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Export fluxes of dissolved, colloidal and particulate organic carbon, major and trace elements from the Ob River and its tributaries across seasons

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ABSTRACT

Riverine export fluxes of organic carbon (OC), major and trace elements remain at the forefront of environmental research in Arctic and subarctic regions, due mostly to high sensitivity of river hydrochemical parameters to climate warming and, at the same time, global importance of OC, nutrients and toxicants delivered by rivers to the Arctic Ocean. In contrast to reliable information on export fluxes of carbon and metals from the mainland to the Arctic Ocean by large and mid-size Arctic rivers, the majority of these studies quantify either dissolved ($< 0.45 \mu\text{m}$) or particulate suspended matter (PSM) fluxes, without mechanistic analyses of element speciation in most labile, low molecular weight (LMW) or colloidal form. Here we assessed colloidal versus LMW ($< 3 \text{ kDa}$) and suspended ($> 0.45 \mu\text{m}$) export of OC, major and trace elements in a large Siberian river (Ob) and its smaller tributaries, situated within a boreal taiga / wetland zone. The main differences between Ob and its small tributaries are (i) higher dissolved OC and dissolved and particulate Fe concentrations in tributaries, due to input from surrounding bogs, (ii) much higher PSM load (clays) in the large river (Ob) compared to smaller tributaries; and (iii) strong underground water input for the Ob River, especially during baseflow, which is less pronounced for its tributaries. These major environmental factors were largely responsible for specific features of colloidal vs particulate export for the Ob River and its tributaries.

Annual export fluxes normalized to the watershed area (yields) were similar for most elements in dissolved ($< 0.45 \mu\text{m}$) fraction between the Ob and the tributaries, exempting Fe, Mn, Co and Zn which were higher in tributaries essentially due to input from wetlands. Export of Mo, V, W and U was higher in the Ob River due to pronounced groundwater influence. Colloidal (3 kDa – $0.45 \mu\text{m}$) yields were also generally higher in the tributary compared to Ob, except for those soluble elements of groundwater input (Sr, Mo, W, U). The particulate suspended ($> 0.45 \mu\text{m}$) yield of all elements, except Mn, was much higher in the Ob River when compared to its smaller tributaries. Overall, elemental fluxes of small wetland-draining tributaries of the Ob River can be considered analogous to the small rivers of the permafrost-free portion of the Arctic coast. Such small rivers are more sensitive to processes occurring at the watershed level, hence being an efficient potential sentinel for environmental changes. Fluxes in large Arctic coast rivers are more conservative and are strongly controlled by the effects of PSM interaction with river water at high flow and groundwater loading at base flow. Global significance of our findings is that elemental dissolved ($< 0.45 \mu\text{m}$) yields of small Arctic rivers draining coastal wetlands and boreal forests can be adequately (within a factor of 2 to 3, comparable to inter-annual variations and uncertainties) approximated by those currently available for mid-sized and large rivers.

1. Introduction

Biogeochemistry of dissolved organic carbon, major and trace elements in large Arctic rivers has remained at the forefront of Arctic

research for more than two decades due to the high importance of soluble and suspended particulate fluxes for Earth's carbon and nutrient cycles and the strong vulnerability of lotic systems in high latitudes to on-going climate warming (Gordeev et al., 1996, 2004; Dittmar and

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Kattner, 2003; Holmes et al., 2000, 2001; Tank et al., 2012; Drake et al., 2018; Kipp et al., 2020; Larkin et al., 2021; Moskovchenko et al., 2024). The majority of available studies characterize fluxes of dissolved and particulate elements in all large (Holmes et al., 2012; Gordeev et al., 2024; Juhls et al., 2025) and several mid-sized (Bagard et al., 2011; Chupakov et al., 2020, 2023; Pokrovsky et al., 2010, 2022b) Arctic rivers with sufficient seasonal resolution, which allowed for revealing factors controlling C, nutrients and trace element mobilization from the watershed to the river during different seasons and flow regimes.

Unlike large Arctic rivers, smaller river catchments in high-latitude regions—whose numbers increase as size decreases—remain significantly understudied on a seasonal scale. This is primarily due to limited access and logistical challenges associated with regular sampling throughout the year. This is particularly true for the vast Siberian territories, encompassing both permafrost and permafrost-free taiga zones, where most research has focused on summer snapshot campaigns (e.g., Pokrovsky et al., 2006, 2022a; Stolpman et al., 2022). Notable exceptions include seasonally resolved studies on organic carbon (Gandois et al., 2021) and silica export (Pokrovsky et al., 2013). Other available studies of multi-elemental riverine export from small Siberian catchments have dealt with an open-water period of one year (Krickov et al., 2019; 2020; Pokrovsky et al., 2020), therefore neglecting the potentially important, six-month long, winter segment. For these reasons, comparison, in terms of yield of major and trace solutes between large and small rivers, has not been performed sufficiently. Thus, there has been no extrapolation of results between already studied large rivers and numerous smaller rivers, in both the boreal and subarctic zone. This study aims to address this knowledge gap by conducting year-round sampling to provide higher seasonal resolution for a large Arctic river—the middle course of the Ob River (watershed area: 262,000 km²)—and two of its small tributaries: the Andrevka River (catchment size: 257 km²) and the Rybnaya River (catchment size: 98 km²).

In what is conventionally called the ‘dissolved’ form of a solute in the river (< 0.45 μm), two geochemical pools can be distinguished: the first, low molecular weight (LMW) form, which includes ions and simple molecules less than a few kilodaltons (several nm), and the second — operationally defined as the ‘colloidal’ pool — having sizes ranging between several nm and 0.45 μm. Over past decades, sizeable research efforts were devoted towards characterizing OC, nutrient and metal distribution among aquatic colloids (Guo et al., 2001; Aiken et al., 2011; Aufdenkampe et al., 2011; Philippe and Schaumann, 2014; Gottselig et al., 2017; 2020; Cuss et al., 2020). In high-latitude regions, colloids have received particular attention given their importance as major carriers of C, micronutrients and toxic elements to the Arctic Ocean (Ingri et al., 2000; Stolpe et al., 2013b; Pokrovsky et al., 2016b; Cuss et al., 2018; Jenssen et al., 2021; Wang et al., 2022; Chauhan et al., 2024). However, quantitative assessment of colloidal and LMW export of solutes to the Arctic Ocean is not yet possible. While for European mid-sized Arctic rivers (Severnaya Dvina and Pechora), the environmental factors controlling the OC and trace elements distribution among colloidal, dissolved and particulate pools have been recently characterized (Pokrovsky et al., 2010; Chupakov et al., 2020), the other rivers of the Arctic remain virtually unknown. A few exceptions are snapshot studies in Siberia, where the Yenisey tributaries (Pokrovsky et al., 2006; Bagard et al., 2011), Ob (Kolesnichenko et al., 2021) and the Lena River (Hirst et al., 2017; 2023) main stem and tributaries were characterized for some trace elements and Fe. Other examples include western Siberian rivers across a permafrost gradient (Krickov et al., 2019), some Scandinavian (Dahlqvist et al., 2004, 2007) and Canadian/Alaskan rivers (Stolpe et al., 2013a, b; Ghotbizadeh et al., 2022). In this regard, comparison between large and small rivers is especially important, chiefly because small rivers exhibit a disproportionately high discharge (Vonk et al., 2023), but also because their elevated Dissolved Organic Carbon (DOC), Fe and, potentially, colloidal yields (Brown et al., 2020; Pokrovsky et al., 2020). However, the colloidal versus dissolved and particulate export by small rivers is still poorly quantified, primarily due

to lack of high seasonal resolution from year-round measurements. Given the difficulty, if not virtual impossibility, of year-round access to small rivers in high latitudes of Siberia, here we chose small tributaries of the Ob River that can be representative of small rivers in the permafrost-free part of the Arctic, or those draining to mires and lakes and otherwise not integrating their signal to a large river. Primarily, we aimed at assessing mean multi-annual dissolved (< 0.45 μm) yields of major and trace elements in a large Siberian river and its smaller tributaries by comparing these yields with those of large and mid-sized rivers of Northern Eurasia. The second aim of this study was to quantify the relative contribution of LMW<sub>3 kDa, colloidal (3 kDa – 0.45 μm) and particulate (> 0.45 μm) forms of OC, major and trace elements, including micronutrients, toxicants and geochemical tracers in both a large Siberian river (the Ob) and its smaller tributary.

We hypothesized that strongly pronounced groundwater versus surface water input of a large river compared to a small tributary, coupled with sizable transport of PSM by the former, will control the seasonal pattern of the relative share of colloidal, low molecular weight and particulate export of carbon and other elements. We also hypothesized that variations in the elemental composition of colloids, reflecting their chemical nature and source, would primarily depend on river size and be influenced by the balance between hyporheic discharge and surface runoff from bogs, which varies seasonally. Through selecting a large boreal river and its smaller tributaries at a location with similar climate conditions and forest/wetland coverage of the watershed, we anticipated revealing the factors controlling element export at the watershed scale. We also expected to be able to extrapolate calculated annual yields of the main pools of elements to still unknown small rivers of high latitudes therefore allowing better constraining the overall export of dissolved, colloidal and particulate matter from the land to the Arctic Ocean at the scale of entire Northern Eurasia.

2. Methods

2.1. Environmental context of the Ob River middle course and its small tributaries

The middle course of the Ob River belongs to the boreal taiga biome. At Kaibasovo (INTERACT Research Station), the Ob River has a watershed of 260,000 km² including permafrost-free taiga forest and wetlands. The main stem was sampled in the vicinity of the research station (57.246 °N, 84.184 °E, Fig. 1). The mean annual temperature is −0.1 °C with an annual precipitation of 590 mm in 2017–2018. The soils are predominantly alluvial and are overlain by a humic layer (~30 cm) including fluvisols, podzols, and histosols. Two small right tributaries of the Ob River, located approximately 10 km upstream of the main stem sampling point, originating from upland peat bogs and draining through typical taiga forest were also chosen for regular sampling. The Andrevka River has a watershed of 257 km² and a mean annual discharge of 2.3 m³ s⁻¹. Its catchment includes birch-pine forest on wetlands (56 %), *Larix* 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 ($S_{\text{watershed}} = 98 \text{ km}^2$; mean annual discharge is 2.0 m³ s⁻¹) originates in a large bog in upland of the second Ob terrace and is also covered by birch-pine forest on wetlands (67 %), mixed pine-birch forest (20 %), fir-pine forest (5 %), and meadows (2 %). In both catchments, soils are histosols on peatlands (67 %), alluvial (5 %), and podzols (28 %). The significantly higher annual runoff (2 ×) of the Rybnaya River compared to the Andrevka River may be attributed to the higher proportion of wetlands and lower meadow coverage in the Rybnaya watershed. This difference likely results in much lower evapotranspiration in the Rybnaya River watershed.

Daily and monthly discharges of the Ob River at Kaibasovo Station were assessed via extrapolation from gauged stations associated with the Russian Hydrological Survey Nikolskoe, located 11 km upstream of Kaibasovo. Typical uncertainty of Ob River discharge is between 1 and 5

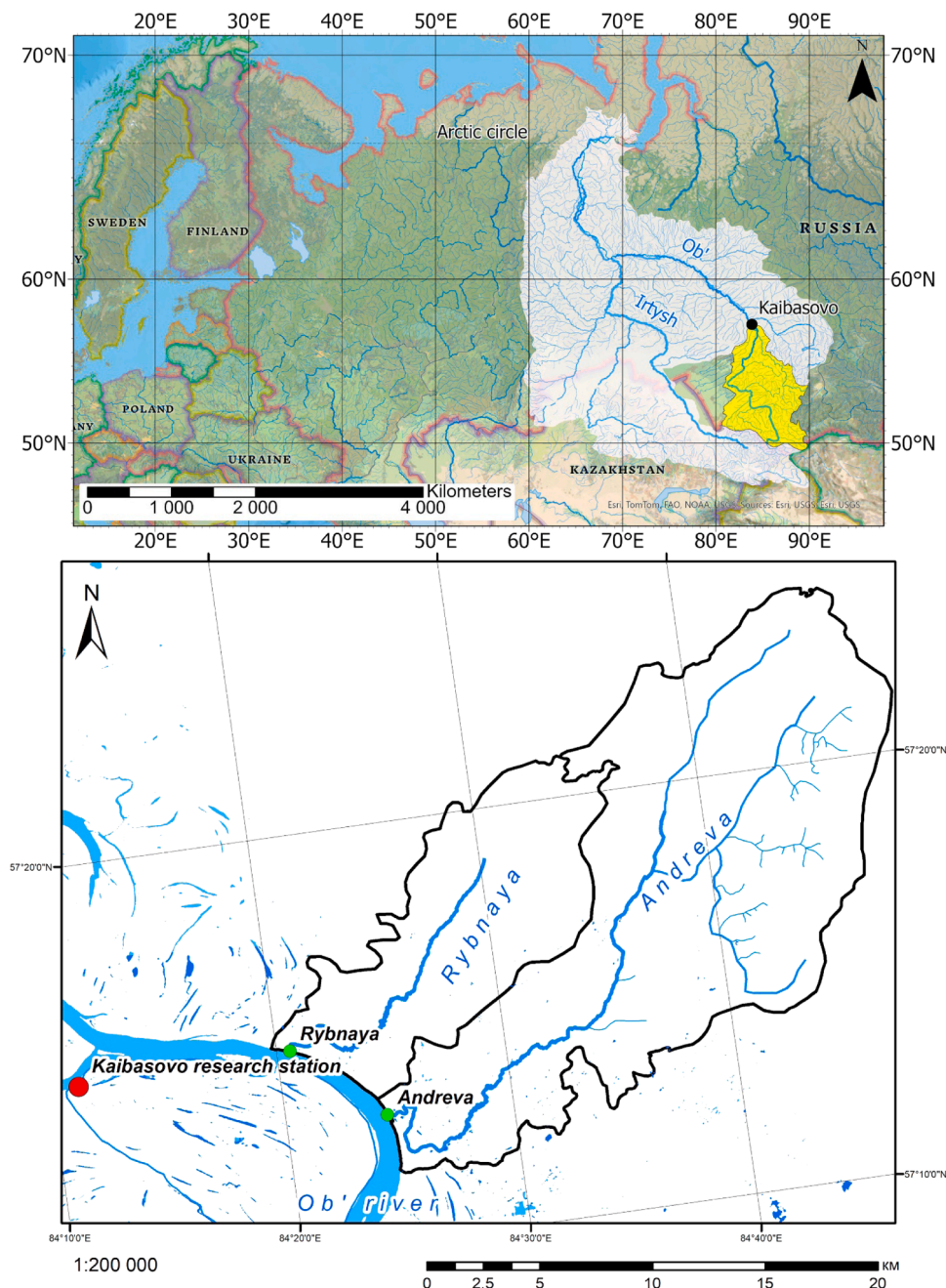


Fig. 1. Map of the study site including the watershed of the middle Ob River (yellow area in the upper panel), and its two small tributaries, the Andreva and the Rybnaya Rivers (bottom panel). Sampling sites are shown by red and green circles (Ob and tributaries, respectively).

%. The discharges of the Andreva and Rybnaya River were modelled using analogous gauged rivers of the region, with similar size and land cover in terms of forest, wetland and lake proportion on the watershed as described in details elsewhere (Krickov et al., 2022). In brief, for constructing the hydrograph of two small Ob's tributaries, we used four gauged rivers of similar environmental context (elevation, land cover, type of soil and vegetation) located within 50 km of Kaibasovo: Latat (46 km length, 296 km² watershed area), Itatka (64 km, 411 km²), Kuzherbak (65 km, 513 km²) and Oyash (88 km, 1240 km²) whose daily discharges are available from Russian Hydrological Survey. Estimated uncertainty on these discharges are between 10 and 15 %, which is linked mostly to difficulties in approximating discharge during peak spring flood and autumn rains.

2.2. Water sampling procedure

During the period May 2016 – September 2019, we collected about 320 samples from the middle of the Ob River and the middles of the Andreva and Rybnaya Rivers, all at approximately 0.5 m depth. Over this period, we sampled for the dissolved (< 0.45 μm) composition 1–9 times per month during winter baseflow (November to April), 2–30 times per month during spring flood (April –June), 5–30 times per month during summer (July and August) and 3–10 times per month during autumn (September–October). An additional 2–18 samples per month were collected during baseflow, 1–13 times per month were collected during spring flood and 1–2 times per month were collected during autumn. River suspended matter was collected using pre-weighed polycarbonate filters (0.45 μm) in order to measure the total suspended sediment (TSS) concentration. Colloidal separation was

performed on 0.45 µm filtered waters, typically once per month, over the entire year of 2018 on Ob and Andreva.

2.3. Sampling and analyses of particulate suspended matter (PSM)

Sampling of particulate suspended matter from the Ob and Andreva Rivers was performed in the same sites as dissolved fraction collection, as described in details elsewhere (Krickov et al., 2018, 2020). In brief, 30 to 50 L of water were collected in pre-cleaned barrels from the middle of the river at 0.5 m depth and the PSM was separated via frontal filtration using an Inox, Teflon® PTFE-coated filtration unit (AISI 304; Fisher Bioblock). This unit was fitted with 142 mm Sartorius membranes (0.45 µm; acetate cellulose) and operated at 5 bars. A peristaltic pump (MasterFlex B/T) with Teflon tubing created an average flow rate of 1–2 L/h. Collected PSM was then immediately frozen and freeze-dried upon arrival to the laboratory.

Elemental composition of the PSM was assessed via full acid leaching in a clean room (class A 10,000) followed by ICP-MS (Agilent 7500 ce) analyses using methods for organic-rich natural samples employed in GET laboratory (Toulouse) which are described in detail in Krickov et al. (2020). We used Mars 5 microwave system (CEM, France) to digest the PSM via a mixture of concentrated HNO₃, HCl and HF. To control the accuracy of analyses, we used 2711a Montana II Soil standard and LKSD sediment as certified samples. The concentration of major and trace elements (TE) in digestion products was measured using an ICP-MS Agilent 7500ce with ~3 µg/L of In and Re as internal standards. Uncertainty for TE measurement ranged from 5 % at 0.1–100 µg/L to 10 % at 0.001–0.01 µg/L. In addition to total chemical analysis using acid digestion, the PSM was analyzed for total Si and Al; wet chemistry was used with photometric detection after fusion of a 20 mg sample with borax in Pt crucibles. Detection limits were 0.02 mass % for Al and 0.04 mass % for Si, with an uncertainty of 3 to 4 %.

2.4. Analyses of river water solutes

Electrical Conductivity (E.C.) and pH were measured using a Hanna HI991300 conductivity meter and a WTW portable pH meter with combined electrode. DOC and DIC concentrations were measured by Shimadzu TOC-VCSN analyzer, using methods for boreal organic-rich water samples (Chupakov et al., 2020). Major anion concentrations (Cl and SO₄) were measured by ion chromatography (HPLC, Dionex ICS 2000) with an uncertainty of 2 %. Filtered solutions for major and trace element analyses were acidified (2 %) with ultrapure HNO₃ and were stored in pre-washed HDPE bottles. The preparation of bottles for sample storage was performed in a clean bench room (ISO A 10,000). Blanks were performed to control the level of pollution induced by sampling and filtration. Major cations (Ca, Mg, Na and K), Si, and TE were determined with an ICP-MS Agilent ce 7500 with 3 µg L⁻¹ of In and Re as internal standards and 3 external in-house standards. These were placed each 10 samples per series of river water. The Milli-Q blanks were routinely processed to monitor for any potential contamination introduced by our sampling and handling procedures. Detection limits (d.l.) of trace elements were determined as 3 times the blank signal. Specifically, the d.l. was ≤ 0.1–1 ng L⁻¹ for Cd, Ba, Y, Zr, Nb, rare earth elements (La–Lu), Hf, Pb, Th and U; 1 ng L⁻¹ for Ga, Ge, Rb, Sr and Sb; ~ 10 ng L⁻¹ for Ti, V, P, Cr, Mn, Fe, Co, Ni, Cu, Zn and As). The typical uncertainty for elemental concentration measurements was 5 % at 1–1000 µg L⁻¹ and 10 % at 0.001 – 0.1 µg L⁻¹. The SLRS-6 (Riverine Water Reference Material for Trace Metals certified by the National Research Council of Canada) was used to check the accuracy and reproducibility of analyses (Yeghicheyan et al., 2019).

2.5. Ultrafiltration via centrifugation for assessing colloidal forms of elements

For size fractionation procedure and assessing colloids versus LMW

forms, the river water was first filtered through disposable sterile Nalgene filter unit (0.45 µm, regenerated cellulose). The filtrate was subjected to centrifugal ultrafiltration through pre-cleaned 3 kDa single-used Amicon Ultracell cartridges. See description of the preparation and cleaning procedure and discussion of possible artifacts of ultrafiltration in Oleinikova et al. (2017). Prior to sample filtration, the cartridges were rinsed 3 times by Milli-Q water (3 × 15 mL). We verified that the DOC and trace metal blanks were 3 to 10 times lower than the minimal concentrations of these components in the river water samples. The first portion of the sample filtrate (15 mL) was discarded. In centrifugal ultrafiltration (UF) devices, no retentate remains after the filtration process. However, we confirmed that the concentrations of DOC, Fe, Al, and other trace metals in the permeate were consistent regardless of the volume of solution filtered, similar to findings with other frontal filtration techniques (Iliina et al., 2013; 2016). This indicates that there were no sorptive losses for trace elements, which could otherwise lead to an overestimation of colloidal abundance. One fraction of the filtrate was acidified for ICP MS analysis, and another one was used for DOC analyses. The centrifugal ultrafiltration was run at 20 °C using Eppendorf 5920 centrifuge (4000 rpm, 20 min). All filtrations and colloidal separations were run in a protected laboratory environment within 24 h of collection from the river. The proportion of colloids in the dissolved (< 0.45 µm) fraction of the river for a trace element (TE) was calculated as

$$([\text{TE}]_{<0.45\mu\text{m}} - [\text{TE}]_{<3\text{kDa}}) / ([\text{TE}]_{<0.45\mu\text{m}}) \times 100\%$$

Note that while dissolved and particulate suspended (> 0.45 µm) concentration and fluxes were assessed for all three rivers (Ob, Andreva and Rybnaya), the colloidal and LMW fraction was measured only on the Ob and Andreva Rivers.

2.6. Data treatment and flux calculation

Element export fluxes were calculated based on measured (Ob) or calculated (Andreva and Rybnaya) discharges at the site of sampling and concentrations over the period of observation (May 2016 – September 2019 for Ob; August 2017 – September 2019 for Andreva and Rybnaya). Based on these data, we first estimated the daily load (mass of component day⁻¹) obtained from a time series of paired river flow and constituent concentration data, then calculated mean monthly loads. Annual element fluxes were estimated using thus calculated monthly element loads. The more common LOADEST approach (Holmes et al., 2012) could not be applied due to an insufficient number of measurements throughout the year, particularly for the tributaries. However, the similarity of this method to LOADEST for flux estimation has been demonstrated in other Arctic and subarctic rivers, such as the Severnaya Dvina (Chupakov et al., 2020) and the Taz (Pokrovsky et al., 2022b), where extensive coupled hydrochemical and daily discharge data were available over several consecutive years. Based on obtained size fractionation data on river solutes, we also calculated the mean monthly concentrations of all measured solutes in the < 0.45 µm and < 3 kDa fractions, which allowed for quantification of monthly and annual export flux of the colloidal, dissolved and particulate suspended forms of major and trace elements.

3. Results

3.1. Dissolved (< 0.45 µm) element dependence on river discharge

For both the Ob River and its tributaries, the maximum discharge occurred during the spring flood in May, while the minimum discharge was observed in February–March. However, the Ob River exhibited significant inter-annual variations in peak discharge timing (Fig. S1 of the Supplement). The seasonal dynamics of major and trace element dissolved (< 0.45 µm) concentrations demonstrated 3 groups of solutes.

These groups were distinguished via examining the Pearson correlations between element concentration and discharge (Table S1). They were detectable in both the Ob River and its tributaries, although some elements differed between the main river and each of the tributaries. Group 1 was represented by highly mobile elements and demonstrated maximal concentrations in winter during low discharges and minimal concentrations in spring flooding and autumn rains during high discharges. It included major anions (Dissolved Inorganic Carbon (DIC), Cl, SO_4), alkali, alkaline earth metals, and trace (oxy)anions [B, Ge, As, Mo, and U^{VI}] (Fig. 2). Group 2 included elements having maximal concentration during the spring flood (May) and positively correlated with discharge: DOC, trivalent and tetravalent hydrolysates (Al, Ti, Fe, Nb, Y, Zr, REEs, Zr, Hf and Th) as illustrated in Fig. 3. A number of elements also belonged to transitional Group 3 as they combined features from groups 1 and 2 in terms of their concentration dependence on discharge, or they did not exhibit any specific seasonal dynamics and their concentrations were independent of river discharge: P, Ni, Rb, Cd, Cs, W, Tl and Pb. High concentrations of dissolved iron were observed during

winter baseflow (Fig. S2 of the Supplement), similar to elements of the Group 1. Redox-sensitive Mn had maximal concentrations ($> 1000 \mu\text{g L}^{-1}$ in the tributaries) during baseflow in winter and summer and generally decreased during spring flood.

3.2. Mean annual element concentration and export fluxes ($< 0.45 \mu\text{m}$)

The primary difference in mean annual concentration of the main stem and two tributaries is a factor of 2 to 4 higher DOC, P and Si and a factor of 10 to 40 higher Fe, Mn and Co concentrations in both tributaries compared to the Ob River (Table 1). In contrast, the Ob River exhibited a factor of 2 to 5 higher mean annual concentrations of major cations (Na, Mg, Ca and K), and anions (DIC, Cl and SO_4), Sr and some trace anionic elements (V, Mo, Sb and W). Annual export fluxes (yields) of the Ob River and its tributaries also exhibited systematic differences (Table 2). Dissolved organic C, Si and P and a number of TE, including divalent heavy metals and low solubility-low mobility hydrolysates (Ti, Cr, Co, Ni, Zn, Ga, Ge, As, Rb, Y, Zr, Nb, Cs, REEs, Hf, Pb and Th)

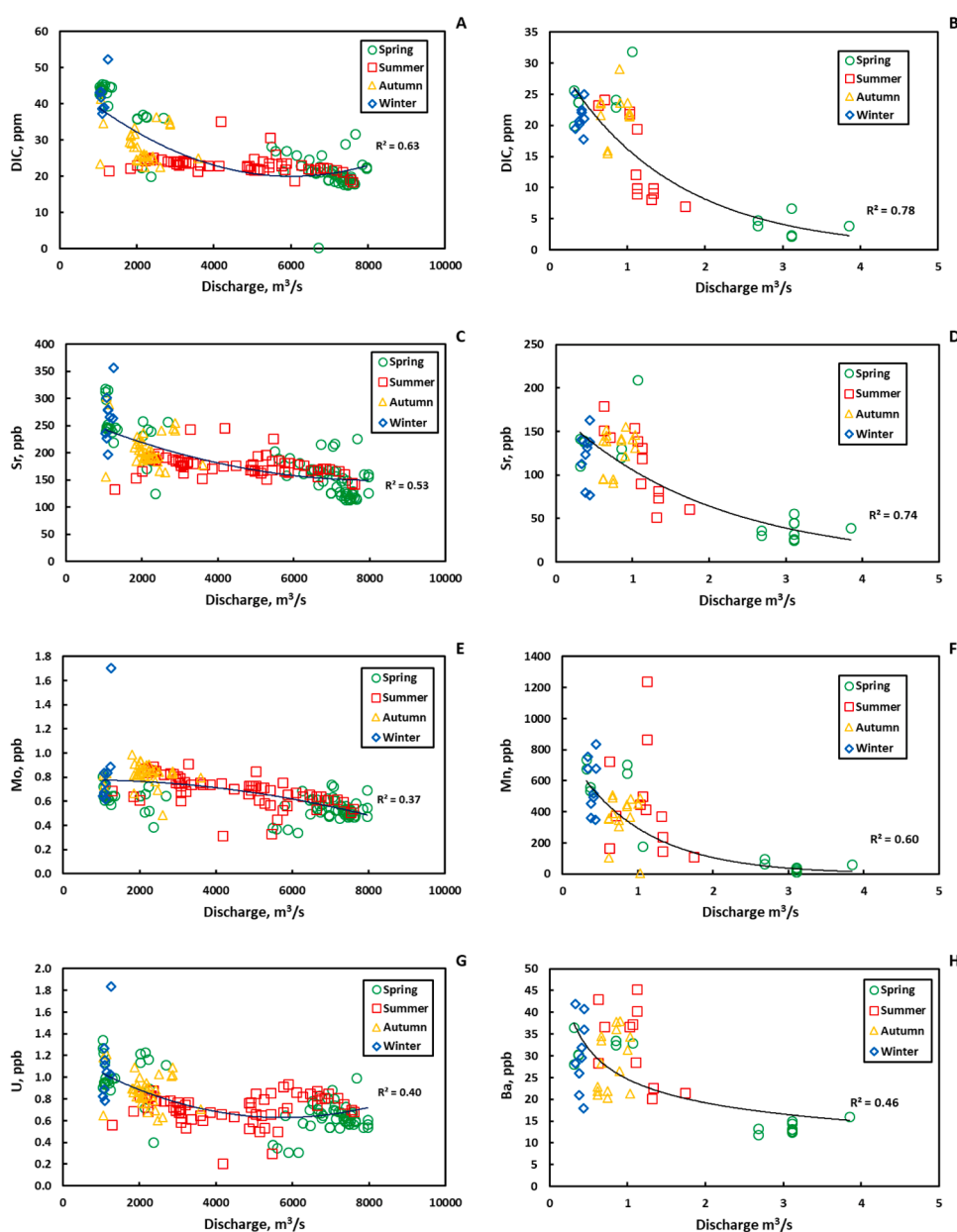


Fig. 2. Examples of first group element concentration plotted as a function discharge over entire observation period in the Ob (left column) and Andreeva (right column) for DIC, Sr, Mo (Ob and Andreeva), Mn (Andreeva), U (Ob) and Ba (Andreeva).

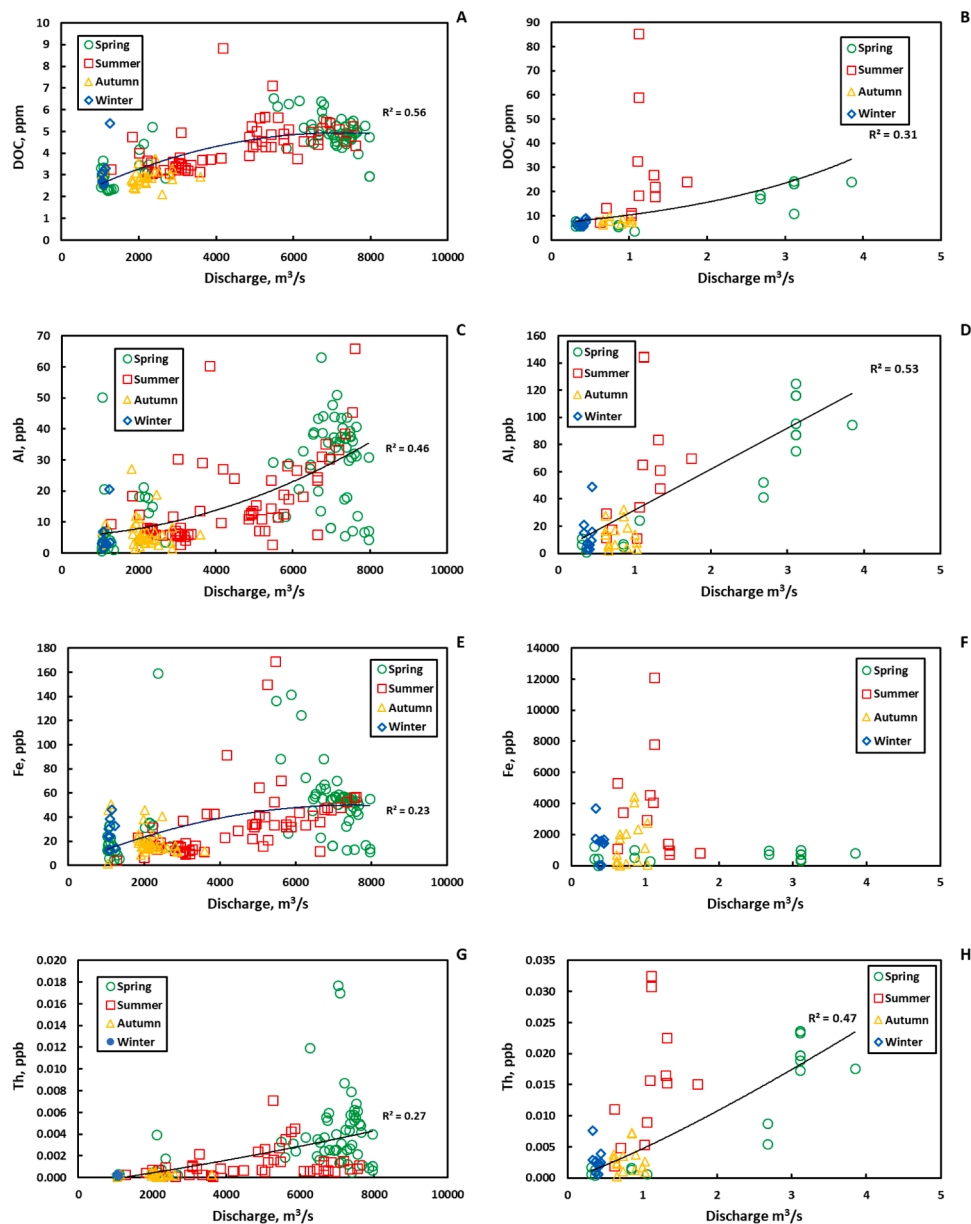


Fig. 3. Examples of second group element concentration plotted as a function discharge over entire observation period in the Ob (left column) and Andreeva (right column) for DOC, Al, Fe, and Th.

exhibited less than a factor of 2 to 3 difference in annual yields. At the same time, inter-annual variations of mean monthly yields for the same river achieved a factor of 1.5 to 3.0 for both labile groundwater-originating elements and surface export-dominated, colloidal-controlled trace metals (Table S2).

Mean annual yields of the Ob, Rybnaya and Andreeva rivers are generally consistent with previous estimations of major and trace elements for the Ob River (Vorobyev et al., 2019) and three mid-sized Arctic rivers that have been assessed using high frequency multi-annual sampling (the Severnaya Dvina, Pechora and Taz rivers; Chupakov et al., 2020, 2023; Pokrovsky et al., 2022b) as detailed in Table S3. The yields are similar, within a factor of 3 to 5, for most elements among these rivers. The main difference is observed for Fe, Mn, Cr and U, which can be explained by a combination of lithology (i.e. carbonate rock compositions for Severnaya Dvina and Pechora rivers) the proportion of wetlands and forest within the watershed and permafrost coverage. This information is detailed in Section 4.2.

Unfortunately, obtained yields of the Ob, Rybnaya and Andreeva

ivers cannot be compared with those measured exclusively for the open-water period in western Siberia across a large permafrost gradient (Pokrovsky et al., 2020). In Pokrovsky et al. (2020), the contribution of the 6 month winter period has not been taken into account, which can sizably underestimate the yield of soluble highly mobile elements, notably in the southern part of the Western Siberia Lowland (Frey et al., 2007; Pokrovsky et al., 2015). Similarly, a quantitative comparison between trace element yields measured in this study and those assessed for large Arctic rivers based on limited number of samplings per year, with an uncertainty as high as 50 % (Gordeev et al., 2024) is unwarranted. However, we note that yields for most major and trace elements of the Ob River's middle course are similar, within a factor of 2 to 5, to those of 4 large Arctic Rivers at their terminal gauging stations, as well as the mean of 7 Eurasian rivers (Taz, Pechora, Severnaya Dvina, Ob at Salekhard, Yenisei, Kolyma, and Lena; Table S3).

Table 1

Mean (\pm SD) annual concentrations of solutes ($< 0.45 \mu\text{m}$) of the Ob River and its two small tributaries Rybnaya and Andrevka. SD is standard deviation.

	Ob		Andrevka		Rybnaya	
	Mean \pm SD	N	Mean \pm SD	N	Mean \pm SD	N
DIC (ppm)	29.1 \pm 9.09	169	19.3 \pm 7.77	45	21.7 \pm 9.11	31
DOC (ppm)	3.76 \pm 1.13	169	12.4 \pm 9.78	45	14.7 \pm 13	30
Cl (ppm)	5.68 \pm 3.02	164	0.766 \pm 1.33	47	0.68 \pm 0.635	37
SO ₄ (ppm)	13.5 \pm 4.85	164	1.54 \pm 4.05	47	0.734 \pm 0.887	37
Li (ppb)	3.2 \pm 0.931	184	2.19 \pm 1.4	52	1.86 \pm 0.714	38
Be (ppb)	0.022	163	0.0115	52	0.0107	38
	\pm 0.0392		\pm 0.0147		\pm 0.0173	
B (ppb)	26.2 \pm 7.96	184	18.8 \pm 11	52	17.8 \pm 7.51	38
Na (ppb)	9520 \pm 2800	184	4940 \pm 2790	52	4650 \pm 1558	38
Mg (ppb)	7060 \pm 2060	184	3920 \pm 1330	52	3900 \pm 1390	38
Al (ppb)	25.3 \pm 72.7	184	28.1 \pm 28.4	52	19.2 \pm 21.2	38
Si (ppb)	2810 \pm 905	184	9300 \pm 2980	52	9320 \pm 3260	38
P (ppb)	21.9 \pm 12.6	176	124 \pm 96.2	47	159 \pm 167	36
K (ppb)	1580 \pm 1170	181	651 \pm 282	43	720 \pm 315	35
Ca (ppb)	33,800 \pm 7460	184	22,800 \pm 7150	52	26,600 \pm 9640	38
Ti (ppb)	0.509 \pm 0.854	183	0.888 \pm 0.388	52	0.846 \pm 0.389	38
V (ppb)	1.22 \pm 0.52	184	0.311 \pm 0.228	52	0.277 \pm 0.227	38
Cr (ppb)	0.214 \pm 0.189	183	0.284 \pm 0.154	52	0.276 \pm 0.185	38
Mn (ppb)	26.4 \pm 28	184	424 \pm 210	52	694 \pm 438	38
Fe (ppb)	32.7 \pm 24.2	184	1794 \pm 1657	51	2240 \pm 2480	38
Co (ppb)	0.0537	184	0.349 \pm 0.297	52	0.584 \pm 0.371	38
	\pm 0.0225					
Ni (ppb)	0.818 \pm 0.343	183	2.65 \pm 6.09	52	1.23 \pm 1.48	38
Cu (ppb)	1.82 \pm 1.95	184	0.557 \pm 0.623	52	1.1 \pm 1.94	38
Zn (ppb)	6.3 \pm 5.19	184	8.28 \pm 6.66	52	8.81 \pm 5.55	38
Ga (ppb)	0.0115	183	0.0224	52	0.030 \pm 0.016	38
	\pm 0.007		\pm 0.0107			
Ge (ppb)	0.00945	183	0.0135	52	0.0147	37
	\pm 0.004		\pm 0.013		\pm 0.022	
As (ppb)	1.29 \pm 0.496	184	1.51 \pm 1.12	52	4.3 \pm 4.7	38
Rb (ppb)	0.602 \pm 0.196	184	0.753 \pm 0.24	52	0.669 \pm 0.256	38
Sr (ppb)	203 \pm 53.8	184	120 \pm 40	52	130 \pm 43.8	38
Y (ppb)	0.0325	184	0.0717	52	0.049 \pm 0.043	38
	\pm 0.0179		\pm 0.054			
Zr (ppb)	0.0161	182	0.0634	52	0.0486	38
	\pm 0.0129		\pm 0.056		\pm 0.043	
Nb (ppb)	0.00124	169	0.0027	47	0.0021	37
	\pm 0.0012		\pm 0.0028		\pm 0.0022	
Mo (ppb)	0.693 \pm 0.177	184	0.108 \pm 0.186	52	0.123 \pm 0.202	37
Cd (ppb)	0.0214	184	0.017	52	0.0156	38
	\pm 0.0502		\pm 0.0237		\pm 0.0204	
Sb (ppb)	0.115	184	0.0368	50	0.0356	38
	\pm 0.0253		\pm 0.0347		\pm 0.0306	
Cs (ppb)	0.00213	184	0.00405	52	0.00276	37
	\pm 0.00097		\pm 0.00798		\pm 0.0013	
Ba (ppb)	25.8 \pm 4.79	184	29.3 \pm 7.71	52	34.3 \pm 12.1	37
La (ppb)	0.0238	184	0.0673	52	0.0337	36
	\pm 0.0219		\pm 0.0847		\pm 0.035	
Ce (ppb)	0.0393	184	0.116 \pm 0.116	52	0.0751	37
	\pm 0.0407				\pm 0.0804	
Pr (ppb)	0.00442	184	0.0107	52	0.00795	37
	\pm 0.0043		\pm 0.0095		\pm 0.0084	
Nd (ppb)	0.0187	184	0.0466	52	0.0337	37
	\pm 0.018		\pm 0.042		\pm 0.036	
Sm (ppb)	0.00826	183	0.0161	51	0.0148	37
	\pm 0.0053		\pm 0.012		\pm 0.012	
Eu (ppb)	0.00306	184	0.00504	52	0.00439	37
	\pm 0.0012		\pm 0.0025		\pm 0.0022	

Table 1 (continued)

	Ob		Andrevka		Rybnaya	
	Mean \pm SD	N	Mean \pm SD	N	Mean \pm SD	N
Gd (ppb)	0.00503	184	0.0128	52	0.00918	37
	\pm 0.0044		\pm 0.0106		\pm 0.0091	
Tb (ppb)	0.000732	184	0.00181	52	0.00138	37
	\pm 0.00061		\pm 0.0015		\pm 0.0013	
Dy (ppb)	0.00439	184	0.011	52	0.00775	37
	\pm 0.0035		\pm 0.0091		\pm 0.0075	
Ho (ppb)	0.00096	184	0.00242	52	0.00167	37
	\pm 0.00071		\pm 0.0019		\pm 0.0015	
Er (ppb)	0.00277	184	0.00732	52	0.00493	37
	\pm 0.002		\pm 0.0054		\pm 0.0041	
Tm (ppb)	0.000447	184	0.00113	52	0.000749	38
	\pm 0.00030		\pm 0.00079		\pm 0.00057	
Yb (ppb)	0.00276	184	0.00745	52	0.00464	38
	\pm 0.0017		\pm 0.0051		\pm 0.0034	
Lu (ppb)	0.00047	184	0.00114	52	0.000768	38
	\pm 0.00027		\pm 0.00073		\pm 0.00052	
Hf (ppb)	0.00103	151	0.0024	52	0.00171	38
	\pm 0.00092		\pm 0.0021		\pm 0.0015	
Ta (ppb)	0.00025	113	0.000161	26	0.000253	24
	\pm 0.00014		\pm 0.00023		\pm 0.00021	
W (ppb)	0.0401	181	0.0109	49	0.00802	36
	\pm 0.053		\pm 0.016		\pm 0.0038	
Pb (ppb)	0.145 \pm 0.217	184	0.203 \pm 0.283	51	0.233 \pm 0.333	38
Th (ppb)	0.00115	133	0.00628	52	0.00405	38
	\pm 0.0014		\pm 0.0066		\pm 0.0046	
U (ppb)	0.803 \pm 0.259	184	0.0565	52	0.0231	38
			\pm 0.149		\pm 0.0414	

3.3. Colloidal, $< 3 \text{ kDa}$ LMW, and particulate export of elements

The mean annual proportion of colloids in the tributary was sizably higher than that in the main stem (Table 3). The seasonal pattern of the colloidal proportion was also different between the Ob and Andrevka (Table S4) Rivers. Colloidal fluxes of redox-sensitive elements (Fe and Mn) and those originating from groundwater input and subjected to dilution during high discharge events (alkalis, alkaline-earths and anions) were strongly seasonally-variable in the Ob River compared to its smaller tributary (Fig. 4). The contrast between the Ob and its tributary was noted for labile elements with groundwater origin (Ca, V, Ba, Sb, Mo, W and U), and especially Fe, which demonstrated essentially LMW_{<3 kDa} export during winter baseflow for the Ob River.

There were two elemental groups demonstrating a positive relationship of the percentage of colloidal form (relative to dissolved $< 0.45 \mu\text{m}$ fraction) and the river discharge (CF-D) as detailed in Table S5: Group 1_{CF-D} included alkaline-earth and alkali elements (Ca, Sr, Ba, Rb and Cs) while Group 2_{CF-D} was Fe and low mobility trivalent and tetravalent hydrolysates and U (Fig. 5A–C). Two similar primary groups were observed for the Andrevka River (Fig. 5D–F), with DOC also increasing its colloidal fraction with river discharge and Cr and V decreasing their colloidal share at high discharges.

In terms of mean annual percentage of colloids in the dissolved flux (CF-F), three groups of elements were identified (Table S6; Fig. 6): Group 1_{CF-F} was alkalis, alkaline-earth metals, anions and neutral molecules (DIC, Si, Cl, SO₄, Mo and U) that were weakly affected by colloids (0–20 %); Group 2_{CF-F} included DOC, some trace metals (V, Ti, Mn and Co) and oxyanions (As, V and Mo) which were sizably impacted by colloids (20 to 60 %). Finally, low solubility-low mobility elements – trivalent and tetravalent hydrolysates, some trace metals (Be, Cr, Cu, Zn, Ni and Cd), P, and W constituted the Group 3_{CF-F}, that was strongly dominated by colloids (60 to 100 %). The largest contrast in the share of colloidal flux between the Ob River and its tributary were observed for U, Mo and Ge, whose relative proportions strongly decreased during baseflow season due to sizable groundwater influx of low molecular forms of these trace elements.

When considering all three main pools of elements in the river, there

Table 2

Mean annual export fluxes (yields, kg km⁻² y⁻¹) of solutes (< 0.45 μm) in the Ob River and its two small tributaries. *n* represents the number of measurements used to constrain the flux calculations.

Component	Ob	<i>n</i>	Andreva	<i>n</i>	Rybnaya	<i>n</i>
DIC	8496	169	1777	45	2045	31
DOC	1260	169	1670	45	1910	30
Cl	1624	164	87.3	47	75.3	37
SO ₄	4080	164	218	47	91.3	37
Li	1.01	184	0.229	52	0.182	38
Be	0.0083	163	0.0012	52	0.00095	38
B	8.38	184	2.01	52	1.74	38
Na	2840	184	490	52	444	38
Mg	2114	184	371	52	361	38
Al	12.6	184	4.75	52	3.14	38
Si	891	184	894	52	875	38
P	7.65	176	12.2	47	17.1	36
K	470	181	70.0	43	77.0	35
Ca	10,180	184	2131	52	2481	38
Ti	0.111	183	0.104	52	0.0893	38
V	0.421	184	0.0405	52	0.0354	38
Cr	0.0776	183	0.0355	52	0.0329	38
Mn	5.48	184	36.0	52	54.6	38
Fe	10.0	184	183	51	234	38
Co	0.0156	184	0.0353	52	0.0524	38
Ni	0.263	183	0.336	52	0.324	38
Cu	0.494	184	0.0774	52	0.120	38
Zn	1.65	184	0.927	52	1.01	38
Ga	0.00426	183	0.00239	52	0.00282	38
Ge	0.00286	183	0.00165	52	0.00176	37
As	0.395	184	0.163	52	0.465	38
Rb	0.192	184	0.0831	52	0.0760	38
Sr	60.2	184	11.3	52	12.2	38
Y	0.0122	184	0.00974	52	0.00646	38
Zr	0.00623	182	0.00950	52	0.00658	38
Nb	0.000401	169	0.000413	47	0.000306	37
Mo	0.216	184	0.0131	52	0.0232	37
Cd	0.00494	184	0.00174	52	0.00163	38
Sb	0.0369	184	0.00523	50	0.00518	38
Cs	0.000715	184	0.000545	52	0.000316	37
Ba	8.10	184	2.87	52	3.22	37
La	0.00892	184	0.00770	52	0.00455	36
Ce	0.0150	184	0.0136	52	0.0108	37
Pr	0.00188	184	0.00155	52	0.00112	37
Nd	0.00802	184	0.00664	52	0.00471	37
Sm	0.00307	183	0.00215	51	0.00191	37
Eu	0.00110	184	0.000607	52	0.000498	37
Gd	0.00207	184	0.00179	52	0.00126	37
Tb	0.000298	184	0.000253	52	0.000189	37
Dy	0.00181	184	0.00150	52	0.00106	37
Ho	0.000393	184	0.000335	52	0.000226	37
Er	0.00111	184	0.00100	52	0.000653	37
Tm	0.000173	184	0.000151	52	0.000101	38
Yb	0.00109	184	0.000995	52	0.000614	38
Lu	0.000180	184	0.000153	52	0.000101	38
Hf	0.000319	151	0.000372	52	0.000231	38
W	0.0111	181	0.00127	49	0.000847	36
Pb	0.0466	184	0.0227	51	0.0255	38
Th	0.000421	133	0.00102	52	0.000641	38
U	0.242	184	0.00651	52	0.00254	38

was a drastic contrast in the relative proportion of LMW (< 3 kDa), colloidal (3 kDa – 0.45 μm) and particulate suspended matter (PSM, > 0.45 μm) forms of elements in total annual fluxes (and relevant yields) between the Ob River and its tributary (Fig. 7). For >30 low solubility – low mobility elements, the share of their annual colloidal fluxes in the tributary was much higher than that in the Ob River. In contrast, particulate yield was far higher in the Ob River compared to the Andreva River for virtually all elements with the exception of Mn (Fig. 7C).

Comparisons of annual elemental yields in various forms (dissolved, colloidal and particulate) between the Ob River and its tributary exhibited the following features (Table S7): 1) for the LMW (< 3 kDa) form, only Mn and Zn were lower in the Ob River compared to its tributary; all other elements were either similar (± 30 %) among the

Table 3

Mean annual proportion of colloids in the Ob River and its small tributary Andreva. See data for each specific month in Supplementary Table S1.

	Ob, % colloid mean±SD	<i>n</i>	Andreva, % colloid mean±SD	<i>n</i>
DOC	36.3 ± 19	14	65.8 ± 13	14
SO ₄	21.1 ± 16	4	52.1 ± 22	3
Li	4.56±9.1	14	9.91±13	13
Be	48.6 ± 39	11	64±28	13
B	8.38±11	14	9.89±22	13
Na	8.16±12	14	10.6 ± 13	13
Mg	6.28±9.4	14	10.9 ± 15	13
Al	74.8 ± 21	13	73.5 ± 24	14
Si	8.13±10	14	6.47±11	13
P	76.9 ± 19	5	94.9 ± 3.8	6
K	12.1 ± 17	14	18.8 ± 14	11
Ca	4.74±5.7	14	15.1 ± 21	13
Ti	35.4 ± 26	12	36.8 ± 31	13
V	9.01±11	14	54.5 ± 27	14
Cr	34.3 ± 23	14	77.3 ± 15	14
Mn	43±37	13	30.8 ± 32	14
Fe	58.9 ± 21	13	99±0.76	14
Co	43.3 ± 22	14	59.1 ± 22	14
Ni	47.5 ± 12	14	71.6 ± 19	14
Cu	67.1 ± 17	14	67.2 ± 30	14
Zn	61.7 ± 27	14	82.5 ± 18	12
Ga	39.6 ± 29	14	32.9 ± 30	13
Ge	21±28	14	47.4 ± 30	10
As	18.3 ± 14	14	60.5 ± 16	14
Rb	12.1 ± 13	14	15±15	13
Sr	5.18±7.1	14	14±20	13
Y	63.1 ± 17	14	87.7 ± 7.1	14
Zr	75.5 ± 24	14	97.8 ± 1.7	12
Nb	86.6 ± 9.1	3	94.9 ± 4.5	5
Mo	12±12	14	51.4 ± 38	11
Cd	65.6 ± 26	13	60.3 ± 27	14
Sb	12.6 ± 9.9	14	40.9 ± 39	12
Cs	29.6 ± 25	14	38.8 ± 32	13
Ba	3.3 ± 5.1	14	19.9 ± 21	14
La	88.3 ± 7.9	12	92.4 ± 8.4	14
Ce	82.9 ± 27	13	94.5 ± 5.3	14
Pr	81.5 ± 19	14	92.4 ± 6.6	14
Nd	81.2 ± 24	14	91.7 ± 8.7	11
Sm	91.2 ± 7.0	14	91.3 ± 13	10
Gd	64.2 ± 28	14	88±11	12
Tb	84±12	13	86.7 ± 14	12
Dy	69.2 ± 29	14	89.6 ± 7.9	14
Ho	72.7 ± 26	13	87.8 ± 10	12
Er	62.7 ± 31	11	92±7.36	14
Tm	61.8 ± 22	14	79.6 ± 20	13
Yb	47.1 ± 36	14	80.5 ± 14	13
Lu	66.3 ± 22	11	84±10	12
Hf	42.9 ± 31	8	46.3 ± 40	6
W	24.3 ± 19	14	78.3 ± 22	5
Pb	70.5 ± 28	13	64.1 ± 38	14
Th	72.5 ± 45	4	97.9 ± 1.5	5
U	14±14	14	54.6 ± 42	13

main stem and tributary (trace metals, trivalent and tetravalent hydrolysates, geochemical tracers), or 3 to 10 times higher in the Ob River compared to the Andreva River, as especially typical for alkalis, alkaline earth metals, and anionic TE such as V, As, Mo, Sb, W and U (Fig. 7A); 2) the colloidal yield of elements was similar (within a factor of 2) in both rivers for OC, some macro- and micro-nutrients (Si, P) and divalent metals (Ni, Zn, Ba, Cd and Pb) and lithogenic elements (Be, Cr, Ti, Y, Zr, Hf and REEs); 3) the yield of soluble labile elements (DIC, alkalis, alkaline-earths, B, Cu, micro-anions (Mo, Sb and W) and U) was sizably (x 3 to 20) higher in the main stem compared to tributary; 4) in contrast to 2, the colloidal yield of Fe, Mn and Co were a factor of 3 to 10 higher in the Andreva River compared to the Ob River (Fig. 7B; Table S7); and 5) the particulate yield of most elements was a factor of 2 to 20 higher in the Ob River compared to its tributary except for Mn (Fig. 7C). Note here that Ca, Sr, Ba and Sb exhibited comparable suspended yields between

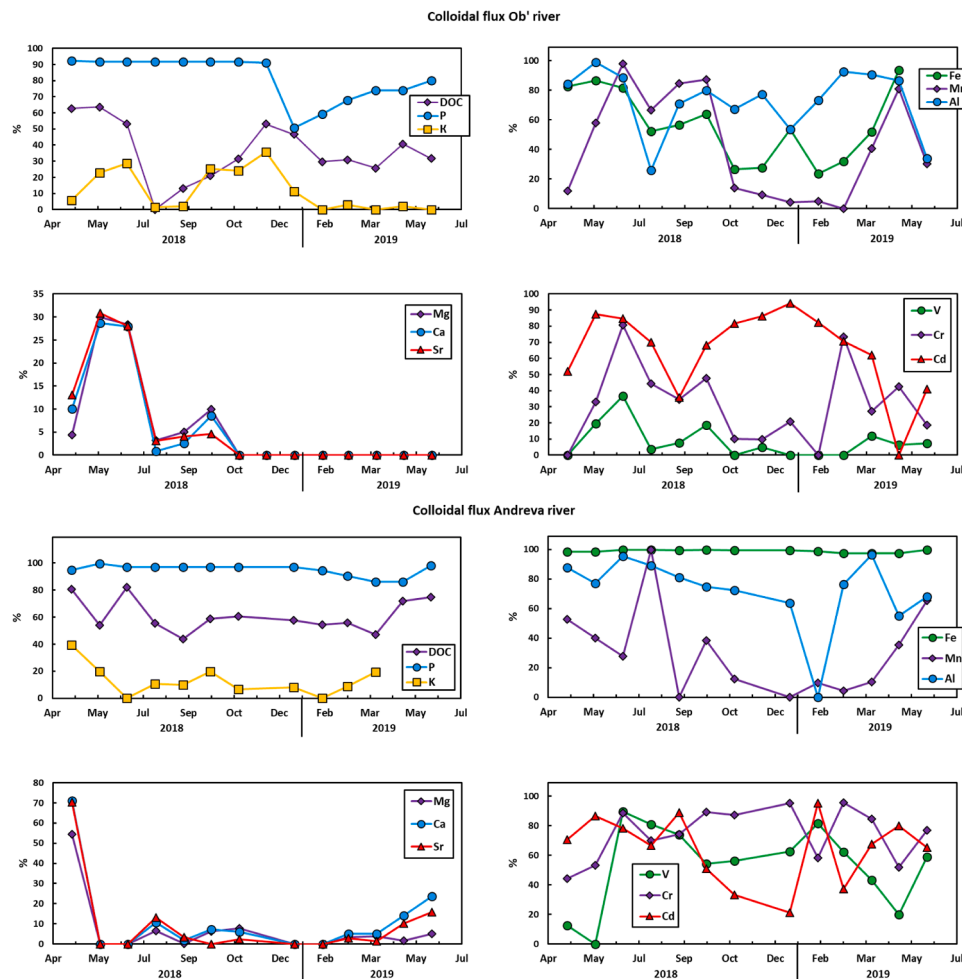


Fig. 4. Change of the proportion of colloidal forms of major and trace elements in overall export flux over the period of observation, from April 2018 to July 2019 in the Ob River (upper 4 panels) and its small tributary the Andrevka River (bottom 4 panels).

the Ob River and its tributary, whereas the share of suspended fluxes for Mo and U was lower in the main stem compared to the tributary.

The stoichiometry of major colloidal constituents (OC, Al, Fe and P) systematically evolved across seasons (Fig. S3) depending on river discharge (Fig. 8). Colloids of the tributary were strongly enriched (by a factor of 10 to 100) in Fe relative to Al, whereas the Ob River's colloids were enriched in OC relative to Fe when compared to Andrevka River. For both rivers, colloids were enriched in Al relative to OC at high discharges (compared to baseflow), due to Al mobilization from PSM into the solute pool. Colloids were enriched in Fe and P during baseflow, likely due to an influx of groundwater and Fe(II) oxidation into organo-ferric colloids. In the Ob River, we noted a decrease in colloidal OC during the summer and early autumn periods, compared to the spring flood.

4. Discussion

4.1. Seasonal aspects and elemental yields – comparison between Ob and tributaries for dissolved and particulate fluxes

Much higher dissolved ($< 0.45 \mu\text{m}$) yields of Fe, Mn and Co (the latter is known to follow Mn in boreal humic waters; Pokrovsky et al., 2012) in the tributaries compared to the main stem likely reflects an enhanced mobilization of these elements from partially anoxic mires dominating the watersheds of the tributaries. This is especially pronounced during winter baseflow, under ice (see illustrations of element concentrations across seasons in Fig. S2). During this period, the wetlands which feed the tributaries do not freeze completely and become

capable of delivering sizable amounts of dissolved Fe and Mn to the rivers via shallow subsurface flow (Pokrovsky et al., 2016b; 2020). During summer baseflow, peaks in Mn concentrations in the tributary (Fig. 2F) might be linked to rewetting of dried peat soils as it is known from other temperate catchments (i.e., Heal et al., 2002). In contrast, the high yield of soluble labile elements (major cations and major and trace anions) of the Ob River compared to its tributaries stems from a much stronger hydrological connectivity of the large river to deep underground reservoirs (Vorobyev et al., 2015), which contain high concentrations of these elements due to leaching of carbonate-bearing rocks of the basement (Pokrovsky et al., 2015).

For the same reasons, the higher share of soluble labile cations and anions (alkaline-earth metals), Mo and U in the dissolved compared to particulate fraction in the large river is because these solutes likely originate from deep underground water reservoirs. These reservoirs are mostly pronounced during baseflow, as has been established across a sizable latitudinal gradient of small and large rivers of western Siberia (Frey et al., 2007; Pokrovsky et al. 2015). This strong hydrological connectivity of large rivers with groundwater reservoirs demonstrated by water isotopic signatures in rivers of western Siberia (Ala-aho et al., 2018a; Ala-aho et al., 2018b) can also explain the higher seasonal variability of the colloidal proportion of certain elements in the Ob River compared to its smaller tributaries. This was especially pronounced for redox-sensitive Fe, which could be present partially in ionic Fe(II) forms, alkalis and alkaline-earth metals. Hence, an increase in the colloidal fraction of Fe, Mn and U with discharge (Fig. 5) reflects low colloidal transport of these elements in winter, when the river is essentially fed by

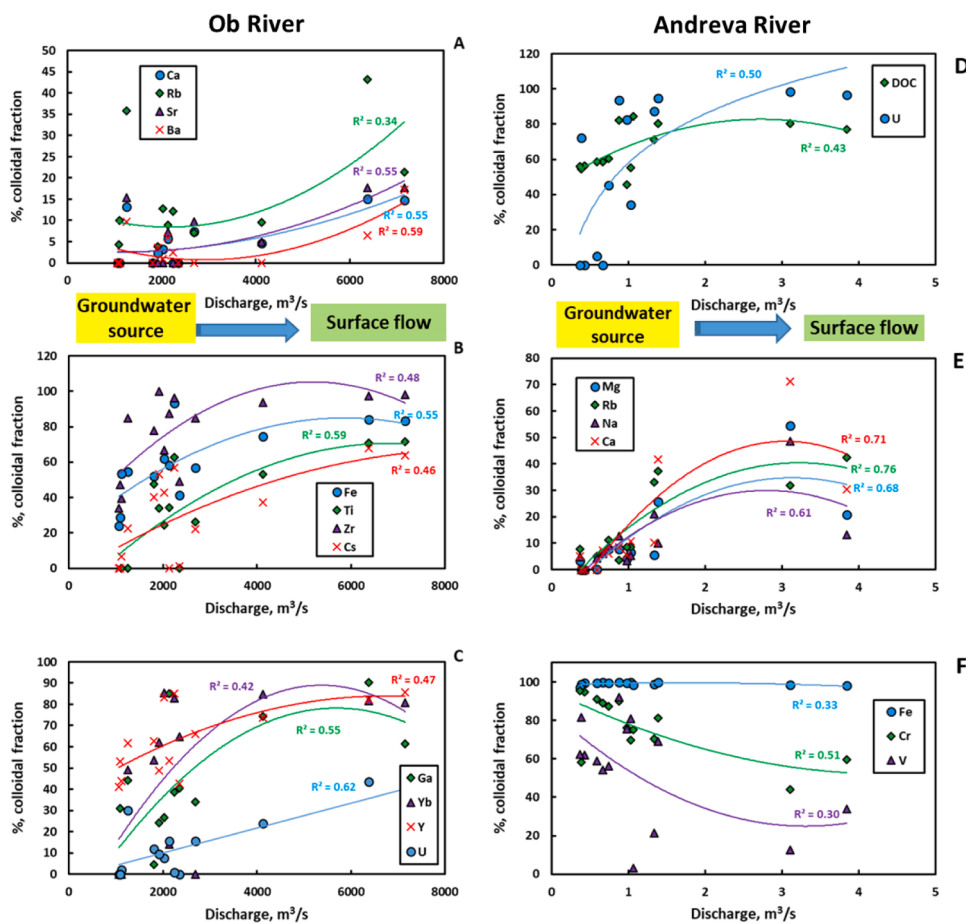


Fig. 5. Proportion of colloidal forms of some major and trace elements as a function of discharge in the Ob River: A: alkaline-earth metals; B: lithogenic elements (Fe, Ti, Zr, Cs); C: Ga, Yb, Y and U. Proportion of colloidal forms of some major and trace elements (D: DOC and U; E: Mg, Rb, Na and Ca; F: Fe, Cr and V) as a function of discharge in the Andrevka River. Solid lines represent a fit to the data over the course of the year with empirical 2nd order polynomial dependence ($\% \text{ colloid} = a \times Q^2 + b$, where Q is discharge, a and b are empirical constants specific to each element).

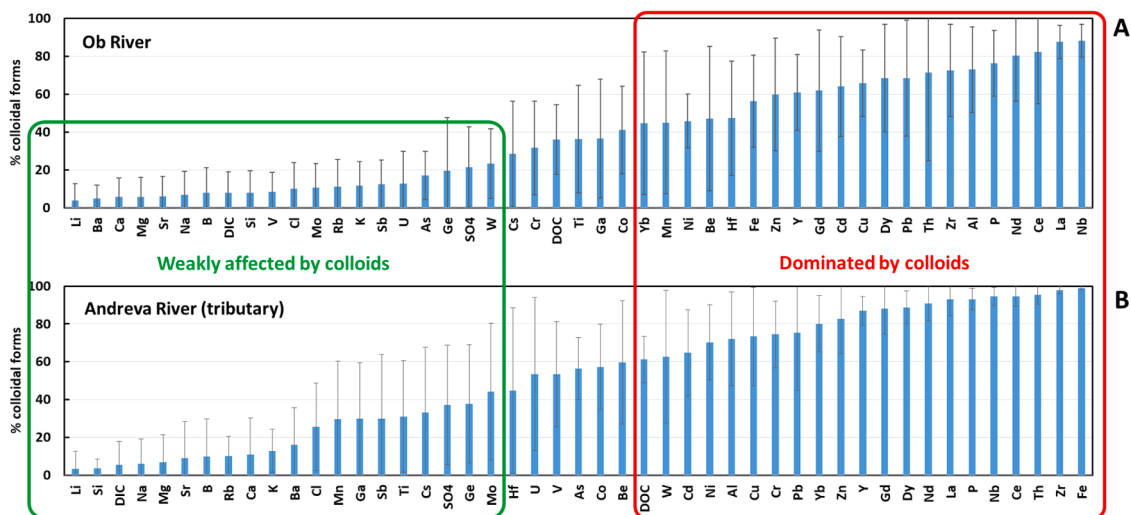


Fig. 6. Mean annual proportions of colloids (3 kDa – 0.45 μm) in the Ob River (A) and its small tributary Andrevka (B). Error bars represent s.d. across different months over the year, from May 2018 to June 2019 ($n = 12$ to 14). Two main groups of element in terms of their affinity to colloidal fraction are highlighted in color frame.

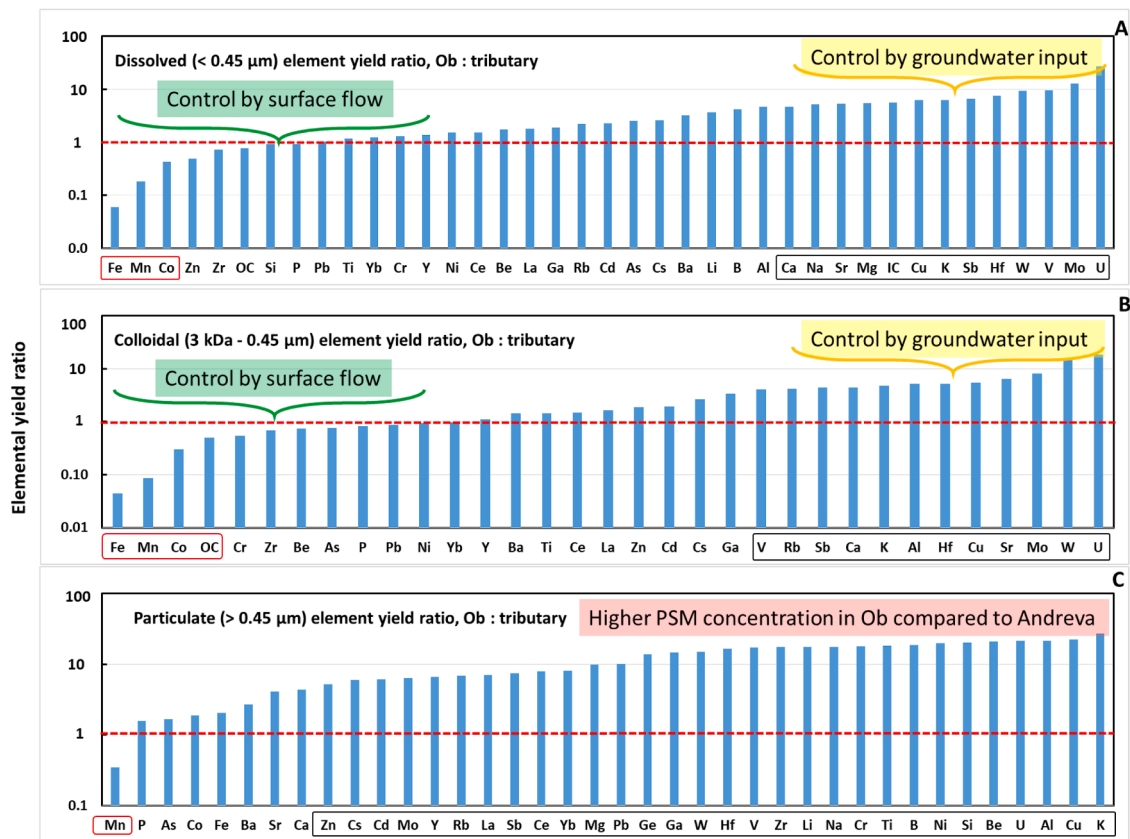


Fig. 7. Ratio of the elemental yields (dissolved, A; colloidal, B; particulate, C) in the Ob River to that of the tributary (Andreva). Black and red boxes highlight the elements exhibiting significantly ($p < 0.05$) higher and lower yields, respectively, in the Ob River compared to its tributary.

deep groundwater containing a very low proportion of colloids.

4.2. Dominance of colloidal fluxes in overall elemental export and relevant mechanisms

The dominance of organic and organo-mineral (ferric and aluminum) colloids in boreal and subarctic waters is a well-established feature (Lyvén et al., 2003; Stolpe et al., 2013a, b; Cuss et al., 2017, 2018; Javed et al., 2017). This study adds new dimension to the knowledge of colloidal speciation of OC and metals across seasons in boreal rivers (Porcelli et al., 1997; Ingri et al., 2000; Pokrovsky et al., 2010; Bagard et al., 2011), via comparing, using a uniform methodology, the colloidal versus $LMW_{<3\text{ kDa}}$ export between a large river and its small tributary, both having similar environmental context in terms of lithology, vegetation and climate. Consistent with previous observations on small permafrost rivers of western Siberia (Krickov et al., 2019), the $LMW_{<3\text{ kDa}}$ fraction of total dissolved OC increased in the order spring < autumn < summer (Fig. 4). Such a trend likely reflects progressive replacement of allochthonous medium and high molecular weight colloids in spring and autumn high flow by autochthonous LMW organic ligands in summer baseflow. While large size allochthonous organic colloids originate from soil litter and vegetation leaching, autochthonous LMW organic ligands are likely represented by exometabolites of plankton and periphyton.

Seasonal variability of colloidal elemental stoichiometry demonstrated a decrease in the OC : Al ratio with increased river discharge, for both the Ob River and its smaller tributary. Relative enrichment of colloids in Al at high discharges likely reflects the mobilization of this element from aluminosilicate minerals dominating PSM during spring flood (i.e., Krickov et al., 2023). Colloidal enrichment in Fe and P at low discharges may reflect the formation of colloids via mixing of surface DOM-rich waters with groundwater, delivered in the riparian and

hyporheic zone of the river during summer and winter baseflow. This includes oxidation of Fe(II) into Fe(III) high molecular weight colloids, stabilized by DOM (i.e., Chen et al., 2014, 2016) and incorporating, via coprecipitation, dissolved P and a number of low-solubility typically immobile elements. These processes were hypothesized to be the major factors of colloid formation in permafrost-free rivers of the boreal zone (Pokrovsky and Schott, 2002; Pokrovsky et al., 2010; Vasyukova et al., 2010). Such a coagulation of Fe hydroxide together with DOM at the redox interface in wetlands (Riedel et al., 2013; Koretsky et al., 2006), boreal lake sediments (Herzog et al., 2024) and at the riverbank surface (Ratié et al., 2019) is fairly well known. It has been also demonstrated that at high Fe/OC ratios in temperate streams, the $< 0.45\ \mu\text{m}$ colloidal fraction is dominated by Fe(III) (hydr)oxides stabilized by organic matter (Gaffney et al., 2008).

For both the main stem and the tributary, REEs demonstrated particular features of their LMW colloidal and particulate flux. The share of LMW and PSM fluxes for light REE (LREE) such as La, Ce and Pr was higher than that of heavy REEs (Er, Tm and Yb). In contrast, HREE exhibited a more important contribution of colloidal flux compared to that of LREE (Tables S6 and S7). A likely reason for these differences is the higher affinity of LREE to solid surfaces and the stronger complexation ability of HREE with organic ligands (Bau, 1999), as also demonstrated in works on organic and organo-mineral colloids in boreal and subarctic waters (Vasyukova et al., 2010; Pokrovsky et al., 2016) including small western Siberia rivers of the permafrost zone (Krickov et al., 2019).

The results of the present study on colloidal fractionation of elements are generally consistent with former works on western Siberia rivers across a large permafrost gradient (Krickov et al., 2019) which demonstrated a decrease of Fe in the colloidal fraction during baseflow in larger rivers. This was interpreted due to the discharge of Fe(II) ions and inorganic complexes from underground waters. Similarly, a

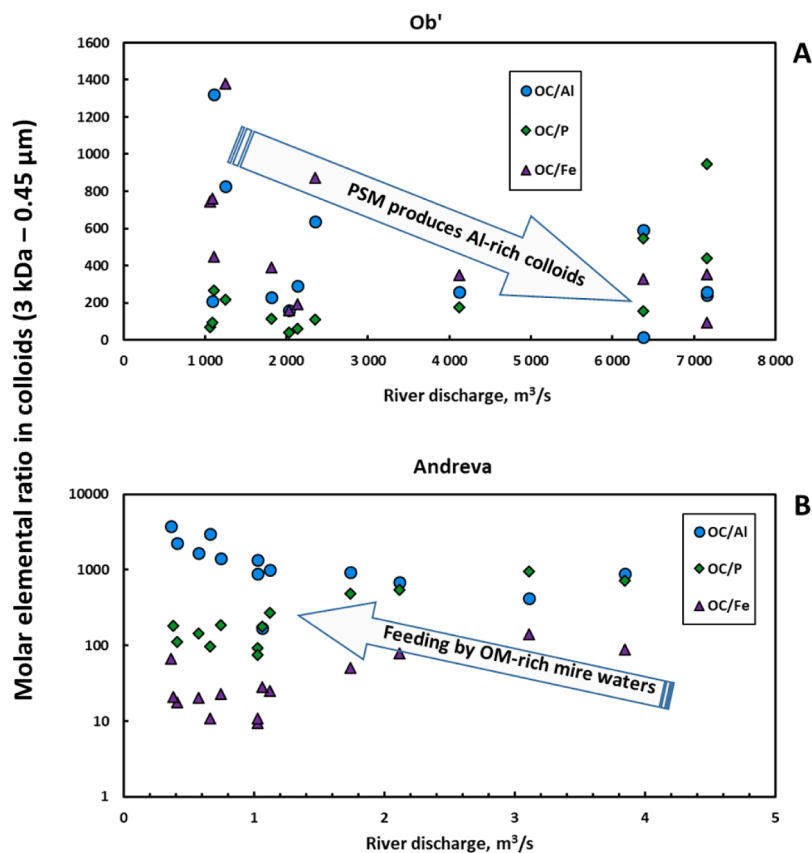


Fig. 8. Stoichiometric molar ratio of major colloidal (3 kDa – 0.45 μm) constituents in the Ob River (A) and its tributary (B), as a function of river discharge. Note a log Y scale for the Andreva River. PSM is particulate suspended matter.

decrease in the colloidal fraction of soluble high mobility elements (alkaline-earth metals), macro- (P) and micro-anions (Mo) and U at low discharges (Fig. 5) likely stems from increased connectivity between the river water and underground reservoirs; this is known from water isotope tracing in western Siberia (Ala-aho et al., 2018a, b). These reservoirs are enriched in ionic, LMW forms of labile elements (Frey et al., 2007) notably because of the presence of carbonate concretions and shells in sedimentary strata of the southern regions of western Siberia (Pokrovsky et al., 2015; 2016b). Note that an increase in low solubility trivalent and tetravalent TE with an increase in discharge of the Ob River (Fig. 5) likely reflects an increase in the concentration of main colloidal carriers—organic matter and Fe(III) oxy(hydr)oxides—for these elements, given that TE^{3+} and TE^{4+} are essentially present in the form of high molecular weight organo-ferric colloids (Stolpe et al., 2013b; Pokrovsky et al., 2016a). Overall, large-sized organo-Fe-Al colloids as main carriers of trace element have been evidenced from macroscopic and spectroscopic observations in the wetlands and river coastal zones of temperate regions (Pourret et al., 2007; Pédrot et al., 2008; Guénet et al., 2017; Vantelon et al., 2019).

The middle course of the Ob River is known to have sizeable underground loading by Fe(II)-enriched partially anoxic ground waters that are influenced by interaction with limestone-rich sedimentary rocks (Vorobyev et al., 2019). These rocks do not impact the loading of Andreva and Rybnaya rivers, whose watersheds, covered predominantly by bog and forest, are disconnected from the groundwater reservoirs, similar to other small-sized WSL rivers (Pokrovsky et al., 2020). As a result, the dissolved ($< 0.45 \mu\text{m}$) yields of labile major (Ca and Sr) and trace (oxyanions and U) are sizably higher in the Ob River compared to its smaller tributaries. Furthermore, across the seasons, the degree of connection between these groundwaters and the river could control the relative proportion of some colloidal metals at the expense of LMW ionic

forms. Thus, we observed a lower percentage of colloidal forms of alkaline-earth metals, Fe, Mn, V and Cr at low discharges compared to high flow (Fig. 5). This was especially pronounced for U, which likely changed its dominant speciation from uranyl-carbonate (LMW) complexes at the baseflow to U(VI)- organo-ferric colloids during flood flow. Similar behavior of U has been evidenced across the boreal and subarctic river waters (Pokrovsky et al., 2010; Bagard et al., 2011; Chupakov et al., 2023).

The extensive mire coverage in the Andreva River watershed resulted in significantly higher DOM concentrations (Pokrovsky et al., 2015), which likely explains the increased proportion of colloids in this small tributary compared to the main stem. The most likely mechanisms for the bogs control on riverine colloids is that they decrease the connectivity of rivers to groundwater reservoirs in this region (Ala-Aho et al., 2018a). A decrease of groundwater loading diminishes the delivery of soluble and labile elements, present in the ionic forms, to the river thus increasing relative share of their colloidal forms. It is worth noting that bogs mobilize colloids during all seasons because of the permafrost-free zone; therefore, the difference in elemental colloidal patterns between the main stem and its small tributaries persists over the entire period of observation.

The molar ratio of major constituents for colloids (3 kDa - 0.45 μm) is useful in constraining the climate and environmental controls on colloid generation in river water (Krickov et al., 2019). In both rivers, the highest colloidal phosphorus was observed during low discharges (Fig. 8), which can be explained via mobilization of organic forms of P from sediments in the riparian zone. Notably, a high proportion of colloidal P (30–70 %) has been reported in organic-rich soil porewaters of Siberian peatlands (Raudina et al., 2021). In the Ob River catchment, organic P may be generated in riparian and riverbed sediments, where organic matter mineralization and P release to the water column occur

simultaneously. However, the speciation of P in colloids and its role in the formation of Fe-Al-organic colloids remain poorly understood.

Elevated OC relative to Al in colloids of the Ob and Andrevka Rivers at low discharges likely reflected loading of these rivers by neighboring mire waters. This contrasted with mobilization of Fe and Al, likely from suspended minerals, into the colloidal pool during spring flood, at high PSM load. Higher OC : P colloid ratio at higher discharges suggests that P at high discharges is being mobilized in particulate ($> 0.45 \mu\text{m}$) rather than dissolved form. Overall, we observed organic-rich colloids during baseflow and Al-rich colloids at high discharges. For both Ob River and its small tributary, this likely reflected seasonally dependent export of solutes from organic rich bogs, podzol soils and suspended particulate mineral leaching within the river water column. This is consistent with the high capacity of the Ob River's PSM to generate organo-mineral colloids rich in Al, Fe and lithogenic elements, when interacting with the DOM-rich waters of the tributaries or the floodplain (Lim et al., 2024).

4.3. Small wetland-dominated boreal rivers as analogues of Arctic coastal rivers: comparison of dissolved yields across Northern Eurasia

Annual elemental dissolved ($< 0.45 \mu\text{m}$) yields, assessed for the middle course Ob River and its two small tributaries, when compared with detailed year-round estimations of major and trace element yields in other rivers of Northern Eurasia (mid-sized Severnaya Dvina, Pechora, Taz and large Arctic rivers at their terminal gauging stations (Ob, Yenisey, Lena and Kolyma) are not that drastically different despite huge contrast in river size, environmental context, lithology, climate and permafrost presence. At the same time, it should be highlighted that inter-annual variations in mean monthly yields often achieve a factor of 5 to 10 (Table S2). However, for most major and trace elements, mean annual yields were within the same order of magnitude, and did not vary more than a factor of 3 to 5 among studied boreal/subarctic rivers. Exceptions are labile groundwater-originated alkalis and alkaline-earth metals (Sr, Rb), oxyanions (B and Mo), U, redox sensitive Fe, Mn and Cr whose yields could range from a factor of 10 to 20 among different Eurasian rivers. This likely stemmed from the highly variable source of the winter period loading of the rivers (Pokrovsky et al., 2016b), the different size of the riparian/floodplain zone from which the mobilization of redox-sensitive elements occurred (Pokrovsky et al., 2022b), or the different lithology of the watersheds in terms of coverage by granites, basalts, or sedimentary carbonates (Gordeev et al., 2024). It should further be noted that there were almost uniform levels of Si yields in all rivers, likely due to Si regulation by boreal and subarctic forest litter leaching and plant uptake (i.e., Pokrovsky et al., 2013). An alternative explanation is Si buffering via dissolution of primary and secondary clay minerals, given the rather similar Si release rates from both clay dominated soils (Lim et al., 2023) and individual silicate minerals (Heřmanská et al., 2023) in the circumneutral pH range, which is most relevant to natural weathering conditions.

The small tributaries of the Ob River's middle course investigated in this study are poorly connected to groundwater reservoirs and are essentially controlled by input from wetlands and boreal forests via surface and shallow subsurface flow. Therefore, they can be tentatively used as analogues of small streams and rivers of the Eurasian Arctic coast, including those draining through permafrost wetlands. The freshwater flux by small rivers amounts to 40 % of overall discharge to the Arctic Ocean (Vonk et al., 2023); however, the overwhelming majority of them are ungauged and virtually inaccessible for year round hydrochemical survey. For these reasons, there is not a single estimate of major and trace element yields by Arctic coastal rivers which takes into account the entire yearly period. Recently assessed high temporal resolution elemental yields in three Arctic mid-sized rivers (the Severnaya Dvina, Pechora and Taz rivers; Chupakov et al., 2022, 2023; Pokrovsky et al., 2022b) *a priori* cannot be used as analogues for calculating the missing yields of small rivers. Further, 25 small Canadian Arctic rivers

assessed by Brown et al. (2020) could not be used for this comparison due to their low representability in terms of season (snap shot summer sampling) and low number of solutes (8 major cations and anions and only Sr and Ba).

The Andrevka and Rybnaya rivers, two of the more pristine Ob River tributaries sampled in this work with sufficient seasonal resolution, can help to fill this knowledge gap by providing tentative estimations of chemical yields in small rivers. Through a quantitative comparison of elemental yields of these small rivers with Great Arctic Rivers recently assessed via the PARTNERS program (Gordeev et al., 2024) and the mid-sized rivers cited above, we conclude that, for a large suite of elements, large rivers can serve as a reasonable analogue of small rivers. In fact, the inter-annual monthly variation of elemental yields for the same river (a factor of 2 to 5; see Table S2) and intrinsic uncertainties (at least 50 %) on yields estimated for the large rivers based on $< 6-7$ samplings per year (Gordeev et al., 2024) are comparable with the differences between mean values for 7 Arctic rivers and the two small tributaries of the Ob River studied in this work (Table S3). Generally, for Arctic rivers, due to the strong spatial-temporal variability of dissolved trace element concentrations in their waters and a relatively small number of measurements, only differences in mean values as high as a factor of 3 are considered significant (Savenko and Savenko, 2024).

Uncertainties and inter-annual variations of yields available for three mid-sized rivers (Severnaya Dvina, Pechora, and Taz) based on high-resolution multi-annual sampling (Chupakov et al., 2020; 2023; Pokrovsky et al., 2022b) are smaller than those for large Arctic Rivers (20 to 30 %); however, such precise estimations for large Arctic Rivers are unlikely to be achieved in the near future. Taken together, we conclude that the mean annual yields of 4 great and 3 mid-sized Eurasian Arctic rivers—for > 50 elements—can be used to approximate yields of unknown small rivers which provide the missing 40 % of freshwater discharge. Exceptions include redox-sensitive elements (Fe and Mn) whose yields in Ob River tributaries exceeded those of large Arctic rivers by a factor of 10 to 20 and that of mid-sized by a factor of 2 to 5. The yield of U, originated from groundwater interactions with carbonate-rich rocks, was substantially (a factor of 10 to 40) lower in small rivers compared to the average of large ones.

Considering these comparisons, elementary yields of small Arctic rivers draining peatlands and boreal forests can be adequately approximated from data available for mid-sized and Great Arctic rivers. The uncertainty on this approximation is within a factor of 2 to 3, with the exception of Fe and Mn, whose true fluxes to the Arctic Ocean can be an order of magnitude higher than those inferred exclusively from large rivers. Enhanced manganese delivery by currently unaccounted for small rivers can partially explain the missing Mn source to the Arctic Ocean (Midday et al., 2011), inferred from oceanographic studies. Similarly, the colloidal yield of insoluble trace metals and lithogenic elements can be sizably (a factor of 3 to 10) underestimated if only large rivers are used to calculate the export from the entire Arctic territory. In this regard, the Fe(III) - small aquatic humic ligand (SAHL) complexes, originated from coastal soils (e.g., Krachler and Krachler, 2021) and carried by both large and small rivers, can be of the utmost importance for the nutrient balance of the Arctic Ocean. In contrast, the dissolved yield of labile Sr, Mo, W and U can be moderately (a factor of 2 to 3) overestimated when extrapolating mean large river values for the entire North Eurasian subarctic. Finally, the suspended flux of small rivers cannot be calculated based on that available for large rivers, given the much higher particulate element yields of the latter (Fig. 7C).

5. Conclusions

In an effort to better understand factors controlling major and trace element export in rivers of the boreal Siberian region, we quantified seasonal variability of concentrations, calculated mean annual yields and characterized colloidal versus < 3 kDa dissolved and suspended fluxes of C and major and trace elements for the middle course of the Ob

River and its small tributaries. In terms of the mean annual percentage of colloids in the < 0.45 μm dissolved flux, 3 groups of elements were identified: 1) alkalis, alkaline-earth metals, anions and neutral molecules (DIC, Si, Cl, SO_4 , Mo and U), weakly affected by colloids (0–20 %); 2) DOC, some trace metals (V, Ti, Mn and Co), and oxyanions (As, V and Mo) which were sizably impacted by colloids (20 to 60 %) and 3) low solubility-low mobility elements; trivalent and tetravalent hydrolysates, trivalent trace metals (Be, Cu, Zn, Ni and Cd), P, Cr and W, which were strongly dominated by colloids (60 to 100 %).

There was a drastic contrast in the relative proportion of LMW (< 3 kDa), colloidal (3 kDa – 0.45 μm) and particulate suspended matter (PSM, > 0.45 μm) elemental forms in total annual fluxes between the Ob River and its tributaries. Colloids constituted a larger proportion of the total dissolved fluxes for over 30 low-solubility, low-mobility (lithogenic) elements in the tributaries compared to the Ob River. The main reasons for this difference are the higher colloidal pools of OC and Fe in the tributaries, where these elements are mobilized through surface runoff, and the strong groundwater input in the Ob River. Colloidal fluxes of redox-sensitive elements (Fe and Mn) and those originated from groundwater input (alkalis, alkaline-earths and anions) were strongly seasonally-variable in the Ob River compared to its smaller tributary. Colloids were enriched in Al relative to OC at high discharges, due to Al mobilization from PSM into the solute pool, and they were enriched in Fe and P during baseflow, likely due to an influx of groundwater and Fe(II) oxidation into organo-ferric colloids.

The small boreal rivers draining pristine wetlands are likely to be an important and still poorly quantified source of some nutrients and redox-sensitive elements to the Arctic ocean given that up to 40 % of freshwater discharge occurs from ungauged small rivers of the Arctic coast, and that these rivers demonstrate a factor of 5 to 20 higher yields of Fe, Mn, Cr and P compared to large and mid-sized rivers. At the same time, the delivery of alkaline earth metals, alkalis, trace anions (Mo and W) and U by small rivers is likely to be much lower than that of large rivers.

Data availability

Primary hydrochemical data of sampled sites are provided in Supplementary excel file.

CRedit authorship contribution statement

Ivan V. Krickov: Writing – original draft, Investigation, Data curation. **Sergey N. Vorobyev:** Writing – review & editing, Methodology, Investigation, Funding acquisition, Formal analysis. **Larisa G. Kolesnichenko:** Methodology, Investigation, Formal analysis, Data curation. **Yuri Kolesnichenko:** Visualization, Software, Methodology, Funding acquisition. **Dmitri Zinchenko:** Methodology, Investigation. **Liudmila S. Shirokova:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation. **Oleg S. Pokrovsky:** Writing – review & editing, Writing – original draft, Supervision, Conceptualization.

Declaration of competing interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2025.123221.

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