.8	10.2	9.18	12.1	14.2	10.4	23	0.53	0.62	0.45
Heavy metals											
Mn	24.3	52.4	206	6.15	22.2	8.78	4.06	34	0.65	0.26	0.12
Fe	286	568	543	65.5	180	80.0	51.5	66	2.73	1.21	0.78
Co	0.119	0.102	0.225	0.040	0.078	0.058	0.046	0.148	0.53	0.39	0.31
Ni	1.66	1.04	1.20	0.61	1.03	0.58	0.91	0.80	1.29	0.73	1.14
Cu	1.89	0.80	0.68	1.41	1.54	1.13	1.11	1.48	1.04	0.76	0.75
Zn	4.09	–	7.48	0.61	2.20	1.86	0.93	0.60	3.67	3.10	1.55
Cd	0.011	0.0054	0.0082	0.0039	0.0067	0.0056	0.0046	0.080	0.08	0.07	0.06
Tl	0.0025	–	0.0013	0.0040	0.0033	0.0053	0.0021	0.007	0.47	0.76	0.30
Pb	0.110	0.157	0.076	0.091	0.099	0.073	0.086	0.079	1.25	0.92	1.09
Hydrolysate elements											
Al	15.6	35.6	26.8	17.5	17.7	76.2	42.7	32	0.55	2.38	1.33
Ga	0.0076	–	0.020	0.0045	0.0063	0.013	0.016	0.030	0.21	0.43	0.53
Y	0.185	–	0.150	0.101	0.135	0.299	0.081	0.040	3.38	7.48	2.03
Ti	0.27	0.39	0.54	0.46	0.39	0.70	0.56	0.49	0.80	1.43	1.14
Zr	0.098	–	0.090	0.170	0.140	0.196	0.079	0.039	3.59	5.03	2.03
Hf	0.0090	–	0.0030	0.0042	0.0060	0.017	0.0039	0.0059	1.02	2.88	0.66
Th	0.031	–	0.0090	0.022	0.025	0.106	0.014	0.041	0.61	2.59	0.34
U	0.275	–	0.016	0.237	0.242	0.313	0.038	0.372	0.65	0.84	0.10

Table 3. Cont.

Element	Kara Sea Watershed					Laptev Sea Watershed (C _{LS})	East Siberian Sea Watershed (C _{ESS})	Rivers Worldwide ⁴ (C _{GR})	C _{KS} C _{GR}	C _{LS} C _{GR}	C _{ESS} C _{GR}
	Ob Bay		Yenisei Bay		Mean for the Rivers of the Kara Sea Watershed (C _{KS}) ²						
	Ob River: 1993–2001 ¹ [15], 2007 [16], 2004–2006 [17], 2009–2021 [18], 2016 [19], 2020–2021 [20]	Pur River: 2013–2014 [21]	Taz River: 2013–2014 [21], 2015–2020 [22]	Yenisei River: 1993–2001 ¹ [15], 2009, 2010, 2016 [7], 2004–2006 [17], 2009–2021 [18]							
Rare earth elements											
La	0.138	0.145	0.080	0.118	0.125	0.499	0.047	0.120	1.04	4.16	0.39
Ce	0.233	–	0.150	0.221	0.223	0.786	0.087	0.262	0.85	3.00	0.33
Pr	0.038	–	0.020	0.035	0.036	0.118	0.015	0.040	0.90	2.95	0.38
Nd	0.158	–	0.100	0.116	0.131	0.459	0.066	0.152	0.86	3.02	0.43
Sm	0.039	–	0.030	0.028	0.032	0.086	0.020	0.036	0.89	2.39	0.56
Eu	0.010	–	0.0070	0.0080	0.0087	0.016	0.0053	0.0098	0.89	1.63	0.54
Gd	0.041	–	0.030	0.036	0.038	0.086	0.022	0.040	0.95	2.15	0.55
Tb	0.0056	–	0.0040	0.0048	0.0051	0.011	0.0028	0.0055	0.93	2.00	0.51
Dy	0.034	–	0.020	0.033	0.033	0.059	0.017	0.030	1.10	1.97	0.57
Ho	0.0065	–	0.0050	0.0061	0.0062	0.012	0.0031	0.0071	0.87	1.69	0.44
Er	0.019	–	0.010	0.020	0.019	0.032	0.0093	0.020	0.95	1.60	0.47
Tm	0.0040	–	0.0020	–	0.0038	0.0052	0.0009	0.0033	1.15	1.58	0.27
Yb	0.017	–	0.014	0.019	0.018	0.028	0.0078	0.017	1.06	1.65	0.46
Lu	0.0024	–	0.0020	0.0029	0.0027	0.0041	0.0012	0.0024	1.13	1.71	0.50
Anionogenic elements											
F	86.0 ⁶	–	–	145	122	101 ⁷	84.9	100	1.22	1.01	0.85
B	17.9	12.4	11.0	9.90	12.9	5.01	2.96	10.2	1.26	0.49	0.29
Ge	0.0092	–	0.030	0.0076	0.0091	0.010	0.012	0.0068	1.34	1.47	1.76
V	0.94	–	0.50	0.96	0.93	0.51	0.26	0.71	1.31	0.72	0.37
As	0.88	0.31	0.72	0.35	0.56	0.28	0.45	0.62	0.90	0.45	0.73
Sb	0.126	–	0.020	0.030	0.066	0.017	0.068	0.07	0.94	0.24	0.97
Cr	0.24	0.31	0.32	0.17	0.21	0.24	0.073	0.70	0.30	0.34	0.10
Se	–	–	0.031	–	0.031	–	0.085	0.07	0.44	–	1.21
Mo	0.36	–	0.09	0.50	0.43	0.22	0.14	0.42	1.02	0.52	0.33
W	0.0096	–	0.0040	0.0080	0.0084	0.0065	0.0034	0.10	0.08	0.07	0.03

¹ The concentrations of P_{min} and Si were averaged using monitoring data for 1975–1995 and expeditionary research data for 1993–2003. Averaging of Cu, Zn, Cd, and Pb concentrations was performed using data [11] for 1998. ² Taking into account the ratio of the volumes of the long-term average water runoff of rivers according to [30]. ³ Generalization of data [23–26] on Mn, Fe, Ni, Cu, Zn, Cd, and Pb in [33]. ⁴ P_{min} [31], Si [4], F [5], and other trace elements [6]. ⁵ The obtained data are of the same order with the estimates [28] of the long-term average concentrations of P_{min} and Si, equal to 76.1 and 3670 µg/L for the Ob River, 8.6 and 3110 µg/L for the Yenisei River, 6.8 and 2030 µg/L for the Lena River, and 5.0 and 2690 µg/L for the Kolyma River, respectively; for the Pur and Taz rivers, the long-term average concentrations are given according to [28] for 1980–2012. ⁶ Weighted mean concentration considering the river water runoff for 2018–2020 [8]. ⁷ Mean concentration for 1995 and 2021 [10].

Considering the data on the mouth reaches of the rivers of the White and Pechora sea watersheds, it can be argued that the concentrations of most of the trace elements dissolved in their waters have similar values. The mean concentrations of P, Si, Li, Rb, Be, Mn, Fe, Co, Ni, Cu, Cd, Pb, Ga, Y, rare earth elements, B, Ge, As, Sb, Se, and Mo differ by less than two times the average. Concentrations of Cs, Sr, Ba, Tl, Al, Ti, Zr, Hf, Th, U, V, and Cr in the Pechora Sea watershed are 2–3 times lower, and the Zn concentration is 2.8 times higher compared to the White Sea watershed. Significant differences are found only for W, the content of which in the Pechora River waters is eight times less than that in the rivers of the White Sea watershed. In general, the concentrations of dissolved trace elements in the Pechora River are slightly lower than the mean values of the rivers of the White Sea watershed (Figure 2a), which can be associated with the presence of continuous permafrost in the Pechora River watershed (7% [34]), leading to a decrease in the intensity of the processes of chemical element mobilization. At the same time, based on the similarity of the trace element composition of river waters, the White and Pechora sea watersheds can be generalized into a conjoint watershed of the European territory of the Russian Arctic.

In the watersheds of the Asian territory of the Russian Arctic (Figure 2b,c), the concentrations of many dissolved trace elements (Li, Rb, Cs, Be, Sr, Ba, Mn, Fe, Zn, Cd, Pb, and B) are lower than those in the watersheds of the corresponding European territory. These elements are characterized by a tendency to decrease in concentration from west to east, i.e., with increasing climate severity and the prevalence of continuous permafrost. This trend is not seen for hydrolysate elements (Al, Y, rare earth elements, Zr, Hf, Th, and U) and Tl due to their increased concentrations in the Lena River waters of the Laptev Sea watershed (Figure 2b), and it is also not clearly observed for Co, Ni, Cu, Ga, Ti, and anionogenic elements (F, P, Si, Ge, V, As, Sb, Cr, Se, Mo, and W), the content of which is not systematically varied, differing in the studied watersheds by no more than 5–7 times the average. Along with this, the concentrations of dissolved trace elements in the river waters of the easternmost watershed of the East Siberian Sea (the Kolyma River) are generally 3.1 times lower than for the White and Pechora sea watersheds, and 1.8 times lower compared to the Kara and Laptev sea watersheds (Figure 3):

$$C_{ESS} = 0.32C_{WPS}, \quad r = 0.82, \quad (1)$$

$$C_{ESS} = 0.54C_{KLS}, \quad r = 0.94. \quad (2)$$

A comparison of the mean chemical composition of the waters of the mouth reaches of rivers of the Russian Arctic sea watersheds and the global river runoff shows a fairly close correspondence between the concentrations of most trace elements (Figure 2, Tables 2 and 3). The largest and systematic discrepancies were found for W, Cs, Zn, and Cd.

The W and Cs content in river waters carried to all seas of the Russian Arctic is significantly lower than estimates [6] for the global river runoff. Since the concentrations of W and Cs in river waters were rarely determined using modern, high-sensitivity analytical methods, it can be assumed that the average content of these elements in the global river runoff is overstated; however, an alternative explanation is also possible and is related to the overall lower content of dissolved trace elements in the river runoff from the Russian Arctic sea watersheds.

Another systematic discrepancy was noted for Zn and Cd. The mean Zn concentrations in the river waters of different seas of the Russian Arctic watersheds are in the range of 0.9–11.5 µg/L, and the minimum values (0.9–2.2 µg/L) refer to the watersheds of its Asian territory, which are characterized by the low intensity of weathering processes and experience the least anthropogenic impact. According to [6], the average Zn content in the global river runoff is equal to 0.6 µg/L, which is 7 and 19 times lower than the estimate for the river runoff leading into the White and Pechora seas. The reason for this discrepancy is not clear. It is possible that the estimate [6] is low, since the mean Zn concentration in the global river runoff is noticeably lower than that of Cu, which is detected extremely rarely in river waters (usually the opposite relationship occurs). In addition, other estimates of

the mean Zn concentration in the global river runoff (20–30 µg/L [35,36]) are an order of magnitude higher than the value suggested in [6]. For Cd, an element with similar chemical and geochemical properties to Zn, its average concentration in rivers of the world, on the contrary, is much higher than in the runoff from the Russian Arctic sea watersheds, and the discrepancy increases from west to east, reaching a maximum for the East Siberian Sea watershed.

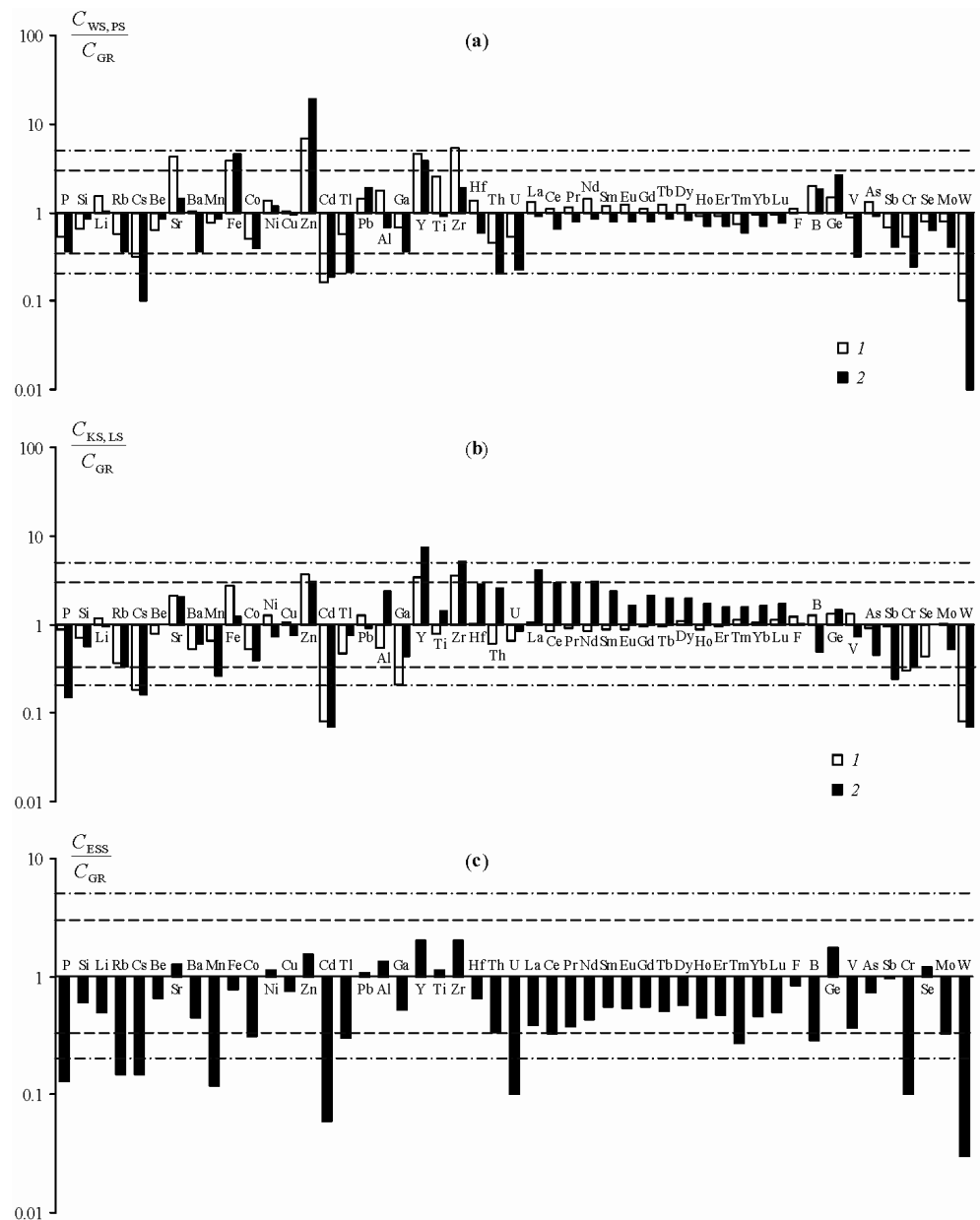


Figure 2. Comparison of the mean concentrations of dissolved trace elements (µg/L) in the waters of mouth reaches of rivers of the Russian Arctic sea watersheds with the global runoff (C_{GR}). (a) Watersheds of the White and Pechora seas: (1) C_{WS} is the mean for the rivers of Kandalaksha Bay, Onega, Kyanda, Severnaya Dvina, Kuloy, Mezen, and Semzha, taking into account the ratio of the volumes of their long-term average water runoff; (2) C_{PS} is the mean for the Pechora River. (b) Watersheds of the Kara and Laptev seas: (1) C_{KS} is the mean for the Ob, Pur, Taz, and Yenisei rivers, taking into account the ratio of the volumes of their long-term average water runoff; (2) C_{LS} is the mean for the Lena River. (c) Watershed of the East Siberian Sea: C_{ESS} is the mean for the Kolyma River. Dash and dot-and-dash lines show three- and fivefold differences, respectively.

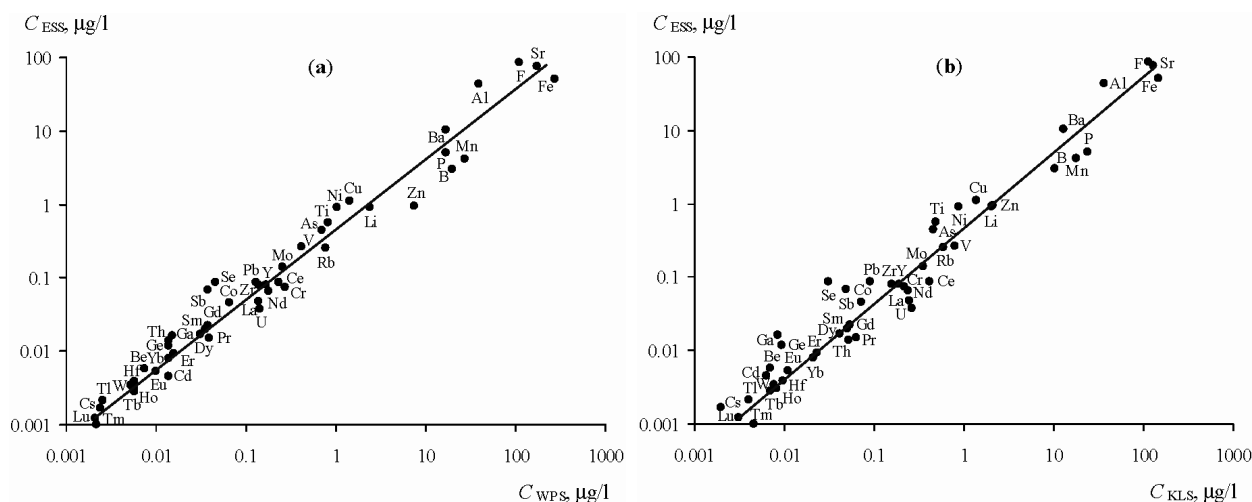


Figure 3. Relationship between the mean concentrations of dissolved trace elements in the waters of mouth reaches of rivers of the different Russian Arctic sea watersheds. **(a)** Watershed of the East Siberian Sea (C_{ESS} is the mean for the Kolyma River) and watersheds of the White and Pechora seas (C_{WPS} is the mean for the rivers of Kandalaksha Bay, Onega, Kyanda, Severnaya Dvina, Kuloy, Mezen, Semzha, and Pechora, taking into account the ratio of the volumes of their long-term average water runoff). **(b)** Watershed of the East Siberian Sea (C_{ESS} is the mean for the Kolyma River) and watersheds of the Kara and Laptev seas (C_{KLS} is the mean for the Ob, Pur, Taz, Yenisei, and Lena rivers, taking into account the ratio of the volumes of their long-term average water runoff).

Many authors believe that anthropogenic sources have a strong influence on the concentrations of Zn and Cd in terrestrial surface waters. From this point of view, the decrease in Zn and Cd concentrations in the river runoff from west to east of the Russian Arctic territory has a logical explanation since the intensity of anthropogenic processes and associated anthropogenic pollution decreases in the same direction; however, this assumption is contradicted by the weak variability of Pb concentrations in all studied watersheds of the Russian Arctic, which is consistent with the world average value given in [6].

Thus, the data presented in this review show a fairly close correspondence between the mean concentrations of dissolved trace elements in the river runoff from the Russian Arctic sea watersheds and those in the river waters of the world. Significant discrepancies were established only for W, Cs, Zn, and Cd.

4. Conclusions

The concentrations of dissolved trace elements (P, Si, Li, Rb, Be, Sr, Ba, Mn, Fe, Co, Ni, Cu, Tl, Pb, Al, Ga, Y, Ti, Zr, Hf, Th, U, rare earth elements, F, B, Ge, V, As, Sb, Cr, Se, and Mo) in the river runoff from the Russian Arctic sea watersheds are generally consistent with estimates of their average content based on the global river runoff. Significant systematic differences in the mean chemical composition of river waters in the Russian Arctic sea watersheds and that of the river waters of the world (up to an order of magnitude) are observed only for dissolved W, Cs, Zn, and Cd.

Correlation relationships between the mean concentrations of dissolved trace elements in the waters of the considered Arctic watersheds show a tendency to decrease in the direction from west to east. The concentrations of dissolved trace elements in the river waters of the easternmost watershed of the East Siberian Sea are generally 1.8 times lower than those of the Kara and Laptev sea watersheds, and 3.1 times lower compared to those of the White and Pechora sea watersheds.

Author Contributions: A.V.S. conceived the study; A.V.S. and V.S.S. jointly carried out the research and wrote the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by a grant from the Russian Science Foundation No. 24-27-00275, <https://rscf.ru/en/project/24-27-00275/> (accessed on 23 January 2024).

Data Availability Statement: Data supporting the reported results can be found in the studies cited in the manuscript.

Acknowledgments: The authors are grateful to N.A. Demidenko and M.N. Kozhin for collecting water samples from the rivers of the White Sea watershed for chemical analyses.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Livingstone, D.A. Chemical Composition of Rivers and Lakes. U.S. Government Publishing Office: Washington, DC, USA, 1963; 440, pp. 1–64. [\[CrossRef\]](#)
- Alekin, O.A.; Brazhnikova, L.V. *Dissolved Matter Runoff from the Territory of the USSR*; Nauka: Moscow, Russia, 1964; pp. 1–144. (In Russian)
- Meybeck, M. Pathways of major elements from land to ocean through rivers. In *River Inputs to Ocean Systems*; United Nations: New York, NY, USA, 1981; pp. 18–30.
- Meybeck, M. Global occurrence of major elements in rivers. In *Treatise on Geochemistry*; Drever, J.I., Holland, H.D., Turekian, K.K., Eds.; Elsevier–Pergamon: Amsterdam, The Netherlands, 2004; Volume 5, pp. 207–223.
- Gordeev, V.V. *Geochemistry of the River–Sea System*; IP I.I. Matushkina: Moscow, Russia, 2012; pp. 1–452. (In Russian)
- Gaillardet, J.; Viers, J.; Dupre, B. Trace elements in river waters. In *Treatise on Geochemistry*, 2nd ed.; Holland, H.D., Turekian, K.K., Eds.; Elsevier: Amsterdam, The Netherlands, 2014; Volume 7, pp. 195–235.
- Savenko, A.V.; Pokrovsky, O.S. Distribution of dissolved matter in the Yenisei estuary and adjacent Kara Sea areas and its inter-annual variability. *Geochem. Int.* **2019**, *57*, 1201–1212. [\[CrossRef\]](#)
- Savenko, A.V.; Savenko, V.S.; Efimov, V.A. Present-day fluorine concentration in the Ob River water. *Lomonosov Geography J.* **2023**, *78*, 132–138.
- Savenko, A.V.; Savenko, V.S.; Efimov, V.A.; Pokrovsky, O.S. Trace element composition of the waters of the mouth of the Kolyma River. *Doklady Earth Sci.* **2023**, *508*, 102–105. [\[CrossRef\]](#)
- Savenko, A.V.; Savenko, V.S.; Efimov, V.A. Fluorine concentrations in the Lena R. water from 1995 to 2021. *Water Resour.* **2023**, *50*, S172–S176.
- Guay, C.K.H.; Zhulidov, A.V.; Robarts, R.D.; Zhulidov, D.A.; Gurtovaya, T.Y.; Holmes, R.M.; Headley, J.V. Measurements of Cd, Cu, Pb and Zn in the lower reaches of major Eurasian arctic rivers using trace metal clean techniques. *Environ. Pollut.* **2010**, *158*, 624–630. [\[CrossRef\]](#) [\[PubMed\]](#)
- Pokrovsky, O.S.; Viers, J.; Shirokova, L.S.; Shevchenko, V.P.; Filippov, A.S.; Dupre, B. Dissolved, suspended, and colloidal fluxes of organic carbon, major and trace elements in the Severnaya Dvina River and its tributary. *Chem. Geol.* **2010**, *273*, 136–149. [\[CrossRef\]](#)
- Chupakov, A.V.; Pokrovsky, O.S.; Moreva, O.Y.; Shirokova, L.S.; Neverova, N.V.; Chupakova, A.A.; Kotova, E.I.; Vorobyeva, T.Y. High resolution multi-annual riverine fluxes of organic carbon, nutrient and trace element from the largest European Arctic river, Severnaya Dvina. *Chem. Geol.* **2020**, *538*, 119491. [\[CrossRef\]](#)
- Chupakov, A.V.; Pokrovsky, O.S.; Moreva, O.Y.; Kotova, E.I.; Vorobyeva, T.Y.; Shirokova, L.S. Export of organic carbon, nutrients and metals by the mid-sized Pechora River to the Arctic Ocean. *Chem. Geol.* **2023**, *632*, 121524. [\[CrossRef\]](#)
- Gordeev, V.V.; Beeskow, B.; Rachold, V. Geochemistry of the Ob and Yenisey estuaries: A comparative study. *Berichte Polar- und Meeresforsch.* **2007**, *565*, 1–235. [\[CrossRef\]](#)
- Demina, L.L.; Gordeev, V.V.; Galkin, S.V.; Kravchishina, M.D.; Aleksankina, S.P. The biogeochemistry of some heavy metals and metalloids in the Ob River estuary—Kara Sea section. *Oceanology* **2010**, *50*, 729–742. [\[CrossRef\]](#)
- Gordeev, V.V.; Pokrovsky, O.S.; Zhulidov, A.V.; Filippov, A.S.; Gurtovaya, T.Y.; Holmes, R.M.; Kosmenko, L.S.; McClelland, J.W.; Tank, S.E. Dissolved major and trace elements in the largest Eurasian Arctic rivers: Ob, Yenisey, Lena, and Kolyma. *Water* **2024**, *16*, 316. [\[CrossRef\]](#)
- McClelland, J.W.; Tank, S.E.; Spencer, R.G.M.; Shiklomanov, A.I.; Zolkos, S.; Holmes, R.M. Arctic Great Rivers Observatory. Water Quality Dataset. Version 20230314. Available online: <https://arcticgreatrivers.org/data> (accessed on 16 January 2024).
- Kolesnichenko, I.; Kolesnichenko, L.G.; Vorobyev, S.N.; Shirokova, L.S.; Semiletov, I.P.; Dudarev, O.V.; Vorobev, R.S.; Shavrina, U.; Kirpotin, S.N.; Pokrovsky, O.S. Landscape, soil, lithology, climate and permafrost control on dissolved carbon, major and trace elements in the Ob River, Western Siberia. *Water* **2021**, *13*, 3189. [\[CrossRef\]](#)
- Soromotin, A.; Moskovchenko, D.; Khoroshavin, V.; Prikhodko, N.; Puzanov, A.; Kirillov, V.; Koveshnikov, M.; Krylova, E.; Krasnenko, A.; Pechkin, A. Major, trace and rare earth element distribution in water, suspended particulate matter and stream sediments of the Ob River mouth. *Water* **2022**, *14*, 2442. [\[CrossRef\]](#)
- Pokrovsky, O.S.; Manasypov, R.M.; Loiko, S.V.; Krickov, I.A.; Kopysov, S.G.; Kolesnichenko, L.G.; Vorobyev, S.N.; Kirpotin, S.N. Trace element transport in western Siberian rivers across a permafrost gradient. *Biogeosciences* **2016**, *13*, 1877–1900. [\[CrossRef\]](#)

22. Pokrovsky, O.S.; Manasypov, R.M.; Chupakov, A.V.; Kopysov, S.G. Element transport in the Taz River, western Siberia. *Chem. Geol.* **2022**, *614*, 121180. [[CrossRef](#)]
23. Martin, J.M.; Guan, D.M.; Elbaz-Poulichet, F.; Thomas, A.J.; Gordeev, V.V. Preliminary assessment of the distributions of some trace elements (As, Cd, Cu, Fe, Ni, Pb and Zn) in a pristine aquatic environment: The Lena River estuary (Russia). *Marine Chem.* **1993**, *43*, 185–199. [[CrossRef](#)]
24. Guieu, C.; Huang, W.W.; Martin, J.M.; Yong, Y.Y. Outflow of trace metals into the Laptev Sea by the Lena River. *Marine Chem.* **1996**, *53*, 255–267. [[CrossRef](#)]
25. Holemann, J.A.; Schirmacher, M.; Prange, A. Dissolved and particulate major and trace elements in newly formed ice from the Laptev Sea (Transdrift III, October 1995). In *Land–Ocean Systems in the Siberian Arctic: Dynamics and History*; Kassens, H., Bauch, H.A., Dmitrenko, I.A., Eicken, H., Hubberten, H.-W., Melles, M., Thiede, J., Timokhov, L.A., Eds.; Springer-Verlag: Berlin, Germany, 1999; pp. 101–111.
26. Holemann, J.A.; Schirmacher, M.; Prange, A. Seasonal variability of trace metals in the Lena River and the southeastern Laptev Sea: Impact of the spring freshet. *Glob. Planet. Change* **2005**, *48*, 112–125. [[CrossRef](#)]
27. Vorobyev, S.N.; Kolesnichenko, Y.; Korets, M.A.; Pokrovsky, O.S. Testing landscape, climate and lithology impact on carbon, major and trace elements of the Lena River and its tributaries during a spring flood period. *Water* **2021**, *13*, 2093. [[CrossRef](#)]
28. Bryzgalo, V.A.; Nikanorov, A.M.; Kosmenko, L.S.; Reshetnyak, O.S. *Estuary Ecosystems of Large Rivers in Russia: Anthropogenic Load and Ecological State*; Southern Federal University Press: Rostov-on-Don, Russia, 2015; pp. 1–164. (In Russian)
29. Ivanov, V.V.; Bryzgalo, V.A. Hydrological and hydrochemical regime of the White Sea watershed. In *The White Sea and Their Watershed under Influences of Climate and Anthropogenic Impact*; Filatov, N.N., Terzhevnik, A.Y., Eds.; Karelian Research Center of RAS: Petrozavodsk, Russia, 2007; pp. 119–145. (In Russian)
30. Magritsky, D.V.; Frolova, N.L.; Evstigneev, V.M.; Povalishnikova, E.S.; Kireeva, M.B.; Pakhomova, O.M. Long-term changes of river water inflow into the seas of the Russian Arctic sector. *Polarforschung* **2018**, *87*, 177–194. [[CrossRef](#)]
31. Savenko, V.S.; Savenko, A.V. *Geochemistry of Phosphorus in the Global Hydrological Cycle*; GEOS: Moscow, Russia, 2007; pp. 1–248. (In Russian)
32. Gordeev, V.V.; Filippov, A.S.; Kravchishina, M.D.; Novigatsky, A.N.; Pokrovsky, O.S.; Shevchenko, V.P.; Dara, O.M. The geochemical peculiarities of the river discharge to the White Sea. In *The White Sea System*; Lisitzin, A.P., Nemirovskaya, I.A., Eds.; Nauchny Mir: Moscow, Russia, 2012; Volume 2, pp. 225–308. (In Russian)
33. Gordeev, V.V. Trace elements in water, suspended matter and bottom sediments of the Ob and Yenisey estuaries and the Lena delta and in the adjacent areas of the Kara and Laptev seas. In *System of the Laptev Sea and the Adjacent Arctic Seas: Modern and Past Environments*; Kassens, H., Lisitzin, A.P., Thiede, J., Polyakova, Y.I., Timokhov, L.A., Frolov, I.E., Eds.; Moscow University Press: Moscow, Russia, 2009; pp. 202–224. (In Russian)
34. Dolgoplova, E.N. The role of permafrost in the formation of the hydrological and morphological regime of river mouths in the Arctic Ocean watershed area. *Arct. Ecol. Econ.* **2018**, *32*, 55–70. [[CrossRef](#)]
35. Gordeev, V.V. *River Runoff into the Ocean and Specifics of Its Geochemistry*; Nauka: Moscow, Russia, 1983; pp. 1–160. (In Russian)
36. Martin, J.M.; Meybeck, M. The content of major elements in the dissolved and particulate load of river. In *Biogeochemistry of Estuarine Sediments*; Forstner, U., Muller, G., Stoffers, P., Eds.; UNESCO Press: Paris, France, 1978; pp. 95–110.

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