Chemical Geology 614 (2022) 121180

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Element transport in the Taz River, western Siberia

Oleg S. Pokrovsky [a,*], Rinat M. Manasypov [b], Artem V. Chupakov [c], Sergey Kopysov [b]

[a] Geosciences and Environment Toulouse, UMR 5563 CNRS, 14 Avenue Edouard Belin, 31400 Toulouse, France
[b] BIO-GEO-CLIM Laboratory, Tomsk State University, Tomsk, Russia
[c] N. Laverov Federal Center for Integrated Arctic Research, Russian Academy of Sciences, Arkhangelsk, Russia

ARTICLE INFO

Editor: Dr. Don Porcelli

Keywords:
Arctic
Discharge
Season
Export
Flux
Carbon
Nutrient
Trace metal

ABSTRACT

The riverine export fluxes of dissolved carbon, nutrient and metals from the land to the Arctic Ocean are fairly well quantified for five large Arctic rivers but remain virtually unknown for mid-sized Eurasian rivers, notably those draining through the permafrost zone. Because such rivers can most rapidly respond to on-going climate warming and permafrost thaw in the Arctic, their current hydrochemical composition and elemental yields are badly needed for judging the level of changes in the very near future. Towards quantifying the annual export fluxes and assessing the mechanisms of seasonal variability of river solutes, we monitored the pristine subarctic Taz River ($S_{watershed}$ = 150,000 km^2), which drains through boreal forest and peatlands in the discontinuous and continuous permafrost zone, on a weekly to monthly basis over a 3 year period.

Based on seasonal pattern of riverine solutes (< 0.45 μm) and their dependence on discharge, 3 groups of elements were distinguished. These groups of solutes were consistent with several main sources of elements in the main stem of the Taz River such as deep groundwater, riparian zone and floodplain lake sediments, plant litter, mineral soil water, and peatwater from the peatlands. The 1st group was represented by dissolved inorganic carbon (DIC), specific conductivity, and some nutrients (NO_3, NH_4, N_{tot} and Si) and soluble elements that originated from groundwater and deep soil mineral horizons (Cl, SO_4, Li, B, Na, Mg, Ca, Si, K, Rb, Mn, Co, Sr, Mo, Cs, Ba and W) and showed maximal concentration at the end of winter, before the spring ice-off. This group showed negative correlation to discharge. The 2nd group included dissolved organic carbon (DOC), low-mobile hydrolysates and organically-complexed trace metals (Al, Be, V, Ni, Y, Se, Zr, Nb, REEs, Hf, Pb and Th) which demonstrated maximal concentrations during the spring flood and autumn high flow and minimal values during winter. The concentration of these elements generally increased with water discharge, presumably due to their mobilization in the form of organic and organo-mineral colloids by surface flow through forest litter and via suprapermafrost flow from peatlands. And lastly, the 3rd group of solutes included macronutrients (P, N), Fe, Ti, Cr, Ga, Ge, As, Pb, and U which exhibited features of first two groups and originated from both surface and underground sources. This group showed the strong impact of autochthonous biotic processes in the river channel and soils of the watershed (nutrients, Si).

Similar to other Arctic rivers, the spring flood (May and June) provided 30–40% of annual export for DOC, macronutrients and most major and minor solutes. The exceptions are DIC, Si, Ca, Mg and Fe which exhibited essential (30–40%) export during winter baseflow, whereas >70% of annual Mn flux occurred in winter. A number of elements present in the snowpack exhibited sizable (> 45%) export during spring flood (Zn, Cu, Pb, Cd, Sb and Cs). The 3 years mean export fluxes (yields) of dissolved components were comparable to or 30–50% lower than those of other large and medium sized Arctic rivers. This was due mostly to a lack of fresh unaltered rocks and a dominance of peatlands within the Taz River watershed. Elevated concentrations of redox-sensitive micro-nutrients (such as Fe and Mn) occurring during winter baseflow can be linked to disproportionally large floodplain zone of this river which can act, especially in the river's lower reaches, as a stratified lake thereby releasing high amounts of redox-sensitive elements from the sediments. The role of suboxic zones in the Arctic boreal riverine landscape may be more important than previously thought, and may allow explaining anomalously high concentrations of some metals (i.e., Mn) reported in Arctic Ocean surface waters. It is anticipated that

* Corresponding author.
E-mail address: oleg.pokrovsky@get.omp.eu (O.S. Pokrovsky).

https://doi.org/10.1016/j.chemgeo.2022.121180
Received 31 July 2022; Received in revised form 4 October 2022; Accepted 14 October 2022
Available online 19 October 2022

climate warming in the region may increase the contribution of winter flow and enhance the export of soluble elements and some nutrients (such as Si, Mn and Co).

1. Introduction

Mobilization of dissolved organic carbon (DOC), macro- and micronutrients and trace metals and CO_2 from the frozen peat to surface waters in the permafrost zone is expected to enhance under on-going permafrost thaw and active layer thickness deepening in high latitude regions (Bense et al., 2012; Pokrovsky et al., 2012a; Vonk et al., 2015, 2019; Cochand et al., 2019; Juhls et al., 2020; O'Donnell et al., 2021). The riverine export fluxes of dissolved carbon, nutrient and some trace metals from the land to the Arctic Ocean are fairly well quantified for five large Arctic rivers (MacKenzie, Kolyma, Lena, Yenisey, and Ob), thanks to thorough work of the American and Russian State Hydrological Survey and multi-annual sampling within the PARTNERS/ARCTIC GRO programs (Raymond et al., 2007; Cooper et al., 2008; Holmes et al., 2013; McClelland et al., 2015; Tank et al., 2016; Behnke et al., 2021). The other Arctic rivers, notably the *middle eight* (Indigirka, Yana, Olenek, Khatanga, Taz, Pur, Pechora, Severnaya Dvina, covering a total watershed area of 1.9 million km^2 with an average population density of 1.13 people km^{-2}) remained virtually unknown to the scientific community with the exception of some recent work on the Severnaya Dvina River (Chupakov et al., 2020; Gordeev et al., 2021). Other studies addressed small rivers draining organic-rich permafrost peatlands in western Siberia (Frey et al., 2007; Pokrovsky et al., 2015). Such rivers are most sensitive to climate warming and may turn out to be very important indicators of terrestrial response to the on-going environmental changes and sizable vectors of C, nutrients and trace metal export to the Arctic Ocean (Krickov et al., 2018, 2019, 2020). However, the mid-sized rivers of this territory remain poorly studied. Three such rivers—the Taz, the Pur and the Nadym—demonstrated 'mysteriously' high yield (watershed-area-normalized export) of major nutrients (N and P) that was more than an order of magnitude higher than that of large Arctic Rivers (Holmes et al., 2000, 2001). It was proposed that inadequate sampling and storage procedure by the State Hydrological Survey was among the possible reasons for this anomalous yield (Holmes et al., 2001); however, independent verification of this procedure was never attempted mainly due to the limited accessibility to this territory. It is important to note that these rivers possess disproportionally large floodplain zones which can act, especially in the river's lower reaches, as a stratified lake that is capable of releasing a high amount of redox-sensitive elements from the sediments and sediment pore water. Indeed, high concentrations of redox-sensitive elements such as Mn, Fe and P are reported in organic-rich seasonally stratified lakes in the bottom layer and at the sediment – water interface (Pokrovsky et al., 2012a; Shirokova et al., 2013b). In western Siberia, it is evident for the middle course of the Ob River (non-permafrost zone) with its huge floodplain (Vorobyev et al., 2019). Furthermore, it remains unclear which other potential macro- and micronutrients (Si, Fe, Mn, Mo, other trace metals) can exhibit elevated yield and how it can affect the overall nutrient and elemental export to the Kara Sea and Artic Ocean. Note for instance that elevated Mn concentrations in the surface layer of the Arctic Ocean are linked to fresh water input (Middag et al., 2011) yet the large Artic Rivers do not exhibit anomalously high Mn export flux. It is thus not excluded that small and medium sized coastal rivers of the Siberian lowlands act as an important—and still poorly known—source of this and other redox elements to the coastal seas.

The present study attempts to fill these aforementioned knowledge gaps through considering a medium sized river (the Taz River, $S_{watershed} = 150{,}000$ km^2) that is not subjected to any anthropogenic influence (population < 1 person/km^2 and lacks of hydrocarbon exploration on the watershed, contrary to the Pur and Nadym Rivers). The Taz River drains through a representative gradient of forest and tundra landscapes, permafrost zones (from sporadic and isolated in the south to continuous in the north) and can be considered as a model river for quantifying the areal yield of solutes and testing the environmental factors controlling the seasonal pattern of export fluxes. Note that the majority of the Taz River basin is in the discontinuous permafrost zone, which is most vulnerable to thaw (Spence et al., 2020) due to the extended vertical and lateral conduction (Devoie et al., 2021) such that even slight increases in temperature can lead to pronounced permafrost degradation (Wright et al., 2022).

Although the basic hydrochemical properties and export fluxes of the Taz River have been assessed based on the Russian Hydrological Survey program in the 1970s [which included multiple samples per year over several years (Gordeev et al., 1996)] and more recent hydrological studies of the Taz River (Zakharova et al., 2011; Nasonova et al., 2019) and hydrochemical studies of some nutrients and toxicants in the mouth zone of this river (Bryzgalo et al., 2011). However, these more recent studies were of insufficient seasonal resolution and did not allow reliable assessment of elementary export fluxes. It has been demonstrated by many authors that much higher frequency sampling of river water is necessary to quantify riverine export of solutes (Horowitz, 2013; Yanai et al., 2015; Kerr et al., 2016; Chupakov et al., 2020; Vorobyev et al., 2019; Juhls et al., 2020; Gandois et al., 2021).

The main objective of this study is to quantify the annual and seasonal export fluxes of C, nutrients, and major and trace elements by a pristine river draining permafrost peatlands and to characterize the main environmental drivers responsible for seasonal variations of riverine solutes. Information obtained may help to foresee the impact of climate warming on organic and inorganic solute export via using the gradients in temperature, vegetation and permafrost across the river watershed.

2. Study site, materials and methods

2.1. Taz River basin and river discharge

The Taz River originates on the Siberian Uvaly, a hilly region in the central part of the Western Siberian Lowland (WSL), and drains through mires (40%) and forests (60%) of the north-eastern part of the WSL. It is located entirely within the permafrost zone, discontinuous in the south and continuous in the north. The river has a broad valley and extended floodplain zone, where the permafrost does not occur, except in the peatlands bordering the main stem. Its overall length is 1400 km and its watershed area equals 150,000 km^2. The average discharge at the river mouth is 1450 m^3 s^{-1} and strongly varies across seasons (from 6600 to 157 m^3 s^{-1} between spring flood and winter baseflow). The spring flood, summer and winter baseflow provide 60, 21 and 19%, respectively, of annual discharge (Fig. 1). The mean annual air temperature (MAAT) is -5.4 ± 0.9 °C and the mean annual precipitation is 540 ± 20 mm y^{-1}. The lithology of the catchment is dominated by clays, silts and sands which are overlayed by quaternary deposits (loesses, fluvial, glacial and lacustrine deposits). The dominant soils are podzols in forest areas and histosols in peatland regions.

The daily discharge of the Taz River at Tazovsky site was calculated from daily discharges measured at the Russian Hydrological Survey (https://gmvo.skniivh.ru) gauging station at Sidorovsk (150 km upstream of Tazovsky, without any major tributary on this river section), following the methodology elaborated for Western Siberia (Rozhdestvensky et al., 2003; Kopysov et al., 2020) and taking into account daily precipitation and temperature from the Tazovsky meteorological station following Bulygina et al. (2021). The daily discharge reconstruction for the period from June 2017 to August 2020 at the Tazovsky sampling site was performed via a Windows-based HBV-light model (Bergström, 1992; Seibert and Vis, 2012). For a suitable analogue river to verify reliability of discharge modeling, we used the neighboring and similar sized Pur River, for which the measured daily discharges are available at the Urengoy gauging station of Russian Hydrological Survey (https://gmvo.skniivh.ru).

2.2. Sampling and analyses

Between 2018 and 2020, during high flow of the spring flood (May) we sampled the river every 2–3 days, whereas during summer, autumn and winter baseflow we sampled weekly. From 2016 to 2017, we sampled once a month and weekly during high flow. Altogether, 41 samples were collected during spring flood, 70 samples were collected during summer-autumn baseflow and 127 samples were collected under ice during winter. Water samples were taken 200 m offshore from 0.3 m depth in pre-cleaned polypropylene bottles and were immediately filtered through sterile, single use Minisart® filter units (Sartorius, acetate cellulose filter) with a pore size of 0.45 μm. The water temperature, pH and conductivity were measured using a Hanna HI991300 conductivity meter and a WTW portable pH meter with combined electrode. The DOC and DIC were measured by a Shimadzu® TOC-VCSN (total combustion at 950 °C with Pt catalyzer and via acid addition without combustion), with a detection limit of 0.1 mg L^{-1} and an uncertainty of 5%. The SUVA was measured via ultraviolet absorbance at 245 nm using a 10-mm quartz cuvette on a Bruker CARY-50 UV-VIS spectrophotometer. Major anion concentrations (Cl and SO_4) were measured by ion chromatography (Dionex ICS 2000) with an uncertainty of 2%. Internationally certified water samples (ION-915, MISSISSIPPI-03, RAIN-97) were used to check the validity and reproducibility of analysis. Good agreement between our replicated measurements and the certified values was obtained (with relative difference < 10%).

Filtered (< 0.45 μm) samples for nutrient (N, P) analyses were frozen on-site and transported to the laboratory in the frozen state. Nutrient analyses were based on colorimetric assays (Koroleff, 1983a, 1983b). Total dissolved organic nitrogen (DON) was measured from the difference between the total dissolved nitrogen (persulfate oxidation) and the total dissolved inorganic nitrogen (DIN, or the sum of NH_4^+, NO_2^- and NO_3^-). Uncertainties of dissolved N analyses were between 5 and 10% and detection limits were equal to 10 μg L^{-1} for N-NO_3 and N_{tot}, 2 μg L^{-1} for N-NH_4 and 0.5 μg L^{-1} for N-NO_2. The P-PO_4 analyses were based on the formation of molybdenum blue complex from the reaction of orthophosphate and ammonium molybdate followed by reduction with ascorbic acid in an aqueous sulfuric acid medium, with an uncertainty of 5% and a detection limit of 2 μg L^{-1}.

Filtered solutions for cation analyses were acidified (pH ~ 2) with ultrapure double-distilled HNO_3 and stored in pre-washed high-density polyethylene (HDPE) bottles. The preparation of bottles for sample storage was performed in a clean bench room (International Organization for Standardization (ISO), A 10,000). Blanks were performed to control the level of pollution induced by sampling and filtration. Major cations (Ca, Mg, Na, K), Si, P, and about 40 trace elements were determined with an inductively coupled plasma mass spectrometry (ICP-MS) Agilent ce 7500 with a collision cell, using In and Re (~ 3 ppb) as

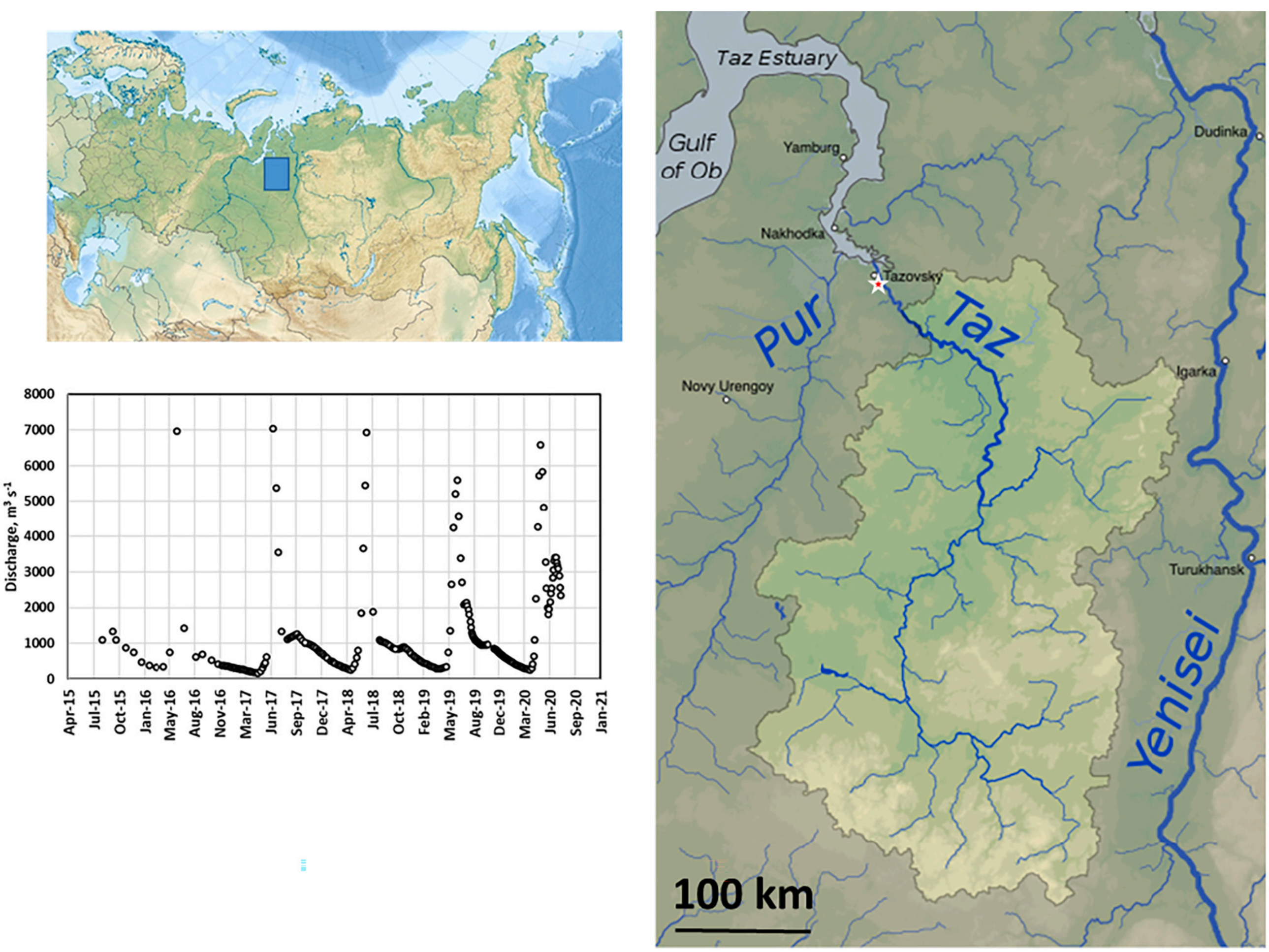

Fig. 1. Map of the studied Taz River watershed and daily discharge (Q) at the terminal gauging stations, Tazovsky in 2015–2020. White/red asterisk denotes the position of sampling point. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

internal standards. We used 3 external in-house standards, which were placed after each 10 river water samples. Detection limits of TE were determined as 3× the blank concentration. The typical uncertainty for elemental concentration measurements ranged from 5% at 1–1000 μg L^{-1} to 10% at 0.001–0.1 μg L^{-1}. The Milli-Q field blanks were collected and processed to monitor for any potential contamination introduced by our sampling and handling procedures. The Riverine Water Reference Material for Trace Metals (SLRS-6, certified by the National Research Council of Canada) was used to check the accuracy and reproducibility of analyses (Yeghicheyan et al., 2019). It was analyzed each 20 samples and satisfactory agreement (relative difference ≤ 15%) was obtained for all certified major and trace elements.

2.3. Data treatment and flux calculation

Annual element fluxes were estimated similar to LOADEST method (https://water.usgs.gov/software/loadest/, Holmes et al., 2012) from calculated daily element loads. The latter were obtained from a calibration regression, applied to daily discharge from the RHS. The calibration regression was constructed from time series of paired streamflow and measured element concentration data for 2017 to 2020 following the methodology elaborated for a similar data set of another medium-size Arctic river, the Severnaya Dvina (Chupakov et al., 2020). A multivariate extension of the nonparametric Mann-Kendall rank test was used for detecting relationships between element concentration and discharge. Because of the high seasonal variation in water chemistry - time series, trend tests were performed separately for three seasons (winter, November–May; spring, June–July; summer, August–October) and the full available data set over the 3 years.

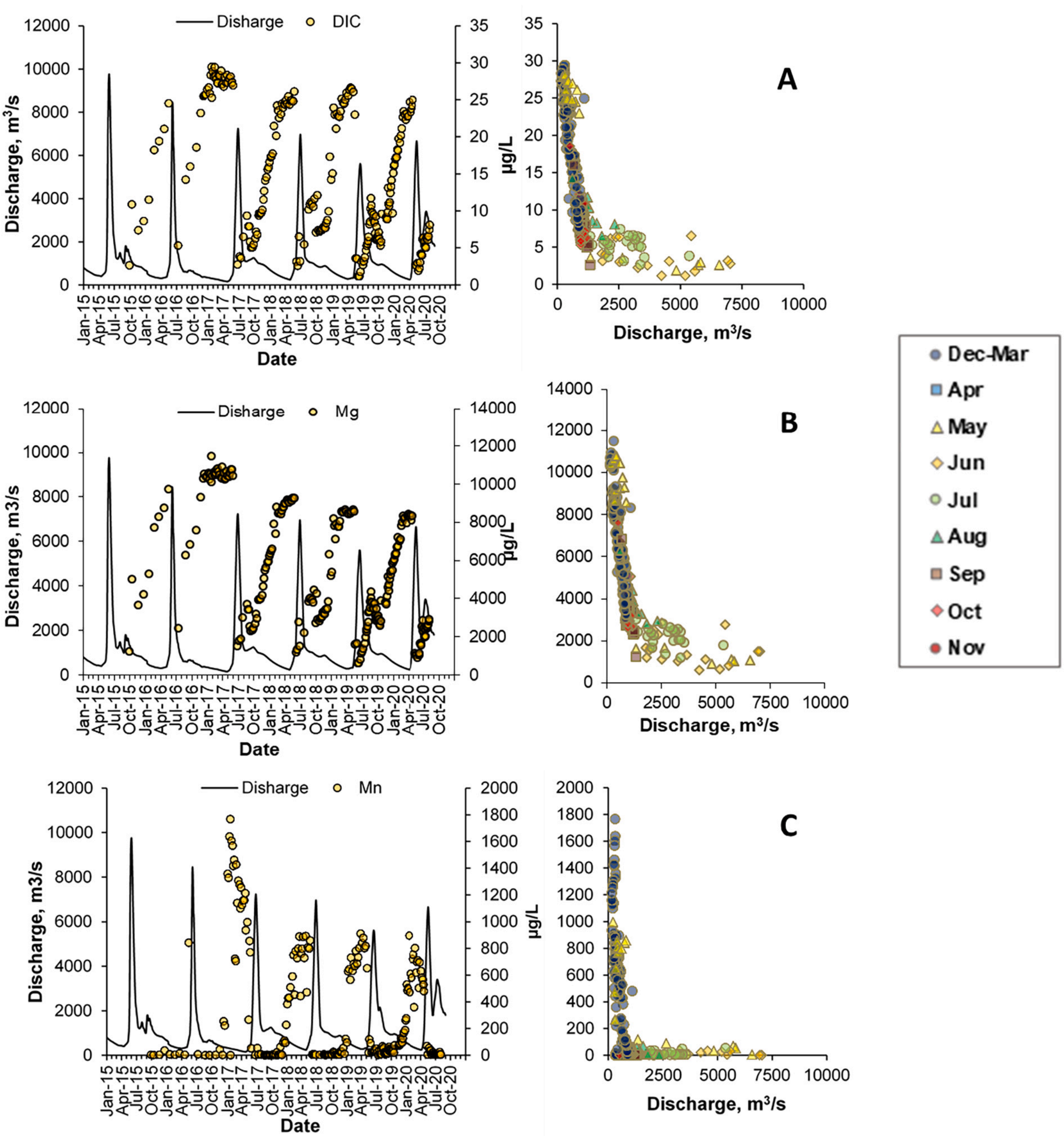

Fig. 2. The concentration- discharge relationships of elements of the 1st group: DIC (A), Mg (B) and Mn (C) of the Taz River in 2015–2020.

3. Results

3.1. Seasonal features of element export by the Taz River and element relation to the discharge

All the primary data on dissolved (<0.45 μm) element concentration in the Taz River together with discharges are available from the Mendeley Repository (Pokrovsky et al., 2022). Seasonal patterns in concentration variation and pairwise (Pearson) correlations over the full period of our observations indicate 3 group of solutes. The 1st group was represented by dissolved inorganic carbon (DIC), specific conductivity, some nutrients (NO_3, NH_4, N_{tot} and Si) and soluble elements presumably originated from groundwater and soil mineral horizons (Cl, SO_4, Li, B, Na, Mg, Ca, Sc, Si, K, Rb, Mn, Co, Sr, Mo, Cs, Ba and W). This group showed a maximum in the end of winter, before the spring ice-off, and negatively correlated with discharge (Fig. 2 and **Fig. S1**). Particular elements of the 1st group included K, Rb and Cs that showed a less pronounced link to discharge compared to alkaline-earth metals and demonstrated an occasional peak during the spring flood.

The 2nd group positively correlated with discharge and included dissolved organic carbon (DOC), SUVA, Al, Be, V, Y, Zr, Nb, REEs, Hf, Pb and Th. The concentration of these elements demonstrated two maxima: 1) during the spring flood (2nd half of June) and 2) during the autumn high flow or before the ice-on (November). The 2nd group demonstrated one minimum during winter (Fig. 3 **A, B** and **Fig. S2** of the Supplement). An important feature of elements in the 2nd group is the strong spring

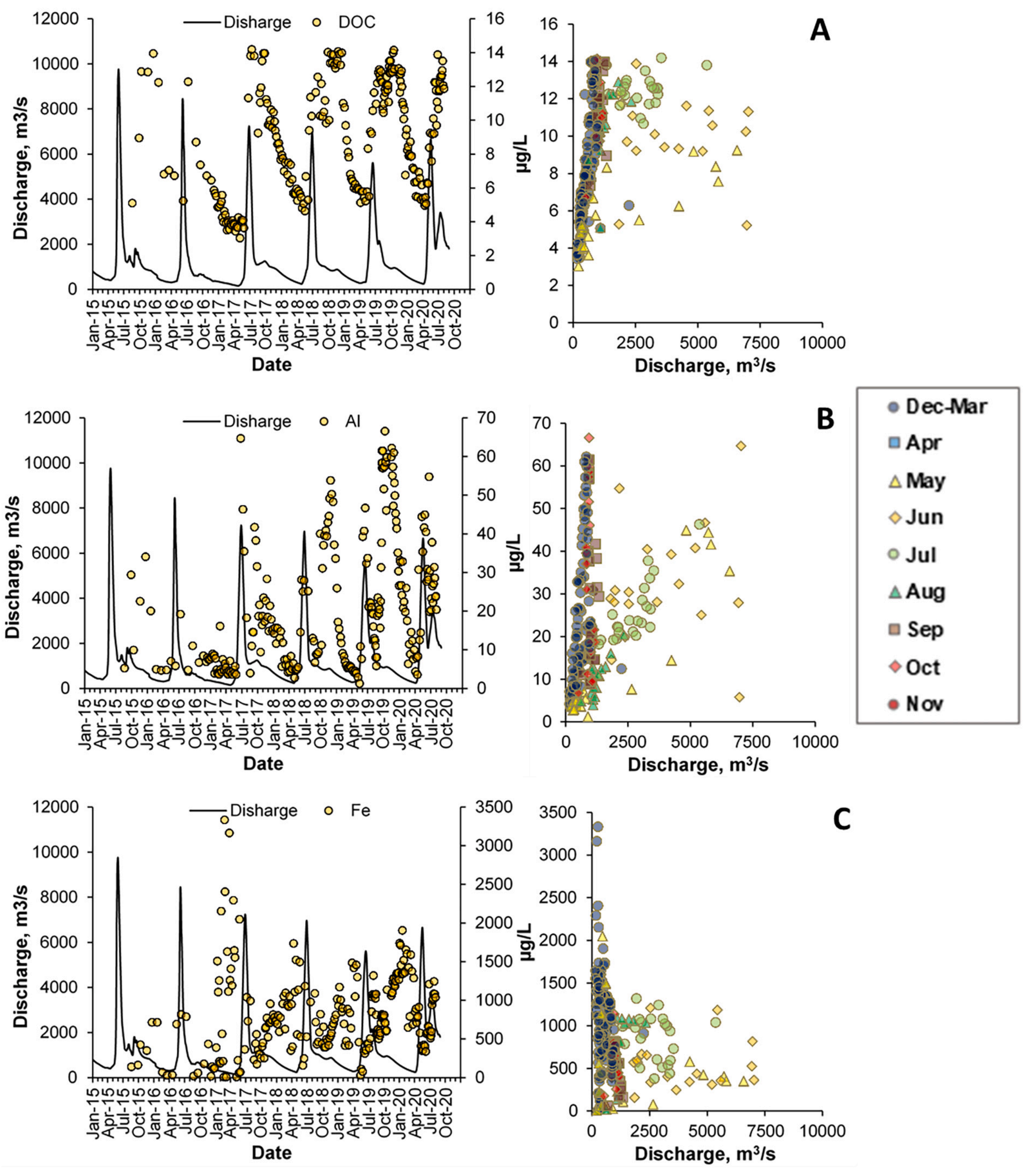

Fig. 3. The concentration- discharge relationships of elements of the 2nd group: DOC (A), Al (B) and Fe (C) of the Taz River in 2015–2020.

pulse (abrupt, > 10-fold concentration rise) and a summer maximum, occurring, for example, with Zn, Cd and Pb. For a number of biologically-active metals (V, Ni, Zn), the existence of the summer maximum decreased the overall correlations between these element concentrations and the river discharge. It is worth noting that heavy trace elements (REEs, Hf, Th) exhibited the late autumn maximum which was more pronounced than that of the early season (spring flood).

Finally, the 3rd group of elements included PO_4^{3-}, P_{tot}, NO_2^-, K, Cr, Cu, Ni, Rb, As, Sb and Se that did not demonstrate any significant dependence on the discharge (shown as examples of Fe in Fig. 3C, Ni, Cu and Rb in Fig. 4 and K, Sb, As in **Fig. S3** of the Supplement). The concentrations of these elements did not show any systematic seasonal variations and exhibited several non-reproducible peaks. It is the existence of several distinct peaks during hydrologically-contrasting seasons (winter, spring flood, summer, autumn) that led to a very complex pattern of element concentration dependence on discharge and did not allow obtaining statistically significant correlations with river discharge. For example, Fe belongs to this group of elements with complex behavior as it exhibited two maxima of concentration, one at the end of spring flood in June and another at the end of winter (March to April) at the minimal flow under ice (Fig. 3 **C**).

The proposed classification into these 3 groups was primarily based on element evolution over the season and linkage of their concentration to river discharge. The existence of these groups was further supported by the pairwise correlation coefficients of riverine solutes over the full time of observation (**Table S1**). The first group of elements, whose

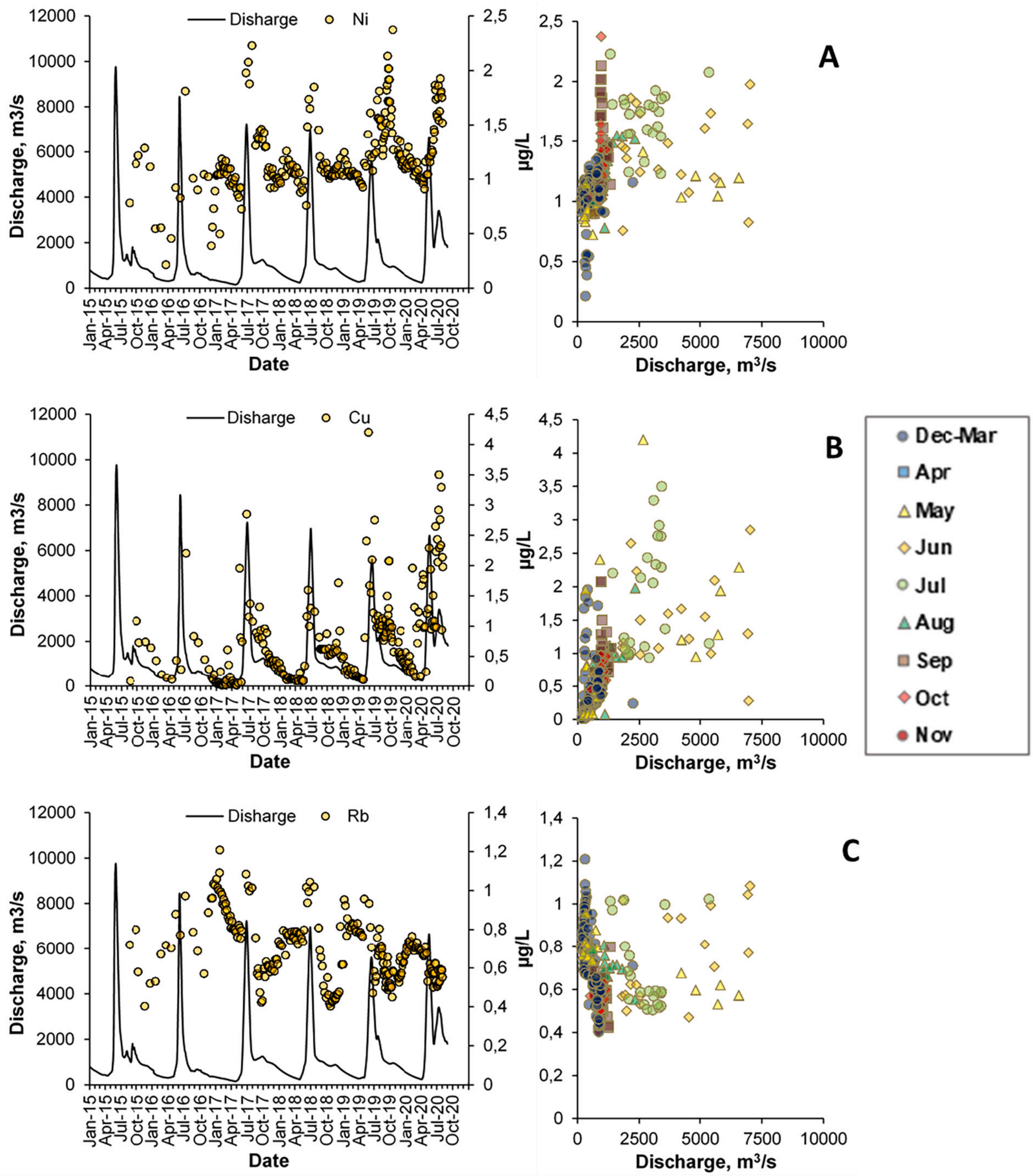

Fig. 4. The concentration-discharge relationships of elements of the 3rd group: Ni (A), Cu (B), and Rb (C) of the Taz River in 2015–2020.

concentrations increased with a discharge decrease, were strongly ($p < 0.05$) correlated with DIC and specific conductivity and included anions and simple molecules (Cl, SO_4, B, Si, Mo and W), alkalis (Li, Na, K, Rb and Cs), alkaline-earth elements (Mg, Ca, Sr and Ba), Sc, Mn, Co and Cu, as illustrated in Fig. 5 **A-D** for B, Si, Mn and Sr. The highest pairwise correlations ($R^2 > 0.91$, $p < 0.001$) were observed between DIC and B, Na, Mg, Si, Ca and Sr.

The 2nd group of elements, those that positively correlated with the discharge, could be adequately approximated by DOC concentrations and included trivalent and tetravalent hydrolysates (Al, Y, all REEs, Ti, Zr, Hf and Th) and trace metals bound to organic complexes or colloids (Be, V, Ni, Nb and Se) as illustrated in Fig. 5 ***E*-H** for Al, V, Y and La. The strongest ($R^2 > 0.60$, $p < 0.01$) correlations of DOC were observed with Be, Y, Hf, Th and REEs. Note that the R^2 of REE increased from light to heavy REE (0.72–0.65 for La and Ce to 0.80 for Er and Yb).

The 3rd group of elements demonstrated the most complex and non-systematic seasonal pattern and lack of correlation with the river discharge correlated neither with groundwater proxies (S.C. and DIC) nor with trace element carrier (DOC). These included macro-nutrients (N, P), Fe, a number of trace metals such as toxicants (Cr, Zn, Cd, Tl, Pb and Bi), less common TE (Sn, Te and W) and U. Dissolved Fe did not demonstrate any sizable correlations with other elements except As ($R^2 = 0.41$, $p < 0.01$). Note that, although Al also exhibited significant ($p < 0.05$) correlations with some insoluble elements (Ti, Y, Zr, REEs, Nb, Hf and Th), these correlations were still lower than those between these insoluble elements and DOC (**Table S1**).

3.2. *Mean multi-annual yields of dissolved carbon, major and trace elements*

Based on an overall five years of monitoring (2016–2020), we calculated mean multi-annual export fluxes for all major and trace dissolved components of the Taz River (summarized in Table 1 and listed for each month of the year in **Table S2** of the Supplement). The mean annual distribution of export fluxes among three main hydrological seasons in terms of share of annual flow (Table 2**)** demonstrated the following features. The spring flood (May–June) accounted for 36% of annual water flow and provided between 30 and 45% of annual flux of DOC, Cl and SO_4, macronutrients (K, N and P) and most major and minor solutes. A number of elements present in the snowpack exhibited essential (> 45%) export during spring flood (Zn, Cu, Pb, Sb and Cs), with Cd exhibiting as much as 85% of annual flux during the spring flood period. All soluble, highly mobile elements (DIC, Si, Li, B, Na, Mg, Ca, Sr and Co) exhibited sizable (30–40%) export during winter baseflow. Manganese presents an exceptional case because the share of its winter – time yield was as high as 72%. The elements with maximal export during summer baseflow are Fe, Zn, V, As and light REE.

The elementary export flux by the Taz River calculated based on monthly-averaged discharge and concentrations and daily discharges with interpolated concentrations were generally (within ±20–30%) similar (not shown). However, ignoring strong variations in discharge at the transitional periods between winter baseflow and spring flood, or the summer baseflow and autumn flood may produce sizable biases (in both directions) in major and trace element seasonal export.

To the best of our knowledge, multi-elemental annual yields of all major and trace elements for the permafrost-affected rivers of similar size and physio-geographical context based on high-frequency sampling are not available in the literature. Therefore, the obtained yields of DOC, DIC, macro-nutrients, major cations and ~ 30 trace elements could be compared with a few available measurements of year-round fluxes in the largest European subarctic river, Severnaya Dvina (Chupakov et al., 2020), small rivers of the permafrost zone of the WSL (Pokrovsky et al., 2020) and the Ob River in its middle course draining through permafrost-free forest and peatlands (Vorobyev et al., 2019). The permafrost-free Severnaya Dvina River draining through taiga and wetlands on carbonate and sedimentary rocks demonstrates a 2 to 3 times higher yield of soluble highly mobile elements such as DIC, Ca, K, Mg, Sr and U compared to the Taz River and 30–50% higher DOC and other trace elements, except Fe, Mn and Co whose export is 2 to 3 times higher in the Taz River. Small rivers of the WSL permafrost zone are sizably (a factor of 2 to 3) enriched, in terms of annual yield, in DOC, Al, Ti, Ba and Zr, but the export of other elements by small rivers was generally comparable (± 30%) to that of the Taz River. Finally, the annual yields of DOC, Si, Al, Ti, Cr, Cu, Ni and Co in the Taz River were 3 to 4 times higher than those of the Ob River in its middle course, whereas the annual yield of P, Y, REE and Pb was an order of magnitude higher in the Taz River compared to the Ob River. Iron and Mn yields in Taz River again stand out as they were 40 and 20 times higher, respectively than those in the Ob River. In contrast, several soluble, highly mobile elements (DIC, Ca, Sr, Sb and Mo) exhibited 2 to 4 higher yields in the Ob River compared to the Taz River, whereas Ba and U export by Ob was a factor of 8 and 20 times higher, respectively, than that by Taz.

4. Discussion

4.1. *Environmental factors controlling seasonal pattern of major and trace elements in the Taz River*

In general, the groups of elements identified in the Taz River depending on their relation to discharge and seasonal concentration patterns were consistent with previous classifications of major and trace elements in boreal and subarctic rivers (Pokrovsky et al., 2010, Pokrovsky et al., 2012b). However, several unique features of the Taz River basin (lithology, peat, permafrost, large floodplain zone, short open-water period) bring about specific behavior of a number of mobile, organic-bound and redox-sensitive elements. Thus, soluble, highly mobile elements (oxyanions and neutral molecules, alkalis and alkaline-earth metals) which are typical for the first group of elements, and exhibit negative correlation with the discharge, generally originate from high-DIC groundwaters (Bagard et al., 2011; Pokrovsky et al., 2015, 2016b, 2020). Such a relationship is typical for solutes subjected to strong dilution without hemostasis during export from the watershed (Thompson et al., 2011; Moatar et al., 2017; Rose et al., 2018). However, in the Taz River this group also included Mn which showed a strong accumulation in winter, under ice, but did not include uranyl.

In contrast, the elements of the 2nd group (DOC, lithogenic low-soluble trivalent and tetravalent hydrolysates) and organically-bound trace metals (Be, V, Cr, Co, Ni, Cu, Cd, Pb and Nb) exhibited maximal concentrations during peaks of spring and autumn flood, being positively correlated with river discharge (Fig. 3 and **Fig. S2**). Such a behavior of elements of the 2nd group is presumably due to their mobilization from topsoil in the form of organic and organo-mineral colloids by surface flow through forest litter during spring flood and storm events and thawed soil mineral layers during summer baseflow, similar to other permafrost-dominated Siberian watersheds (Bagard et al., 2011). The mobilization of these DOM - associated solutes occurs from riparian zone, floodplain sediments, and shallow soil layers (Mei et al., 2012; McLaughlin and Kaplan, 2013); these processes might be responsible for positive relationship between DOC and discharge in various catchments across the world (Moatar et al., 2017; Musolff et al., 2015; Rose et al., 2018). The most intense leaching of organically-bound trace metal from ground vegetation and forest litter occurs during storms and floods (Ciszewski and Grygar, 2016). Note that the late autumn maximum of heavy lithogenic elements (REEs, Hf, Th) which was more pronounced than that of the early season indicates preferential mobilization of these elements from deep mineral soil horizons, during the time of maximum thawing depth.

A local maxima of heavy metal concentrations was noted for Zn, Cd and Pb during spring flood; on some days of high flow, concentration of these elements raised 10- to 100-fold. This increase may be linked to massive mobilization of these elements from the melt snow. In fact, recent analysis of the snow collected from large territory of western

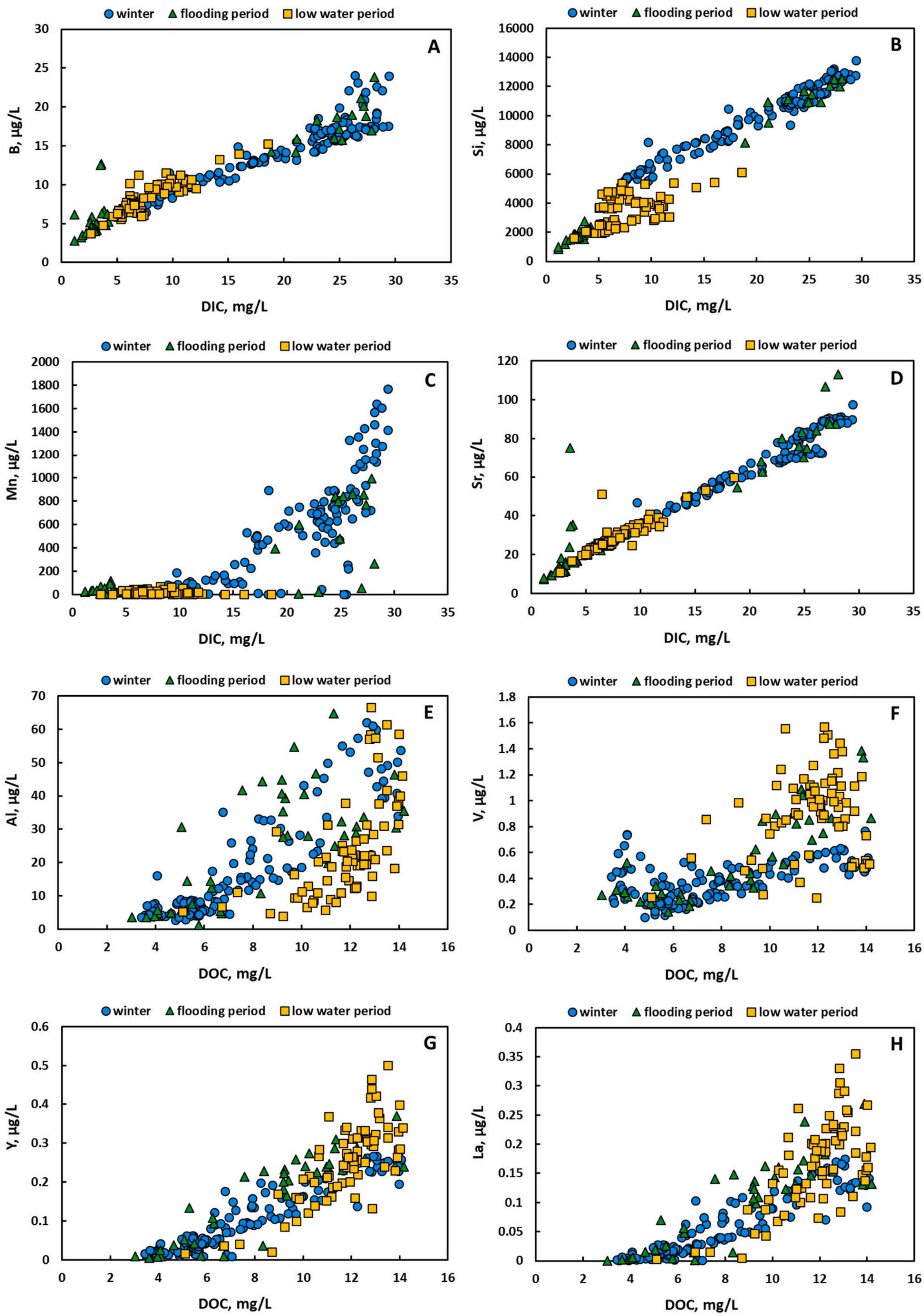

Fig. 5. Correlations between element concentrations in the Taz River: B (A), Si (B), Mn (C), and Sr (D) as a function of DIC concentration and Al (E), V (F), Y(G) and La (H) as a function of DOC concentration. Blue circles, green triangles and yellow squares represent three main hydrological seasons – winter baseflow, spring flood and summer-autumn low water period, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Mean multi-annual concentration (C) and yields (F) of the Taz River watershed (150,000 km^2). For most elements we used the most complete data set of 2017 to 2019. The nutrients were calculated based on full period of observation (2015 to 2020) due to insufficient number of measurements during last three years.

Solute	C, μg L^{-1} (±SD)	F, kg km^{-2} y^{-1} (±SD)	Solute	C, μg L^{-1} (±SD)	F, kg km^{-2} y^{-1} (±SD)
DOC	9040 ± 3340	2670 ± 70	Se	0.031 ± 0.008	0.003 ± 0.004
DIC	14,900 ± 8870	2160 ± 220	Rb	0.7 ± 0.2	0.20 ± 0.02
Li	1.1 ± 0.3	0.22 ± 0.02	Sr	51 ± 26	8.6 ± 1.7
Be	0.007 ± 0.005	0.0028 ± 0.0001	Y	0.15 ± 0.10	0.053 ± 0.003
B	12 ± 5	2.2 ± 0.2	Zr	0.09 ± 0.05	0.031 ± 0.002
N_{tot}	410 ± 71	107 ± 38	Nb	0.002 ± 0.001	0.0006 ± 0.0001
N-NO_3	235 ± 117	45 ± 18	Mo	0.09 ± 0.04	0.018 ± 0.003
N-NH_4	15 ± 8	3.4 ± 2.5	Cd	0.013 ± 0.003	0.009 ± 0.005
N-NO_2	4 ± 1	1.3 ± 0.5	Sb	0.02 ± 0.01	0.0069 ± 0.001
Na	3720 ± 1800	615 ± 79	Cs	0.0012 ± 0.0006	0.00028 ± 0.00005
Mg	5640 ± 3090	866 ± 112	La	0.08 ± 0.07	0.032 ± 0.003
Al	21 ± 17	7.4 ± 1.2	Ce	0.15 ± 0.12	0.057 ± 0.01
Si	7250 ± 3850	1103 ± 99	Pr	0.02 ± 0.02	0.0092 ± 0.0009
P_{tot}	67 ± 57	19 ± 4	Nd	0.10 ± 0.08	0.039 ± 0.002
P-PO_4	49 ± 16	12 ± 5	Sm	0.03 ± 0.02	0.0093 ± 0.0009
SO_4	1690 ± 930	421 ± 92	Eu	0.007 ± 0.004	0.0024 ± 0.0002
Cl	798 ± 255	165 ± 34	Gd	0.03 ± 0.02	0.010 ± 0.001
K	514 ± 191	128 ± 24	Tb	0.004 ± 0.003	0.00145 ± 0.00008
Ca	13,100 ± 6640	2120 ± 323	Dy	0.02 ± 0.02	0.0089 ± 0.0004
Ti	0.7 ± 0.3	0.19 ± 0.01	Ho	0.005 ± 0.003	0.00182 ± 0.00008
V	0.5 ± 0.3	0.19 ± 0.01	Er	0.01 ± 0.01	0.0053 ± 0.0002
Cr	0.4 ± 0.2	0.10 ± 0.06	Tm	0.002 ± 0.001	0.00074 ± 0.00005
Mn	350 ± 439	29 ± 1	Yb	0.014 ± 0.009	0.0048 ± 0.0001
Fe	789 ± 429	166 ± 15	Lu	0.002 ± 0.001	0.00075 ± 0.00002
Co	0.3 ± 0.3	0.04 ± 0.01	Hf	0.003 ± 0.002	0.0010 ± 0.0001
Ni	1.2 ± 0.3	0.36 ± 0.03	W	0.004 ± 0.003	0.00057 ± 0.00037
Cu	0.69 ± 0.63	0.30 ± 0.06	Tl	0.0013 ± 0.0009	0.00032 ± 0.00006
Zn	9 ± 15	4.2 ± 2.5	Pb	0.1 ± 0.1	0.036 ± 0.01
Ga	0.02 ± 0.01	0.004 ± 0.002	Bi	0.003 ± 0.002	0.00032 ± 0.00025
Ge	0.03 ± 0.02	0.007 ± 0.004	Th	0.009 ± 0.007	0.0037 ± 0.0003
As	0.8 ± 0.3	0.20 ± 0.01	U	0.016 ± 0.004	0.0043 ± 0.0003
Ba	5.2 ± 2.4	1.1 ± 0.1			

Siberia and mass-balance calculations demonstrate that, during the spring flood, the snowmelt of the region is capable providing >100% of riverine discharge of Zn, Cd and Pb (i.e., these elements can be entirely originated from the snow water, Krickov et al., 2022). A second maximum of some elements in this group could be linked to leaching from the litter fall, especially pronounced for deciduous needle-leaf forest of the river basin, similar to what is known for other parts of Siberia (Viers et al., 2013).

The elements of the 3rd group exhibited the features of two first groups and originated from both surface and underground sources with strong impact of autochthonous biotic processes in the river channel and soils of the watershed (nutrients, Cr, Rb, As, Sb and Se). Indeed, the role of autochthonous in-stream processes on nutrients and some metals is well known (Behrendt and Opitz, 2000; Vink et al., 1999). The behavior of these elements reflected a superposition of multiple source and transport factors such as redox processes, biotic uptake, groundwater input and surface colloidal export. For example, Fe exhibited a strong winter maximum but also another maximum during spring flood. The winter maximum could be linked to accumulation of reduced Fe under the ice; this Fe(II) is most likely mobilized from riparian sediments and within the river hyporheic zone, at sites of local anoxia (Dong et al., 2020). The spring-time maximum of Fe is tentatively linked to its transport in the form of large size Fe(III)-OM colloids, as is known in small rivers (Krickov et al., 2019) and soil porewaters (Raudina et al., 2021) of the region.

Finally, macro- and some micro-nutrients exhibited complex features without statistically significant linkage to discharge on an annual scale. For example, nitrate and Mn demonstrated one maximum at the end of winter and one minimum during the summer (July–August). While the summer minima of nutrients such as N, P and Mn are induced by biological uptake or enhanced photo-coagulation in warm waters as it is known in other organic-rich boreal lakes and rivers (Pokrovsky and Shirokova, 2013; Vorobyev et al., 2017; Chupakov et al., 2020), the winter baseflow maximum can be linked to specific hydrological setting of the Taz River's lower reaches, possessing a huge floodplain zone. We noted high Mn accumulation during winter baseflow; under the ice the dissolved concentration of this element achieved 800 to 1800 μg L^{-1}. These concentrations are 2 orders of magnitude higher than the world river average (Laxen et al., 1984; Gaillardet et al., 2005), and, during this period of the year, comparable to Fe concentrations. A recent hydrochemical study of the northern part of the Taz River basin demonstrated that Mn was the only element that could migrate from topsoil and suprapermafrost water to surface water and river water, indicating that Mn may be a proxy for predicting processes occurring in the active layer during summer-autumn thawing (Ji et al., 2020). Another explanation is enhanced mobilization of manganese from the riparian zone/floodplain (Björkvald et al., 2008) which becomes partially anoxic under the long-lasting ice/snow regime of the Taz River floodplain. It is interesting that equally high concentrations of reduced Fe and Mn occur in bottom layers (hypolimnion) of seasonally stratified subarctic lakes (i.e., Pontér et al., 1992; Pokrovsky et al., 2012b). Although the hydrochemistry of floodplain lakes of the Taz River's lower reaches is totally unknown, it can be hypothesized that an influx of waters rich in Mn and some other redox-sensitive elements from these lakes to the main stem may provide elevated concentrations of these elements during glacial baseflow period. We believe that this is a specific feature of permafrost peatland rivers having large floodplain zone, hence the Taz River's selection for further seasonally-resolved study of both hydrochemistry and hydrological connectivity.

Another striking example of the seasonal behavior of riverine solutes is uranyl: in boreal rivers, it is known to demonstrate the features of the 1st group of labile elements, being strongly accumulated under ice during winter time, due to enhanced mobility of U(VI) in the form of uranyl-carbonate complexes (Pokrovsky et al., 2016a; Krickov et al., 2019; Vorobyev et al., 2019). For this reasons, U concentration in seasonally frozen rivers subjected to groundwater feeding is strongly

Table 2
Percentage of element yield during each season of the year: winter (November–April), spring flood (May–June), summer (July–August), and autumn (September–October).

Index	winter	spring flood	summer	autumn	Index	winter	spring flood	summer	autumn
Flow	21	36	29	14	Se	22	29	26	22
DOC	18	32	34	16	Rb	18	41	32	9
DIC	42	26	19	13	Sr	34	30	24	12
Li	30	29	26	15	Y	13	35	35	16
Be	12	37	36	14	Zr	16	34	34	17
B	31	32	24	13	Nb	16	33	38	13
$N-NO_3$	32	33	20	16	Mo	24	34	31	11
$N-NH_4$	27	29	29	16	Cd	3	85	10	2
$N-NO_2$	17	46	25	11	Sb	12	43	32	14
N_{tot}	27	38	22	13	Cs	22	47	23	8
Na	36	30	21	14	Ba	27	35	25	13
Mg	39	27	21	13	La	12	35	38	16
Al	17	42	26	15	Ce	12	37	36	15
Si ICP	42	26	17	14	Pr	12	36	37	15
$P-PO_4$	29	30	27	14	Nd	12	36	37	15
P_{tot}	17	37	36	10	Sm	13	36	36	16
Cl	27	34	24	15	Eu	13	35	36	15
SO_4	20	42	28	10	Gd	13	36	35	16
K	19	42	30	8	Tb	13	35	36	16
Ca	37	28	22	13	Dy	13	36	36	15
Ti	20	32	32	15	Ho	13	35	36	16
V	11	34	43	12	Er	13	35	36	16
Cr	17	39	33	11	Tm	14	35	36	16
Mn	72	22	4	2	Yb	14	36	35	16
Fe	29	24	35	12	Lu	14	36	34	16
Co	45	29	18	9	Hf	15	36	33	16
Ni	16	36	35	13	W	21	42	26	11
Cu	7	55	29	9	Tl	21	37	32	9
Zn	6	44	45	5	Pb	4	48	43	5
Ga	28	32	25	15	Bi	28	41	23	8
Ge	27	28	27	17	Th	11	39	34	15
As	20	29	38	14	U	17	39	32	12

correlated with DIC (Chupakov et al., 2020). However, this was not the case for the Taz River: no sizable correlation of U concentration with DIC, DOC or discharge was established. A tentative explanation for this is that the continuous to discontinuous permafrost of the Taz River precludes sufficient contact with deep groundwaters similar to what is known for small rivers of the WSL (Frey et al., 2007; Pokrovsky et al., 2015, 2016a, 2020). Furthermore, the mother rocks developed on the Pur-Taz interfluve and the Taz watershed are essentially clays, sands, silts and diatomites with no sizable amount of carbonate concretions or loesses (Volkova, 2014). This contrasts with the presence of carbonate rocks in rivers of the southern part of the WSL, or in the largest European Arctic river Severnaya Dvina, draining through forest and wetlands, where strong winter-time enrichment in UO_2(VI) is well established (Pokrovsky et al., 2016a; Vorobyev et al., 2019; Chupakov et al., 2020).

4.2. *Element correlations and forms of export*

The groups of elements described above were consistent with pairwise correlations across the seasons that revealed two main indicators: (*i*) DIC, that positively correlated with deep groundwater-originated highly labile elements and soluble salts (S.C.) such as anions and neutral molecules (Cl, SO_4, Si, B, Mo and W), alkalis (Li, Na, K, Rb and Cs), alkaline-earth metals (Mg, Ca, Sr and Ba) and some other mobile elements (Sc, Mn, Co and Cu), and (*ii*) DOC, whose presence enhanced the transport of trivalent (Al, Ga, Y and REE), tetravalent (Ti, Zr, Hf and Th) elements and some organic-bound trace elements (Be, V, Ni, Se, Y, Nb and Ta).

An increase in correlation coefficients between REE and DOC from light (LREE) to heavy (HREE) is consistent with preferential transport of LREE in the form of ferric and organo-ferric colloids and higher affinity of HREE to the organic complexes as is known across boreal surface waters including the WSL (Vasyukova et al., 2010; Pokrovsky et al., 2016b) and stems from the change in chemical binding properties of the REE (Bau, 1999).

A lack of correlations between the elements of the 3rd group, notably of macro-nutrients or heavy metals (Zn, Cd, Pb and Bi) and DOC (or DIC) was due to the existence of multiple concentration peaks, notably during spring flood and summer baseflow. These peaks are linked to local autochthonous activity or mobilization with snowmelt, in contrast to more conservative patterns of DOC, DIC or total salts (specific conductivity).

In addition to DOM, dissolved Fe is often considered as a proxy of organo-ferric colloids in the boreal river water (Dahlqvist et al., 2007; Vasyukova et al., 2010; Bagard et al., 2011; Stolpe et al., 2013). These colloids accommodate numerous insoluble trace elements, notably trivalent and tetravalent hydrolysates such as those known in small rivers (Krickov et al., 2019), surface waters (Shirokova et al., 2013a; Pokrovsky et al., 2016b) and soil porewaters (Raudina et al., 2021) of western Siberia. However, in the case of the Taz River, no significant correlation of DOC with Fe, or Fe with any other trace element for that matter, was observed (**Table S1**). We believe that the main reason for this incoherent behavior of Fe is due to multiple counterbalanced factors controlling its delivery to and transport in the river water. First, Fe can be mobilized in the reduced form from riparian sediments via the shallow groundwater of the floodplain at the end of autumn and under the ice in winter resulting in peaks in its concentration during these periods of the year. Second, Fe can be transported in the form of organic complexes, produced via topsoil and plant litter leaching by snow meltwater during the spring flood when its concentration may increase together with DOC and the river discharge. Third, Fe can be exported from shallow subsurface waters (suprapermafrost flow) from adjacent peatlands (Raudina et al., 2018) which produces a peak in concentration at the end of summer. It is interesting that only As followed the behavior of Fe ($R^2 = 0.41$) suggesting a similar mechanism of mobilization from reduced groundwaters and via organic-rich surface colloids, as consistent with high affinity of As to both DOM and Fe oxy-hydroxides in inland waters (Bose and Sharma, 2002; Bauer and Blodau, 2006; Barral-Fraga et al., 2020).

4.3. Elementary yields of the Taz River basin compared to other boreal and subarctic rivers

The obtained yields of DOC and DIC (2.7 ± 0.07 and 2.2 ± 0.2 t C km^{-2} y^{-1}, respectively) were in reasonable agreement with earlier estimations of mean multi-annual values from long-term monitoring by the Russian Hydrological Survey (1.9 and 3.8, t C km^{-2} y^{-1}; Gordeev et al., 1996). The DOC yield of Taz is sizably higher than that reported for Ob, Yenisey and Lena (1.4, 1.9, and 2.3 t C km^{-2} y^{-1}, respectively; Holmes et al., 2012). This can be explained by enhanced mobilization of allochthonous aromatic organic matter to the main stem of the Taz River from surrounding peatlands, as also confirmed by elevated SUVA (4 to 5 mg C^{-1} m^{-1} L), stable over the course of the year.

The range of values for the riverine C yield in discontinuous to continuous permafrost zone of western Siberia, estimated from 3-season open water period (May to October) measurements in small rivers (< 100,000 km^2 watershed) are 3–5 and 0.5–1 t km^{-2} $period^{-1}$ for DOC and DIC, respectively (Pokrovsky et al., 2020). The higher annual DIC export from the Taz River assessed in this study is due to considerably higher winter baseflow and the much larger size of the river, with more pronounced hydrological connectivity to underground DIC-rich reservoirs compared to small WSL rivers of the permafrost zone.

Although the total number of nutrient concentration measurements in this study was an order of magnitude lower than that of other components, within a reasonably uncertainty (Table 1), we did not evidence anomalously high ammonia yields, as it was suggested by Holmes et al. (2000) based on the United Federal Service for Observation and Control of Environmental Pollution (OGSNK/GSN) of Russian Hydrological/Hydrochemical Survey. Even the winter-time concentrations of $N\text{-}NH_4$ were an order of magnitude lower than those of $N\text{-}NO_3$ (Table 1 and **S2** of the Supplement). We believe that analysis of unfiltered river water samples employed by Russian Hydrochemical Survey, and long storage of collected samples prior the analysis, while not strongly affecting DIC, DIC, major cations, anions, and silica (Zakharova et al., 2005, 2007; Pokrovsky et al., 2010; Chupakov et al., 2020), may create sizable bias in concentration of nutrients and thus interpretation of such data is not warranted. At the same time, the annual yield of $N\text{-}NO_3$ and $P\text{-}PO_4$ in the Taz River obtained in this study (45 and 12 kg km^{-2} y^{-1}, respectively) are sizably higher than those in the Yukon (26 and 2.5 kg km^{-2} y^{-1}, respectively) and Mackenzie (21 and 1.3 kg km^{-2} y^{-1}, respectively), as reported by Holmes et al. (2000) and Dornblaser and Striegl (2007). Nutrient mobilization from riparian lake sediments and herbaceous plant litter in the low reaches of the floodplain can be the cause of this elevated N and P flux in the Taz River.

The mean multi-annual total dissolved cation (TDS_c = Na + K + Ca + Mg) flux of the Taz River (3.7 ± 0.3 t km^{-2} y^{-1}) is comparable to 6-months of open-water period yield for small WSL rivers in the permafrost-free zone (2.6 ± 0.6 t km^{-2} y^{-1}, Pokrovsky et al., 2020) but sizably lower than the fluxes of Central Siberian rivers of the same latitude, draining basaltic rocks (5 to 8 t km^{-2} y^{-1}, Gordeev et al., 1996), large Siberian rivers such as Yenisey and Lena (6.2 and 6.8 t km^{-2} y^{-1}, respectively, Gordeev et al., 1996), the Ob River in its middle course (6.0 t km^{-2} y^{-1}, Vorobyev et al., 2019), and the permafrost-free Eurasian Arctic rivers draining through forest and peatlands underlain by sedimentary rocks (Severnaya Dvina, 9.5 t km^{-2} y^{-1}, Chupakov et al., 2020; Pechora, 6.6 t km^{-2} y^{-1}, Gordeev et al., 1996). However, the TDS_c yield of the permafrost-affected Taz River is comparable with previous estimations of other permafrost peatland-affected, mid-sized Siberian rivers (2.8, 2.5, and 2.3 t km^{-2} y^{-1} for Kolyma, Indigirka and Anabar, respectively, Gordeev et al., 1996). The main reason for the relatively low cationic flux of the Taz River compared to other large rivers of Northern Eurasia of similar runoff are *i)* low connectivity of this permafrost-affected river with underlying bedrocks and groundwater, due to thick peat layer and permafrost, and *ii)* the essentially weathered character of silicate rocks (sands, clays, silts) with a negligible amount of divalent cation-rich primary silicate and carbonate minerals in the northern part of western Siberia. The same reasons can be applied for the lower export flux of other soluble, highly mobile elements such as Sr, Ba, Mo, Sb and U in the Taz River compared to the permafrost-free Ob River or the Severnaya Dvina River, both exhibiting similar runoff and forest/peat land coverage.

The outstandingly high yield of Fe, Mn and Co (the latter is co-mobilized with Mn) of the Taz River compared to small rivers of the permafrost-affected WSL region and permafrost-free subarctic rivers may be linked to the highly developed floodplain zone of the Taz River, where winter-time mobilization of redox-sensitive elements occurs. This is consistent with reports on high level of Fe(II) in the low reaches of the Ob River where periodic hypoxia occurs (Telang et al., 1991). It is possible that, across the lower reaches of the Arctic rivers, a complex redox barrier is formed at the interface between oxic and anoxic zones in the riparian and floodplain sediment – water interface, notably during winter stagnation. Because this interface regulates the solute transfer from the watershed to the river main stem, it clearly can affect numerous biogeochemical processes, notably of redox-sensitive elements. One of such elements is manganese, which is a major component in this zone, and can act as a significant oxidant for organic carbon. To further verify this possibility, however, information on 1) in-situ redox conditions, especially under ice in winter, 2) degree of redox stratification of both river water column and floodplain lakes, and 3) hydrological connectivity between the floodplains lakes or stagnant riparian zone and the main stem are needed which is beyond the scope of this study.

Extremely high Mn and Fe yields of the Taz River, revealed in the present study, may contribute to better understanding of unknown sources of Mn in the surface layers of the Arctic Ocean (Middag et al., 2011). Small and medium size rivers account for 30 to 50% of total freshwater discharge to the Arctic Ocean (Feng et al., 2021). However, as shown in this study, these rivers may have order of magnitude higher annual yield of Fe and Mn, compared to great Arctic rivers and thus can provide sizable and currently non-accounted for source of dissolved metals to the coastal zone. At the same time, essential part of dissolved (< 0.45 μm) Fe may be removed in the estuary, whereas the behavior of Mn is more conservative with smaller losses during freshwater-seawater mixing. Furthermore, the bioavailable low molecular weight fraction ($LMW_{<1\text{–}3\ kDa}$) of metal micronutrients is not subjected to coagulation and removal in the estuary (Pokrovsky et al., 2014). In western Siberian rivers, including Taz, this LMW fraction accounts for 40 to 60% of total dissolved Mn (Krickov et al., 2019) during open water period and thus can represent important input of this metal to the Arctic Ocean from small and medium size coastal rivers similar to Taz. We admit that winter-time measurements of metal colloidal transport in Siberian rivers, never attempted so far, are needed to quantify the bioavailable flux of redox-sensitive metal micronutrients to the Arctic Ocean.

4.4. Possible consequences for assessing the climate change impact on riverine fluxes

Results of the present study allowed identification of several sources of elements, depending on transport mechanisms operating within the watershed such as deep groundwater, riparian zone and floodplain lake sediments, plant litter, mineral soil water, and peatwater from the peatlands. The partial contribution of each source to the annual export flux is different among elements, depending on their susceptibility to redox reactions or far-range atmospheric transfer. Among these sources, plant litter and topsoil act on the largest number of elements, provided that these elements are not exclusively affected by redox transformations, atmospheric input or groundwater feeding.

Despite the differences in elementary yields by various contrasting rivers (in terms of permafrost coverage, climate and rock lithology) of the boreal and subarctic zone, the numbers measured in previous studies and new data acquired here allow to suggest the existence of some kind of regulating/buffering mechanism(s) responsible for similar (ca., within half an order of magnitude) annual export fluxes (in mass of element per watershed km^2) of major/nutrients (Na, K, Si, Ca, Mg, DIC and DOC) and many trace elements. This similarity is noteworthy in view of the drastically (many orders of magnitude) different reactivity in aqueous solutions of major rock-forming minerals such as carbonates, clays and primary silicates (Schott et al., 2009). A likely explanation for such a similarity in elementary yield is overwhelming control of plant litter degradation (leaching) on most chemical element delivery to the river water, especially in boreal and permafrost-bearing catchments (Pokrovsky et al., 2012b). The mass-balance estimations in pristine Siberian watersheds allow the majority of annual flux of solutes being delivered from vegetation rather than direct lithological source (Pokrovsky et al., 2006). This is further confirmed by extremely high reactivity of plant litter in aqueous solutions and rather similar mass-normalized release rate from various plant species of elements like Ca and Si, as demonstrated by laboratory experiments (Fraysse et al., 2010). Given sizable and labile reservoir of major and trace elements in plant litter and topsoil organic layer, the element delivery to the river from the watershed is limited by hydrological transport and largely controlled by water flux during the open – water period thus maintaining rather narrow range of elementary yields among different rivers. The exceptions to these mechanisms are elements that mark a direct impact of groundwaters from carbonate rock reservoirs (Sr, U^{VI}) and redox-sensitive elements (Fe, Mn) that can be locally accumulated during winter baseflow and mobilized to the river water from anoxic sediments of the floodplain (riparian) zone. The yield of these elements can be drastically ($>$ 10 times) different between different rivers depending on local lithological and redox environment.

Within the context of climate warming and permafrost thaw in the northern part of the WSL, Taz River hydrochemistry may shift towards a more important contribution of mineral-hosted groundwater in the winter time, given the pan-Arctic increase in rivers runoff during glacial period of the year (Nasonova et al., 2019; Mack et al., 2021). As a result, the ratio DOC: DIC may decrease whereas the export of soluble highly mobile elements including nutrients such as Mn and Si may increase. The change in low mobile trivalent and tetravalent trace elements and divalent organically-bound metal export by the Taz River will depend on the change in DOM export and quality as well as the increase in the thickness of the active layer. In a case where thawing of the peat deposits overlaying the silts and clays occurs, one may expect an enhanced export of lithogenic elements originated in deep mineral deposits facilitated by organic and organo-mineral colloids. At the same time, it remains totally unclear, to which degree the floodplain lake winter-time stratification may affect the delivery of redox-sensitive elements to the main stem of the Taz River. These processes strongly depend on hydrological connectivity within the floodplain and require extensive spatially-resolved sampling during both open water and ice-covered baseflow periods of the year.

Taken together, results obtained from multi-annual riverine yields of C, nutrients, major and trace elements—on the first mid-sized permafrost affected river in northern Eurasia to be studied—represent an important baseline for assessing future changes in element export, and allow for extrapolation with other unknown rivers draining permafrost peatlands in Central and Northern Siberia.

5. Conclusions

We performed a temporally unprecedented investigation [5 years span, typical frequency once a week or 2–3 times a week at high flow] of the Taz River which is a pristine mid-sized Arctic river impacted by permafrost. We assessed seasonal features of ~40 major and trace elements and calculated multi-annual elementary yields. Three main groups of organic and inorganc solutes were established reflecting elemental correlations with either DOC or DIC and relationship to river discharge. Dissolved inorganic carbon and specific conductivity were a good proxy for soluble, highly mobile elements, whereas DOC positively correlated with low mobility trivalent and tetravalent hydrolysates and some trace metals (V, Ni, Se, and Nb). According to the element pathways between the source and the main stream, we distinguished: (1) deep groundwater, supplying DIC-correlated labile elements; (2) riparian zone and floodplain sediments, affecting N and P macronutrients, Fe, Mn, and other redox sensitive trace metals; (3) plant litter, controlling the release of micronutrients but also some major elements such as Ca, Si; (4) soil water from mineral horizons under forest, supplying low-mobility lithogenic elements, whose transport is enhanced by organic colloids originated from (5) DOC-rich suprapermafrost waters from peatlands. The latter also provided many divalent trace metals, including atmospheric pollutants.

Although in general, the seasonal pattern of elementary concentration and the degree of element dependence on discharge were consistent with those established for other subarctic rivers, the Taz River demonstrated distinct features impacting the behavior of a number of biologically- and geochemically-important elements (nutrients, Mn, Co, Fe and U). Permafrost was found to diminish the connection between the groundwater and the river water, whereas its large riparian (floodplain) zone acted as a sizable reservoir of redox-sensitive elements during glacial seasons. The late-season (autumn) peak of organically-bound metals (trivalent and tetravalent trace elements, Be, V, Cr, Co, Ni, Cu and Nb) was most likely originated from enhanced mobilization of these elements from falling plant litter, which is highly reactive in aqueous solution. However, some discharge from the peatlands (or lake sediments), during downward freezing of shallow water bodies cannot be excluded. Occasional spring-time pulses in Zn, Cd, Sb and Pb were linked to these metals mobilizing from snow meltwater. Anomalously high winter time concentration of Mn produced an annual yield of this element which was an order of magnitude higher than that reported in large Arctic rivers. Given sizable contribution of small and medium size rivers in total freshwater discharge to the Arctic Ocean, results on Taz catchment may help to explain elevated Mn concentrations in surface layers of the Artic Ocean.

Together with the available multi-element yields on Severnaya Dvina and six large Arctic rivers, the dataset generated in this study provides a solid background for upscaling C, nutrient and metal export from other mid- and small sized Eurasian rivers. The overall watershed area of these rivers exceeds two million km^2, and this information should allow monitoring future changes in riverine export from the land to the Arctic Ocean and foreseeing the hydrochemical response to ongoing climate warming and permafrost thaw.

Authors contribution

OP and RM designed the study and wrote the paper; RM and OP performed sampling, analysis and their interpretation; AC and SK performed hydrological characterization of the Taz River basin and calculated elementary export fluxes.

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

Data availability

Posted on Mendeley: Pokrovsky, O.S. et al., 2022. : Mendeley Data, V1, doi: 10.17632/gwmyt2kmw3.1:

Acknowledgements

We acknowledge support from RSF grant No 22-17-00253 and the Tomsk State University Development Program “Priority-2030”. We thank two reviewers for very thorough and constructive comments.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemgeo.2022.121180.

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