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Seasonal Variations of Mineralogical and Chemical Composition of Particulate Matter in a Large Boreal River and Its Tributaries

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Abstract: Despite the importance of river suspended matter (RSM) for carbon, nutrient, and trace metal transfer from the land to the ocean, the mineralogical control on major and trace element speciation in the RSM remains poorly constrained. To gain a better understanding of environmental and seasonal factors controlling the mineral and chemical composition of riverine suspended load, we studied, over several hydrological seasons, including winter baseflow, the RSM of a large boreal river in Western Siberia (Ob in its middle course) and its two small tributaries. The concentration of RSM increased from 2–18 mg/L in winter to 15–105 mg L^{-1} during the spring flood. Among the dominant mineral phases of the RSM in the Ob River, quartz (20–40%), albite (4–18%), smectite (2–14%), and chlorite (6–16%) increased their relative proportions with an increase in discharge in the order "winter $\leq$ summer < spring flood"; illite (5–15%) was not affected by seasons or discharge, whereas the abundance of calcite (0–30%) decreased with discharge, from winter to summer and spring. Seasonal variation of elemental composition of the Ob River's RSM allowed distinguishing three main groups of elements. Sodium, K, Si, Al, trivalent, and tetravalent hydrolysates increased their concentrations in the RSM with an increase in discharge, reflecting enhanced contribution of lithogenic material during high flow, whereas the concentration of alkaline-earth metals (Ca, Sr, Ba), P, Mn, and As decreased with discharge, reflecting accumulation of these elements in the suspended matter under ice. At the same time, a number of nutrients and trace elements demonstrated progressive accumulation in the RSM during winter (Ca, P, Cu, Zn, Mo, As, Cd, Sb). Micronutrients (V, Co), Fe, and Cr exhibited a minimum during summer, which could reflect both the uptake of these elements by the biota during baseflow (micronutrients) and their enhanced export during winter and spring compared to summer (Fe). The RSM of small tributaries demonstrated quite a different pattern compared to the Ob River main stem. Maximal concentration of suspended matter was observed at low discharges during the winter. During this period, the RSM was dominated by amorphous Fe hydroxides. Overall, the obtained results confirm the overwhelming impact of peatlands on element export in suspended form in small rivers of Western Siberia, and strong seasonal variations of both mineralogy and chemistry of the RSM in the Ob River main stem. Elemental yields (watershed-normalized export), assessed for the first time for the middle course of the Ob River and tributaries, were shifted towards the more important role of particulate vs. dissolved export for a number of trace elements, compared to that of the small and medium-sized rivers of Western Siberia, draining the taiga forest and peatlands of the boreal zone. The contrasting pattern of RSM chemical composition across the year demonstrated the importance of seasonal approach for sampling river suspended matter and calls a need for addressing strongly understudied RSM sources during winter baseflow, under ice.

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1. Introduction

The export of macro- and micronutrients from the land to the ocean in high-latitude regions has attracted significant research efforts [1–5]; however, the majority of these studies are devoted to dissolved rather than particulate fractions of the river load [2,6–9]. This is explained by the fact that, due to generally low flow during most parts of the year, the northern rivers export essentially dissolved forms of elements, in contrast to average continental runoff to the ocean, which occurs preferentially in particulate rather than dissolved form [10–14]. Up to the present time, numerous studies have addressed the "dissolved" organic carbon and macronutrients in terminal gauging stations in large rivers of the circumpolar and boreal zones [3,8,15–19]. In contrast, relatively few studies have dealt with major and trace elements other than C and nutrients in the particulate (>0.22 or 0.45 µm) fraction. Thus, [20] provided an extensive data set for river suspended matter (RSM) concentration and C and N composition in the mixing zone of the Ob and Yenisey Rivers. Only sparse data with very low seasonal resolution are available on the elementary composition of RSM in boreal and subarctic rivers in the European part of Russia [21–25], Central Siberian Plateau [26,27], Eastern Siberian Rivers [28], Canada [29,30], the Mackenzie Basin [31], and six large Arctic rivers (data of PARTNERS and ARCTIC GRO; [32,33]. The Russian Hydrological Survey provided numerous data on RSM concentrations in large and small rivers across Northern Eurasia, with sufficient seasonal resolution (monthly to bi-monthly sampling); however, no data for chemical composition are available [34–36]. Much less is known about the mineral composition of the RSM in boreal and subarctic regions of northern Eurasia. In particular, although the mineralogy of suspended matter in many of the world's rivers is fairly well characterized, the information on seasonal variations in RSM mineralogy and chemistry is rather limited.

The first compilations described the proportion of clastic and clay minerals in the RSM of 14 rivers in the former USSR [37]. Over the last 30 years, clay minerals in suspended matter from the Ob and Yenisei Rivers [38] and Khatanga, Lena, and Yana [39] were investigated. More recent, also occasional, low seasonal resolution studies of clay minerals in RSM of Central Siberian rivers of the Yenisei eastern tributaries were reported in [40]. A much better understanding of mineralogy in RSM was achieved for the Severnaya Dvina (NW Russia) suspended load [41–49]. However, a detailed combination of both the mineralogical and bulk chemical composition of RSM, with high seasonal resolution, has not been attempted. Boreal and subarctic rivers are especially important for suspended carbon and major and trace element transport as they: (i) are strongly susceptible to ongoing environmental changes; (ii) act as major conduits of soil C and nutrient export from the watershed; and (iii) may respond in a still poorly known way to increases in discharge, precipitation, soil erosion, vegetation shift, and permafrost thaw.

The Western Siberian Lowland (WSL) stands apart from other high-latitude regions because the chemical composition of its rivers was recently assessed across a gradient of permafrost zones [50]. Despite the relatively pristine character of the world's largest peatland, it has a sufficiently developed road infrastructure that allows collecting RSM across a sizable territory with non-prohibitive sample transport and preservation costs. There are multiple features that make the WSL a unique test site for studying riverine export of material. Initially, it stores a sizeable amount of organic carbon (OC) in thawed and frozen peat [51]. This OC can be mobilized to the river and become biodegradable [52] thus enhancing the CO_2 emissions from the territory [53]. Second, the WSL provides a large amount of freshwater to the Arctic Ocean [54–56] and exhibits high fluxes of greenhouse gases from the inland waters to the atmosphere [57–59]. Third, the permafrost in the WSL is much warmer (ground temperature close to 0 °C) and highly vulnerable to thawing, compared to other Siberian regions [60]. As such, ongoing climate warming is likely to have a significant impact on the pattern of dissolved but also particulate solids in the WSL rivers due to the alteration of hydrological regimes [61,62] and enhancement of element releases caused by widespread permafrost thawing [7].

The first comprehensive study of major and trace elements in the RSM of Western Siberia was performed about 20 years ago on the Irtysh River, the major tributary of the Ob [63]. During summer baseflow, these authors observed typical Al, Si-rich suspended matter composition in the middle course of the river and the presence of Fe-organic amorphous components in RSM of the tributaries in the low reaches of the Irtysh River, where it drains through abundant mires. Gordeev et al. [63] also reported that dissolved P and As are carried by organic- and Fe-rich components, which were identified as specific features of rivers in the peatland zone. Recently, an extensive study of 33 small- and medium-sized rivers during spring flood, summer baseflow, and autumn flood was performed over a 1700 km gradient of climate and permafrost in Western Siberia [50]. These authors found that the presence of forest in the permafrost-bearing zone increased particulate concentrations of all alkalis and alkaline-earth elements, trace elements (TE) such as B, As, Nb, Mn, Co, trivalent and tetravalent hydrolysates (TE^{3+}, TE^{4+}) and related this observation with element mobilization from mineral horizons that become available for interacting with soil fluids under forested regions. They also found that the concentration of lithogenic low-soluble elements (TE^{3+}, TE^{4+}) in the RSM strongly increased with the river size (watershed area). Overall, compared to the world RSM average, the WSL rivers exhibited lower concentrations of all elements except Mn and P and a low share of suspended elements relative to total (suspended + dissolved) forms of trace metals and of low-mobility (lithogenic) elements. Krickov et al. [50] explained these features by: (1) low runoff and low RSM concentration as there is no rock and mineral substrate exposed to physical weathering in WSL peatland; (2) organic, rather than mineral, nature of surrounding "solid" substrates and, as a result, organic rather than silicate nature of RSM; and (3) high dissolved OC and Fe concentrations leading to high concentrations of typically low-soluble elements in the dissolved (<0.45 µm) fraction in which they are carried by colloids.

The majority of these factors are likely to operate in the permafrost-free zone where the Ob River and its small right tributaries sampled in this work are located. However, given the larger size and faster flow velocity of the Ob River main stem compared to small tributaries, we hypothesize a sizable contrast in the mineral and elemental composition of the suspended matter in the Ob River compared to that of small tributaries. In particular, we expect lower concentrations of lithogenic material and higher concentrations of OC, Fe, and Mn in small rivers draining the upland mires, which are rich in dissolved OC and Fe, compared to the Ob River middle course. We further expect systematic evolution of both the mineralogical and chemical composition of the RSM given the importance of a long, winter period of baseflow under ice with possible oxygen anoxia and enhanced feeding from the groundwater, followed by a strong increase in RSM transport at high flow during spring flood. Towards this goal, we studied the mineral and chemical composition of RSM collected in the Ob River middle course and its two small tributaries across the main hydrological seasons. The main novelty of this work relative to previous studies of the RSM in Western Siberia and across the subarctic consists in considering the full length of the hydrological season, including the winter baseflow, and relating the chemical and mineralogical variations of the RSM to the season and the discharge. We aimed at addressing the following specific objectives: (1) assess the mineral composition of the suspended matter of the Ob River and its two tributaries across seasons; (2) quantify the concentration of major and trace elements in the RSM as a function of river discharge; (3) calculate the annual riverine yields (export fluxes) of elements in suspended form and compare these fluxes to other similar regions of the world as well as with dissolved export; and (4) identify potential environmental sources of suspended material in the river water and characterize the possible transformation of the RSM between the tributaries and the main stem across the seasons.

2. Materials and Methods

2.1. Study Site: The Ob River Middle Course and Its Two Small Tributaries

The permafrost-free (middle course) part of the Ob River catchment is located within the boreal taiga biome. The floodplain forms a system of interconnected shallow ephemeral lakes and primary and secondary water channels that extend over 5–10 km from the main water channel [64–66]. The Ob River at Kaibasovo drains a 260,000 km^2 permafrost-free area of taiga forest and wetlands. For this study, we sampled the main stem in the boreal zone of the Ob River within the research station (Kaibasovo), which is a part of the INTERACT network (57.246° N, 84.184° E, Figure 1). The climate is semi-continental with a mean annual temperature of -0.1 °C and annual precipitation of 589 mm in 2018. The width of the floodplain in this part of the Ob River is between 10 and 30 km. The soils are predominantly alluvial, overlain by a thin (~30 cm) humic layer, and include fluvisols, podsols, and histosols. The vegetation is represented by trees (*Betula, Salix,* and *Populus*, etc.), shrubs (*Rosa canina, Viburnum, Ribes*, etc.), and grasses (*Calamagrostis, Phleum, Veronica longifolia*, etc.). Grasses are abundant in the elevated and most remote parts of the floodplain, while trees and shrubs are confined to the banks of lakes and river channels. The flow velocity of the main channel is between 5 and 5.6 km h^{-1} during the flood and 2.7 and 3 km h^{-1} during the baseflow, which is typical for the Ob River in general.

Two small right tributaries of the Ob River, located within 12 km of the main stem sampling point, were chosen to represent the small terrace streams originating from upland peat bogs and draining through typical taiga forest with minimal residence time on the floodplain. The Andreva River ($S_{watershed}$ = 257 km^2; length = 38 km; mean annual discharge is 2.3 m^3 s^{-1}) drains through dense, pristine taiga forest and birch/willow along the narrow floodplain. The watershed is covered by birch-pine forest on wetlands (31%), ryam (local name for low pine forest on peatland, 25%), larch trees (20%), meadows (19%), and fir-pine forest (5%). The dominant soils are histosols of peatlands (88%), alluvial (9%), and hydromorphic podzols (3%). The Rybnaya River ($S_{watershed}$ = 98 km^2; length = 15 km; mean annual discharge is 2.0 m^3 s^{-1}) originates in a large bog in the upland of second Ob's terrace and is also covered by birch-pine forest on wetlands (58%), ryam (low pine forest on peatland, 9%), mixed pine-birch forest (20%), fir-pine forest (5%), and meadows (2%). Soils are histosols on peatlands (67%), alluvial (5%), and podzols (28%). The clear-cutting of forest does not exceed 2% of both watershed territories. The typical water residence time in wetlands that feed both watersheds is equal to 4.7 years.

2.2. Sampling of RSM

Sampling of suspended matter was performed in 2018–2019, both from the main stem (28 samples) and tributaries (10 samples), but the frequency of sampling in the tributaries was much lower due to limited access to Rybanya and Andreva during high flow and the inter-seasonal period. Large water samples were collected from the middle of the river at 0.5 m depth in pre-cleaned polypropylene jars (from 30 to 50 L). The RSM was collected via direct filtration of large volumes (20–30 L) of the river water with an Inox (AISI 304) Teflon® PTFE-coated filtration unit (Fisher Bioblock, Illkirch, France) equipped with 142 mm acetate cellulose Sartorius membranes (0.45 µm) and operated at 5–7 bars. An average flow rate of 1–2 L/h was created by a peristaltic pump (MasterFlex B/T) with Teflon tubing. For the total concentration of suspended material determination, smaller volumes of freshly collected river water (1–2 L) were filtered on-site (at the river bank or in the boat) with pre-weighted acetate cellulose filters (47 mm, 0.45 µm) and Nalgene 250 mL polystyrene filtration units using a Mityvac® manual vacuum pump.

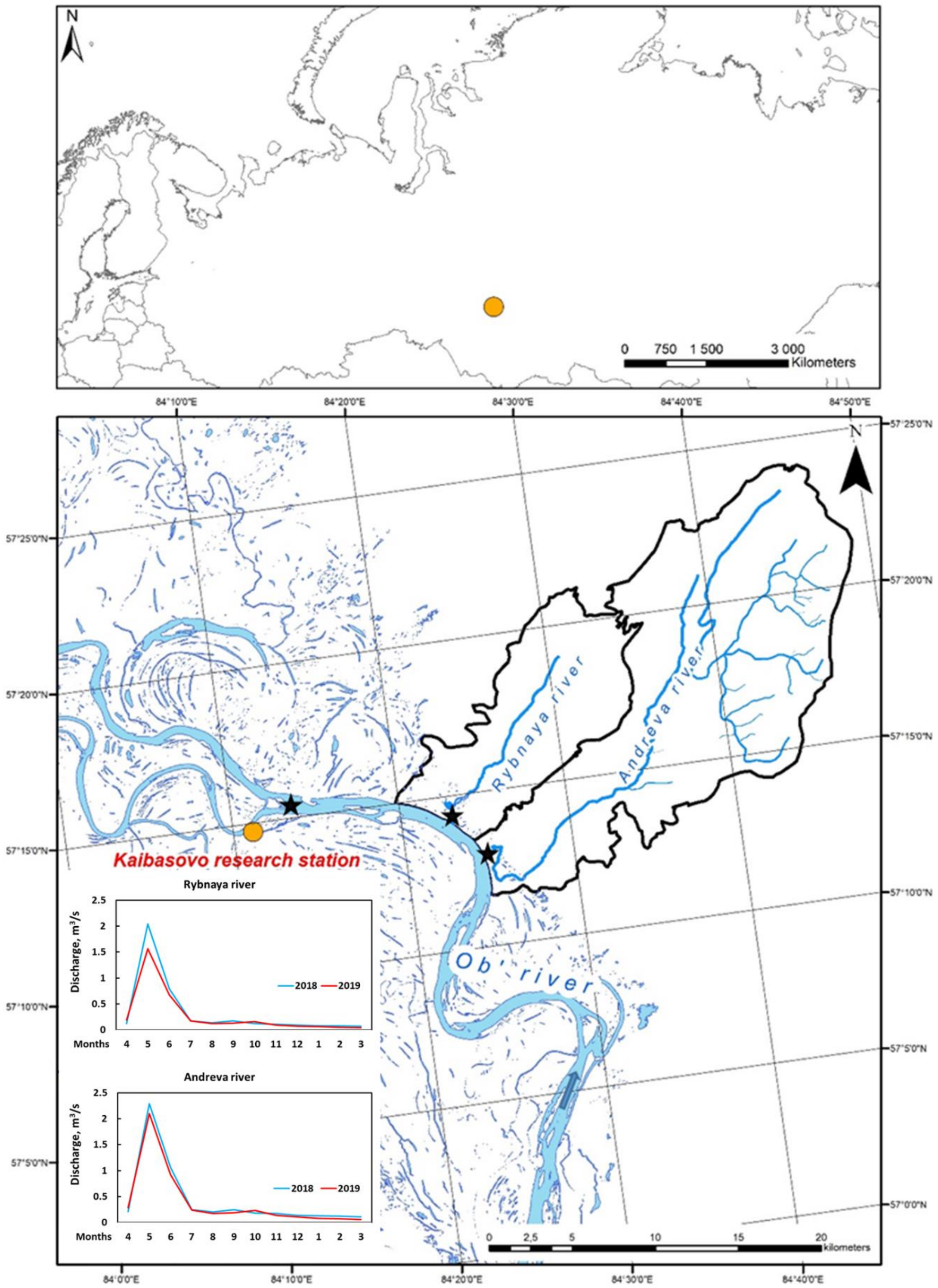

Figure 1. Map of the Ob River middle course (Western Siberia). Black asterisk denotes the sites of the main stem and two tributaries. Two inserts represent monthly hydrographs of the Rybnaya and Andreva rivers.

2.3. Analyses

Eight major and 45 trace element concentrations in the RSM collected from the large-volume separation procedure were measured after full acid leaching in a clean room (class A 10,000), followed by ICP-MS (Agilent 7500ce, Santa Clara, CA, USA) analyses using methods for organic-rich natural samples employed in the GET laboratory (Toulouse, France). The 100 mg dry weight powders were reacted for 30 min in an ultrasonic bath prior to full digestion using a Mars 5 microwave digestion system (CEM, Matthews, NJ, USA) using a mixture of 6.5 mL concentrated HNO_3, 3.5 mL concentrated HCl, and 0.5 mL concentrated HF. HNO_3 and HCl were bi-distilled in the clean room, and HF was of commercially ultra-pure quality (Fluka). For digestion, 10 samples of RSM, 1 certified 2711a

Montana II soil standard [or LKSD sediment]. and 1 blank sample were loaded into Teflon reactors and treated at 150 °C for 20 min. After completing the digestion, the contents of the reactors were transferred into 30 mL Savilex vials and evaporated at 70 °C. The residue was dissolved in 10 mL of 10% HNO_3 and diluted with 2% HNO_3 prior to analysis. The concentration of major and trace elements (TE) in filter digestion products was measured using an ICP-MS Agilent 7500ce with ~3 µg/L of In and Re as internal standards. Four in-house external standards were analyzed for every 10 samples. The uncertainty for TE measurement ranged from 5% at 0.1–100 µg/L to 10% at 0.001–0.01 µg/L.

We interpreted the results for the elements that exhibited a good agreement between the certified or recommended values and our measurements within acceptable uncertainty levels $([X]_{\text{recommended or certified}} - [X]_{\text{measured}})/(([X]_{\text{recommended or certified}} + [X]_{\text{measured}})/2) \times 100 \leq 10\%)$, or for cases in which we obtain a good reproducibility (the relative standard deviation of our various measurements of standards lower than 10%), even if no certified or recommended data are available. All certified major (Ca, Mg, K, Na) and trace elements (Al, As, B, Ba, Co, Cr, Cu, Fe, Ga, Li, Mn, Mo, Ni, Pb), all REEs, Sb, Sr, Th, Ti, U, V, Zn) concentrations of the SLRS-6 standard [67] and the measured concentrations agreed with an uncertainty of 10–20%. Agreement for Cd, Cs, and Hf was between 30 and 50%. For all major and most trace elements, concentrations in blanks were below analytical detection limits (≤0.1–1 ng/L for Cd, Ba, Y, Zr, Nb, REE, Hf, Pb, Th, U; 1 ng/L for Ga, Ge, Rb, Sr, Sb; ≤10 ng/L for Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As).

In addition to total chemical analysis after HF + HNO_3 digestion, the RSM samples were processed for total Si and Al using wet chemical analysis with photometric detection after the fusion of 20 mg sample with borax in Pt crucibles, with a detection limit of 0.02 mass % for Al and 0.04 mass % for Si, and standard deviation of 3 to 4% [68,69].

The content of 8 minerals (quartz, albite, potassium feldspars, amphibole, pyroxene, muscovite, calcite, smectite, illite, kaolinite, chlorite, and vermiculite) in the particulate fraction was studied by X-ray powder diffractometric method on a D8 ADVANCE (Bruker AXS) X-ray diffractometer (Cu-Kα radiation, with Ni 0.02 filter, at 40 kV and 40 mA) equipped with a LYNXEYE linear detector [70]. For primary treatment, deciphering of spectra, and calculation, the program DIFFRAC.EVA was used. For quantitative analyses of total RSM samples, the corundum numbers from the PDF-2 ICDD (International Centre for Diffraction Data) database were employed. First, a suspension of non-ground RSM was prepared in alcohol and deposited on silica monocrystal support for phase analyses of a small amount of solid material. After scanning (discrete regime with step 0.02° θ, exposition 8 s/step in the interval 2.5–70° 2θ with rotation), the samples were saturated by ethyleneglycole over 24 hrs in order to identify smectite and mixed-layer minerals of smectite family. The scanning was performed between 2.5 and 14° 2θ with a step of 0.02° and exposure of 4 s/step. The uncertainty of the relative proportion of mineral composition was 1–2%, and the detection limit was 0.5% for layer silicates and 1–2% for clastic minerals. Identification of clay minerals was performed following standard procedures [71].

2.4. Data Treatment and Discharge Assessment

Statistical analysis was used to quantify the relationship between major and trace element concentrations in RSM, its mineral composition, and riverine discharge. Nonparametric statistics were used because, based on the Shapiro–Wilk test of the normality of variables, data on major and trace element concentrations in the RSM across the seasons were not normally distributed. For these reasons, we used the median, 1st, and 3rd quartiles to trace the dependence of element concentrations in the RSM on seasons. Correlations between element concentration in the RSM and its mineral composition or discharge were tested using Pearson coefficients at $p < 0.05$ for the Ob River main stem and its small tributaries. The differences in suspended element concentration between different seasons and between the Ob River and small rivers were tested using a Mann–Whitney U test for a paired data set with a significance level of 0.05.

In order to calculate the annual export of elements in suspended form, first we obtained the mean monthly multi-annual element concentration in the RSM and multiplied it by the mean monthly total RSM concentration and by the mean monthly discharge. The total riverine suspended flux of elements (in kg per month) was summed up for the entire year and divided by river watershed area to obtain the mean annual yields of each major and trace element, separately for the Ob River and its small tributaries. In previous works on elemental export fluxes by boreal and subarctic rivers, we demonstrated that mean monthly concentrations and discharges allow an adequate approximation of the total annual export of both dissolved and particulate load from large, medium, and small rivers [24,65,72–74].

For the Ob River main stem, the daily discharges were available from the Nikolskoe gauging station of the Russian Hydrological Survey, located within 20 km upstream of the sampling site. The discharge of small tributaries was modeled based on the average altitude of the watershed and climate characteristics using the parameters obtained for neighboring gauged rivers, following the approaches outlined in previous works on small WSL rivers (e.g., Ref. [72]). The river hydrographs were modeled using the HBV Light program package. For small-gauged rivers of the middle course of the Ob River, the model parameters allowed to calculate the daily runoff based on water temperature and precipitation from average data of adjacent meteostation at Nikolskoe. The data for reproducing the water discharge at key sites were taken from hydrological yearbooks and the automatic information system of state monitoring of water objects, whereas the daily air temperature and precipitation were taken from the Russian Hydrometeocenter (URL: https://en.wikipedia.org/wiki/Hydrometeorological_Centre_of_Russia, accessed on 1 December 2022). First, we verified that the HBV model adequately reproduces the seasonal dynamics of runoff (quality criteria of 0.75 to 0.90). Then, we applied this model to the Rybnaya and Andreva rivers, based on the primary landscape and climate parameters available for these rivers. The uncertainties on the discharge of these two ungauged rivers amount to 20–30% and stem from the lack of precision in the determination of the watershed area due to a lack of precise topographic information, which is not a trivial task for the quite flat watershed with sizable coverage of wetlands.

3. Results

3.1. Total Concentration and Mineral Composition of RSM

The concentration of RSM in the Ob River increased from 2–18 mg L^{-1} in winter to 15–105 mg L^{-1} during the spring flood (Figure 2A). The mineral composition of the RSM from the Ob River and tributaries is provided in Table S1 of the Supplement. Among the dominant mineral phases of the RSM in the Ob River, quartz (20–40%), albite (4–18%), smectite (2–14%), and chlorite (6–16%) increased their relative proportions with the discharge increase in the order winter $\leq$ summer < spring flood; illite (5–15%) was not affected by seasons or discharge, whereas the abundance of calcite ($\leq$30%) decreased with discharge, from winter to summer and spring (Figure 2B–G).

The RSM of small tributaries demonstrated quite a contrasting pattern compared to the Ob River main course. The maximal concentration of suspended matter was observed at low discharges during the winter (20 to 70 mg/L) and minimal during the spring flood (Figure S1A). The proportion of Na-feldspar and illite increased with an increase in discharge, being maximal during the spring flood, whereas the proportion of chlorite decreased (Figure S1B–D, respectively).

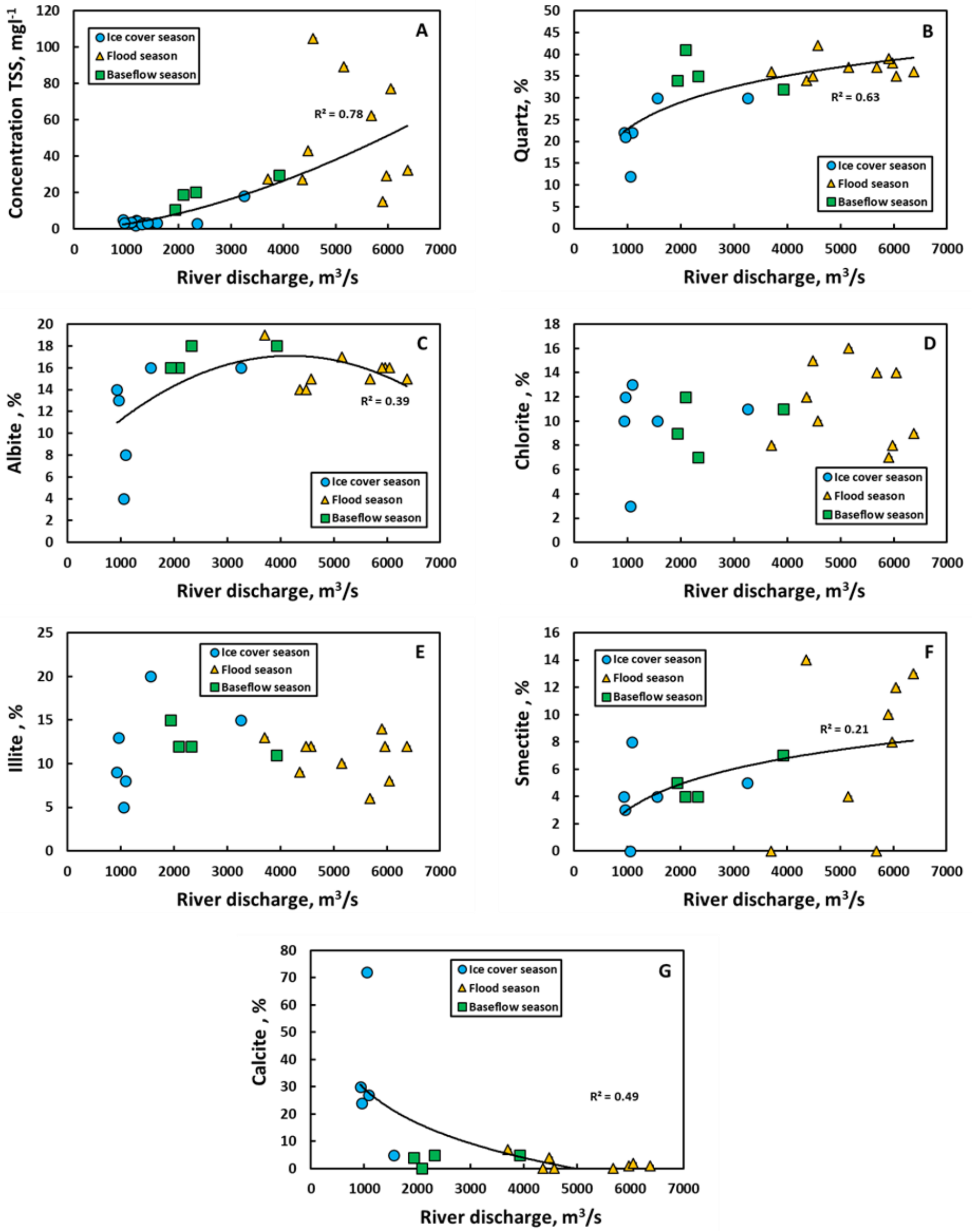

Figure 2. Mass percentage of different minerals in the RSM of the Ob River during winter (blue circles), spring flood (yellow triangles), and summer baseflow (green squares), as a function of river discharge. (**A**) Total suspended solid; (**B**) quartz; (**C**) albite; (**D**) chlorite; (**E**) illite; (**F**) smectite, and (**G**) calcite. For better visualization of possible trends in the data, we used empirical logarithmic or power regression, where this trend was significant ($p < 0.05$).

3.2. Element Concentration in the RSM as a Function of Season and River Discharge

The chemical composition of RSM across all seasons in the Ob River and its tributaries is provided in Table 1, whereas all primary data are listed in Supplementary Table S2. Considering all seasons together, the Mann–Whitney U test showed that there was no significant difference (at $p < 0.05$) in element concentrations and proportions of dominant minerals in the RSM of Rybnaya and Andreva. However, the RSM of the Ob River and that of its tributaries demonstrated strong differences in most components ($p < 0.05$, Supplementary Table S3). This allowed us to consider both of these small tributaries when comparing their chemical and mineral composition with those of the Ob River main stem. Seasonal variation of the elemental composition of the Ob River's RSM allowed distinguishing three main groups of elements. Sodium, K, Si, Al, trivalent, and tetravalent hydrolysates increased their concentrations in the RSM with an increase in discharge, whereas the concentration of alkaline-earth metals (Ca, Sr, Ba), P, Mn, and As decreased with discharge, as illustrated in Figure 3A–H. A number of elements in the suspended load of the Ob River did not show any correlation with discharge (e.g., B, Cr, Ni, Co, Cu, Mo, Zn, Pb, Cd, Sb, Y, REEs, Ti, Zr, Hf, Th, U). At the same time, most of these elements exhibited strong variation in concentration (e.g., by a factor of 5 to 10) at low discharge during the winter period (Figures 4A–H and S2A–F) .

Specific temporal patterns in the course of the year could be revealed for some macro- and micronutrients and trace elements. There was a progressive accumulation in the RSM during winter (Ca, P, Cu, Zn, Mo, As, Cd, Sb) as illustrated in Figure 5A–D. Trace metal micronutrients (Rb, V, Co), Fe and Cr exhibited a clear minimum during summer, which could reflect both the uptake of these elements by the biota during baseflow (micronutrients) and their enhanced export during winter and spring compared to summer (Fe).

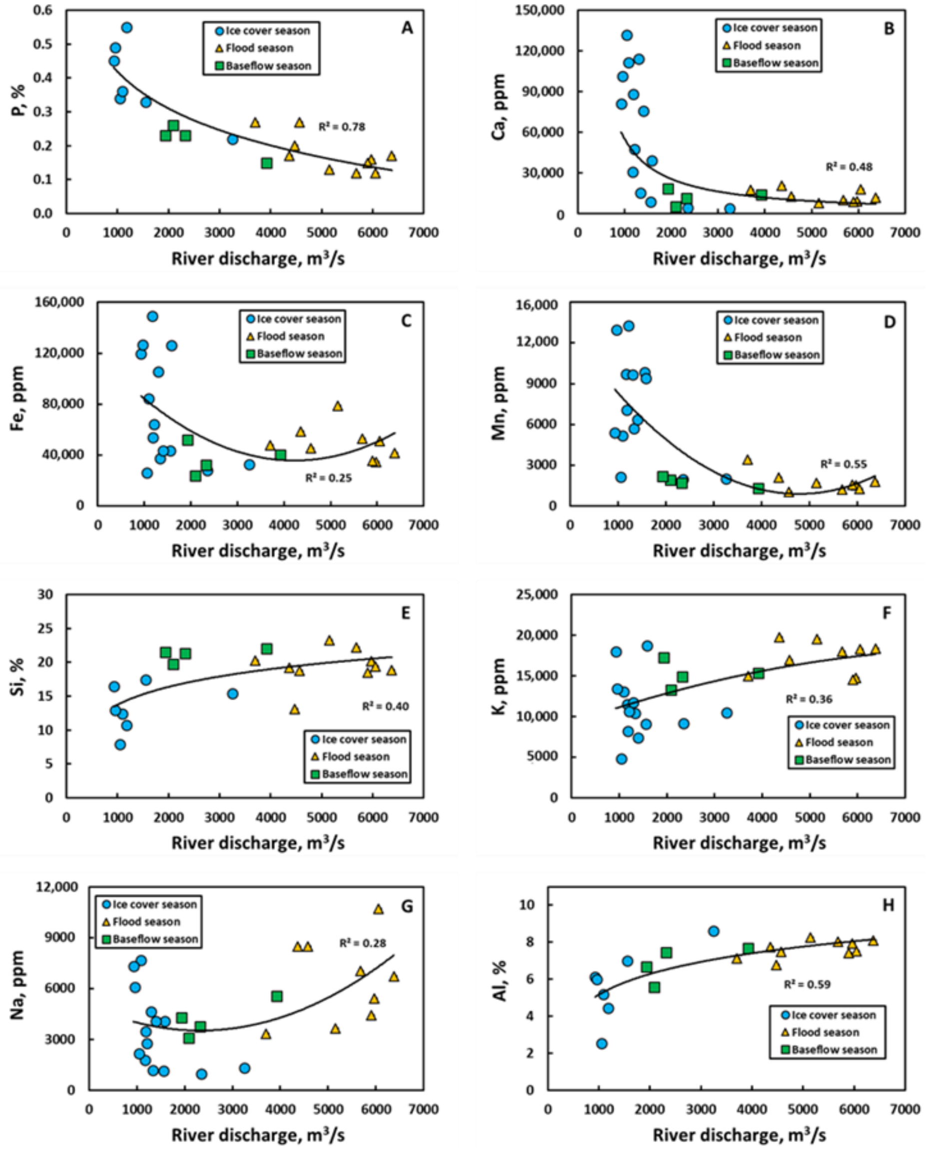

Figure 3. Major element concentration ((**A**) phosphorus; (**B**) Ca; (**C**) Fe; (**D**) Mn; (**E**) Si; (**F**) K; (**G**) Na, and (**H**) Al) in the RSM of the Ob River during winter (blue circles), spring flood (yellow triangles), and summer baseflow (green squares), as a function of river discharge. Significant ($p < 0.05$) trends are visualized via empirical logarithmic or power regression.

Table 1. Mean (±SD) concentrations (ppm dry weight) of elements in RSM of the Ob River and tributaries (this study) and an average value for 30 small and medium-sized WSL rivers studied in Ref. [50].

Element	Ob River	Small Tributaries	WSL Rivers [50]
Si	177,000 ± 41,500	129,000 ± 52,900	209,000 ± 53,400
Li	25.2 ± 10.6	13.4 ± 13.3	11.6 ± 9.46
Be	1.93 ± 0.776	0.890 ± 0.837	–
B	33.3 ± 15.3	18.4 ± 16.4	11.7 ± 12.8
Na	4570 ± 2560	3220 ± 3100	3750 ± 2710
Mg	6680 ± 4180	5290 ± 3570	4430 ± 2810
Al	43,200 ± 27,100	35,400 ± 39,300	25,900 ± 18,400
P	4060 ± 3630	13,200 ± 10,700	4920 ± 4180
K	13800 ± 4090	5130 ± 4520	6480 ± 4270
Ca	37,700 ± 40,300	27,900 ± 18,900	8930 ± 8270
Ti	2210 ± 1140	1340 ± 1720	8110 ± 5730
V	159.3 ± 92.8	76.6 ± 82.1	57.9 ± 33.8
Cr	123.7 ± 89.4	55.5 ± 66.4	41.5 ± 32.2
Mn	4560 ± 3880	34,700 ± 28,100	8020 ± 11,700
Fe	60,400 ± 35,100	237,000 ± 195,000	69,800 ± 44,700
Co	18.6 ± 5.03	52.8 ± 37	24.6 ± 27.6
Ni	58.3 ± 22.7	23.8 ± 20.2	24.1 ± 18.7
Cu	45.5 ± 17.4	13.0 ± 9.35	14.6 ± 11.5
Zn	156 ± 105	119 ± 46.8	90.1 ± 65.0
Ga	16.8 ± 6.90	10.2 ± 8.50	6.65 ± 3.80
Ge	1.19 ± 0.563	0.802 ± 0.865	0.330 ± 0.270
As	55.6 ± 54.8	223 ± 264	19.3 ± 20.0
Rb	19.7 ± 15.5	14.2 ± 8.03	28.8 ± 20.8
Sr	252 ± 243	233 ± 167	132 ± 178
Y	7.69 ± 5.91	8.22 ± 7.34	9.01 ± 4.63
Zr	79.1 ± 41.9	47.9 ± 60.3	34.6 ± 21.7
Nb	11.6 ± 6.2	6.73 ± 8.36	15.1 ± 10.7
Mo	1.31 ± 1.22	1.01 ± 0.583	0.460 ± 0.34
Cd	0.617 ± 0.279	0.484 ± 0.234	0.32 ± 0.19
Sn	6.18 ± 6.11	2.13 ± 1.92	nd
Sb	1.72 ± 1.1	1.13 ± 0.836	0.720 ± 1.17
Cs	1.21 ± 1.21	0.825 ± 0.510	1.65 ± 1.33
Ba	402 ± 203	942 ± 697	409 ± 285
La	12.9 ± 10.2	11.5 ± 11.1	12.6 ± 6.68
Ce	31.7 ± 21.9	28.0 ± 26.7	26.4 ± 14.7
Pr	3.76 ± 2.49	3.21 ± 3.29	2.96 ± 1.66
Nd	15.4 ± 9.82	12.9 ± 13.2	11.6 ± 6.37
Sm	3.21 ± 1.96	2.69 ± 2.73	2.31 ± 1.25
Eu	0.725 ± 0.425	0.682 ± 0.642	0.540 ± 0.280
Gd	2.95 ± 1.83	2.60 ± 2.60	2.28 ± 1.21
Tb	0.407 ± 0.247	0.360 ± 0.365	0.310 ± 0.170
Dy	2.30 ± 1.39	2.08 ± 2.12	1.78 ± 0.950
Ho	0.424 ± 0.254	0.383 ± 0.383	0.330 ± 0.180
Er	1.19 ± 0.717	1.11 ± 1.12	0.990 ± 0.520
Tm	0.162 ± 0.0975	0.157 ± 0.163	0.140 ± 0.070
Yb	1.03 ± 0.622	1.03 ± 1.06	0.930 ± 0.490
Lu	0.145 ± 0.0904	0.146 ± 0.150	0.140 ± 0.0700
Hf	2.95 ± 1.60	1.87 ± 2.33	4.63 ± 2.98
Ta	0.840 ± 0.454	0.505 ± 0.614	1.07 ± 0.760
W	2.74 ± 1.76	1.48 ± 1.29	1.02 ± 1.94
Tl	0.459 ± 0.165	0.205 ± 0.165	0.170 ± 0.110
Pb	35.4 ± 33.2	15.2 ± 8.00	12.8 ± 8.16
Th	3.90 ± 2.87	3.87 ± 3.95	3.02 ± 1.98
U	2.33 ± 0.785	0.866 ± 0.860	0.720 ± 0.440

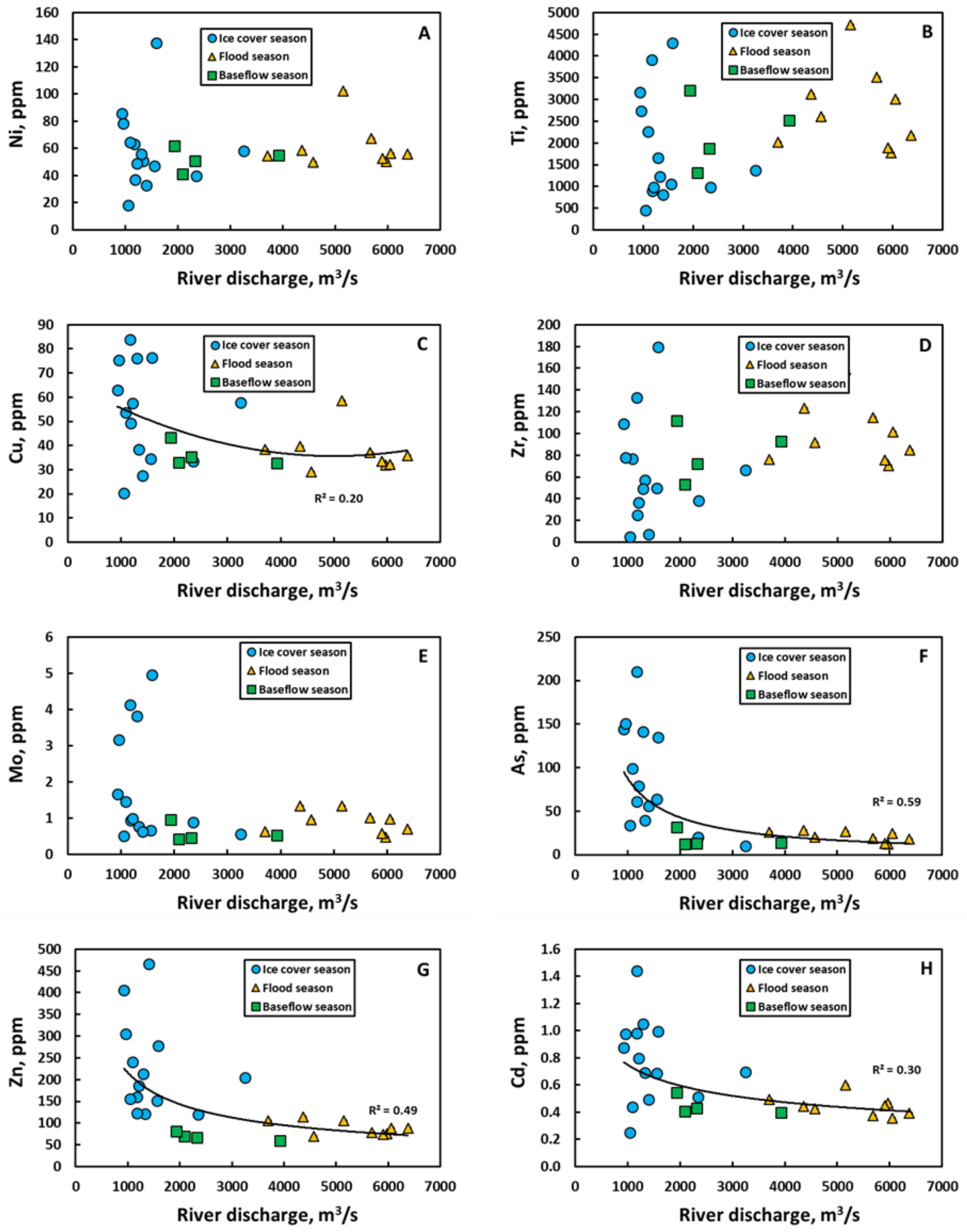

Figure 4. Trace element concentration ((**A**) Ni; (**B**) Ti; (**C**) Cu; (**D**) Zr; (**E**) Mo; (**F**) As; (**G**) Zn, and (**H**) Cd) in the RSM of the Ob River during winter (blue circles), spring flood (yellow triangles), and summer baseflow (green squares), as a function of river discharge. Significant ($p < 0.05$) trends are visualized via empirical logarithmic or power regression.

Element concentration in the Ob River RSM was correlated with the proportion of specific minerals (Table S4). Among trace elements (i.e., non-major constituents of specific minerals), Li, Be, B, Ti, V, Cr, Co, Ni, Cu, Ga, Ge, Zr, Nb, Sb, Hf, and Tl were positively ($p < 0.05$) correlated with the proportion of chlorite in the RSM, whereas smectite positively affected the abundance of middle REE (Sm, Eu, Gd, Tb, Dy) and Th. The other minerals, identified in the Ob River RSM, did not correlate ($R_{\text{Pearson}} < 0.5$; $p > 0.05$) with any trace element.

The elemental composition of the RSM of small tributaries was different from that of the Ob River main stem. Unfortunately, the low number of seasonal samples allowed only a preliminary assessment of element fate in the RSM of small rivers over the course of the year. Calcium, Sr, Ba, Fe, and Mn exhibited quite high concentrations during low flow in the autumn (Figure 6A–D). Typical macro- and micronutrients (Mg, K, V, Cr, Ni, Cu, Zn, Rb, Mo) demonstrated minimal concentration in the RSM at moderate discharges during summer baseflow, as illustrated in Figure S3A–I. Similar behavior was observed for trivalent and tetravalent hydrolysates (Figure S4A–F).

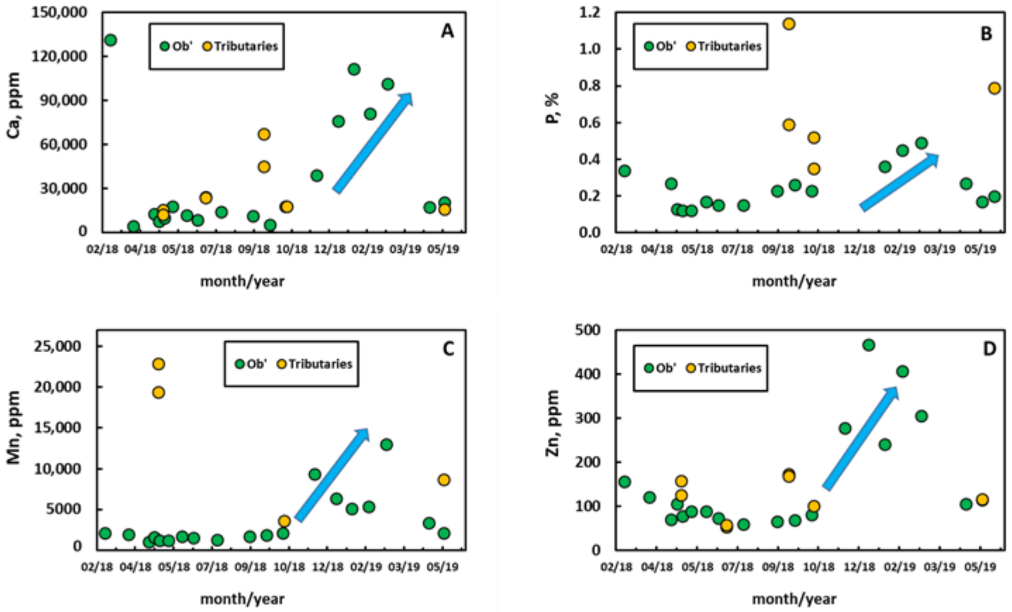

Figure 5. Seasonal pattern of element concentration ((**A**) Ca; (**B**) P; (**C**) Mn; (**D**) Zn) in the RSM of the Ob River (green circles) and two small tributaries (yellow circles). Thick blue arrow signifies the accumulation of element in the Ob River RSM during winter (ice-on) period.

Considering all collected RSM samples in both small tributaries and the main stem, the Pearson correlation table (Supplementary Table S5) identified three main elements marking the abundance of other major and trace components. Aluminum exhibited strong ($R_{Pearson} \geq 0.80$, $p < 0.05$) correlations with major and trace elements (Na, Mg, Li, B) present in the form of feldspars, micas, or secondary clays, but also with lithogenic Ti, Ga, Y, Zr, Nb, REEs, Hf, and Th. In contrast, Fe was sizably ($R_{Pearson} \geq 0.70$, $p < 0.05$) associated with P, heavy metals (V, Cr, Co, Ni, Cu, Zn), trace oxyanions (As, Ge, Mo, Sb, W), and U, potentially reflecting co-precipitation with and adsorption of these trace elements on amorphous iron hydroxides. The latter solid phase dominated the suspended matter, especially during the late autumn/winter period. Calcium strongly ($R_{Pearson} > 0.95$, $p < 0.05$) correlated with Sr as well as with Ba ($R_{Pearson} = 0.7$, $p < 0.05$), reflecting its association with calcite particles. The largest differences in mineral and elemental composition of the Ob River RSM were observed for the winter/spring and winter/summer seasons (Supplementary Table S6).

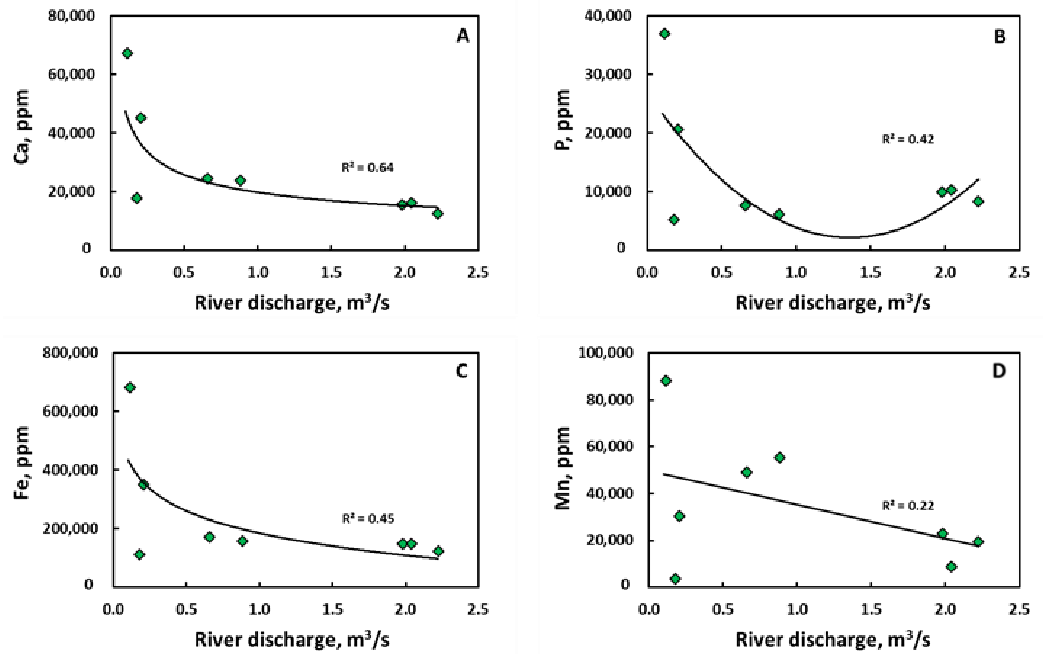

Figure 6. Major and trace element concentration ((**A**) Ca; (**B**) P; (**C**) Fe, and (**D**) Mn) in the RSM of the small tributaries of the Ob River as a function of river discharge. Significant ($p < 0.05$) trends are visualized via empirical logarithmic or power regression.

3.3. Annual Riverine Export of Major and Trace Elements in the Suspended Form

Using measured and interpolated monthly average chemical composition of RSM and tributaries, we attempted to calculate the annual suspended yield of major and trace elements by the Ob River in its middle course and by two small tributaries (Table 2). Thanks to a rather regular sampling of the Ob River, the monthly average chemical compositions of the RSM are available, and estimated uncertainties on the annual yield do not exceed 20–30%. In contrast, there are sizable uncertainties on fluxes in small rivers, for which we do not possess full-year sampling. However, with reasonable interpolation between two adjacent seasons, we could obtain a preliminary estimation of elementary yields for small rivers. The minimal uncertainties on these values are 30 to 50%. Nevertheless, despite such a low resolution in sampling and high uncertainties, we identify clear differences in the annual yields of a number of elements (Table 2).

In the Ob River, the chemical composition of the suspended flux followed the order 'Si > Al > Fe > K > Ca > Mg > Na' and was dominated by Si, Al, and Fe. In contrast, in tributaries, the RSM was dominated by Fe, Mn, and Ca in the order 'Fe > Mn > Ca > Si > P > Al > Mg'. Consistent with this, the yields of P, Fe, Mn, and As were 2 to 10 times higher in the Rybnaya River compared to the Ob's main stem. At the same time, a number of lithogenic elements, toxic metals, and geochemical tracers (e.g., Si, Al, Ga, Ti, Cr, V, Ni, Cu, Zr, REEs, Th, U) exhibited an order of magnitude lower yield in the small tributaries compared to the Ob River main stem.

Table 2. Mean annual elementary yields (watershed-normalized export fluxes) (kg km^{-2} y^{-1}) of the Ob River and its two small tributaries.

	Ob	**Rybnaya**	**Andreva**
Si	2100	96.0	104
Li	0.282	0.0180	0.0160
Be	0.0241	0.00153	0.00114
B	0.384	0.0416	0.0204
Na	59.3	4.70	3.36
Mg	63.0	13.1	6.37
Al	515	49.8	43.5
P	21.1	58.4	13.3
K	170	8.75	6.18
Ca	141	122	32.6
Ti	29.4	1.35	1.59
V	1.65	0.118	0.0965
Cr	1.28	0.0720	0.0716
Mn	17.9	199	51.8
Fe	511	1050	250
Co	0.199	0.302	0.106
Ni	0.647	0.0520	0.0327
Cu	0.394	0.0339	0.0176
Zn	0.898	0.499	0.171
Ga	0.200	0.0265	0.0136
Ge	0.0121	0.00137	0.000868
As	0.223	1.49	0.132
Rb	0.151	0.0450	0.0217
Sr	1.11	0.947	0.269
Y	0.0701	0.0179	0.0106
Zr	1.03	0.0546	0.0585
Nb	0.152	0.00702	0.00790
Mo	0.00869	0.00410	0.00136
Cd	0.00448	0.00269	0.000734
Sn	0.0413	0.00410	0.00297
Sb	0.0155	0.00421	0.00209
Cs	0.00768	0.00308	0.00129
Ba	3.23	3.72	1.19
La	0.107	0.0232	0.0152
Ce	0.309	0.0541	0.0386
Pr	0.0377	0.00525	0.00409
Nd	0.160	0.0211	0.0162
Sm	0.0349	0.00439	0.00335
Eu	0.00788	0.00125	0.000838
Gd	0.0312	0.00445	0.00326
Tb	0.00436	0.000611	0.000450
Dy	0.0245	0.00343	0.00261
Ho	0.00447	0.000673	0.000472
Er	0.0124	0.00187	0.00140
Tm	0.00168	0.000270	0.000197
Yb	0.0106	0.00175	0.00130
Lu	0.00147	0.000254	0.000184
Hf	0.0386	0.00202	0.00231
Ta	0.0109	0.000463	0.000578
W	0.0243	0.00328	0.00162
Tl	0.00548	0.000592	0.000269
Pb	0.250	0.0541	0.0250
Th	0.0429	0.00620	0.00474
U	0.0232	0.00156	0.00108

4. Discussion

4.1. Total Concentration and Mineral Composition of the Ob's and Small Tributaries Suspended Load

A large river such as the Ob exhibits a much higher capacity to carry mineral-suspended material at high discharges during the spring flood as compared to the baseflow in winter and summer. This contrasts with the case of small tributaries, whose capacity to carry mineral loads is rather limited. This finding corroborates previous results for other regions of Western Siberia [50], where we demonstrated a positive link between $S_{watershed}$ and element concentrations in the RSM due to the enhanced capacity of large rivers for physical erosion of river banks and remobilization of riparian zone clay sediments, especially pronounced during high flow. In contrast to large rivers, small rivers of the WSL often flow within peat zones where the water flow does not interact with the mineral substrate [26]. This can explain an order of magnitude difference in RSM concentration between the Ob River and its tributaries during the high flow period of the spring flood. At the same time, elevated RSM concentration in small tributaries during lowest discharges observed in the present study is intriguing as it suggests the presence of some non-mineral phases that are either mobilized from still unfrozen sources such as upland bogs or formed within the water column under ice.

The mineral composition of suspended matter of the Ob River (Figure S5) main stem reflected a super-position of i) lithological control (clays, clastic minerals) from underlying rocks, ii) export by surface flow from soil and river bank erosion, and iii) certain processes within the water column, occurring differently during different seasons. Contrasting the mineral composition of the Ob River's suspended matter and that of its small tributaries may reflect the dominance of podzols in the forest soils of the Ob River and organic-rich histosols in the mires and bogs of Rybnaya and Andreva. The Ob River upstream of Kaibasovo research station receives a sizable amount of clastic mineral particles (quartz, feldspars, pyroxenes, amphiboles) due to the physical erosion of podzol soil mineral horizons. At the same time, the clay mineral composition of both the Ob River and small tributaries was rather similar, which reflects the spatial similarity of lithology in this region of the WSL. We do not exclude the possibility of peat erosion in the upland bogs as a source of minerals in the suspended matter of small rivers. A large variety of minerals have been identified in Western Siberian peat cores of detrital, clay, and authigenic origin [75]. For example, the quartz, feldspars, illite, and chlorite present in the TSS of Rybnaya and Andreva may have originated from the physical erosion of peat layers in the adjacent mires. However, the lack of sulfide minerals in the RSM samples collected in this study contrasts with their occurrence in the peat cores as reported in [75]. It is thus possible that either authigenic sulfides are dissolved and removed in the inland bog waters prior to exporting to the river outlet, or the role of sulfide mineral mobilization is negligibly small due to low runoff and a lack of intensive peat abrasion.

An intriguing finding is the sizable amount of calcite in the Ob River suspended matter during winter at low discharge (Figures 2G and S5). We tentatively explain the appearance of calcite as due to enhanced discharge of the groundwater that carried some amount of $CaCO_3$ particles. It is known that deep base rocks in the permafrost-free part of the WSL contain carbonate concretions, as also reflected by extremely high winter-time Ca and dissolved inorganic carbon (DIC) concentrations in large rivers [26]. Another possible explanation can be the freeze-out of the dominant riverine solutes ($Ca(HCO_3)_2$) and precipitation of $CaCO_3$ at the ice surface and in confined shallow water bodies of the riparian zone of the river. Calcium carbonate precipitation during the winter freezing of river waters is fairly well established in other parts of Siberia [76]. Presumably, much lower concentrations of Ca^{2+} and HCO_3^- ions in the water of Rybnaya and Andreva and the very weak connection of these rivers to the deep groundwater reservoirs, compared to the Ob River main stem, precluded the abundant formation/mobilization of calcite in the suspended load of these small tributaries. In contrast, high RSM concentration (30 to 70 mg L^{-1}) in small rivers during autumn baseflow (Figure S1A) cannot be linked to the presence of crystalline material, be it clastic or clay minerals, but rather reflect some autochthonous amorphous/semi-amorphous precipitates, which are formed due to underground-originated Fe(II) oxidation within the water column. Given the extremely high concentrations of particulate Fe and Mn in these rivers (300,000–700,000 and 30,000–90,000 ppm, respectively), the particulate phase can be entirely composed of amorphous Fe hydroxide with up to 10–30% of Mn hydroxide.

4.2. Chemical Composition of the Suspended Matter of the Ob River and Small Tributaries in Comparison to Other WSL Rivers and World Average

It is known that the chemical composition of the RSM across the world is comparable to that of the upper part of the continental earth crust or shale [13,23,77]. Former studies of the chemical composition of RSM across Central and Eastern Siberia demonstrated strong lithological control [78–82]. The lithological control, however, is less pronounced for the rivers draining through thick peat deposits located within abundant wetlands, as is the case in Western Siberia. The RSM of the small tributaries is impoverished in Cu, Zr, Tl, Pb, and U but enriched in P, Fe, Mn, Co, and As relative to the Ob River in its middle course. Compared to the average value for small and medium-size WSL rivers [50], the small tributaries of the Ob River are strongly enriched in Fe and Mn and, to a lesser degree, enriched in P and As. We believe that the extremely rich content of particulate Fe in the small tributaries derived from the groundwater influx in the hyporheic zone during the lowest discharge in autumn may provide a sizable flux of shallow anoxic groundwater and thus create a favorable environment for the generation of amorphous, OM-stabilized Fe-hydroxide particles due to oxidation of Fe^{2+} and Mn^{2+} and related to this P coprecipitation, as it was invoked for small and medium-size WSL rivers investigated during autumn baseflow [83]. In a large river such as the Ob, this underground signal of Fe hydroxides can be hidden by the high concentration of this element in riverine mineral particles originating from bank abrasion and sedimentary rock physical weathering. Note that coprecipitation of a number of mobile elements such as P, As, and Mo with Fe hydroxide, as also reflected by strong correlation with Fe in the RSM of sampled rivers (Table S5), may explain exceptional enrichment in these elements of the RSM in the tributaries compared to the main stem.

Further, in accordance with numerous previous observations in other parts of the WSL, an enrichment in Fe, Mn, P, and As may stem from the presence of a sizeable proportion of particulate organic matter in Western Siberia rivers [50] and the corresponding impoverishment of suspended matter in elements hosted by silicate (clay) materials [50]. Here, we would like to note that the world average value of the chemical composition of RSM may be biased because it is based on sampling of large rivers. These rivers are enriched in silicate mineral-dominated components because they carry higher proportions of suspended silicate material and smaller fractions of organic-rich particles. Strong enrichment of small- and medium-size permafrost-affected WSL rivers in general [50] and of small Ob's tributaries in particular (this study) in Fe, P, and Mn, together with high C_{org} concentrations (i.e., 10–25%, Ref. [84]), likely reflect the dominance of peat particles and vegetation debris in the suspended load. In addition, the RSM of small tributaries is strongly enriched in Mn hydroxide which is produced by Mn^{2+} oxidation in the surrounding lakes and bogs or formed authigenically in the water column as it was documented in rivers of Northern Europe draining forests and bogs such as the Kalix River [85,86].

The REE upper-crust (UC) normalized pattern of RSM from both the Ob River and its tributaries was rather flat with only a slight Eu–Gd maximum (Figure 7), which originated from feldspar dominance and is generally consistent with other large rivers across the world [13] and similar to the pattern typical for average WSL small- and medium-sized rivers [50]. In agreement with previous studies of permafrost-draining rivers, the Ob's RSM REE pattern reflects a highly homogeneous sedimentary rock substrate (silt and sand) dominating the WSL territory.

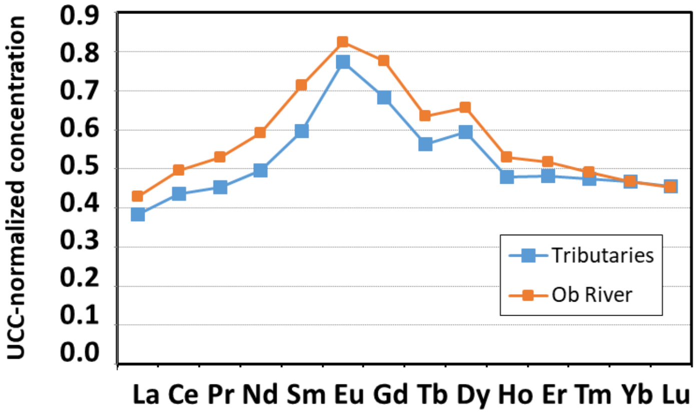

Figure 7. An upper-crust normalized REE pattern of the Ob River suspended matter (orange squares) and its small tributaries (blue squares).

4.3. Seasonal Variation of RSM Elemental Composition in the Ob River and Its Small Tributaries

There was a sizable contrast in the seasonal pattern of element concentration in the RSM between the Ob River and its small tributaries. Thus, Na, K, Si, Al, trivalent and tetravalent hydrolysates increased their concentrations in the RSM of the Ob River with an increase in discharge. This could reflect an enhanced proportion of lithogenic material carried by large rivers during spring floods, when the power of bank abrasion and flow velocity is the highest. This is a well-established feature of most boreal and subarctic rivers (see example for Severnya Dvina River in [24]). An interesting finding was that the concentration of alkaline-earth metals (Ca, Sr, Ba) also increased with decreasing discharge. This could be linked to the accumulation of these elements in the suspended calcite, which was formed during the freezing of $Ca(HCO_3)_2$ waters during winter baseflow at the lowest discharge, as discussed in Section 4.1. A number of other macro- and micronutrients and trace elements demonstrated progressive accumulation in the Ob River's RSM during winter (e.g., P, Cu, Zn, Mo, As, Cd, Sb). In addition to their coprecipitation with calcite (P, Zn, Cu, Cd), oxyanions ($P\text{-}PO_4$, Mo, As, Sb) could be delivered, first, in the dissolved form via deep groundwater discharge in the riparian/hyporheic zone of the river, and then, adsorbed onto surfaces of suspended solids, including carbonate minerals. This is further confirmed by positive Pearson correlations between the total concentrations of these elements and the proportion of calcite in the RSM. Particularly pronounced variability of these elements may reflect poor homogeneity of RSM in the wintertime.

Trace metal micronutrients (Rb, V, Co), Fe, and Cr exhibited a minimum of concentration in the suspended matter of the Ob River during summer, which could reflect both the uptake of these elements by biota in the water column and at the watershed, during baseflow (micronutrients) but also enhanced export during winter and spring compared to summer (Fe). The Fe content in the RSM was controlled by different processes during the winter baseflow and spring flood. Under ice, we hypothesize the formation of Fe(III) hydroxides (amorphous or semi-amorphous compounds, partially stabilized by organic matter), similar to what was observed during the late autumn period in the small tributaries, where suspended Fe concentration achieved 400,000–700,000 ppm. During the spring flood, elevated Fe concentrations were presumably linked to its transport in the form of both adsorbed onto or structurally associated with clays minerals.

In this regard, we note the particular role of chlorite; its concentration in the RSM increased with discharge, and its proportion in the RSM of the Ob River positively correlated with a large number of trace elements (e.g., Li, Be, B, Al, P, K, Ti, V, Cr, Fe, Co, Ni, Ca, Ge, Zr, Nb, Sb, Hf, Ta, Tl). Although pairwise correlations do not necessarily indicate causality, we do not exclude the major role of this mineral in the suspended transport of trace elements, both in the form of elements adsorbed on the surface and incorporated into the structure. Note that the other clay minerals in the Ob River RSM did not demonstrate sizable correlations with trace elements. The exception is smectite, which positively correlated with middle REE and Th. The mechanistic reason for these correlations—primary association in silicate rocks of the watershed or secondary adsorption [87] during mobilization from soils to the river—remains elusive, and its understanding requires in-depth microscopic and spectroscopic analyses combined with sequential leaching of riverine particles.

The seasonal evolution of elemental composition in the small tributaries was quite different from that of the Ob River main stem. A number of macro- and micronutrients (e.g., Mg, K, P, V, Cr, Ni, Cu, Zn, Rb, Mo) demonstrated minimal concentration in the RSM at moderate discharges during summer baseflow. Note here that Rb is known to replace K in vegetation tissues and some enzymes, and its behavior in boreal plants is extremely similar to that of K [88]. This could be linked to the biotic uptake of these elements both in the water column and at the watershed, which occurs during warm vegetative seasons and the maximal development of plankton and periphyton in the river. However, trivalent and tetravalent hydrolysates also exhibited a minimum concentration during summer. This temporal pattern of low mobility and insoluble trace elements could be explained by two maximal concentrations during the two most contrasting seasons: spring flood and late autumn baseflow (Supplementary Figure S6). During the spring flood, these elements are mobilized by high flow and partially stabilized within the suspended load in the form of organo-ferric and organo-aluminum amorphous compounds; some of them can be carried as peat particles, which are less present during summer baseflow. During late autumn–winter, the most likely carriers of TE^{3+} and TE^{4+} are amorphous/semi-amorphous Fe and Mn hydroxides, which are highly abundant in the suspended loads of small tributaries during this period of the year. The high affinity of trivalent hydrolysates such as REE to these solid phases is fairly well known [89].

The results of the present study open the possibility of relating the suspended load of the river to surrounding surface waters such as lakes and to atmospheric precipitation such as snow. On the one hand, we suggest the importance of RSM in controlling the silicate lithogenic material transfer by the Ob River, especially during spring flood, when sizable deposition of suspended matter may occur into the sediments of the floodplain lakes, as it was demonstrated in accompanying study of mineral composition of the floodplain lake sediments [90]. On the other hand, a significant fraction of fine silicate and carbonate material present in the snowpack of Western Siberia and originating from far-range atmospheric transfer [91,92] can be delivered to the river after snowmelt and contribute to the formation of riverine suspended load during freshet.

4.4. Annual Export of Particulate versus Dissolved Elements by the Ob River and Its Tributaries

In permafrost-free watersheds considered in the present study, export of solid particles from the soil to the river occurs via lateral flow through the soil, over surface flow in the forest floor, and by shallow groundwater discharge within the riparian or hyporheic zone [50]. During the winter period, deep underground water, connected to the river, becomes an important source of dissolved load [26]; however, the role of this connection in the formation of suspended loads remains elusive. The annual yields of major and trace elements were sizably different between the Ob River and its small tributaries (Figure 8; Table 2). This can be explained by the different sources of elements. Thus, clastic mineral mobilization from river bank abrasion in the large river strongly enriches its RSM in Si, Al, and lithogenic low mobile elements (trivalent and tetravalent hydrolysates), whereas shallow underground Fe-rich precipitates formed in the hyporheic zone of the small rivers under ice can host a large number of related elements (Mn, As, P). Moreover, due to the high concentration of DOM originating from wetland sources in small humic rivers, some elements that are typically found in the particulate phase (Al) can be strongly stabilized by organic complexes in the dissolved (<0.45 µm) form, thus decreasing the annual particulate yield compared to large rivers such as Ob, which is generally much poorer in DOC.

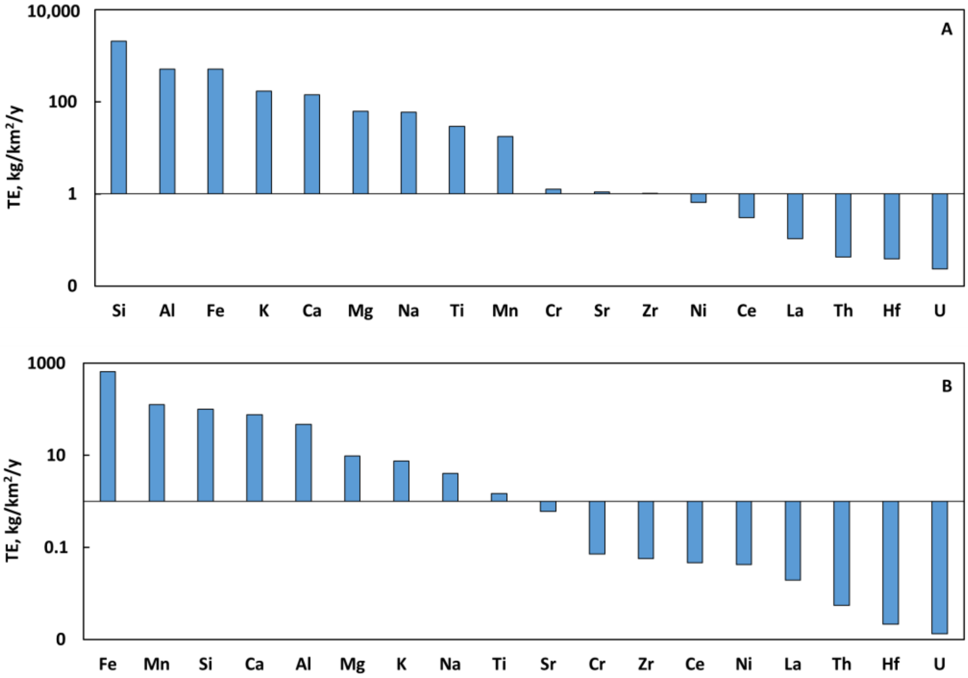

Figure 8. A histogram of annual yields (watershed-normalized fluxes) of some major and trace elements in the suspended matter (>0.45 µm) of the Ob River (**A**) and small tributary (**B**).

Compared to the annual dissolved (<0.45 µm) yield of major and trace elements by the Ob River in its middle course, as previously measured by our group [65], the results of the suspended yields demonstrated the following features. Soluble labile elements (Na, Ca, Mg, Sr, Ba, Zn, and U) exhibited < 30% of total (particulate + dissolved) annual export in the particulate form. These elements mark the presence of carbonate rocks in the groundwater and demonstrated especially high dissolved export during the winter period. Silica, K, Rb, heavy metals of high affinity to DOM (Cu, Ni), As, and Sb were transported in both dissolved and particulate form (the share of particulate form ranged from 30 to 90%). The high share of particulate export of these biogenic elements may stem from the role of plant litter and vegetation debris, especially pronounced during the spring flood. Finally, low-soluble trivalent and tetravalent hydrolysates (Al, Fe, Y, REEs, Ti, Zr, Hf, Th) and elements exhibiting high affinity to Fe hydroxides (P, Cr, V, Co) or clays (Cs, Cd) were entirely (>90%) transported in the suspended form.

It is important to note that these features of element transport by the Ob River in its middle course are different from particulate vs. dissolved flux partitioning in small- and medium-sized WSL rivers, draining both in permafrost-free and permafrost-bearing peatlands [50]. Although the estimations of [50] across the WSL territory may be biased due to a lack of winter-period sampling, a number of factors may be responsible for the observed difference in element export between the Ob River and the small rivers of the WSL. In the latter case, much larger amounts of trace metals were transported in the dissolved rather than suspended form, due mostly to: (1) lower concentration of RSM in small rivers compared to Ob; (2) essentially organic rather than mineral silicate nature of RSM in small rivers compared to Ob; (3) much higher concentration of DOM and relevant organic and organo-mineral colloids, carrying insoluble trace elements in small rivers and lack of these colloids in the DOM-poor Ob River. Furthermore, in the Ob River, an overwhelming role of particulate Fe and Mn hydroxide, accommodating a large number of both low soluble (TE^{3+}, TE^{4+}) and mobile (P, As, Sb) elements during the long winter period, may strongly shift the overall export from dissolved to particulate forms. It is clear that further assessment of high-frequency (at least, bi-weekly) sampling of RSM in small and medium-sized WSL rivers is needed to fully constrain the partitioning of major and trace elements between solid and aqueous forms.

Under ongoing climate warming, we can hypothesize a certain evolution of the suspended element fraction over the dissolved form. With warmer winters and higher baseflow discharge, one can expect an increase in water connectivity between deep underground reservoirs and rivers. Although this will essentially occur in the northern part of the WSL [61], similar tendencies are observed in the permafrost-free zone of high latitudes. This may increase the input of dissolved elements, thereby further decreasing the share of particulate forms in total element export, not only by the Ob River middle course but also by its small tributaries, as already noted across the territory of Western Siberia [50] and further confirmed in the present study of permafrost-free rivers draining through taiga and peatlands.

5. Conclusions

To better understand natural factors shaping the river suspended matter and quantify the annual yield of particulate elements in pristine boreal taiga/wetland regions, we studied the mineral and chemical (major and trace elements) composition of RSM collected in the Ob River middle course and its two small tributaries across the main hydrological seasons. In addition to traditional sampling during the 6-month open water period, here we unprecedentedly collected suspended material during several months of the winter baseflow period, under ice. The obtained results confirmed the first hypothesis of this study, which focused on the sizable contrast in mineral and elemental composition of the suspended matter of the Ob River compared to that of its small tributaries. We discovered extremely high concentrations of particulate Fe and Mn in small humic rivers during winter baseflow, presumably linked to amorphous, organically bound Fe and Mn hydroxide precipitation in the water column, fed by the discharge of metal-rich anoxic shallow groundwater. We also confirmed the second hypothesis on the systematic evolution of both the mineralogical and chemical composition of the RSM over the course of the year, as we found extremely high concentrations of calcite in the Ob River suspended matter during winter, under ice. This could be tentatively linked to $CaCO_3$ enrichment due to deep groundwater discharge, most pronounced during baseflow, or carbonate mineral precipitation during ice formation and freeze-out of dominant solutes in the river water. The proportion of sodium feldspar and illite increased with an increase in discharge, whereas the proportion of chlorite decreased. A number of macro- and micronutrients demonstrated minimal concentration in the RSM at moderate discharges during summer baseflow: Mg, K, P, V, Cr, Ni, Cu, Zn, Rb, and Mo, which could be linked to biotic uptake of these elements both in the water column and at the watershed. Similar behavior was observed for trivalent and tetravalent hydrolysates, which could be controlled by OM-enhanced transport during spring flood and Fe and Mn hydroxide-enhanced transport during winter, with minimal concentrations during the summer baseflow.

The annual elemental yield (watershed area-normalized downstream export flux) in the suspended form was drastically different between the Ob River main stem and small tributaries. This could be related to both different sources of particulate matter, namely soil and bank erosion and underground water discharge in Ob, and feeding from upland bogs in small tributaries. We stress the importance of the winter ice-on period for shaping element speciation in the suspended matter and assessing particulate element export in this permafrost-free part of Western Siberia. This calls for a need for more complex, microscopic, and spectroscopic studies of amorphous organic, metal-rich particles, and nanoparticles dominating the suspended and dissolved loads of wetland-affected Siberian rivers during winter.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15040633/s1, Figure S1: Mass percentage of different minerals in the RSM of two small tributaries of the Ob River as a function of river discharge; Figure S2: Elements, showing lack of discharge-concentration dependence in the RSM of the Ob River during winter, spring flood, and summer baseflow; Figure S3: Major and trace element concentration in the RSM of the small tributaries of the Ob River as a function of river discharge; Figure S4: Major and trace element concentration in the RSM of the small tributaries of the Ob River as a function of river discharge; Figure S5: Seasonal pattern of total suspended solid (A) and mass percentage of different minerals (quartz, (B); albite, (C); chlorite, (D); illite, (E); smectite, (F); calcite, (G) in the RSM of the Ob River. Figure S6: Seasonal pattern of element concentration in the RSM of the Ob River. Table S1: Mineralogical composition of sediments and RSM concentration in the Ob River and tributaries; Table S2: Chemical composition of sediments and RSM concentration in the Ob River and tributaries; Table S3: Mann-Whitney (U-test) for the difference in mineralogical and chemical composition of the RSM from the Ob River main stem and two small tributaries; Table S4: Pairwise Pearson linear correlation between element concentration in the RSM of the Ob River and percentage of constituting minerals; Table S5: Pairwise Pearson linear correlation between element concentration in the RSM of the Ob River and small tributaries. Table S6: Mann-Whitney (U-test) for the difference in mineralogical and chemical composition of the RSM from the Ob River main stem by seasons. Significant ($p < 0.05$) differences are shown by red color. TSS is total suspended solid.

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