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Permafrost coverage, watershed area and season control of dissolved carbon and major elements in western Siberian rivers

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Abstract

Analysis of dissolved organic and inorganic carbon (DOC and DIC, respectively), pH, Na, K, Ca, Mg, Cl, SO_4 and Si in ∼ 100 large and small rivers (< 100 to $\leq 150\,000\,km^2$) of western Siberia sampled in winter, spring, summer and autumn over a more than 1500 km latitudinal gradient allowed for establishing the main environmental factors controlling the transport of dissolved river components in this environmentally important region, comprising continuous, discontinuous, sporadic and permafrost-free zones. There was significant latitudinal trend consisting in general decrease of DOC, DIC, SO_4, and major cation (Ca, Mg, Na, K) concentrations northward, reflecting the interplay between groundwater feeding (detectable mostly in the permafrost-free zone, south of 60° N) and surface flux (in the permafrost-bearing zone). The trend of inorganic components was mostly pronounced in winter and less visible in spring, whereas for DOC, the trend of concentration decrease with latitude was absent in winter, and less pronounced in the spring flood than in the summer baseflow. The latitudinal trends persisted over all river watershed sizes, from < 100 to $> 10\,000\,km^2$. This suggested that in addition to groundwater feeding of the river, there was a significant role of surface and shallow subsurface flow linked to plant litter degradation and peat leaching.

Environmental factors are ranked by their increasing effect on DOC, DIC, $\delta^{13}C_{DIC}$, and major elements in western Siberian rivers as the following: watershed area < season < latitude. Seasonal fluxes of dissolved components did not significantly depend on the river size and as such could be calculated as a function of watershed latitude. Unexpectedly, the DOC flux remained stable around $3\,t\,km^{-2}\,yr^{-1}$ until 61° N, decreased two-fold in the discontinuous permafrost zone (62–66° N), and increased again to $3\,t\,km^{-2}\,yr^{-1}$ in the continuous permafrost zone (67° N). The DIC, Mg, K and Ca followed this pattern. The total dissolved cation flux (TDS_c) ranged from 1.5 to $5.5\,t\,km^{-2}\,yr^{-1}$, similar to that in central Siberian rivers of the continuous permafrost region. While Si concentration was almost unaffected by the latitude over all seasons, the

Si flux systematically increased northward, suggesting a decreasing role of secondary mineral formation in soil and of vegetation uptake.

The dominating effect of latitude cannot however be interpreted solely in terms of permafrost abundance and water flow path (deep vs. surface) but has to be considered in the context of different climate, plant biomass productivity, unfrozen peat thickness and peat chemical composition. It can be anticipated that, under climate warming in western Siberia, the maximal change will occur in small ($< 1000\,\text{km}^2$ watershed) rivers DOC, DIC and ionic composition, and this change will be mostly pronounced in summer and autumn. The wintertime concentrations and spring flood fluxes and concentrations are unlikely to be appreciably affected by the change of the active layer depth and terrestrial biomass productivity. Assuming a conservative precipitation scenario and rising temperature over next few centuries, the annual fluxes of DOC and K in the discontinuous permafrost zone may see a maximum increase by a factor of 2, whereas for DIC and Mg, this increase may achieve a factor of 3. The fluxes of Ca and TDS_c may increase by a factor of 5. At the same time, Si fluxes will either remain constant or decrease two-fold in the permafrost-bearing zone relative to the permafrost-free zone of western Siberia.

1 Introduction

The Western Siberian Lowland (WSL) can be considered as one of the most vulnerable permafrost-bearing territories with respect to ongoing climate change, due to (i) the dominance of discontinuous, sporadic and intermittent permafrost coverage rather that continuous and discontinuous permafrost of central and eastern Siberia and the Canadian High Arctic, (ii) its flat area and high impact of flooding and thermokarst development and most importantly (iii) its high stock of older and recent organic carbon in the form of partially frozen peat deposits. Due to the importance of the boreal and sub-arctic continental zones in the Earth's carbon cycle and the high vulnerability of circumpolar zones to climate warming, the majority of conducted works has been devoted to the biogeochemistry of organic carbon and sediments in large rivers of the Russian boreal circumpolar zone (Gordeev et al., 1996, 2004; Moran and Woods, 1997; Lobbes et al., 2000; Dittmar and Kattner, 2003; Gebhardt et al., 2004; Cooper et al., 2008; Magritsky, 2010; Nikanorov et al., 2010a, b; Holmes et al., 2000, 2001, 2012; Pokrovsky et al., 2010; Feng et al., 2013). While these studies have allowed for the quantification of the carbon and major element delivery fluxes from the continent to the Arctic Ocean, the mechanisms responsible for carbon and metals mobilization from the soil/groundwater to the rivers remain very poorly understood. The WSL offers a unique site to test various hypotheses of element sources and to reveal related mechanisms as it presents the full gradient of permafrost coverage, climate and vegetation over the homogeneous sedimentary basement rock, essentially peat soil, flat orography and similar annual precipitation. Taking advantage of these features, in their pioneering studies, Frey et al. (2007a, b) and Frey and Smith (2005) provided a first-order assessment of the relative contributions of shallow surface water and deep groundwater to small western Siberian rivers. Their study was conducted during the summer baseflow season presenting the largest contrast between permafrost-free and permafrost-affected rivers. This allowed them to conclude that climate warming should shift the permafrost-affected part of the region from surface feeding to groundwater feeding while the permafrost-free zone may remain unaffected.

However, unlike many regions of the world, the boreal and subarctic river regions exhibit extreme seasonal variations in discharge and chemical elements concentrations (see Voronkov et al., 1966; Gordeev and Sidorov, 1993; Gordeev et al., 1996; Gislason et al., 1996; Gaillardet et al., 2003; Rember and Trefry, 2004; Zakharova et al., 2005, 2007; Bagard et al., 2011, 2013; Prokushkin et al., 2011; Guo et al., 2004b, 2007; Olefeldt and Roulet, 2012). The quantitative description of these systems, therefore, requires an understanding of how weathering rates and riverine fluxes of major and trace elements as well as their main carrier (organic carbon) vary seasonally. High seasonality implies significant variations in the source of the elements in river flow over the year, which is further accentuated by high variability of the depth of the active layer and relative contributions of mineral soil weathering and the leaching of the soil organic horizon. As such, the chemistry of fluxes on the seasonal scale depends on the relative role of mineral dissolution vs. plant litter (organic soil) leaching. Although several recent studies have used isotopic techniques in an attempt to resolve the sources of elements in subarctic rivers (Engstrom et al., 2010; Keller et al., 2010; Pokrovsky et al., 2013a; Mavromatis et al., 2014), the relative contributions of mineral and plant litter/organic soil components remain poorly constrained particularly for boreal watersheds.

The purpose of the present work is to improve our understanding of western Siberian river transport of organic and inorganic carbon and major elements (Ca, Mg, K, Si) via studying numerous watersheds across the 1500 km latitudinal profile during four main hydrological seasons: winter and summer baseflow, spring flood and autumn. As a working hypotheses, we assume, following the previous works of Frey et al., that the permafrost controls riverine chemical composition via regulating the degree of (i) groundwater feeding and (ii) leaching of elements from unfrozen (active) soil layers. Because groundwater in the permafrost zone are discharged to the river via unfrozen *taliks* underneath the river bed (Anisimova, 1981; Bagard et al., 2011, 2013), it can be suggested that the larger the river, the stronger the impact of groundwater via taliks. As a result, the contrast in groundwater-related element concentrations between rivers of different latitudes is expected to be the largest during winter baseflow. Therefore, the first objective of this study was to test the effect of the watershed area on inorganic river water components across the permafrost gradient. The second objective was to assess the effect of the active layer depth, peat thickness and permafrost coverage on dissolved organic carbon (DOC), dissolved inorganic carbon (DIC) and its isotopic composition in rivers during different seasons. Specifically, during the spring flood, when the majority of the soil layer is frozen, only surface flux should be important and concentrations should reflect the degree of DOC and element leaching from plant litter. The largest contrast between rivers of different sizes is therefore expected in August, whereas the spring flood should exhibit the lowest differences in terms of DOC transport by rivers of different climate and permafrost zones. Finally, the third objective of this study was a first-order assessment of the river fluxes across the 1500 km latitudinal profile. Here, we expect, in accordance with general knowledge of weathering and DOC export fluxes dependence on temperature, vegetation and permafrost distribution (White and Blum, 1995; Dessert et al., 2003; Gaillardet et al., 2003; Millot et al., 2003; Oliva et al., 2003; Smedberg et al., 2006; Frey and McClelland, 2009; Prokushkin et al., 2011; Beaulieu et al., 2012; Tank et al., 2012a, b; Olefeldt et al., 2014), a gradual or stepwise decrease of the fluxes of all river water constituents northward, from permafrost-free to discontinuous and continuous permafrost zones. Verifying the correctness of these research statements should allow for the quantitative prediction of the degree of river water composition modification in response to changing environmental conditions, notably the increase in the thickness of the active (unfrozen) layer, increasing the winter discharge and augmenting plant biomass and productivity.

2 Study site and methods

2.1 Geographical setting

The Western Siberian Lowland (WSL) is the largest flood zone of the world, after the Amazon's varzea. The rivers (mainly the tributaries of the Ob, Pur, and Taz) drain Pliocene sands and clays, covered by thick (1 to 3 m) peat and enclose three main zones of the boreal biome, taiga, forest–tundra and tundra. Quaternary clays, sands, and aleurolites ranging in thickness from several meters to 200–250 m have alluvial, lake–alluvial and, rarely, aeolian origins south of 60° N and fluvio-glacial and lake–glacial origins north of 60° N. The older, Paleogene and Neogene, rocks are rarely exposed at the Earth's surface and are represented by sands, aleurolites and clays, where carbonate material is present as concretions of individual shells (Geologicheskoe Stroenie, 1958). The climate is humid semi-continental with a mean annual temperature (MAT) ranging from −0.5 °C in the south (Tomsk region) to −9.5 °C in the north (Yamburg), with a rather similar annual precipitation over more than 1500 km of latitudinal gradient from 400 to 460 mm. The annual river runoff gradually increases northward, from 160–220 mm yr^{-1} in the permafrost-free region to 284–320 mm yr^{-1} in the Pur and Taz river basins located in the discontinuous to continuous permafrost zone (Nikitin and Zemtsov, 1986). A detailed physicogeographical, hydrology, lithology and soil description can be found in earlier works (Botch et al., 1995; Smith et al., 2004; Frey and Smith, 2005, 2007; Frey et al., 2007a, b; Beilman et al., 2009) and in our recent limnological and pedological studies (Shirokova et al., 2013; Manasypov et al., 2014, 2015; Stepanova et al., 2015). A detailed map of studied region together with main permafrost provenances and river runoff in the WSL is given in Fig. 1, and the list of sampled rivers grouped by watershed size and season is presented in Table 1.

2.2 Chemical and isotope analyses

Altogether, 96 rivers were sampled in early June 2013 (spring flood), August 2013 and 2014 (summer baseflow), October 2013 (autumn) and February 2014 (winter baseflow) along the 1500 km latitudinal gradient (Table 1). The watershed area of sampled rivers ranged from 2 to 150 000 km^2, not considering the Ob River in its medium course zone. Collected water samples were immediately filtered in pre-washed 30 mL PP Nalgene® flasks through single-use filter Minisart units (Sartorius, acetate cellulose filter) with a diameter of 25 mm and a pore size of 0.45 µm. The first 20 to 50 mL of filtrate were discarded. Filtered solutions for cation analyses were acidified (pH ∼ 2) with ultrapure double-distilled HNO_3 and 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. The DOC blanks of filtrate never exceeded 0.1 mg L^{-1} which is quite low for the organic-rich river water sampled in this study (i.e., 10–60 mg L^{-1} DOC). pH was measured in the field using a combined electrode calibrated against NIST buffer solutions (pH of 4.00 and 6.86 at 25 °C). The accuracy of pH measurements was ±0.02 pH units. DOC and DIC were analyzed using a total carbon analyzer (Shimadzu TOC VSCN) with an uncertainty better than 3 %. Special calibration of the instrument for analysis of both forms of dissolved carbon in organic-rich, DIC-poor water was performed as described elsewhere (Prokushkin et al., 2011). Major anions (Cl, SO_4) concentrations were measured by ion chromatography (HPLC, Dionex ICS 2000) with an uncertainty of 2 %. Major cations (Ca, Mg, Na, K) and Si were determined with an ICP-MS Agilent ce 7500 with In and Re as internal standards and three various external standards, placed each 10 samples in a series of river water. Approximately 30 % of samples were analyzed for Ca, Mg and Na concentrations using atomic absorption spectroscopy (flame) with an uncertainty of 2 %. Reasonable and non-systematic agreement (between 5 and 10 %) with the results of ICP MS analyses was achieved. Aqueous Si concentrations were also determined colorimetrically (molybdate blue method) with an uncertainty of 1 % using a Technicon automated analyzer. The SLRS-5 (Riverine Water Reference Material for Trace Metals certified by the National Research Council of Canada) was used to check the accuracy and reproducibility of each analysis (Yeghicheyan et al., 2014).

The ^{13}C in dissolved inorganic carbon was analyzed in filtered river water sampled in bubble-free sealed glass bottles by gas chromatography and isotope mass spectrometry, using Delta V Advantage and Finnigan GasBench II in order to determine $\delta^{13}C_{DIC}$ (per mil relative to VPDB; Fritz and Fontes, 1980). For these measurements, 0.1 mg of 100 % H_3PO_4 was added to the borosilicate vial and flushed with He (purity of 7.0) for 400 s. Afterwards, 1 mL of the sample was injected into the vial and shaken for 36 h at 24 °C. Standard samples of C-O-1 and NBS-19 were routinely analyzed to test the accuracy of our measurements; typically, a disagreement of less than 0.3 ‰ between the measured and certified values was observed, with a total estimated measurement uncertainty of ±0.2 ‰.

2.3 Hydrological parameters

The daily, seasonal and annual discharges of some of the studied rivers are available from systematic surveys by the Hydrometeorological State Committee of the former USSR Goskomgidromet and Roskomgidromet (now the Russian Hydrological Survey, RHS). These data are published in the annual issues of the State Water Cadastre

(Hydrological Yearbooks) and generalized in the "Resources of surface waters of the USSR, 1970 and 1972". Given the limited number of observations over the year, the river discharge for each river was averaged for each of the four seasons of sampling (May to June, July to September, October, and November to April). For this, we used available monthly average discharges from the RHS gauging stations in the Kara Sea basin from the data base of R-AcricNET (www.r-arcticnet.sr.unh.edu), which is based on mean-multiannual data of the RHS. The southern, permafrost-free part of western Siberia is relatively well covered by RHS stations. In contrast, the density of stations, especially on small rivers, is much lower in the northern, permafrost-affected part of the WSL. However, a systematic hydrological study of State Hydrological Institute in 1973–1992 in the northern part of western Siberia allowed for the reliable evaluation of discharges from small- and medium-sized rivers (Novikov et al., 2009). In the case of the RHS gauging station location which was different from our sampling point of this river, we used an interpolation of the discharge taking into account the watershed area change along the main course of the river (Methodical, 2007; Svod pravil, 2004). In the absence of the gauging station at the river, we used either an analogous river approach or mean values for the area-normalized discharge in the region, given the rather homogeneous geographical setting of the WSL (see runoff distribution in Fig. 1). For small- and medium-sized rivers of the palsa and polygonal bogs of the permafrost zone, we used empirical formulas accounting for hydrological parameters of these watersheds (Novikov et al., 2009).

2.4 Statistical treatment

The concentrations of carbon and major elements in rivers were treated using the least squares method, Pearson correlation and one-way ANOVA (SigmaPlot version 11.0, Systat Software, Inc). Regressions and power functions were used to examine the relationships between the elemental concentrations and the watershed area, river discharge, average latitude of the watershed and seasons. Comparison of element concentrations in rivers sampled in three main permafrost zones (continuous, discontinuous and permafrost-free regions), during four main seasons and of different watershed size classes was conducted using the non-parametric Kruskal–Wallis H statistic.

Principal component analysis (PCA) was used for the full set of sampled rivers for all seasons simultaneously and for each season individually. In this treatment, the main numerical variables were average latitude of the watershed, specific conductivity, pH and DOC, DIC, Cl, SO_4, Si and major cation concentrations. These PCA analyses were applied in order to derive a distinctive view of the influence of various parameters, notably latitude and season, on lake water DOC and major chemical composition variability. Both the normed and non-normed PCA treatments were used to compute and interpret the spatial structures using the STATISTICA package (http://www.statsoft.com).

3 Results

3.1 Statistical analysis of the effect of river size, season and latitude on DOC and element concentration

Results of major element analysis in rivers are listed in Table S1 of the Supplement. First, we separated the watershed into four main classes encompassing all studied rivers (except Ob): < 100, 100 to 1000, 1000 to 10 000 and > 10 000 km^2. We considered three main season in six different latitude ranges (56 to 58° N, 58 to 60° N, 60 to 62° N, 62 to 64° N, 64 to 66° N and 66 to 68° N). We checked for the variation of measured parameters of each watershed size as a function of latitude, separately in each season. Based on the Kruskal–Wallis H statistic, the differences between the seasons and between different latitudes were found to be significantly higher (p level < 0.0001) for most elements than the differences between watershed size classes, within each seasons and within each latitude range. This is illustrated for pH, DOC, DIC and $\delta^{13}C_{DIC}$ in Figs. 2, 3, 4 and 5, respectively which show the measured value as a function of latitude for different watershed classes, individually for each main season. Similar plots for major cations (Ca, Mg, K) and Si are given in Fig. S1, S2, S3 and

S4, respectively. There is a clear and significant trend of concentrations with latitude; the differences between different latitude ranges are significant at $p < 0.0001$ for all elements, and at $p < 0.05$ for Si. The effect of the watershed size on river water chemical composition in summer, winter and spring is much smaller than that of latitude ($9 < H < 12$, $p < 0.05$ and $20 < H < 50$, $p < 0.001$, respectively). Considering all rivers simultaneously, the effect of the season is clearly seen at $p < 0.001$ for all elements except DOC; the latter, however, is also statistically significant ($H = 10.6$, $p = 0.014$). Considering full data set of all seasons and watershed sizes, we distinguished three geographical zones in terms of the permafrost abundance: continuous, discontinuous and absent. For most river water parameters (pH, DIC, DOC, major anions and cations) the differences between three zones are significant ($30 < H < 95$, p level < 0.001). Si concentrations exhibited lower but statistically significant differences between different zones ($H = 9.5$, $p = 0.0086$).

The PCA analysis of individual seasons (spring, summer, and winter) and all seasons simultaneously allowed us to distinguish three factors contributing to observed variations in element concentrations (i.e., 6–7, 2—3 and 2.2 %, respectively) as listed in Table S2 of the Supplement. Considering all rivers and all seasons simultaneously, the first factor which is presumably latitude, controls pH, specific conductivity, DIC, Mg, K and Ca. This factor remains important in spring and winter but decreases in influence in summer. The second FACTOR of low importance (2 to 3 % of variation) is linked to Cl, Na and SO_4, and may mark the influence of marine aerosols rather than groundwater since its role is the highest during open-water seasons. The third factor, pronounced during all seasons except summer consisted of the size of the watershed and always includes SO_4^{2-}. In summer, this factor becomes linked to the latitude rather than to the watershed size and exhibited strong control on K. The DOC seems to be controlled by F1 in summer and partially in spring, while this control disappears in winter (Table S2), in accord with the weak effect of latitude on DOC concentrations during these seasons (Fig. 3). According to PCA results, latitude exhibited a negligible effect on Si concentrations in all seasons expect summer (Table S2), although it is less visible in the graphical plot (Fig. S4), whereas K is mostly dependent on the latitude in spring (Table S2 and Fig. S3).

3.2 Effect of the permafrost abundance on DOC, DIC, $\delta^{13}C_{DIC}$, Si and major cation concentrations

An assessment of the role of permafrost type and abundance on river water chemical composition is possible via separating all the sampled watersheds on three categories according to the permafrost distribution in WSL: permafrost-free, discontinuous and continuous permafrost. For simplicity, we consider all seasons and watershed sizes on the same plot. There is significant decrease of pH, Ca and Mg northward with the largest changes occurring at the beginning of discontinuous permafrost coverage (Fig. 6a–c, respectively). The DOC and DIC also decrease in concentration with the increase in the degree of permafrost coverage (Fig. 7a and b, respectively), whereas the isotopic composition of the DIC becomes progressively more negative northward (from ca. −15 ‰ in the permafrost-free zone to −20–25 ‰ in the continuous permafrost zone, Fig. 7c). In contrast, the effect of the permafrost on Si concentrations is not clearly seen; the scatter of the data between different seasons and watersheds does not allow for determining any significant trend (Fig. S5).

The optical properties of DOC remain essentially constant throughout the full range of watershed sizes, latitudes and seasons (Fig. 8). The largest variation of specific $UV_{280\,nm}$ absorbance occurred in winter, when several DOC-rich water from the southern (permafrost-free) part of the WSL demonstrated quite low concentrations of aromatic (colored) compounds. It is possible that the rivers Vasyugan (RF 63), Shegarka (RF 3) and Vatinsky Egan (RF 57) exhibiting this particular DOC are affected by oil production sites and contain some uncolored products of hydrocarbon oxidation in the underground waters. The other 95 rivers yielded quite uniform distribution of UV_{280} absorbance, thus witnessing the main control of DOC by allochthonous (terrestrial) organic carbon from peat and/or ground vegetation leachates.

3.3 Carbon and major element fluxes in western Siberian rivers

Calculation of element fluxes was based ON mean multiannual monthly average discharge of sampled rivers, measured major chemical composition during three main hydrological seasons (spring flood, summer and winter baseflow) and October, normalized to the watershed area at the point of river sampling. The main uncertainties, quantified as 30 % of the absolute value, stem from the interannual variation of mean monthly discharge, significant change of the watershed area between spring and winter baseflow in the WSL, and an insufficient number of observations over the year, namely during the long winter baseflow, and the hydrologically important spring flood period.

Examples of DOC flux assessment for watersheds of different areas are given in Fig. S6a–c for spring, summer and winter, respectively. It can be seen that the effect of latitude is always more pronounced than that of the watershed area, as also confirmed by the Kruskal–Wallis test ($p < 0.05$). A similar conclusion has been found for other major dissolved components (not shown). This allowed us to define six latitude classes (56 to 58° N, 58 to 60° N, 60 to 62° N, 62 to 64° N, 64 to 66° N and 66 to 68° N) for flux calculations similar to that used for the statistical treatment of river component concentrations (Sect. 3.1). Taking into account the variation of the flux in each latitude class, and neglecting large rivers such as the Ob and Taz, the average export fluxes of DOC, DIC, Si and major cations from WSL can be calculated with a step of 2° N. The number of rivers used for the latitudinal-average flux calculation ranged from 7 to 20 for each latitudinal range. This number was, however, quite low for the southernmost rivers (56–58° N) in summer (two rivers) and northernmost rivers (66–68° N) in spring, summer and winter (3, 4, and 1 river, respectively). This could yield significant uncertainties on the fluxes of most northern rivers. Furthermore, the month of October was sampled only in rivers south of 60° N (12 rivers in total). While the relative contribution of the October period to the total annual flux does not exceed 10 % in the south and likely to be even smaller in the north (the ice is formed by the middle of October), it generates additional uncertainty on the overall flux calculation. However, the dominant factor controlling the uncertainty of seasonal flux in each latitude zone was the standard deviation of the average value of individual rivers. The uncertainty on the annual fluxes was assumed to be the sum of individual uncertainties during each season normalized to the relative contribution of each season to the annual flux.

The average (±2 SD) fluxes of DOC and DIC export from the watershed as a function of average latitude are shown in Fig. 9a and b, respectively. An abrupt decrease of fluxes at 62–64° N does not coincide with the appearance of the relict and isolated permafrost north of 60° N. Rather, this decrease matches the beginning of discontinuous permafrost north of 62° N at the latitudinal transect studied in this work. The re-increase of both DOC and DIC fluxes occurs above 66° N. The fluxes of major cations from western Siberian watershed are shown as a function of latitudinal range for K, Ca, Mg and total dissolved cation flux (TDS_c) in Fig. 10a, b, c and d, respectively. Three main clusters of cation flux–latitude dependence can be outlined, similarly to DOC and DIC: (i) permafrost-free and isolated/sporadic permafrost zone (56–62° N) demonstrating generally similar and elevated fluxes of all rivers, (ii) discontinuous permafrost zone (62 to 66° N) where an abrupt decrease by a factor of 2 to 5 of major cations occur and (iii) continuous permafrost zone north of 66° N exhibiting significant (K, Mg, Fig. 10a and c, respectively) or partial (Ca, Fig. 10b) increases of cation fluxes. The fluxes of dissolved Si exhibited a latitudinal dependence which was contrasting to that of DOC, DIC and major cations with a gradual increase of export fluxes from $\sim 300\,\mathrm{kg\,km^{-2}\,yr^{-1}}$ in the south to $\sim 1400\,\mathrm{kg\,km^{-2}\,yr^{-1}}$ in the north (Fig. 11).

4 Discussion

4.1 General factors controlling river hydrochemical composition in permafrost-free and permafrost-bearing zone

From general knowledge of environmental control on carbon and major element fluxes in rivers of the Russian subarctic (Prokushkin et al., 2011; Pokrovsky et al., 2012) and other boreal and subarctic regions (Laudon et al., 2004; Petrone et al., 2006; Walvoord and Striegl, 2007; Jantze et al., 2013; Giesler et al., 2014), we anticipate a decrease of most element concentrations, including DOC, northward regardless of the season and the river size due to (1) a decrease of chemical weathering intensity with the temperature, well demonstrated for igneous rocks such as basalts (Dessert et al., 2003) and granites (Oliva et al., 2003), (2) a decrease of the thickness of peat deposits in total and the active soil (peat) layer in particular (Beilman et al., 2009; Stepanova et al., 2015 and references therein), (3) a decrease of plant biomass and related plant litter stock on the surface of the soils (Frey and Smith, 2007), (4) a shortening of the unfrozen period of the year and (5) a decrease of the degree of groundwater feeding (Nikitin and Zemtsov, 1986). The factors capable of enhancing element export fluxes in northern (permafrost-bearing) rivers relative to southern (permafrost-free) rivers are (1) the decrease of dissolved organic matter (DOM) respiration by heterotrophs in the water and soil column and thus the increasing removal of allochthonous DOC from the soil to the river, (2) the increase of DOC and related element leaching from plant litter and topsoil (Pokrovsky et al., 2005; Giesler et al., 2006; Fraysse et al., 2010) during more pronounced massive freshet events or summer high flow (Michel and Vaneverdingen, 1994; McClelland et al., 2006; White et al., 2007), (3) the decrease of DOM retention (adsorption) on the mineral soil horizon because the clay horizon is typically frozen in the north (Kawahigashi et al., 2004) and (4) the decrease of authigenic clay mineral and allophane formation in the soil horizons (Targulian, 1971).

At the current, rather limited, stage of knowledge of mineral organic soil horizons and plant biomass chemical composition and reactivity, only a few environmental factors can be quantitatively tested based on river water chemical analyses. Despite significant latitudinal and geographical coverage of western Siberian rivers, the PCA analysis does not explain the observed variability of solute composition, unlike that of the Mackenzie River drainage basin (Reeder et al., 1972). In the latter, however, contrasting lithological and physicogeographical factors (carbonate, gypsum, clays, halite deposits and hot springs) create a distinct component structure. The highly homogeneous environmental context of western Siberia may be responsible for the low capacity of the PCA analysis to explain the variability of river chemistry in this region.

4.2 Effect of latitude (permafrost and vegetation) on major cation, Si and DIC mobilization from the soil profile and groundwater to the river

In the case of the dominance of groundwater feeding of the river, the decrease of element concentrations from water–rock interactions whose transport is not limited by availability of DOM (Ca, Mg, DIC) is expected to be most pronounced in winter, when the groundwater feeding is maximal. Moreover, in the permafrost-bearing zone during the winter baseflow, one should expect a significant difference in element concentrations between small rivers (weakly or not affected by taliks) and large rivers (essentially fed by taliks). In spring, when the active layer is very thin and the majority of the soil column is frozen, the export from the watershed is dominated by surface flow and thus the difference in groundwater-related element concentrations between (i) small and large rivers and (ii) north and south should be minimal. However, the abovementioned hypotheses are not supported by DIC, Ca and Mg concentrations observed in rivers (Figs. 4, S1 and S2). First, the DIC concentrations decrease between permafrost-free and discontinuous/continuous permafrost zones is a factor of 10 in winter (Fig. 4a) and a factor of 20 to 50 in spring (Fig. 4b). Similarly, the decrease of Ca and Mg concentrations between south of 59° N and 62–66° N zones is × 10 in winter and × 20–30 in May. In fact, it is the spring period which exhibits the highest contrast in element concentrations between the south and the north. Second, for the latitude concentration gradient from south to north, the relative DIC, Ca and Mg concentrations change between large ($1000–10\,000\,\mathrm{km}^2$ and $> 10\,000\,\mathrm{km}^2$) and small ($< 100\,\mathrm{km}^2$) rivers in winter is not statistically significant ($p > 0.05$).

North of 66° N, concentrations of Ca, Mg and sulfate increase relative to their concentrations at 62–66° N of the discontinuous permafrost zone. This is especially pronounced during the summer period (Figs. S1c, S2c and Table S1). We do not exclude here the influence of marine sedimentary deposits containing salts in the deep part of the mineral soil profile below the peat layer. This influence, however, cannot be unequivocally proved because (i) DIC concentrations also increase in summer, north of 66° N, although DIC is not likely to be affected by marine deposits, and (ii) chloride, an efficient marker of sea salts, is not increasing in the north (not shown).

The isotopic composition of DIC confirms the general features of DIC and cation concentrations (Fig. 5). The groundwater feeding by taliks in winter is highly uniform over 10° of latitude with the value of $\delta^{13}C_{DIC}$ being equal to -15 ± 5 ‰, reflecting carbonate/silicate weathering and a buildup of CO_2 with a stronger respiratory signal (Finlay, 2003; Striegl et al., 2001; Giesler et al., 2014). During this period, the variability of $\delta^{13}C_{DIC}$ is the highest in small (< 100 km^2) watersheds, but no trend of isotopic composition with latitude could be evidenced at $p < 0.05$ (Fig. 5a). This isotopic signature is preserved in spring for southern (< 60° N) watersheds, whereas in permafrost-affected regions, $\delta^{13}C_{DIC}$ decreases to $\sim -25 \ldots -20$ ‰ regardless of the river size and the type and the abundance of the permafrost (Fig. 5b). Such low values in the permafrost-affected zone could not represent the influence of carbonate/silicate rock weathering by soil CO_2 and likely reflect direct microbial processing of soil and sedimentary organic matter (Waldron et al., 2007; Giesler et al., 2013), with the DIC isotopic signature similar to that of organic carbon in western Siberian subarctic topsoil (-26 ± 2 ‰, Gentsch et al., 2015) and the Ob River organic sediments (-25 to -27 ‰, Guo et al., 2004a).

A plausible explanation for the $\delta^{13}C_{DIC}$ seasonal variation being mostly pronounced in the permafrost zone can be that microbial mineralization of dissolved organic carbon occurs most efficiently during the springtime, when significant amounts of fresh organic matter from ground vegetation are leached by melted snow. The lack of $\delta^{13}C_{DIC}$ decrease in spring relative to winter in the permafrost-free zone may stem from (i) significant input of the carbonate/silicate rock-hosted groundwaters or (ii) the different nature of DOM in the south, where the organic matter which originates from peat leaching is less subjected to microbial processing compared to fresh vegetation in the north, where the peat soil in spring is frozen. One has also take into account that the DIC concentrations in spring are a factor of 30 lower in the permafrost-bearing region relative to permafrost-free region (Fig. 4b). As such, a relatively small input of microbially respired CO_2 will be significantly more visible in the $\delta^{13}C_{DIC}$ value of the northern rivers compared to that of the southern rivers.

The variation of $\delta^{13}C_{DIC}$ along the permafrost/latitude gradient helps to better explain the origin of DIC in rivers in contrasting permafrost zones. Consistent with a progressive decrease of the groundwater feeding of rivers northward (Nikitin and Zemtzov, 1986; Frey et al., 2007b), we observe a distinct trend of $\delta^{13}C_{DIC}$ with latitude during the spring period, reflecting the shift of DIC origin from groundwater in the south to plant litter degradation and soil respiration in surface water north of 62° N (Fig. 5b). In winter, the $\delta^{13}C_{DIC}$ is rather constant within the full latitudinal profile (Fig. 5a) confirming the dominant role of carbonate/silicate mineral weathering by atmospheric and soil CO_2 dissolved in the groundwaters.

Previous hydrological studies in WSL in 1970–1990 revealed that the groundwater feeding of small (< 10 000 km^2 watershed) river decreases from 20–30 % in the discontinuous and sporadic/isolated part of the WSL to 3–6 % in the northern, continuous permafrost zone (Novikov et al., 2009). These numbers agree with estimations based on RHS data of large western Siberian rivers (Nadym, Pur and Taz) and the left tributaries of the Yenisei River (Dubches, Elogyi and Turukhan; Nikitin and Zemtzov, 1986). According to more recent evaluations of Frey et al. (2007b), the groundwater contribution to summertime period river chemical composition ranges between 30 and 80 % for the rivers located between 56 and 58° N. The pH values of 7 to 7.5 in the southern rivers observed both in winter and spring (Fig. 2a and b) are indicative of carbonate/silicate rock input. The spring acid pulse, well established in other permafrost-free boreal regions (Buffam et al., 2007), is not at all pronounced in the south of the WSL but becomes clearly visible in the permafrost-affected, northern regions where the springtime pH decreases to 5...6 (Fig. 2b). This illustrates the more important role of plant and moss leaching in the permafrost-bearing zone on solute export from the watershed. In addition, the dominance of sands north of 62° N may allow for low molecular weight (LMW) organic acids to migrate to the river from the soil profile. In the southern, permafrost-free zone, the dominating clays underneath the peat can adsorb acidic LMW organic compounds and thus do not allow the acid pulse to be clearly visible.

The increase of pH in summer relative to spring period is again less visible in the south than in the north (Fig. 2c) and may reflect the persisting role of bedrock dissolution as well as the change of the river feeding regime, from top soil and vegetation to the peat soil column leaching. The summertime increase of river water pH north of 60° N, in the forest–tundra and tundra zone may be linked to (i) enhanced photosynthesis in the north due to better insolation and (ii) mobilization of DOM and other solutes from soil depressions rather than from watershed divides. The depressions are subjected to intense rinsing during the spring seasons, when the majority of soluble acidic compounds are flushed from the litter and O_e horizon. In contrast, the watershed divides contain significant amounts of organic litter and release organic acids only in spring, when they are covered by temporary ponds of melted snow (see Manasypov et al., 2015). This hydrological scheme of river water feeding was elaborated during the seasonal multiannual observations on frozen bogs of the north of the WSL (Novikov et al., 2009), although the chemical nature of DOM mobilized from different elementary landscapes of the watershed and its acidic properties remain unknown.

The importance of plant litter and ground vegetation as leaching element sources in western Siberian rivers can be assessed from the comparison of K concentrations as a function of latitude during different seasons (Fig. S3). The most significant decrease of K concentrations from the southern ($< 59°$ N) to the northern (61–67° N) watersheds occurs in spring, during intense plant litter leaching. Regardless of latitude, K concentration follows the order spring > winter > summer with the highest concentrations, up to 2500 ppb, recorded in permafrost-free region. Given that the other cations, possibly originating in the water–mineral interaction at some depth, do not exhibit such high concentrations in spring, we interpreted the springtime K "pulse" as indicative of plant litter leaching in the productive taiga zone, which was much less visible in the permafrost zone due to significantly lower biomass and primary productivity of forest–tundra and tundra biomes.

4.3 Latitudinal pattern of DOC in seasonal aspect

The study of organic carbon concentrations in western Siberian rivers collected over various seasons of the year generally confirm the pioneering findings of Frey and Smith (2005). The strong statistically significant ($p < 0.05$) contrast in DOC concentrations among permafrost-free, discontinuous and continuous permafrost zone persists over the course of the year and each season except probably winter (Figs. 3 and 7a). This difference is also seen in $\delta^{13}C_{DIC}$ value among all three zones (Fig. 7c) suggesting, on the annual scale, a more significant contribution of microbial processing of plant and soil organic carbon to HCO_3^- and CO_2 of the river water in the permafrost-bearing zone compared to the permafrost-free zone.

In accordance with the conclusion reached by Frey and Smith (2005), the variation in hydrology may play a limited role in DOC variability and export from the watershed of WSL rivers. The gradient in DOC concentrations along the latitudinal profile remains similar between spring flood and summer baseflow (Fig. 3b and c). Although the winter period does not exhibit such a clear difference between permafrost-free and permafrost-affected regions (Fig. 3a), the contribution of the winter discharge to the annual flux of DOC is between 10 and 15 % and as such does not significantly affect the annual export of DOC from the watersheds.

In contrast, the gradient of organic carbon concentrations along the latitudinal profile in spring will be mostly controlled by the difference in plant litter stock subjected to leaching by melted snow. One would not expect any significant difference between large and small rivers with otherwise similar runoff, vegetation and bog coverage. In this regard, results of western Siberian rivers generally confirm the conclusion of Finlay et al. (2006) on (i) the lack of groundwater contribution to streamflow in arctic watersheds and (ii) that river DOC dynamics are driven essentially by processes occurring at the soil surface. However we doubt the importance of large DOC pool production under very cold conditions as the main reason of sustained high concentrations of DOC at snowmelt suggested by Finlay et al. (2006). Indeed, plant litter degradation in winter, even in the warmest scenario, is minimal and does not contribute significantly to annual litter leaching (Bokhorst et al., 2010, 2013). Instead, we hypothesize fast plant litter and ground vegetation leaching in spring, at the very beginning of the snowmelt. Such a fast enrichment in DOC and colored organic compounds of surface water depressions has been observed in the discontinuous permafrost zone in early June (Manasypov et al., 2015).

An unexpected result of the study of western Siberian watersheds is the lack of the enrichment in DOC of small headwater streams, in contrast to what was reported for Scandinavian rivers and streams (Agren et al., 2007, 2014, and references therein). In WSL, especially in the northern, permafrost-affected zone, the small ($< 100\,\text{km}^2$) streams yielded DOC concentrations that were not statistically higher ($p > 0.05$) than those of larger rivers, neither in spring nor in summer baseflow. A number of factors could be responsible for the observed difference between permafrost-free European and permafrost-bearing Siberian watersheds. In the north of western Siberia, the microbial processing of DOM in large rivers may be weakly pronounced. This is confirmed by the observation that the degree of light C isotope enrichment (lowering $\delta^{13}\text{C}_{\text{DIC}}$) in spring is independent ($p > 0.05$) of the size of the river (Fig. 5b), and, correspondingly, of the water residence time on the watershed. According to Kawahigashi et al. (2004), the DOM in northern, permafrost-affected tributaries of the Yenisei River was significantly less biodegradable than that in southern tributaries. This may contribute to better preservation of DOM in the stream and its independence of water residence time. Small watersheds of western Siberia exhibit a runoff and average slope very similar to that of the large rivers, given very flat orographic context of the WSL. This contrasts with the mountain regions of Sweden and Alaska where headwater streams may exhibit higher runoff and thus higher export of the dissolved constituents. Finally, the riparian zone, very important for regulation DOC stock and export in small streams draining glacially formed terrain of NW Europe, is much less pronounced in western Siberia, where generally flat, frequently flooded areas dominate the watershed profile.

4.4 DOC and element fluxes across 1500 km latitude transect of variable permafrost coverage

The elevated DOC fluxes in the continuous permafrost zone observed in the present study (Fig. 9a) are consistent with previous results showing that, with otherwise similar factors, the permafrost areas are a greater source of DOC than the areas with seasonal frost (Carey et al., 2003). In permafrost areas, meltwater travels through organic-rich layers in the form of so called supra-permafrost flow, as opposed to areas without an impermeable permafrost table, where the infiltration of organic-rich surface water to the deep mineral layers and DOC sorption on clay minerals may occur, thus decreasing the overall export of DOC (see Smedberg et al., 2006 for discussion). Given the dominance of peat rather than minerals within the active (unfrozen) layers of soil profile, this difference is even more accentuated in western Siberia.

A sketch of typical soil profiles of western Siberia in the permafrost-free and discontinuous permafrost zone presenting DOC mobilization pathways from the soil to the river in June and August is illustrated in Fig. 12. We hypothesize that plant-litter- and topsoil-derived DOC adsorbs on clay mineral horizons in the southern, permafrost-free and discontinuous/sporadic permafrost zones but lacks the interaction with minerals that occurs in the continuous permafrost zone. This assumption corroborates results found during another latitudinal river transect study of Siberia, along the Yenisei river and its left tributaries draining peatlands of the WSL (Kawahigashi et al., 2004): the northern tributaries exhibited significantly higher DOC concentrations than the southern tributaries of this river. Specifically, given the significant thickness of the peat even in the northernmost part of the WSL and the active layer thickness of < 50 to 80 cm (30 cm on mounds and 80 to 150 m in troughs and depressions; Tyrtikov, 1973; Khrenov, 2011; Novikov et al., 2009), even in the region of continuous permafrost development, peat soil interstitial solutions might not enter into contact with the mineral soil horizon and thus will not decrease their DOC concentrations during migration from the soil column to the river along the permafrost impermeable layer (Fig. 12).

For individual rivers of western Siberia, there is a decrease of DOC flux from the south to the north in May (spring flood), while in summer, the flux increases northward (see Fig. S6a and b). The latter trend reflects elevated DOC concentrations in summer in most northern rivers, on average a factor of 2 higher in 66–68° N that in 62–64° N. Given that the summer period contributes significantly to the annual flux in the north (60 %) rather than in the south (13 to 40 %), the reasons for such an elevated flux in high latitudes are therefore elevated summertime concentrations of DOC. Presumably, the latter are linked to intense leaching of organic matter (OM) from ground vegetation and topsoil with minimal retaining of soluble OM inn sand and clay loam mineral horizons, typical for areas north of 62° N.

In the permafrost zone, the DOC export is strongly controlled by DOC residence time and travel pathway through organic topsoil and lichen, moss and litter leaching vs. peat and mineral layer leaching (Fig. 12). In this case, it is only the thickness of the unfrozen peat and local permafrost coverage that control the DOC export which will be irrelevant to the watershed size and season. It follows that DOC export from peat soils by medium-sized ($< 100\,000\,\mathrm{km}^2$) rivers located entirely in the permafrost zone may be higher than that of the larger rivers, crossing permafrost-free regions. Thus, the DOC fluxes in the permafrost-bearing regions (1.5 to $3.5\,\mathrm{t\,km^{-2}\,yr^{-1}}$) are higher than those suggested for the Ob River ($1.2\,\mathrm{t\,km^{-2}\,yr^{-1}}$, Gordeev et al., 1996). Consistent with this difference, the Pur River, entirely located in the discontinuous permafrost development, exhibits an elevated DOC flux ($2.1\,\mathrm{t\,km^{-2}\,yr^{-1}}$, Gordeev et al., 1996), and the Taz and Nadym rivers show 1.9 and $4.4\,\mathrm{t\,C_{org}\,km^{-2}\,yr^{-1}}$, respectively (calculated based on data of the RHS). Note that the DOC fluxes of the Ob, Pur, Taz and Nadym rivers are based on available time series of the Russian Hydrological Survey (RHS) and represent the multiannual mean of 1960–1980, measured more than 40 years ago. To what degree can the ongoing DOC concentrations and flux rise in rivers linked to climate change and/or acidification as reported in western Europe and Canada (Worrall et al., 2004; Porcal et al., 2009) be applied to WSL is unknown. However, we did not observe any significant (i.e., > 20 %) change of DOC fluxes over past 30 to 40 years either in the boreal non-permafrost pristine region of NW Russia (Severnaya Dvina River, Pokrovsky et al., 2010) or in the central Siberian, continuous permafrost rivers of the Yenisei basin (Pokrovsky et al., 2005). Moreover, a decrease of DOC fluxes in the Yukon River was even reported and suggested to be linked to enhanced mineralization of DOC by biota (Striegl et al., 2005). Note also that the more recent evaluation of the Ob River DOC discharge using a flow-weighted concentrations of 9.4 $\mathrm{mg\,L^{-1}}$, measured in 2003–2007 (Cooper et al., 2008), gives a flux of 1.3 $\mathrm{t\,C\,km^{-2}\,yr^{-1}}$, well comparable with older estimates.

Although river runoff is considered to be one of the major factors of DOC export fluxes (Ludwig et al., 1996; Tank et al., 2012a), the impact of northward increasing runoff in WSL on DOC and DIC annual fluxes is expected to be within the intrinsic uncertainty. First, the fluxes are similar in the range of 56 to 62° N latitude, where the runoff increases two-fold. Second, the main change of the fluxes (by a factor of 2) occurs between 61 and 63° N, where the runoff changes by less than 30 %. Finally, a two-fold increase of the flux from 65 to 67° N occurs at relatively similar runoff (±20 %). These arguments are consistent with available data from the literature of DOC fluxes with relatively low ($<$ 600–800 $\mathrm{mm\,yr^{-1}}$) runoff values. In the temperate zone, the runoff impact of between 100 and 300 $\mathrm{mm\,yr^{-1}}$ on DOC export was rather low (Stets and Striegl, 2012). In the northern boreal zone, no impact on DOC export increase of runoff was detected between 400 and 600 $\mathrm{mm\,yr^{-1}}$ (Giesler et al., 2014). Six large Arctic rivers did not demonstrate a clear dependence of DOC concentrations on runoff below 360 $\mathrm{mm\,yr^{-1}}$ (Holmes et al., 2013). Finally, no direct effect of runoff on DOC export was reported for peatland catchments in subarctic Sweden (Olefeld et al., 2013).

The role of the thermokarst, very common in the WSL north of 62° N, in headwater stream hydrochemistry and known to cause substantial increase of DOC and other solute concentrations in Arctic tundra via soil disruption and DOC removal (i.e., Abbott et al., 2015) seems to be of low importance in western Siberia. First, a decrease of DOC fluxes occurs in the latitude range of 62 to 66° N (Fig. 9a), the main region of thermokarst lake development (Manasypov et al., 2014). Second, thermokarst lakes of western Siberia are poorly connected to the hydrological network even in spring, given their extremely shallow depth and rather flat palsa bog context of the region (Manasypov et al., 2015).

The DIC and major cations follow the pattern of DOC flux as a function of latitude since (i) their concentrations are high in the summer period in the continuous permafrost zone and (ii) the summer period contribution to annual flux is between 60 and 70 %. The cationic fluxes of western Siberian rivers south of 62° N are comparable with those of the other Siberian regions (see Zakharova et al., 2005, for compilation). In the discontinuous permafrost zone, 62 to 66° N, the fluxes are × 3 lower than those of continuous permafrost of central Siberian rivers draining basalts (Fig. 10d). Presumably, the Quaternary deposits of the WSL exhibit the lowest weathering susceptibility and relevant cation fluxes. In any case, one may not compare the intensity of chemical weathering in silicate-rich, organic-poor soils and crystalline rocks (central Siberia and the Lena Basin, Iceland or Alaska) with peat leaching in the majority of WSL watersheds.

The Si fluxes of rivers in the southern part of the WSL (800 $\mathrm{kg\,km^{-2}\,yr^{-1}}$) are comparable to those of the Ob River (616 $\mathrm{kg\ Si\ km^{-2}\,yr^{-1}}$, Guo et al., 2004b) and small rivers of northern Sweden (900 $\mathrm{kg\,km^{-2}\,yr^{-1}}$, Smedberg et al., 2006). In contrast, the fluxes of the permafrost-affected rivers (Fig. 11) contradict the expected trend of a flux decrease with latitude increase; in fact the northern fluxes of the WSL are comparable with those of the temperate rivers such as Mississippi and Yangtze (Guo et al., 2004b). Mean multiannual Si fluxes of Taz and Pur rivers calculated on the RHS data collected in 1970–1975 are equal to 1.4 and 2.4 $\mathrm{t\,Si\,km^{-2}\,yr^{-1}}$, respectively. Note that because Si fluxes in Siberian rivers depend on the runoff in the case of silicate rock weathering (Zakharova et al., 2005), the increase of Si fluxes northward may partially reflect the increase of the specific runoff from ~ 150–200 $\mathrm{mm\,yr^{-1}}$ in the south to ~ 300 $\mathrm{mm\,yr^{-1}}$ in the north (Nikitin and Zemtsov, 1986, see Fig. 1). However, the contribution of this runoff increase cannot exceed 20 % at the overall Si flux increase northward. Additionally, if silicate rock weathering significantly controls element delivery from the soil to the river, such a northward increase would occur for cations as it is known for typical silicate terrains (Zakharova et al., 2007), which is not really seen in Fig. 10.

Two arguments allow us to suggest that such elevated fluxes in the permafrost-affected zone are not measurement or sampling artifacts. First, from a previous study of WSL rivers during the summer baseflow, it is known that Si concentrations are weakly dependent on latitude (Frey et al., 2007), as also confirmed in this work. Second, the gradual increase of annual Si export fluxes (approximately four-fold) from the southern, permafrost-free zone to the northernmost, continuous permafrost zone (Fig. 11) is accompanied by a significant change of the seasonal partitioning structure. The most active, summertime period contributes only 25 % in the south and around 63 % in the north (> 66° N). This period corresponds to the highest seasonal discharge in the north, but also to the highest depth of the active layer in the peat soil. Given that (i) the continuous permafrost context of areas located north of 66° N implies very low groundwater feeding (4 to 6 % of the annual discharge, see Nikitin and Zemtsov, 1986; Novikov, 2009) and (ii) the upper (active) part of the soil profile including its frozen and unfrozen parts is mostly peat rather than clay/sand *Q* sediments, the role of the groundwater–silicate-rock interaction in the Si supply to rivers on the annual scale is quite low. Rather, the progressive increase of Si export flux of rivers from the south to the north of the WSL may be a consequence of the decrease of Si uptake by plants due to the decrease of vegetation biomass northward. The minimal fluxes of dissolved Si are observed in the most southern rivers of the WSL, and may be linked to strong Si retaining by bog and forest vegetation. With this in mind, we postulate, in accordance with the general setting of the WSL recovering from the last glaciation, non-stationary ecosystems with contemporary peat accumulation in the south and frozen peat thawing/degradation in the north.

5 Concluding remarks: possible evolution of western Siberian river chemical composition and fluxes under climate change scenario

An unexpected result of the present study is rather low sensitivity of DOC, DIC, cations and Si concentrations and fluxes to the size of the river. The season also played a secondary role in determining element concentration patterns. The most important governing parameter for both concentrations and fluxes was the latitude, allowing us to distinguish between permafrost-free, discontinuous and continuous permafrost regions. Unusually high fluxes in the northernmost region of studied territory observed for DOC, DIC, Si and cations stem primarily from the fact that the contribution of summer flux to overall annual flux is high. It can be hypothesized that in the continuous permafrost zone of frozen peat bogs, the underlining mineral layer is not reactive, being protected by the permafrost so that the major part of the active layer is located within the organic (peat), not mineral matrix.

The most likely scenario of climate change in western Siberia consists of shifting the permafrost boundary further north and increase of the active layer thickness (Pavlov and Moskalenko, 2002; Frey, 2003; Romanovsky et al., 2010; Vasiliev et al., 2011; Anisimov et al., 2013). The permafrost boundary change, equivalent to the northward shift of the river latitudes in Fig. 9, may decrease the DOC fluxes of the most northern rivers a maximum of two-fold due to the change from continuous to discontinuous permafrost. The change of the fluxes in the permafrost-free or sporadic/isolated permafrost region, south of 62° N, is unlikely at the scale of a century. Indeed, the fluxes of DOC, DIC and even major cations do not seem to be strongly dependent on the latitude south of 62° N (Figs. 9 and 10). The thickness of the active layer is projected to increase more than 30 % during this century across the tundra area in the Northern Hemisphere (Anisimov et al., 2002; Stendel and Christensen, 2002; Dankers et al., 2011). In the WSL, this increase will be most dramatic in the north, where the peat deposits are thinner than those in the discontinuous permafrost zone (Botch et al., 1995; Liss et al., 2001; Novikov et al., 2009; Kremenetsky et al., 2004). The main consequences of this increase may be the involvement of mineral (clay) horizons in water infiltration downward in the soil profile. As a result, the DOC originating from the upper peat layers and plant litter degradation will be retained on mineral surfaces and in the clay interlayers (Kaiser et al., 2007; Oosterwoud et al., 2010; Mergelov and Targulian, 2011; Gentsch et al., 2015). To what degree this change of water hydrological pathways in the soil column may affect the other dissolved components cannot be predicted. However, this effect for inorganic solutes is expected to be lower than that of DOC, given much lower affinity of HCO_3, cations and Si to clay surfaces and the lack of unweathered (primary) silicate rocks underneath the peat soil column. Unfortunately, no time series on the hydrochemistry of rivers of continuous permafrost development north of 66° N are available to test the hypothesis of the impact of climate change on a possible decreasing DOC flux from frozen peatlands due to ongoing decrease of permafrost protection of mineral layer from adsorbing DOC.

An important peculiarity of western Siberian lithology and soil coverage, comprising Quaternary deposits tens to hundreds meters thick and frozen peat soil, is that the effect of rock chemical weathering, CO_2 consumption from the atmosphere, and their response to ongoing climate change may be weakly pronounced. It has been known for a long time that a warmer climate would result in an increasing amount of water available for water–rock interaction at depth due to the increase groundwater discharge over the year (Michel and Vaneverdingen, 1994). The increased thickness of the weathering silicate soil layer is also confirmed by quantitative chemical weathering modeling (Beaulieu et al., 2012). While in massive crystalline rocks of other parts of central and eastern Siberia, Scandinavia or Alaska, this would lead to an increased bicarbonate export, it may not happen in the already strongly weathered sands and clays of western Siberian mineral soil.

Important modifications linked to climate change in boreal and subarctic zones concern the change of the hydrological regime (Karlsson et al., 2015), in particular the increase of the winter baseflow (Yang et al., 2004; Ye et al., 2009; Serreze et al., 2000) due to the increase of groundwater feeding (Frey et al., 2007a, b; Rowland et al., 2010), coupled with the increase of overall precipitation and, consequently, water runoff (Peterson et al., 2002; McClelland et al., 2006). Here, we argue that a 10 to 30 % modification in the annual runoff will be within the variation of the DOC and cation flux between watersheds of various sizes and as such will be difficult to trace.

The increase of vegetation productivity reported for Arctic river basins (Sturm et al., 2001; Tape et al., 2006; Kirdyanov et al., 2012) will most likely proportionally increase the springtime K flux due to its leaching from plant litter but likely decrease the summertime Si flux, especially in the permafrost-bearing regions. The increase of vegetation density in the next decades to centuries may produce a transient uptake of Si by growing vegetation in the discontinuous permafrost zone during the summer period. This potential decrease of the Si export flux may be overweighed by the increasing release of Si from previously frozen mineral horizons, and as such the overall modification of the Si flux in discontinuous/continuous permafrost zone may be smaller than those projected by a simple latitudinal shift.

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Table 1. List of sampled rivers, their watershed area and annual runoff.

Month				Latitude (N)	Longitude (E)	River	Watersheds km^2	Annual runoff $mm\,yr^{-1}$
June	August	October	February					
RJ-22			RF13	61°29′11.1″	74°09′42.9″	Vach-Yagun	1.79	192
RJ-21			RF54	61°29′46.6″	74°15′30.3″	Segut-Yagun	3.37	192
	BL-35			60°44′10.9″	77°22′55.9″	Medvedka	7	173
RJ-20	RA-18		RF55	61°27′17.3″	74°40′23.3″	Kottym’egan	7.18	192
RJ-39			RF31	65°06′48.8″	77°47′58.8″	Tydylyakha	7.46	185
RJ-2		R-2		56°43′15.0″	83°55′35.1″	Chybyr’	8.14	44.8
	BL-28			61°12′19.5″	75°23′06.5″	Er-Yakh	9.35	173
RJ-24			RF52	61°50′28.6″	70°50′28.2″	Vachinguriyagun	9.52	192
RJ-56	BL-25		RF48	62°37′08.4″	74°10′15.9″	Prtriyagun	9.65	192
	RA-6			63°12′43.38″	76°21′27.66″	Goensapur	11	194
RJ-40	RY 14–45		RF30	65°12′17.6″	77°43′49.8″	Tydeyakha	12.0	309
RJ-12		R-12		58°24′38.0″	82°08′46.0″	Istok	12.3	127
	RA-5			63°12′45.96″	76°24′1.32″	Denna	15	194
RJ-36	RY 14–47		RF33	64°32′07.9″	76°54′21.3″	Seryareyakha	15.2	186
RJ-31				64°09′06.4″	75°22′18.1″	Apoku-Yakha	18.8	186
	RA-12			63°9′31.38″	75°3′2.58″	Ponto-Yakha	19	194
RJ-25			RF14	61°58′05.1″	73°47′03.4″	Lyukh-Yagun	21.6	192
RJ-55	BL-23		RF46	62°43′09.9″	74°13′45.9″	Ai-Kirill-Vys’yagun	24.0	192
	BL-34			60°45′58.5″	77°26′12.6″	Saim	26	173
	BL-31			60°50′43.6″	77°05′03.0″	Kaima	31	173
	BL-3			56°54′39.1″	82°33′33.3″	Cherniy Klyuch	32	168
	BL-33			60°47′29.3″	77°19′13.5″	Mishkin Saim	32	173
	RA-15			63°8′34.02″	74°54′29.1″	Nyudya-Itu-Yakha	32	194
RJ-57			RF49	62°33′39.8″	74°00′29.5″	Pintyr’yagun	33.5	192
RJ-52; R-4	BL-19		RF39	63°36′48.2″	74°35′28.6″	Khatytayakha	34.6	194
RJ-46			RF26	65°59′05.7″	77°40′52.6″	Tadym-Yakha	39.9	185
RJ-45			RF25	65°58′54″	77°34′05″	Yude-Yakha	42.4	185
	RA-9			63°13′25.2″	76°5′23.04″	Tlyatsayakha	43	194
	BL-32			60°49′32.3″	77°13 46.3″	Alenkin Egan	44	173
RJ-35			RF34	64°26′05.2″	76°24′37.0″	Kharv’-Yakha	46.4	186
	RY 14–48			64°23′30.6″	76°19′50.1″	Khaloku-Yakha	53	186
RJ-11			RF10	58°23′16.8″	82°11′39.0″	Tatarkin Istok	58.6	33.4
RJ-32				64°12′08.4″	75°24′28.4″	Ngarka-Tyde-Yakha	59.9	186
RJ-3		R-3	RF2	56°46′19.5″	83°57′35.7″	Prud	61.5	44.8
RJ-30			RF36	64°06′50.7″	75°14′17.3″	Ngarka-Varka-Yakha	67.1	186
RJ-33	RY 14–49		RF35	64°17′31.9″	75°44′33.4″	Etu-Yakha	71.6	186
RJ-50; R-3	BL-17		RF41	63°49′58.0″	74°39′02.5″	Khanupiyakha	74	194
RJ-41	RY 14–44		RF29	65°23′34.1″	77°45′46.7″	Ponie-Yakha	78.9	185
	RA-4			63°10′4.68″	76°28′19.08″	Nyudya-Pidya-Yakha	79.5	194
	BL-22		RF45	63°11′19.3″	74°36′25.5″	Pyrya-Yakha	82	194
	RA-10			63°13′12.06″	75°38′52.26″	Yangayakha	88	194
	RA-13			63°10′3.48″	74°45′16.32″	Nekhtyn-Pryn	96	194
RJ-34				64°19′10.1″	76°08′26.7″	Varka-Yakha	105	186
RJ-43			RF27	65°47′48.6″	78°10′09.0″	Almayakha	106	185
RJ-27; Z-86	BL-14; RA-1		RF44	63°47′04.5″	75°37′06.8″	Lymbyd’yakha	115	194
RJ-58	BL-5	R-15	RF65	58°40′46.5″	84°27′56.6″	Vyalovka	117	127

Table 1. Continued.

Month				Latitude (N)	Longitude (E)	River	Watersheds km^2	Annual runoff mm yr^{-1}
June	August	October	February					
	RA-8			63°13′3.66″	76°15′24.6″	Chukusamal	121	194
	RT2 14–30			66°59′20.9″	79°22′30.5″	Malokha Yakha	157	208
	RA-11			63°9′39.84″	75°09′10.86″	Velykh-Pelykh-Yakha	170	194
RJ-53; R-5	RA-16; BL-21		RF38	63°22′01.6″	74°31′53.2″	Kamgayakha	175	194
RJ-8		R-8	RF7	57°52′26.8″	83°11′29.9″	Chemondaevka	177	63.4
	RY 14–42			65°46′34.5″	78°08′25.8″	Khiroyakha	183	185
			RF62	59°41′01.6″	77°44′33.9″	Kornilovskaya	190	133
			RF60	60°08′43″	77°16′53″	Koltogorka	220	155.4
	RA-14			63°11′40.68″	74°38′16.92″	Itu-Yakha	250	194
			RF61	59°44′09.2″	77°26′06″	Levyi Il'yas	253	133
RJ-9		R-9	RF8	57°58′45.7″	82°58′32.2″	Sugotka	275	63.4
RJ-51	BL-18		RF40	63°40′41.8″	74°35′20.7″	Pulpuyakha	281	194
RJ-6			RF5	57°36′43.3″	83°37′02.1″	Malyi Tatosh	302	63.4
RJ-5		R-5	RF4	57°19′20.7″	83°55′53.8″	Brovka	320	63.4
RJ-18	RA-19; BL-27			61°19′41.2″	75°04′0.3″	Ur'evskii Egan	359	272
	BL-9			58°32′05.8″	80°51′26.8″	Karza	473	148
	BL-6			58°37′29.9″	81°06′09.0″	Sochiga	510	148
RJ-49	RT2 14–32			65°59′14.7″	78°32′25.2″	Malaya Khadyr-Yakha	512	278
RJ-54; R-6	BL-24		RF47	63°38′23.4″	74°10′52″	Kirill-Vys'yagun	598	225
	RT2 14–29			67°10′54.8″	78°51′04.5″	Nuny-Yakha	656	312
RJ-14		R-14	RF12	58°33′03.1″	81°48′44.3″	Chigas	689	180
			RF58	60°30′19″	76°58′57″	Sosninskii Yegan	732	199
RJ-29; R-2	BL-16		RF42; RF37	63°51′23.4″	75°08′05.6″	Kharucheiyakha	820	292
RJ-7		R-7	RF6	57°37′17.3″	83°31′53.3″	Bolshoy Tatosh	1020	74.6
RJ-23			RF53	61°34′27.4″	77°46′35.4″	Mokhovaya	1260	192.3
	BL-13			63°43′37.9″	75°59′04.1″	Chuchi-Yakha	1396	292
			RF51	61°59′39″	73°47′39″	Limpas	1648	320
RJ-48	RT2 14–31			66°17′10.8″	79°15′06.1″	Ngarka Khadyta-Yakha	1970	277
	RA-3; RA-7			63°46′22.92″	76°25′28.86″	Vyngapur	1979	324
RJ-17	BL-29; RA-20		RF57	61°11′52.7″	75°25′20.2″	Vatinsky Egan	3190	287
	BL-2			57°02′23.75″	82°04′02.44″	Bakchar	3197	96.1
RJ-13	RA-22	R-13	RF11	58°26′06.9″	82°05′43.6″	Shudelka	3460	211
RJ-42	RY 14–43		RF28	65°41′51.1″	78°01′05.0″	Yamsovey	4030	309
RJ-37	RY 14–46		RF32	64°40′14.0″	77°05′27.2″	Purpe	5110	309
			RF21	67°24′39″	76°21′12″	Khadutte	5190	346
R-1; Z-55; RJ-28	BL-20; RA-2; BL-15		RF43	63°49′54.2″	75°22′47.1″	Pyakupur	9880	324
RJ-26; R-7; R-8	RA-17		RF50	62°07′50.0″	73°44′05.6″	Óromyega	10 770	263
RJ-4; R-10		R-4	RF3	57°06′39.2″	83°54′41.1″	Shegarka	12 000	58.3
RJ-15	RA-21; BL-4	R-17	RF64	58°42′34.5″	81°22′22.0″	Parabel	25 500	131
RJ-38				64°55′55.1″	77°56′08.2 ″	Aivasedapur	26 100	309
RJ-10	RA-23		RF9	58°04′20.8″	82°49′19.7″	Chaya	27 200	95.6
RJ-19; R-9	BL-26		RF56	61°26′13.6″	74°47′39.7″	Agan	27 600	291
			RF63	58°59′37″	80°34′00″	Vasyugan	63 780	177
	BL-30			60°55′41.0″	76°53′49.3″	Vakh	75 090	298
RJ-44	RY 14–41			65°57′05.5″	78°18′59.1″	Pur	112 000	298
RJ-47	RT2 14–40			67°22′13.28″	79°00′25.9″	Taz	150 000	330
RJ-16	BL-36			60°40′28.8″	77°31′29.4″	Ob'	773 200	216
RJ-1		R-1	RF1	56°31′48″	84°09′44″	Ob'	423 100	207

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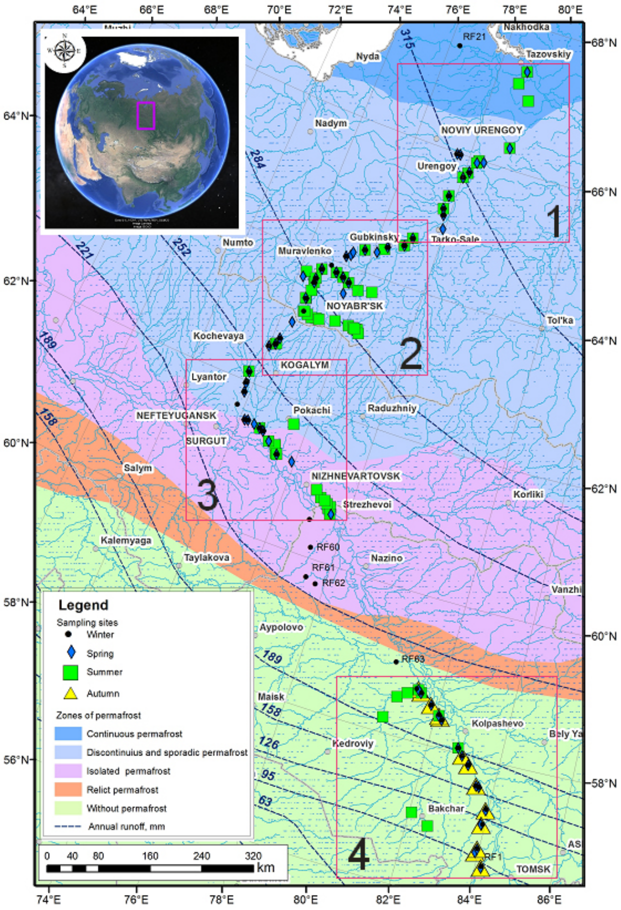

Figure 1a. Map of the study area with permafrost boundaries (Brown et al., 2002; http://portal.inter-map.com (NSIDC)), runoff contour lines (Nikitin and Zemtzov, 1986) and sampling points along the latitudinal transect of the Ob, Pur and Taz river basins.

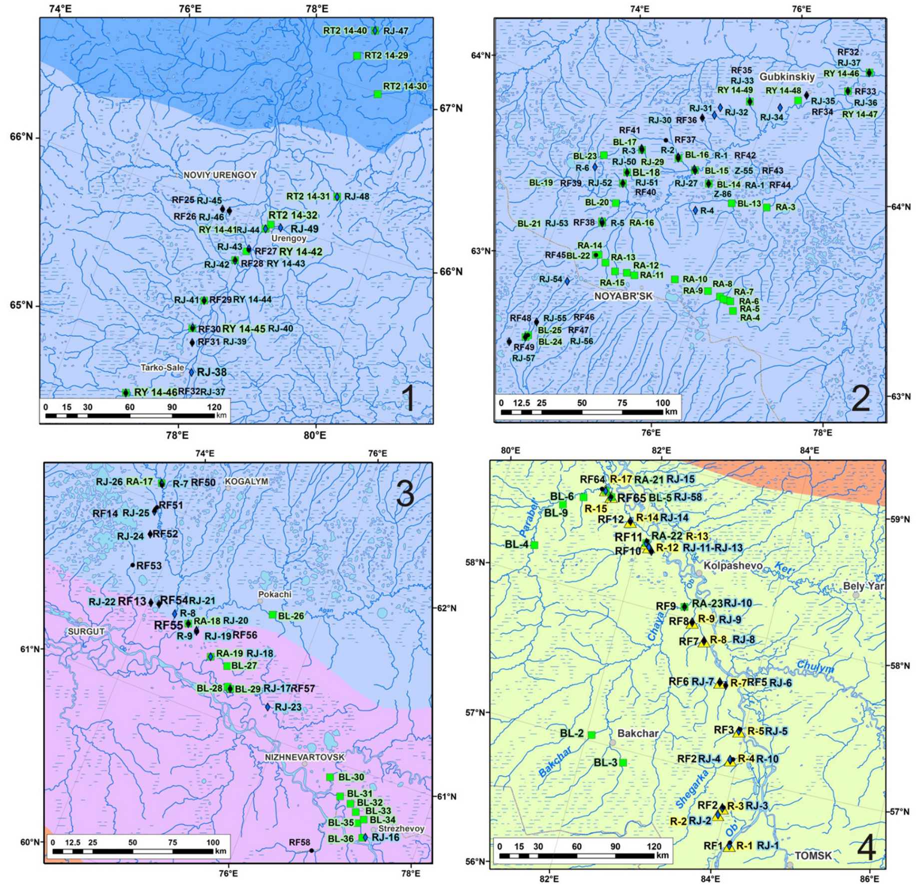

Figure 1b. Continued.

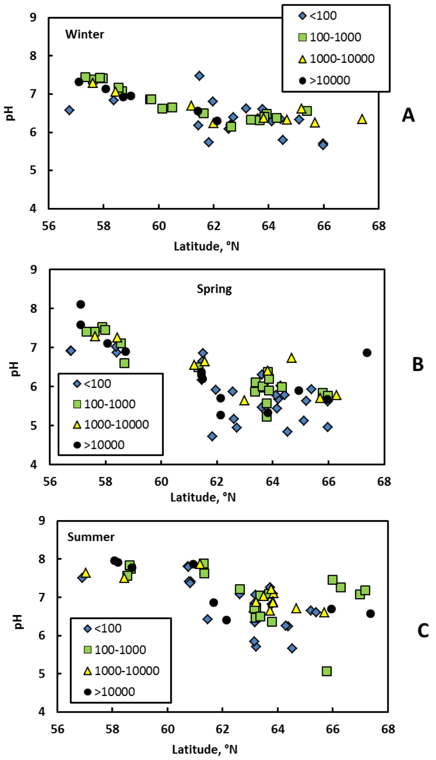

Figure 2. Decrease of river water pH with the increase in latitude during winter **(a)**, spring **(b)** and summer **(c)**. The spring acid pulse is seen only in permafrost-affected rivers north of 62° N **(b)**, and the scatter of the values is maximal during summer **(c)**. The variability among different watershed sizes is smaller than that between the seasons and within the latitude gradient. Diamonds, squares, triangles and circles represent watershed sizes < 100, 100 to 1000, 1000 to 10 000, and > 10 000 km^2, respectively.

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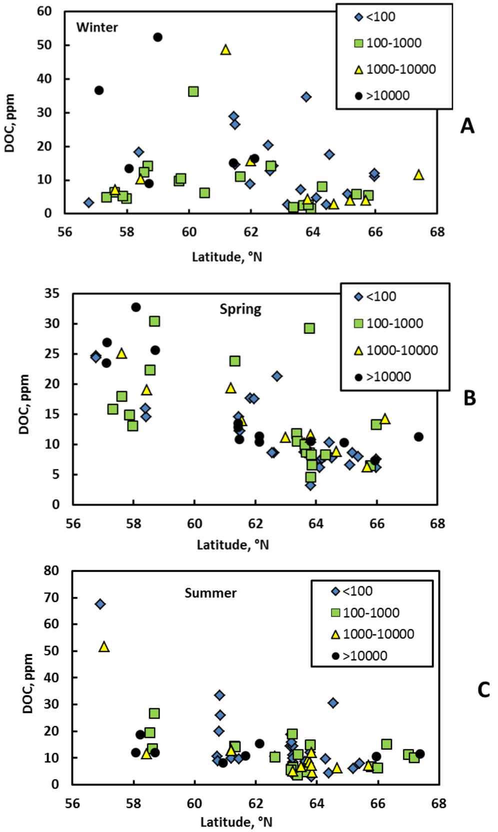

Figure 3. Decrease of DOC with latitude during winter **(a)**, spring **(b)** and summer **(c)**. The latitudinal trend is significant at $p < 0.05$. Considering all seasons together, the differences between different watershed sizes are not statistically significant ($p > 0.05$). The symbols are the same as in Fig. 2.

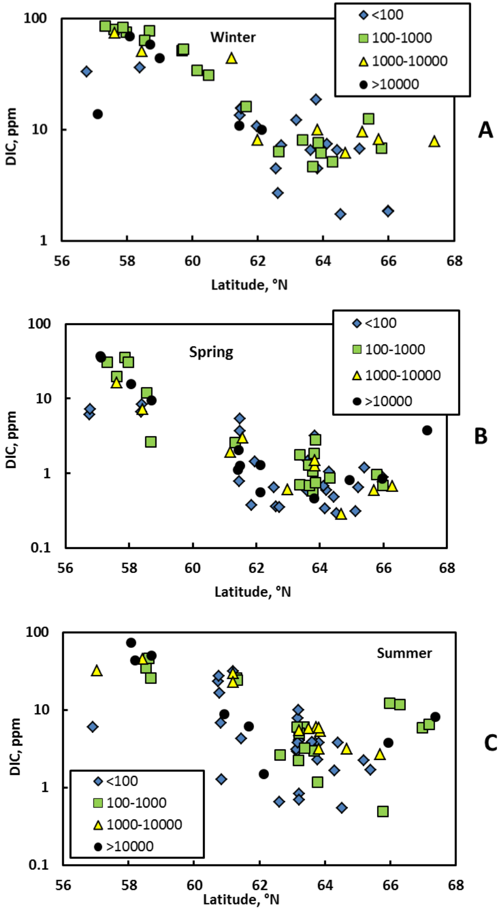

Figure 4. Significant decrease of DIC with latitude during winter **(a)**, spring **(b)** and summer **(c)**. Note the logarithmic scale of concentrations in all three plots. The symbols represent different watershed sizes, see Fig. 2.

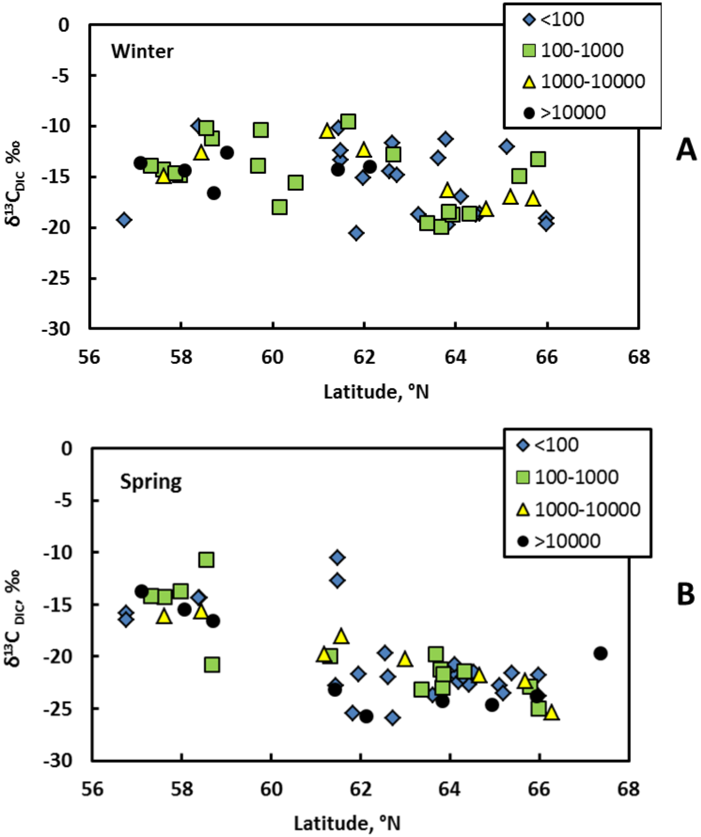

Figure 5. The variation of $\delta^{13}C_{DIC}$ with latitude during winter **(a)** and spring **(b)** for watersheds of different size. The symbols are the same as in Fig. 2. Isotopically light DIC is observed in the permafrost-affected zone during spring, suggesting intense respiration of soil or plant litter carbon (Ob River sediments are from −25 to −27 ‰, Guo et al., 2004a).

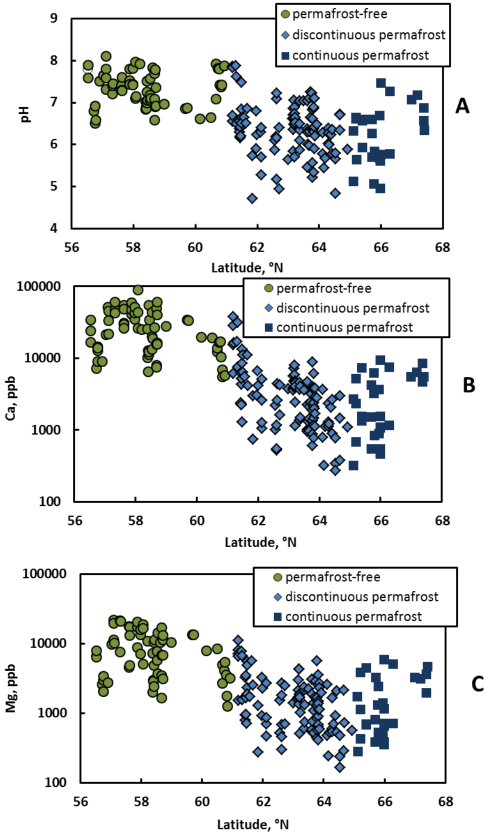

Figure 6. pH **(a)**, Ca **(b)** and Mg **(c)** concentrations in rivers as a function of latitude representing all seasons and all river watersheds. The difference between three permafrost zone are significant at $p < 0.05$. Note the log scale for Ca and Mg concentration as a function of latitude.

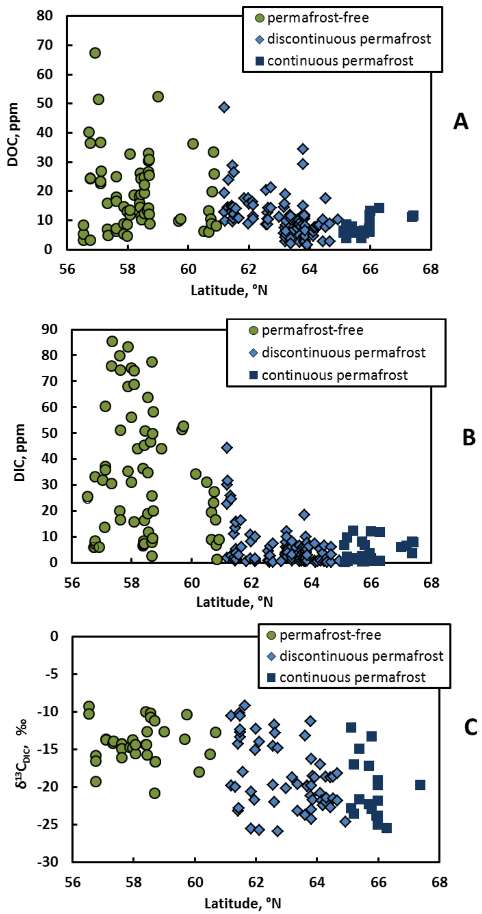

Figure 7. DOC **(a)**, DIC **(b)** and $\delta^{13}C_{DIC}$ **(c)** of all river sizes as a function of latitude comprising all sampled rivers during all seasons. The differences between three groups of sites are significant at $p < 0.05$.

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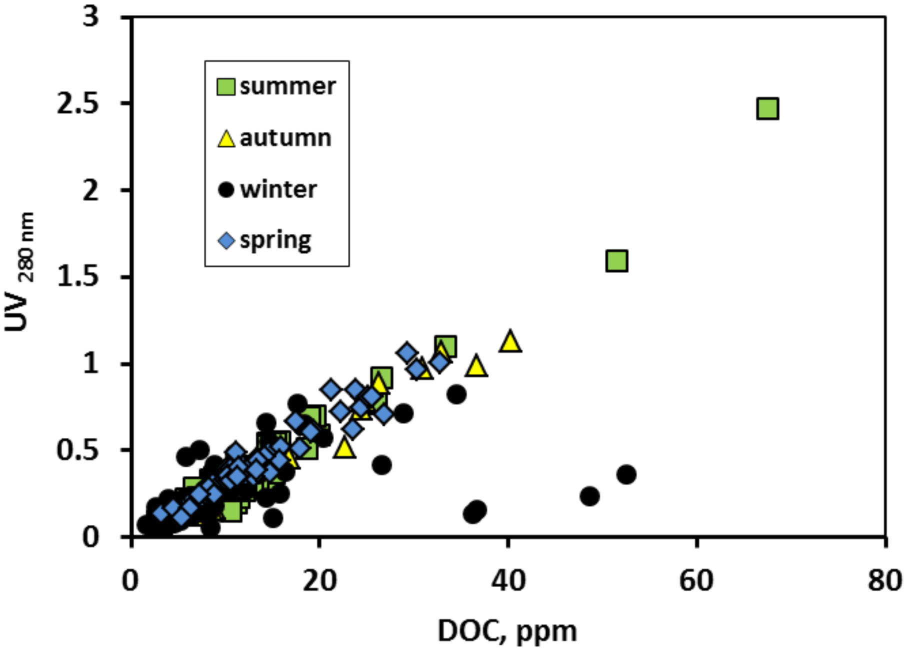

Figure 8. Universal dependence of $UV_{280\,\text{nm}}$ absorbance of DOC concentration in all rivers during all seasons except winter (black circles), where some hydrocarbon degradation products or oil-field organics may produce significant scatter.

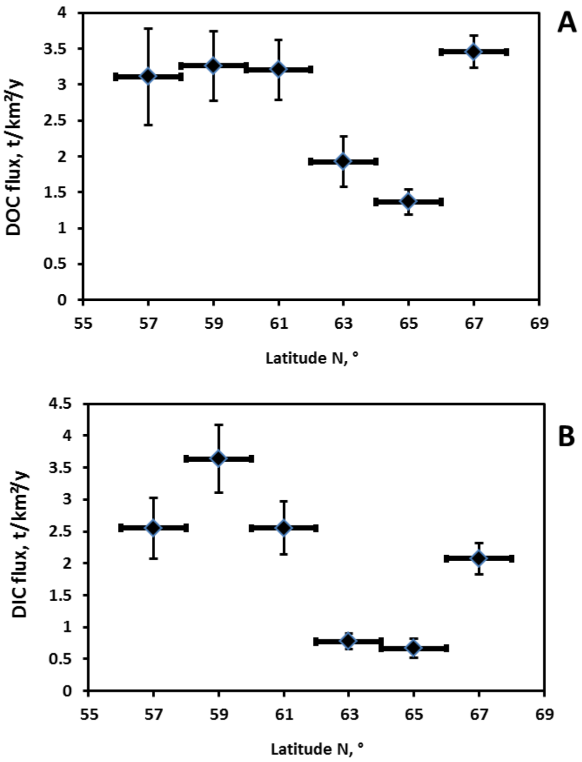

Figure 9. Latitude range-averaged, all river-size-averaged annual fluxes of DOC **(a)** and DIC **(b)** in western Siberian rivers. The increase of DOC and DIC fluxes north of 66° N is due to the significant contribution of the summer period (60 and 50 % for DOC and DIC, respectively). It may be linked to enhanced carbon export from the organic-rich peat layer coupled with the soil respiration/mineralization of fresh DOM from plant litter.

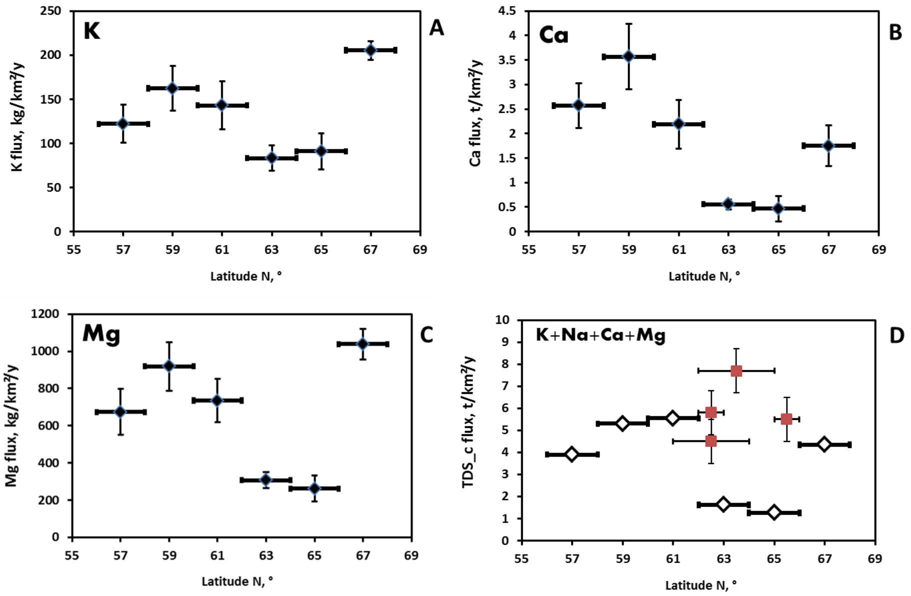

Figure 10. Latitude range-averaged, all river-size-averaged annual fluxes of K **(a)**, Ca **(b)**, Mg **(c)** and TDS_c (total cations, **d**) in western Siberian rivers. Squares in **(d)** represent mean multi-annual TDS_c fluxes of central Siberian rivers draining basalts in the discontinuous/continuous permafrost zone (Pokrovsky et al., 2005).

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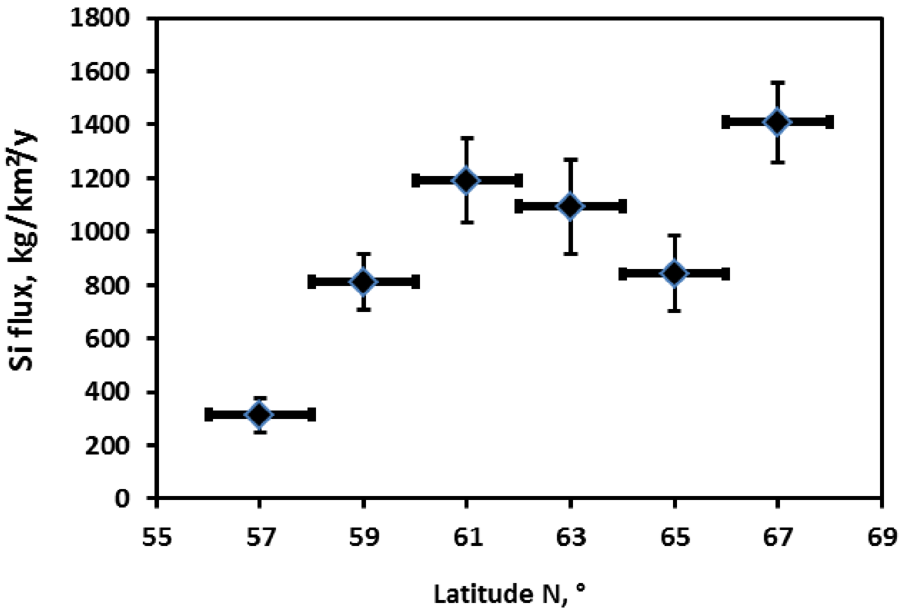

Figure 11. Latitude range-averaged, all river-size-averaged annual fluxes of Si in western Siberian rivers.

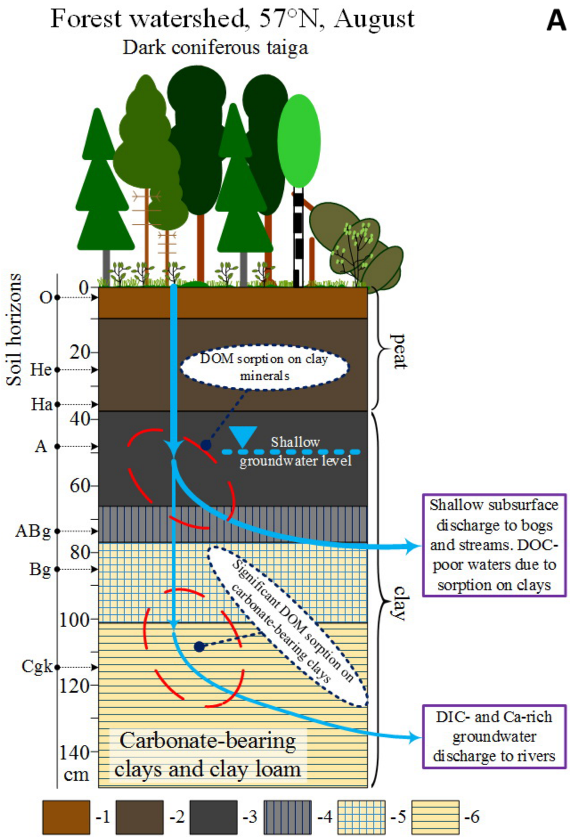

Figure 12a. Scheme of DOC pathways within the soil profile and to the river **(a)**: forest watershed of the southern, permafrost-free zone (57° N). Soil horizons (FAO, 2006): 1, O (Mor, forest litter); 2, medium-decomposed peat (He) transforming into strongly decomposed peat (Ha) in the bottom layer; 3, Mollic humic horizon (A); 4, ABg surface horizons with stagnic properties; 5, Bg middle stagnic horizon; 6, Cgk carbonate-bearing clays and clay loam.

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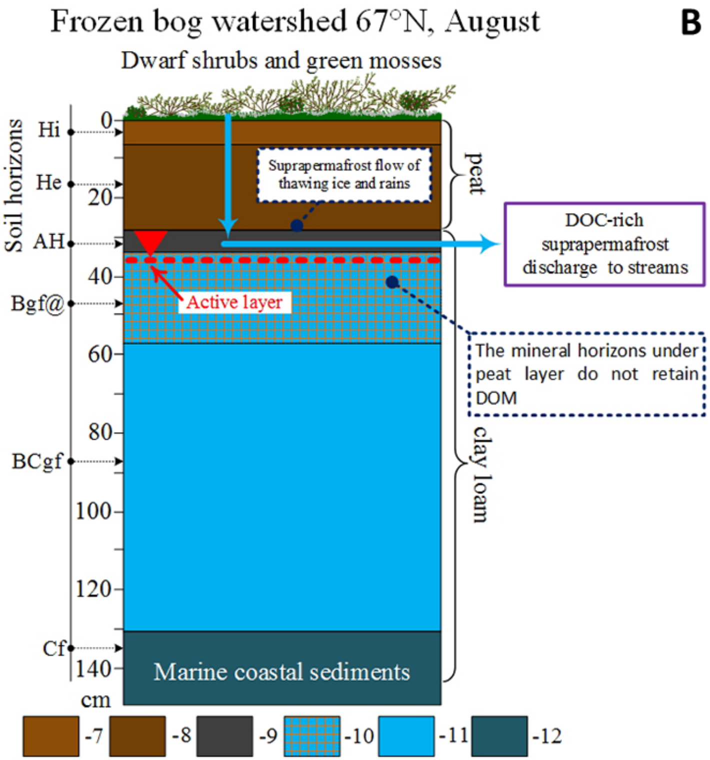

Figure 12b. DOC pathways in frozen bog peatlands of continuous permafrost (67° N). Soil horizons (FAO, 2006): 7, weakly decomposed peat (Hi); 8, partially decomposed peat (He); 9, humic horizons (AH); 10, cryoturbated frozen stagnic horizon (Bgf); 11, frozen stagnic horizon (BCgf); 12 sedimentary deposits (Cf).

In the south, DOC is retained by clay and deep in the soil profile, by clay loam with carbonates. In the north, the active layer depth does not exceed the overall thickness of the peat and thus the leachate of ground vegetation and peat layer do not meet the mineral horizons during their transit to the river.

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