

Dissolved Carbon Concentrations and Emission Fluxes in Rivers and Lakes of Central Asia (Sayan-Altai Mountain Region, Tyva): First Assessment across a Permafrost Gradient and Different Seasons

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Article

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Abstract: Carbon (C) cycle in inland waters, including its concentrations and carbon dioxide (CO₂) emissions from water surfaces are at the forefront of biogeochemical studies, especially in the regions, strongly impacted by on-going climate change. Towards better understanding of C storage, transport and emission in Central Asian mountain regions, extremely poorly studied until now, here we carried out systematic measurements of dissolved C and CO₂ emissions in 15 rivers and 5 lakes located along a macro-transect of various natural landscapes in the Sayan-Altai mountain region, from high mountains of the Western Sayan in the northwest of Tyva to arid (dry) steppe and semi-deserts in intermountain basins of the southeast of Tyva, the border with Mongolia. New data on major hydrochemical parameters, CO₂ fluxes by floating chambers, dissolved organic and inorganic carbon concentrations collected over four main hydrological seasons allowed to assess the current C biogeochemical status of these water bodies in order to judge possible future changes under climate warming. We further tested the impact of permafrost, river watershed size, lake area and climate parameters as well as 'internal' biogeochemical drivers (pH, mineralization, organic matter quality and bacterial population) on CO₂ concentration and emissions in lakes and rivers of this region, and compared them with available data on other subarctic and mountain settings.

Keywords: carbon; concentration; CO₂; emission; rivers; lakes; biogeochemical cycle; Central Asia; Altai-Sayan mountain

1. Introduction

Carbon (C) cycle in inland waters, including its dissolved and particulate concentrations and carbon dioxide (CO₂) emissions are at the forefront of biogeochemical studies, especially in the regions most sensitive to on-going climate changes such as boreal and subarctic zones [1–7] or the tropical/equatorial belt [11–14]. In contrast to these numerous works, the C storage, transport and emission in central continental, mountain and arid regions remain strongly understudied, either due

to limited access and logistics, or still underestimated potential role of these remote territories in C cycling in inland waters. This is especially true for Central Asian mountain system encompassing Tibet, Himalaya, Pamir, Altai and Sayan regions. Exceptions are thorough works on DOC, DIC and POC fluxes in Himalayan Rivers [15–17], and C concentrations and fluxes in thermokarst lakes of Tibetan Plateau [18–23]. However, the northern part of the Central Asian Mountain System remains virtually unexplored from the view point of hydrochemistry and carbon balance in its rivers and lakes.

The Altai-Sayany Mountain system is a specific inland region of the northern part of Central Asia which covers the territory of four countries: Russia, Mongolia, China and Kazakhstan [24]. In Russia, it is located within the Tyva Republic (Russian Federation). It is characterized by a high degree of continentality, aridity, as well as the highest level of endemism under a huge variety of ecosystems and landscapes, many of which are vulnerable to climatic changes [25]. The water bodies such as rivers and lakes are of particular importance for the sustainability, ecosystem services and conservation of the biodiversity of this arid region [26–31]. Particular interest of Altai-Sayan region is that the currently occurring climate changes in this territory contradict existing world models and forecasts. In particular, in the Tyva Republic, our group reported the first ever observed natural phenomenon, the “greening” or afforestation of steppes and bare sands [32,33]. This finding contrasts a number of prediction models which stipulated further progressive drying of the arid Altai- and Sayan regions (ASR), such as Khakassia, Tyva and Mongolia [34,35]. The other existing assessments of future climates in arid regions of Eurasia also predict an increase in aridity and even propose a propagation of desertification in the steppe regions [36–38]. For instance, in the Tyva Republic, the areal extension of steppe ecosystems, including these of dry steppes, is predicted to increase by 20–65%, and the areas of semi-deserts the projected increase achieve several hundred percent compared to their current extent [24].

In contrast to above-mentioned predictions, some other studies suggest an increase in the climatic instability, such as drastic transformation of the main atmospheric circulation in the South Siberia regions and at the border with Central Asia, which could lead to a decrease of the role of atmospheric transport from Atlantic regions hence resulting to blocking of anticyclones, and an increase in meridional atmospheric transport [39,40]. This process, in turn, causes many catastrophic weather events, such as dramatic appearance of rainstorms, hurricanes, water floods, altogether leading to progressive humidification of arid, previously dry, regions [41]. Such catastrophic weather events have been observed over last few years in Khakassia, Tuva and Mongolia [42–44].

It is clear that the ongoing climate changes can drastically impact the current hydrochemical, biogeochemical and hydrological status of inland rivers and lakes of the region. For example, it is known that lakes at high altitudes and cold climate are particularly sensitive to global change [45,46] and modifications in carbon biogeochemistry, including the status of Dissolved Organic Matter (DOM) and C emission fluxes, may strongly alter the role of these lakes in the global C cycle [47–49]. Among the consequences of progressive humification of Central Asian arid regions under on-going climate change, the treeline shift (greening of upland and advancement of treeline) can strongly affect the biogeochemical functioning of lakes, given that 15% of all lakes globally are located at elevations above 500 m above sea level [50]. Further, existing paleo-reconstructions suggest that lake productivity [51] and biogeochemistry [52] are sensitive to changes in DOM input linked to treeline position. Therefore, thorough assessment of today's status of C biogeochemical cycle (concentration, emission from the water surfaces) is necessary to be able to judge the possible future changes in Central Asian regions induced by climate instability.

Over past decade, a few studies in this area addressed hydrochemical [53–58], hydrological and hydrographic [59–61] status of the water bodies, including balneological aspect of mineral springs [62–65]. There are also some studies of water bodies hydrochemistry conducted in adjacent regions of Mongolia [66]. However, the status of aquatic C and CO₂ emissions from the water surfaces of Altai-Sayan region remain unknown. Towards filling this gap in the knowledge, here we assessed the concentration of dissolved organic and inorganic carbon and C emission in lakes and rivers of the Tyva region, via selecting large and small waterbodies, affected by permafrost in a different

degree. Unprecedented physio-geographical and climatic transect of inland water bodies which we implemented in this study extends from the northwest (the highlands of the Western Sayan) to the southeast (the semi-deserts of the Ubsunur Depression on the border with Mongolia). This transect comprises large variety of natural ecosystems and landscapes of the region: from glacial-nival high mountain belts to foothill taiga forests, intermountain basins with mixed herbs and steppe ecosystems, and dry semi-deserts. As a working hypothesis, we anticipated strong environmental control on C biogeochemical parameters of lakes and rivers, including climate, altitude, permafrost extent and size of the watershed as main 'external' drivers of C concentration and emission. We also assessed the link between carbon parameters of the water bodies and possible 'internal' biogeochemical drivers (hydrochemical parameters) such as pH, mineralization, quality of dissolved organic matter and microbial abundance. We tested these controls across four main hydrological seasons (spring, summer, autumn and winter) in 5 lakes and 15 rivers of different size and landscape context.

2. Materials and Methods

2.1. Water bodies of the Tyva Republic

We visited 20 water bodies during four hydrological seasons (autumn 2021 - summer 2022) as shown in Figures 1 and 2. Main physio-geographical parameters of rivers and lakes are listed in Table 1 and 2 and described in details in the Appendix. The Republic of Tyva is located in the Sayan-Altai mountain region, between 50-53 °N and 88-99 °E; the elevations range from 2000 to 500 m, creating a large variety of landscapes, from high-altitude belts to basins with steppes and semi-deserts. The climate of the region is continental, with cold long winters and hot summers; mean monthly temperatures range from -41 in January to +35 °C in July; the precipitation is low (115 to 350 mm y⁻¹), and about 70 % of it falls during the warm season of the year [67].

During the period of our study, the temperatures ranged from -28 °C to 21 °C, whereas the precipitation was equal to 322 and 144 mm during 2021 and 2022, respectively. (http://www.pogodaiklimat.ru/history/36096_2.htm). The water objects sampled in this work include numerous water bodies, mainly belonging to the Yenisei River basin, whereas only a small part belonged to the closed basin of the Ubsunur basin.

The largest river flowing through the region is the Yenisei River, formed at the confluence of the Maly and Bolshoy Yenisei rivers. Most of the rivers of the Yenisei basin are of mountain origin, that is, they mainly have snow and groundwater feeding. The studied lakes are mostly drainless, mainly fed by groundwater, with the exception of Lake Chagytai [68,69]. We collected the water samples during four hydrological seasons, in autumn (24.10.21 – 27.10.21), winter (07.03.22 – 11.03.22), spring (18.05.22 – 22.05.22) and summer (19.08.22 – 23.08.22). Altogether, we sampled 20 water bodies (15 rivers and five lakes). These were selected according to the criteria of proximity to the weather stations throughout the climate/landscape macro-transect of Tyva.

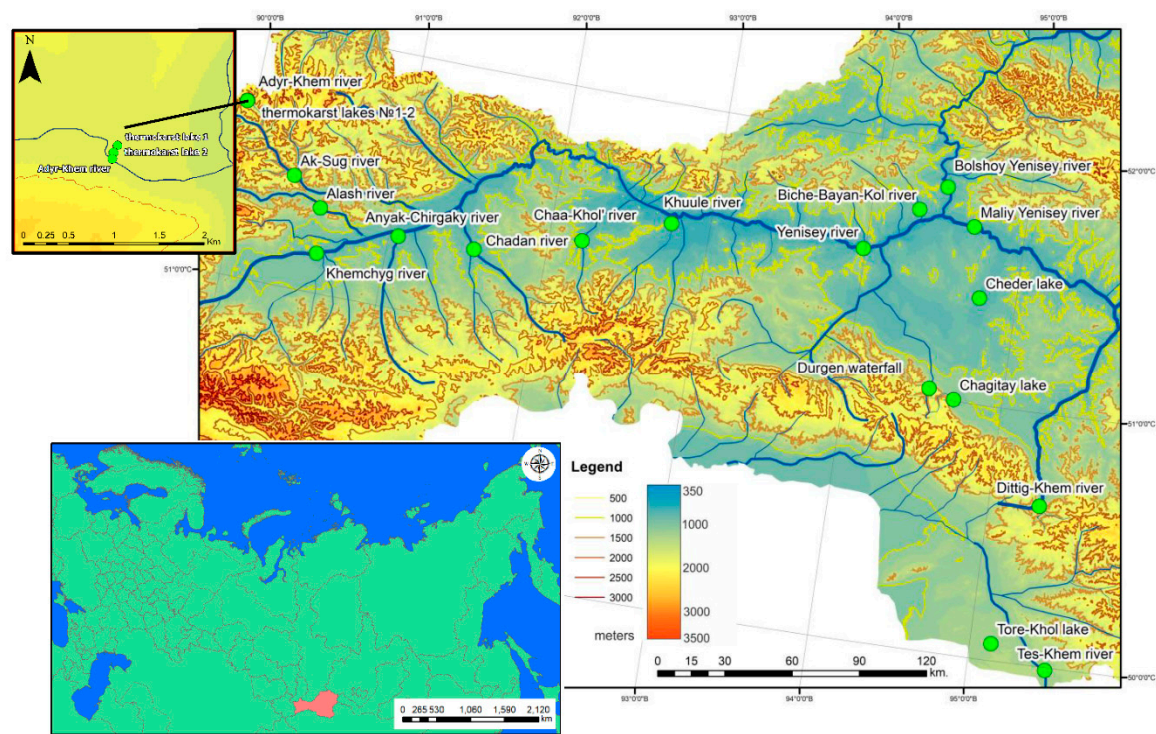


Figure 1. Location of research objects within the Sayan-Altai Mountain system (Central Asia).

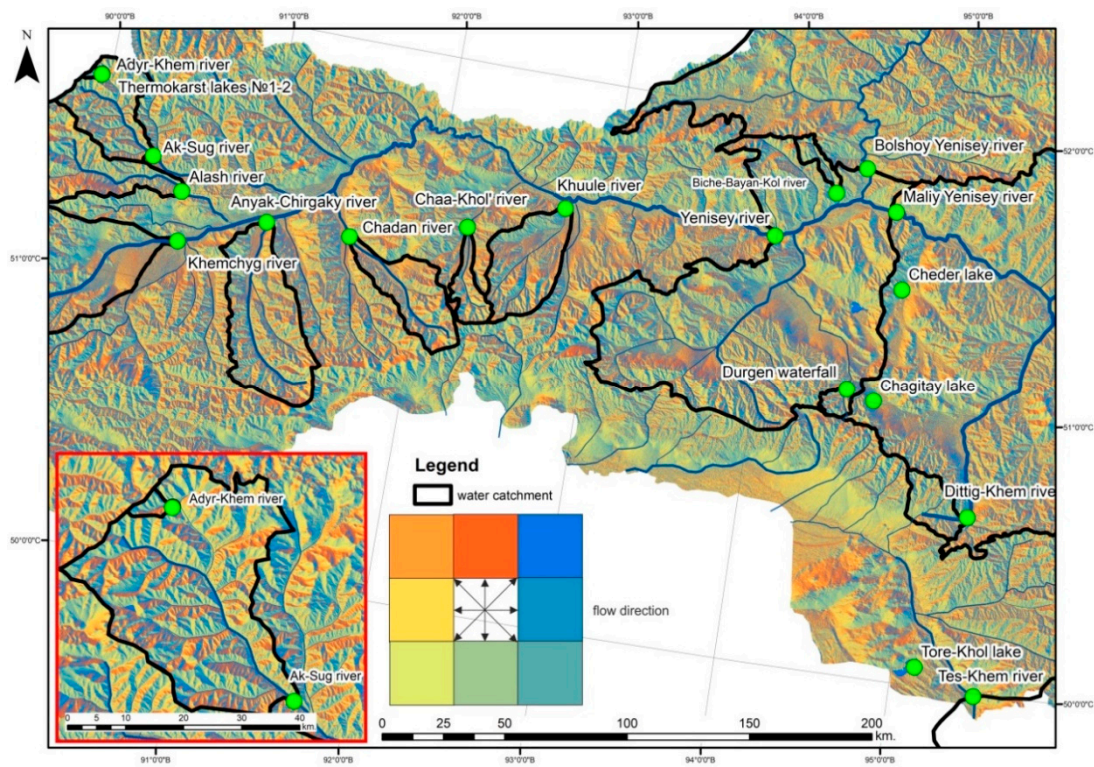


Figure 2. River catchments of the study region. The direction of water flow is shown by different colors.

Table 1. General information about the rivers sampled in this work.

Name	Flow velocity m/s	Depth (m)	Length (km)	Average dis- charge, m ³ /c	Catch- ment area (km ²)	Height at the samp- ling point, m	Aver- age cat- chment height (m)	Slope of the river- bed (m/km)	Location
Yenisei	0.25-2.6	2-3	3487	1020	102806	650	1196	16.8	Ulug- Khem basin
Big Yenisei	1.4-2.4	1.5-4	605	594	57766	630	1448	3.1	Todzhin- skaya basin; Kyzyl basin
Small Yenisei	1.8-2.3	1-2.4	563	411	36395	636	1555	2.8	Sangilen Highlands; Ulugh- Khem basin
Tes-Hem	1.1-2.1	1-2.1	757	55.6	18430	1067	1842	7.9	East Tannu-Ola
Hem- chik	-	0.75-2	320	102	3268	850	1923	14.4	Shapshal ridge; Khemchik basin
Alash	0.43	0.30 -2	172		4741	920	2063	9.2	Alash Plateau
Ak - Sug	0.31	0.25-1	160	14	997.4	1150	1966	26.8	Alash Plateau
Chadan	-	-	98	-	881.5	800	1567	28.8	West Tannu-Ola
Durgen	0.54	0.66 - 1	93	-	121.7	1200	1751	42.3	The northern slope of East Tannu-Ola
Chaa-Hol	0.28	0.5-2	90	-	320.3	540	1694	43.1	The northern slope of the western Tannu-Ola
Huule (Torgalyg)	-	0.4-2	53	-	1090	535	1273	30.9	The northern slope of the Eastern Tannu- Ola; The Central Tuva basin
Anyyak- Chyrgaki	0.173	0.2-2	52	-	1859	800	1519	13.9	West Tannu- Ola
Dyttyg- Hem	-	0.2-0.8	34	-	426.9	1250	1710	36.3	Southern slope of East Tannu-Ola
Biche- Bayan- Kol	0.34	0.3-0.8	32	-	15.3	750	1222	26.0	Uyuk Ridge
Adyr-khem	0.17	0.5-2	8.25	-	8.25	1850	2076	66.2	Alash Plateau

Table 2. General information about the studied lakes [15].

Name	Depth (m)	Water mirror area, km ²	Type	Height (m)	Location
Tore-Khol	6-8 (max. 40 m)	68.8	Freshwater	1148	Ubsunur basin
Chagytai	17	28.6	Freshwater lake	1005	The foot of the northern slope of the Tannu-Ola ridge
Cheddar	1.5-2	4.3	Salt Lake	706	South of the Tuva basin, a drainless depression
Thermokarst.1	4	0.3	Thermokarst Lake	1850	Alash Plateau
Thermokarst. 2	5	0.1	Thermokarst Lake	1850	Alash Plateau

2.2. Analytical methods

The list of measured parameters included temperature, pH, electrical conductivity and concentration of dissolved gases (CO₂ and O₂), dissolved organic (DOC) and inorganic carbon (DIC), isotopic composition of water, optical properties of organic matter, as well as CO₂ emission flux from the water surface. Dissolved oxygen, pH, electrical conductivity and temperature were measured in situ using an EXO2 multiparameter probe and a WTW Multi 3320 multimeter. The measurement of pCO₂ in water was carried out in situ using the GM70 data logger, Vaisala®. The pCO₂ was measured in-situ by an infrared gas analyzer (IRGA, GMT222, Vaisala, Finland) [70]. The sensor was enclosed in a semi-permeable membrane and placed directly into the surface water (30-50 cm depth), where it was allowed to equilibrate for approximately 30 minutes. The sensors were calibrated against standard gas mixtures (0, 800, 3 000, 8 000 ppm) before and after the sampling. Following calibration, results were corrected using water temperature and barometric pressure.

Carbon dioxide emissions from the water surface were measured by direct floating chamber method using SensAir sensors. We used freely drifting chamber (30 cm diameter, covered with aluminum tape). The CO₂ accumulation rate inside the chamber was recorded continuously at 5 sec interval for 5-10 minutes and used to compute (by linear regression if $R^2 > 0.75$) CO₂ flux and k_{CO_2} following Kuhn et al., 2018 [71]. For all calculations, the CO₂ air-water equilibrium was calculated assuming air concentration of 400 ppm. Further details of pCO₂ and fCO₂ measurements in rivers and lakes of adjacent regions are provided elsewhere [1,72–75].

River and lake water was collected from the surface (depth 0.5 m) into a pre-cleaned polypropylene container with a capacity of 1 liter and immediately filtered through nitrate-cellulose filters (<0.45 microns Sartorius Minisart High Flow). DOC and DIC were measured in the BIO-GEO-CLIM Laboratory (TSU), using a total organic carbon analyzer of the TOC-LCSN series, Shimadzu, with an uncertainty of 2%. As indicator of the quality of DOM, we measured UV absorbance using spectrophotometry (Agilent Cary 300 spectrophotometer).

Total microbial cell concentration was measured after sample fixation in glutaraldehyde (in the field, immediately after collection), by a flow cytometry (Guava® EasyCyte™ systems, Merck). Cells were stained using 1 µL of 10 times diluted SYBR GREEN solution (10000x, Merck), added to 250 µL of each sample before analysis. Particles were identified as cells based on green fluorescence and forward scatter.

To build the maps, the DAICHI satellite (ALOS) survey with a resolution of 30 m² was used [www.eorc.jaxa.jp/ALOS/en] together with the 3D Analysis module in the ArcGIS environment. To delineate the catchments of the studied rivers, the Flow Direction module was used in the ArcGIS environment, which calculates flow lines based on data on the heights of nearby points.

3. Results

3.1. Major hydrochemical parameters

The values of pH varied significantly during different seasons of the year ($F = 11.31$, $p = 0.00000$, Figure 3a) and between two major types of the water bodies – lakes and rivers ($F = 10.667$, $p = 0.00000$; Figure 3b, c). The electrical conductivity (E.C.) in the studied water bodies varied widely, and increased in the order thermokarst lakes (29 ± 22) < large rivers (172 ± 97) < small rivers (207 ± 121) < freshwater lakes (534 ± 252) < salt lake (54600 ± 24380).

The water bodies of the Alash plateau, both rivers and lakes, exhibited the lowest E.C. In winter and autumn during low water season, the electrical conductivity was significantly higher than in spring and summer ($F = 3.3$, $p = 0.03$), Supplementary Figure S1, S2. For lakes, a significant relationship ($p < 0.05$) between electrical conductivity and the pH has been established (Figure 4). No such relationship has been revealed for rivers. A strong direct relationship between electrical conductivity and DIC content has been also established (Figure 5), which reflected the dominance of bicarbonate ion in major salt composition of both rivers and lakes (Supplementary Table S1).

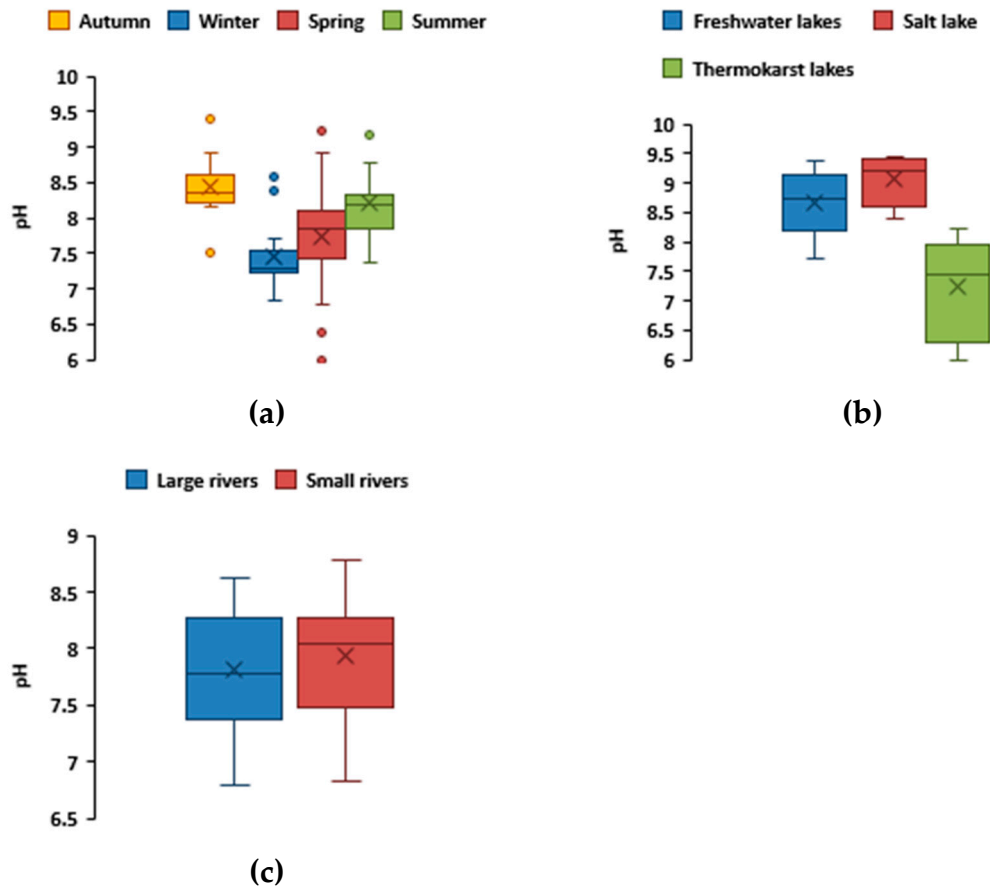


Figure 3. Box plot of median and IQR range (with outliers as dots) of pH values (a) during different seasons of the year (both rivers and lakes); (b) and separately in rivers; (c) and lakes.

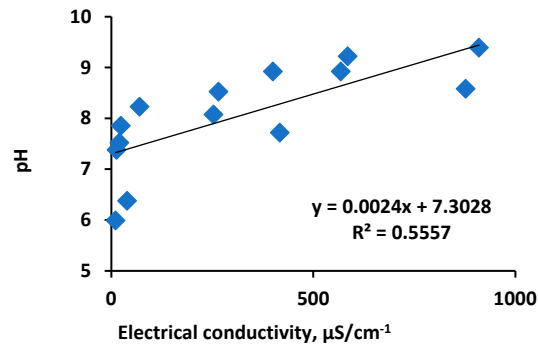


Figure 4. The relationship between electrical conductivity and DIC concentrations in the waters of the studied lakes (Salt Lake Cheder is excluded).

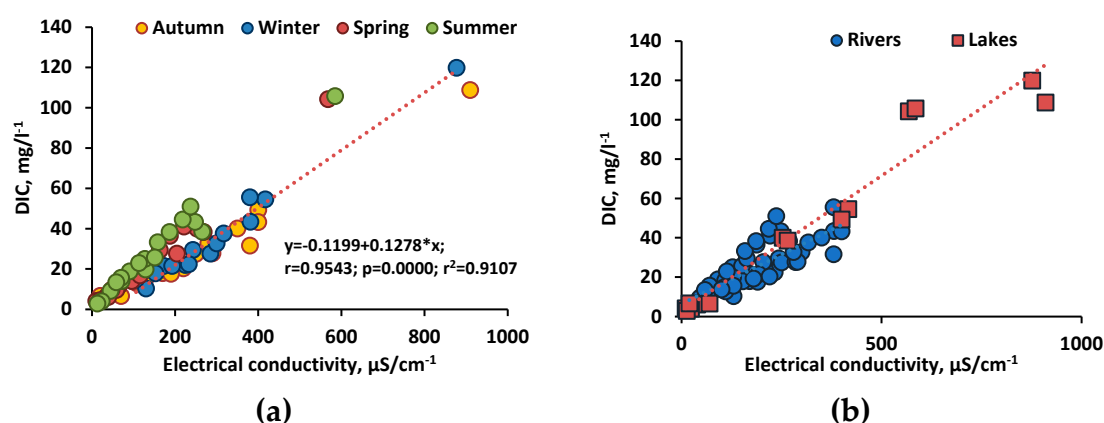


Figure 5. Linear relationship between DIC concentration and electrical conductivity in rivers and lakes of the Tyva region (a) and different seasons (lakes and rivers together); (b) in different types of objects (averaged across seasons).

3.2. DIC u DOC concentrations

Elevated DIC concentrations were observed in freshwater lakes, especially in the Torehol Lake, where they reached 120 mg/L⁻¹, likely due to the impact of carbonate-rich groundwaters, which are reported to occur within the lake watershed (Figure 6a). The minimal DIC values were recorded in the thermokarst lake waters, from 2.8 to 6.6 mg/L⁻¹. The seasonal dynamics of DIC demonstrated rather low variations (within 30 %) with minimal values observed in spring and maximal ones in winter (Figure 6b).

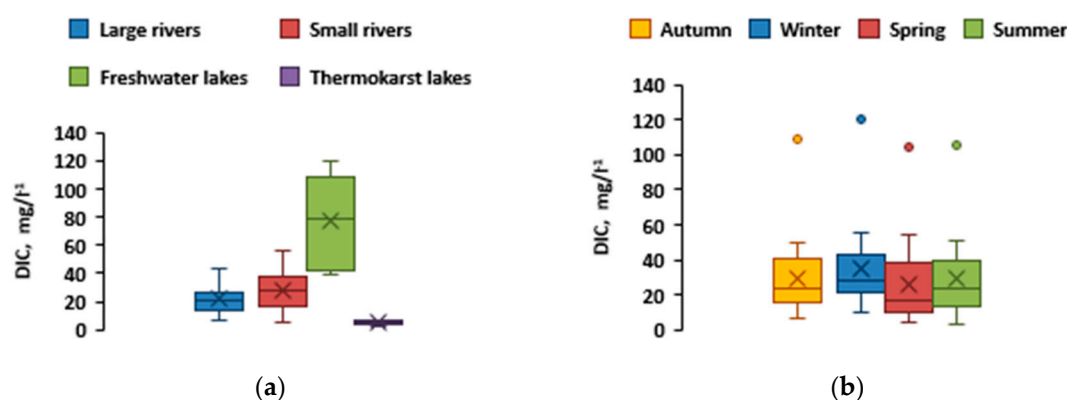


Figure 6. Median (and IQR) boxplots of DIC concentration (mg/L⁻¹) in different types of objects (a), in different types of objects (averaged across seasons) (b) and different seasons (lakes and rivers together).

The maximal DOC values were measured for the waters of the Torehol Lake and thermokarst lakes. Of all the rivers studied, the Dytyg-Khem, Durgen and Biche-Bayan-Kol waters are highly enriched in DOM whereas the majority of the waterbodies ranged from 2 to 6 mg L⁻¹ in DOC concentration. As in the case of DIC spatial and temporal pattern (Figure 7a), the DOC concentrations demonstrated relative stability across seasons (Figures 6b and 7b), with an exception of anomalously low value (14.8 mg L⁻¹) in the Torehol Lake during winter. The highest SUVA₂₅₄ values, which reflect the DOM aromaticity, were observed in the waters of thermokarst lakes, followed by rivers, whereas the minimal values were recorded in freshwater lakes (Figure 8a, b, c). The highest SUVA₂₅₄ was recorded in spring and the lowest in winter (Figure 8b).

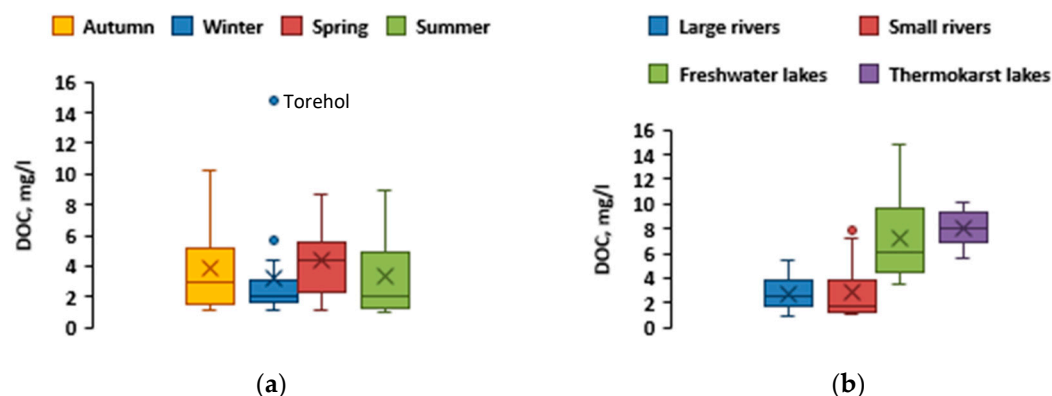


Figure 7. Median (and IQR) boxplots of DOC concentration (mg L⁻¹) in different types of objects (a) and different seasons (lakes and rivers together); (b) in different types of objects (averaged across seasons).

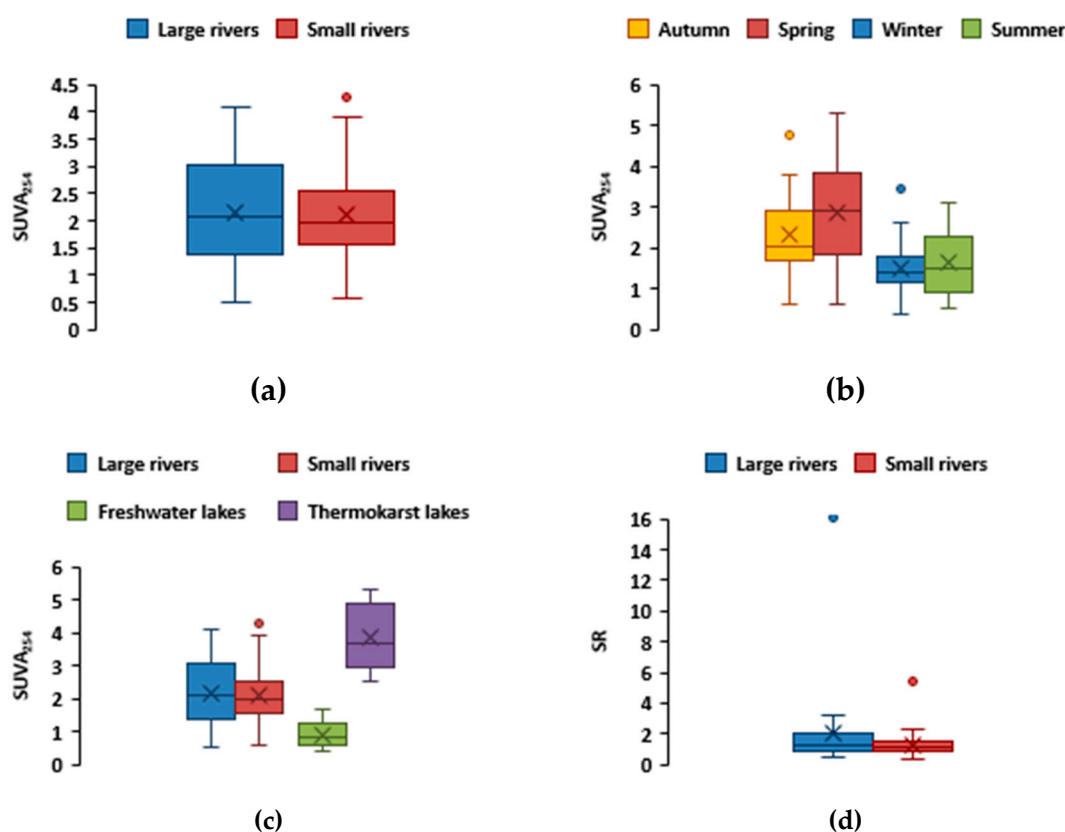


Figure 8. Median (and IQR) boxplots of SUVA₂₅₄ (a) in large and small rivers (averaged across seasons); (b) and different seasons (lakes and rivers together); (c) in different types of objects (averaged across seasons) and SR (d) in large and small rivers (averaged across seasons).

The ratio E₂₅₄:E₄₃₆ is known to indicate the relative role of allochthonous versus autochthonous organic substances in water bodies [76,77]. The DOM composition in the studied water objects was dominated by allochthonous substances, with the exception of the summer and partly spring period, when there was an increase in the E₂₅₄:E₄₃₆ ratio, indicating an active process of photosynthesis and destruction of detritus in the rivers and lakes themselves, leading to an increase in autochthonous organic matter [78,79].

There were no strong variation in the value of SUVA₂₅₄ in the waters of both small and large rivers (Figure 8a). However, small river waters had a lower SR value, which indicated an increased

degree of aromaticity compared to large rivers (Figure 8b). A high index of $SUVA_{254}$ (3.8 ± 1) and a low index of SR (0.9 ± 0.1) in the waters of thermokarst lakes indicated a presence of aromatic compounds. In contrast, freshwater lakes, poor in DOC, exhibited much lower $SUVA_{254}$ and higher SR values compared to thermokarst lakes. The ratio of optical densities $E_{254}:E_{436}$ in rivers followed the order “summer” > spring > autumn > winter (Figure 9a).

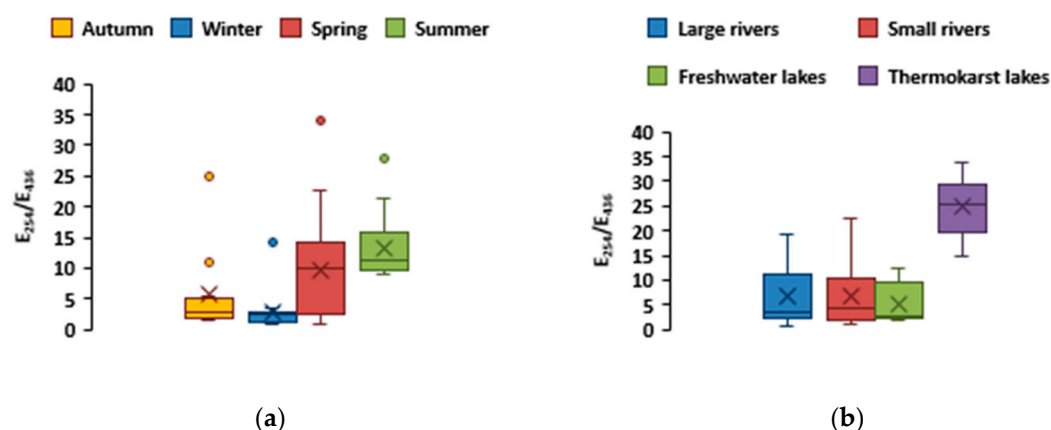


Figure 9. The ratio of optical densities E_{254}/E_{436} in the rivers and lakes of Tyva and (a) different seasons (lakes and rivers together); (b) in different types of objects (averaged across seasons).

3.3. Spatial and seasonal pattern of pCO_2 and fCO_2 in rivers and lakes

The highest values of pCO_2 were noted for a group of small rivers, with a maximum in the Adyr-Khem River, the smallest of the studied rivers draining the mound peat bog (Table 3). A high content of dissolved CO_2 was also noted in the waters of the Chadán River, originating in the western Tannu-Ola and in the waters of the Khule River (Torgalyg), whose source is located on the Eastern Tannu-Ola. This region (Tannu-Ola) is known for its CO_2 -rich underground discharges at the earth surface. The average values of pCO_2 in large rivers differ significantly from small ones; the minimum was marked for the Alash River (Figure 10).

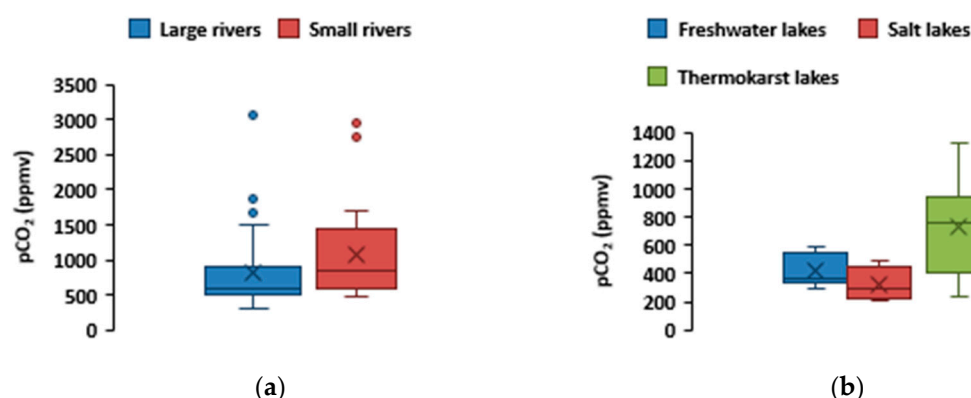


Figure 10. Median (and IQR) boxplots of CO_2 partial pressure (ppmv) (a) in rivers; (b) and lakes (averaged across seasons). Different types of rivers ($F=5.416$, $p=0.02$) and lakes ($F=4.44$, $p=0.03$) are significantly different.

In lakes, the dissolved CO_2 content was sizably lower than that in rivers; the minimum values were noted for the Cheder salt lake and the Tore-Khol Lake, located within a sandy substrate.

Table 3. The values of pCO₂ (ppmv) in rivers and lakes of the region.

Rivers	Average	Median
Large rivers		
Yenisei	689	578
Big Yenisei	860	587
Small Yenisei	790	571
Tes-Khem	672	609
Khemchik	705	715
Alash	563	502
Small rivers		
Ak - Sug	809	552
Chadan	1470	1112
Durgen	739.5	493
Chaa-Hol	778	729
Huule (Torgalyg)	1133	1003
Anyyak-Chyrgaki	909	932
Dyntyg-Hem	840	660
Biche-Bayan-Kol	743	743
Adyr-Khem	2043	2105
Lakes		
Tore-Khol	332,0	336,5
Chagytai	503,8	535,0
Cheder	320,5	292,0
Thermokarst lake 1	754,0	705,0
Thermokarst Lake 2	694,0	806,0

In terms of seasonal variations, both in rivers and lakes, the pCO₂ was significantly higher in winter due to CO₂ accumulation under ice (Figure 11). Note that, because shallow thermokarst lakes freeze solid in winter, measurements of the water column during this period were not possible.

Overall, CO₂ emissions from the surface of rivers and lakes were quite low (median 0.05-0.15 g C m⁻² d⁻¹; Table 4) and did not differ significantly ($p > 0.05$) among different water bodies, including two main categories - rivers and lakes. There was no significant difference in fCO₂ between different seasons of the year (Figure 12c). Exceptionally high CO₂ fluxes were encountered in the Chadan River and Ak-Sug River (12 and 5.6 g C m⁻² d⁻¹, respectively). Despite their small size, these rivers do not freeze solid during ice-on period, and they likely possess sizable bicarbonate/CO₂-rich underground sources that are mostly pronounced during winter baseflow.

Analysis of correlations between O₂ and CO₂ concentrations of all objects across seasons did not show significant relationship ($r = -0.13$, $p > 0.05$); however, when considering solely large rivers and thermokarst lakes, a negative relationship ($r = -0.47$ and $r = -0.95$) was observed (Table S1; Figure S4). In freshwater lakes, pCO₂ also negatively correlated with O₂ level ($r = -0.50$). The water temperature exerted significant ($r = 0.64$, $p < 0.05$) impact on pCO₂ in large rivers (Table S1).

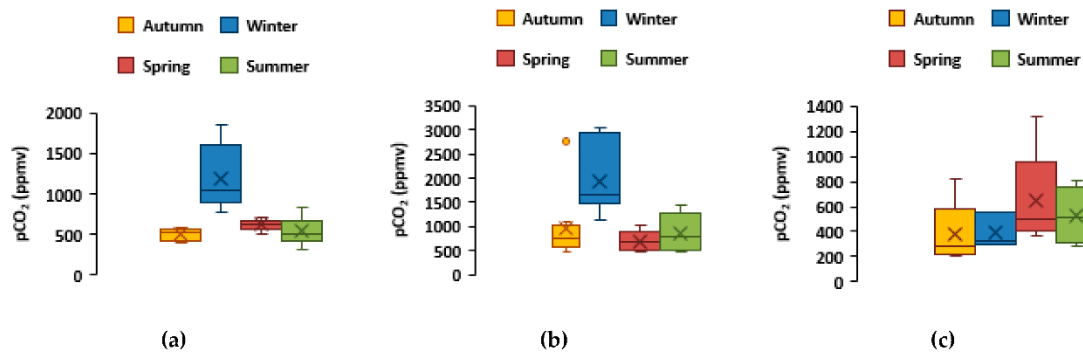


Figure 11. Median (and IQR) boxplots of CO₂ partial pressure (ppmv) in (a) large and (b) small rivers across seasons, statistically different (Large rivers: $F=12.202$, $p=0.001$ and Small rivers: $F=7.8006$, $p=0.001$, accordingly.) (c): Median (and IQR) boxplots of CO₂ partial pressure (ppmv) in lakes across seasons ($F=0.9223$, $p=0.46$).

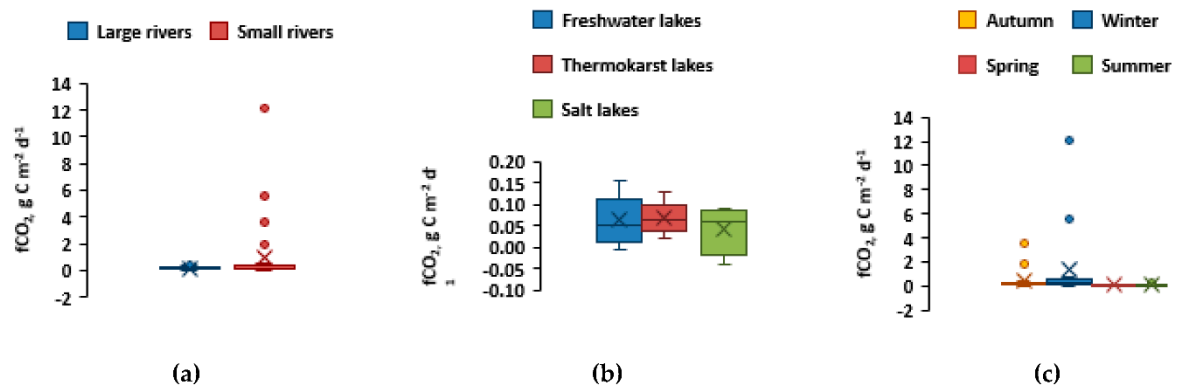


Figure 12. Boxplots (median and IQR range) of fCO₂ (a) in rivers the difference is insignificant at ($F=2.30$, $p=0.13$); (b) in lakes ($F=0.30$, $p=0.74356$); (c) and all types of objects across ($F=2.5448$, $p=0.06369$).

3.4. Testing potential drivers of CO₂ concentrations and fluxes

During summer period, the pCO₂ of the water column in lakes correlated with the lake water surface area ($R^2 = 0.44$, $p < 0.05$), whereas during other seasons, this relationship was not significant ($R^2 = 0.1$ to 0.2 , $p < 0.05$); Figure 13a. The flux of CO₂ positively correlated with lake surface area during the spring ($R^2 = 0.53$, $p < 0.01$) and winter periods ($R^2 = 0.79$, $p < 0.01$) as illustrated in Figure 13b. In thermokarst lakes, pCO₂ and fCO₂ increased with lake surface area in spring, but decreased with S_{area} in summer and autumn (Figure S5), although these qualitative trends could not be statistically supported due to too low number of sampled lakes.

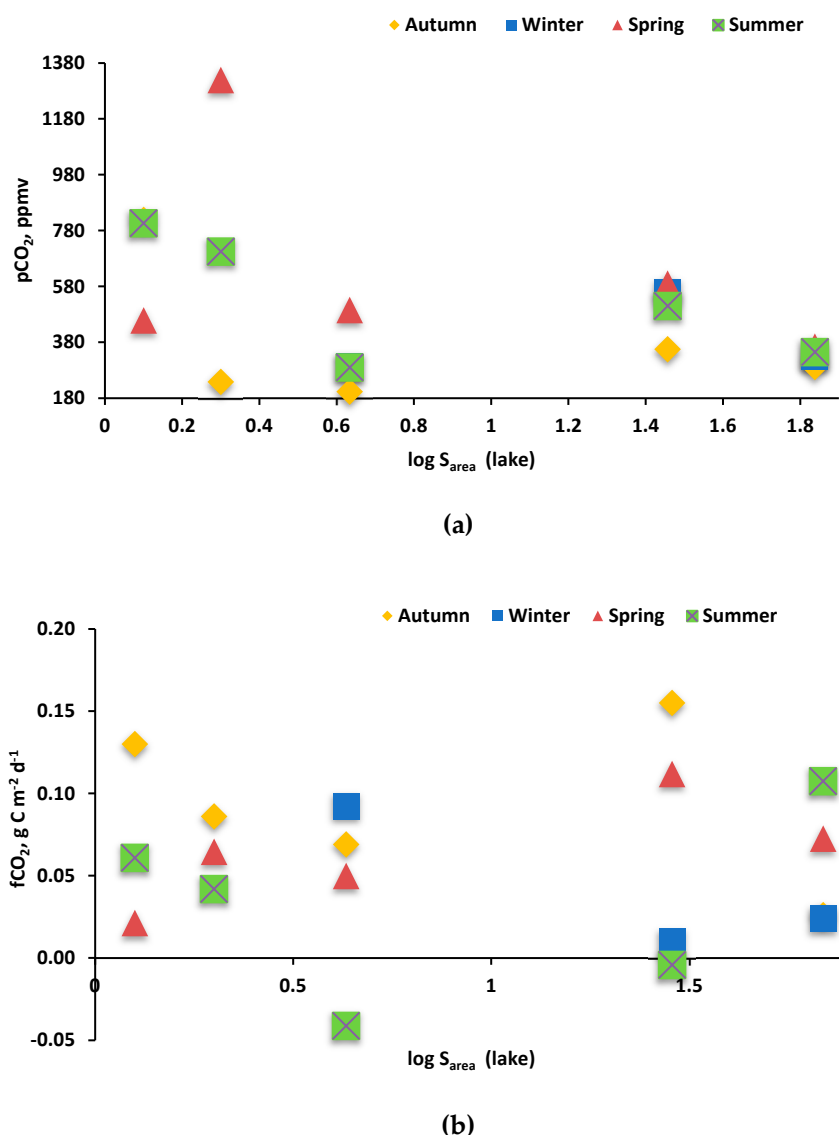


Figure 13. The relationship between (a) pCO₂ and (b) fCO₂ and lake water surface area of the Tyva region (all seasons together).

The river watershed area positively correlated with pCO₂ ($R^2 = 0.38$, $p < 0.05$) and fCO₂ ($R^2 = 0.32$, $p < 0.05$) in the autumn period whereas during other seasons, the correlation was absent ($R^2 < 0.27$; $p > 0.05$) as shown in Figure S6.

Among the “internal” factors likely to control the CO₂ pattern (concentration and fluxes) in the water bodies we tested major hydrochemical parameters of the water column, including pH, conductivity, DIC, DOC, concentration, DOM quality and a microbiological parameter (i.e., total bacterial count) as presented in Table 5. Considering all water objects together, neither pCO₂ nor fCO₂ correlated significantly ($R_{\text{Pearson}} > 0.39$ at $p = 0.05$) with any tested parameter. Note that this result does not contradict several significant relationships of pCO₂ with lake area or O₂, which were evidenced for individual seasons. Individual analyses of group of rivers and lakes demonstrated strong positive control ($p < 0.05$) of E.C. and pH on fCO₂ in large rivers ($r = 0.5$ and 0.64 , respectively) and negative control of pH on pCO₂ in lakes ($r = -0.99$); Table S1 of the Supplement.

Table 5. Pearson correlation coefficients between major hydrochemical and microbiological parameters of the water column, including pH, O₂, S.C., DOC, DIC and optical parameters of DOM reflecting DOM quality. S_{area}, S.C., and TBC represent area of lake surface or river watershed, Specific Conductivity, and Total Bacterial Count, respectively.

All objects													
All	E.C.	T _{water}	pH	O ₂	pCO ₂	TBC	DIC	DOC	SUVA ₂₅₄	E2:E3	E ₂₅₄ :E ₄₃₆	SR	fCO ₂
S _{area}	0.03	0.16	0.23	0.23	-0.18	-0.29	-0.07	-0.46	-0.2	-0.05	-0.41	-0.14	-0.16
S.C.		0.05	0.76	0.25	-0.24	-0.01	0.95	0.23	-0.75	0.72	-0.48	0.85	-0.06
T _{water}			-0.26	-0.69	-0.12	0.02	0.19	0.11	0.01	-0.37	0.12	-0.11	-0.33
pH				0.54	-0.33	0.09	0.7	-0.01	-0.77	0.71	-0.58	0.61	-0.04
O ₂					-0.13	-0.16	0.06	-0.28	-0.42	0.53	-0.46	0.25	0.09
pCO ₂						0	-0.24	-0.28	0.29	-0.07	0.01	-0.15	0.85
TBC							0.14	0.33	0.09	-0.03	0.22	-0.16	0.05
DIC								0.26	-0.72	0.64	-0.44	0.75	-0.08
DOC									0.25	0.03	0.69	0.21	-0.23
SUVA ₂₅₄										-0.61	0.81	-0.56	0.08
E2:E3											-0.51	0.75	0.21
E ₂₅₄ :E ₄₃₆												-0.39	-0.16
SR													0.06
Rivers													
	E.C.	T _{water}	pH	O ₂	pCO ₂	TBC	DIC	DOC	SUVA ₂₅₄	E2:E3	E ₂₅₄ :E ₄₃₆	SR	fCO ₂
S _{area}	0.22	0.38	0.17	0.02	-0.46	-0.23	0.18	0.08	-0.06	-0.04	0.05	-0.06	-0.4
S.C.		-0.16	0.79	0.54	-0.05	-0.11	0.88	-0.21	-0.77	0.42	-0.53	0.34	-0.04
T _{water}			-0.37	-0.71	-0.19	0.16	0.06	0.11	0.18	-0.72	0.28	-0.46	-0.36
pH				0.67	-0.23	-0.18	0.65	-0.18	-0.78	0.61	-0.55	0.46	-0.09
O ₂					-0.07	-0.26	0.16	-0.16	-0.48	0.74	-0.44	0.66	0.06
pCO ₂						0.22	-0.05	-0.3	0.16	0.17	-0.2	0.17	0.93
TBC							0.02	0.32	0.17	-0.17	0.28	-0.4	0.12
DIC								-0.11	-0.68	0.14	-0.39	0.08	-0.08
DOC									0.45	-0.27	0.89	-0.54	-0.24
SUVA ₂₅₄										-0.36	0.75	-0.39	0.11
E2:E3											-0.49	0.65	0.33
E ₂₅₄ :E ₄₃₆												-0.58	-0.2
SR													0.28
Lakes													
	E.C.	T _{water}	pH	O ₂	pCO ₂	TBC	DIC	DOC	SUVA ₂₅₄	E2:E3	E ₂₅₄ :E ₄₃₆	SR	fCO ₂
S _{area}	0.95	0.58	0.72	0.11	-0.31	0.19	0.92	-0.32	-0.93	-0.53	-0.83	0.98	0.17
S.C.		0.56	0.75	0.17	-0.38	0.41	0.99	-0.15	-0.87	-0.25	-0.77	0.92	0.07
T _{water}			-0.07	-0.51	0.19	-0.38	0.57	-0.29	-0.45	-0.14	-0.41	0.46	-0.53
pH				0.59	-0.54	0.65	0.71	0.16	-0.68	-0.28	-0.53	0.75	0.55
O ₂					-0.92	0.54	0.14	0.2	-0.35	-0.03	-0.3	0.18	0.16
pCO ₂						-0.46	-0.35	0.05	0.59	0.08	0.57	-0.36	0.1
TBC							0.45	0.34	-0.19	0.39	-0.16	0.26	0.36
DIC								-0.17	-0.84	-0.19	-0.76	0.9	0.05
DOC									0.48	0.68	0.67	-0.42	0.02
SUVA ₂₅₄										0.58	0.96	-0.94	-0.06
E2:E3											0.59	-0.59	-0.42
E ₂₅₄ :E ₄₃₆												-0.89	-0.02
SR													0.28

4. Discussion

4.1. Major solutes, dissolved organic and inorganic carbon

It is known that inland water systems are sizable sources of CO₂, which is highly important prerequisite for retroactive link between the climate and C cycle in aquatic systems [80–82]. Although at present, the climate changes in the territory of Tyva are already strongly pronounced (e.g., ref. [83], it is not yet possible to quantify this impact on water bodies. However, the present study can provide a solid background for assessing current status of C cycle in order to be able to judge the future changes which are likely to occur over the next decades.

The level of DIC concentration was sizably higher than that of DOC, and hence the C export in studied rivers and C storage in lakes are dominated by inorganic carbon. Only during spring, the DOC concentration was higher than DIC, which could be linked to the snow melt. dilution of the groundwater signal and the dominance of surface flow.

Enhanced DOC delivery to lakes and rivers occurs during melt snow interaction with surface soil, organic-rich litter. This period contrasts shallow subsurface flow in summer and autumn, when the water hydrochemical signal essentially controlled by rock weathering at the watershed. In this regard, the present study corroborates the knowledge of processes controlling river and lake water chemical composition across seasons as established in the boreal, high latitude and subarctic rivers [84–86] and subarctic lakes [87]. Note here that the connection between the groundwaters and the lake, especially in permafrost-covered regions such Altai-Sayany Mountain system, is weaker than that for rivers. A co-mobilization of DIC and other ions from shallow subsurface/ groundwaters, bearing the signal of chemical weathering, for all water objects is confirmed by the observation that the DIC values strongly correlated with the electrical conductivity index. In the Khemchik, Ak-Sug, Alash and Adyr-Khem mountain rivers flowing in the northwestern part of the Republic of Tyva, in the Western Sayans, the values ranged from 4 to 20, and in other rivers from 9–13 to 55. It is possible that a reason for such a reduced DIC values in mountain rivers is an increased precipitation in this area [83], the presence of permafrost [88] and high runoff [89]. An opposite situation is observed in the water bodies of more arid Ubsu-Nur basin: the Tore-Khol Lake and the Tes-Khem River, where the DIC values are the highest. Here, evaporative concentration of major solutes, occurring both within the river watersheds and the lake water column, can be responsible for elevated DIC and S.C. values.

Increased DOC concentrations were observed in lakes, compared to rivers, which may be explained by higher water residence time and autochthonous production of OM. This was especially pronounced in thermokarst lakes, exhibiting the highest SUVA (Figure 8b, c) and the humification index (E_{254}/E_{436} ratio (Figure 9b). According to the ratio of optical densities E_{254}/E_{436} , allochthonous (peat-originated) organic matter prevails in thermokarst lakes, and significantly exceeds the values of the ratios in other water bodies. A decrease of the optical index E_{254}/E_{436} in rivers (Figure 9a) demonstrated the highest allochthonous (terrestrial) source of DOM from forest litter during active period of the year. This likely corresponds to a decrease of the humification index [90] due to biotically-driven degradation of humic-like aromatic components in streams and rivers [91].

4.2. Dissolved C pattern and CO₂ fluxes: driving factors and comparison with other regions

We identified the oxygen regime as one of the main controlling factors of pCO₂ level in both rivers and lakes across seasons. The highest CO₂ concentrations were observed in O₂-impoverished waters, likely due to important impact of partially anoxic sediment respiration on CO₂ regime of the water column. Similar effects are reported in many boreal and subarctic waters across the world, notably in lakes and channels of the Ob River floodplain (i.e., ref. [73]).

The pCO₂ was generally lower in lakes of smaller surface area, which is well –known phenomenon in various lakes of the boreal and subarctic zone [1,75]. This can be linked to enhanced terrestrial input of CO₂-rich waters from the watershed in small lakes and sizable primary productivity of plankton and periphyton/macrophytes in large, mature lakes, as it is known in thermokarst water bodies in the neighboring territory of permafrost peatlands [92].

The seasonal variations of CO₂ concentration were characterized by a maximum pCO₂ during winter in rivers and during spring in lakes. The former can be explained by enhanced underground discharge within the river main stem and CO₂ accumulation under ice, whereas the spring maximum of CO₂ in lakes is likely due to lack of phytoplankton activity and enhanced input of biologically labile terrestrial DOM from the watershed, during freshet. This DOM can be subjected to intensive bacterial processing leading to a maximum of CO₂ emissions [93]. In summer period, lakes act as CO₂ sink due to biological production processes (macrophytes, cyanobacterial bloom) in the water column (e.g., ref. [94]).

The results on carbon (DOC, DIC CO₂) concentrations and CO₂ fluxes in the Altai-Sayany mountain system were compared with data reported for the Qinghai-Tibetan Plateau [18,95,96], since this region has relatively similar climate and also impacted by the permafrost. To account for thermokarst lakes, we also chosen the largest compilation of lakes in sporadic to continuous permafrost zone of the Western Siberia reported in Serikova et al. (2019) [1]. A synthesis of available information is provided in Table 6. The DOC level of river and lakes of the Tuva Republic obtained in this study are quite similar. within the range of natural seasonal and spatial variations. to that in thermokarst lakes of the QTP as well as the Tibetan rivers. The DIC concentrations in lakes and rivers of the Sayan-Altai mountain system are also similar to the values of the Qinghai-Tibetan plateau. with the exception of saline lakes whose C cycle is strongly controlled by local evaporative processes.

Table 6. Comparison of carbon concentration in lakes and rivers and CO₂ (mean and std. deviation) emissions from water surfaces in the Tyva region to other regions of the world. having similar altitudes. climate and landscape characteristics.

Sites	Period	pCO ₂ (ppmv)	fCO ₂ , g C m ⁻² d ⁻¹	DOC (mg L ⁻¹)	DIC (mg L ⁻¹)	Reference
All	Annual cycle	1495±577		3.7±2.9	29±24	This study
Rivers	Annual cycle	929±611	0.60±1.9	2.7±1.7	24.6±12	This study
Lakes	Annual cycle	385±123	0.06±0.05	7.2±3.8	78±35	This study
t/k lakes	Annual cycle	724±368		8±1.6	5±1.6	This study
Fenghuoshan catchment, China	Annual cycle	1260±145	6.3±0.9	17.9±5.5	33±3	[19]
Thermokarst lakes, China	June–September			9.5±5.7	38±35	[96]
The NamCo basin and source area of Yellow River (SAID)	July 2015 (melting of glacier)			2.3±1.3	11.3±10.6	[97]
Yangtze River source region	Biweekly from May to October	1086±275		2.8±0.6	24.4± 1.9	[18]
Qinghai Lake and the inflowing rivers	May 23, 2021			1.0±0.6	13.3±7.7	[21]
Three catchments within the Nam Co watershed	June/July 2018, May 2019, and September 2019			2.4±0.3	8.8±5.5	[98]
76 lakes, Western Siberia Lowland	May- June, August-October	1044±1540	1.7±1.7	16±10	0.7±0.8	[1]
Lena upstream of Kirenga	29 May to 17 June 2016	714±22	0.85±0.06	13.9±1.4	20.0±1.2	[74]
Southwestern and northeastern regions of the QTP (70 lakes, four rivers and one reservoir on the QTP)	20-year period (i.e.. from the 2000s to the 2020s)		0.3±0.2			[95]
Two saline lakes (Qinghai Lake and Hala Lake) in the Tibetan Plateau	Continuously measured on October 20, 23, 2018		13.1±0.4			[20]

In contrast to the DIC and DOC concentrations, for which the results of different regions are fairly comparable, the pCO₂ in Sayan-Altai Mountain region had generally lower values than those observed in the Qinghai-Tibetan Plateau and Western Siberia. It is possible that sizable autochthonous production and CO₂ uptake by plankton in lakes and macrophytes in rivers could be partially responsible for lower CO₂ level in the water bodies of studied region during summer period, when the water warms higher than that in the sub-Arctic western Siberia or high-altitude QTP. At the same time, our results on CO₂ flux are comparable to those Jia et al (2022) [95] for the lakes and rivers of southwestern and northeastern regions of the QTP (0.3±0.2 (g C m⁻² d⁻¹)). However, unlike the maximal flux observed in this work during winter, the latter authors reported the lowest flux during ice-covered seasons. The lowest CO₂ emission is typically observed during cold periods, as

also reported by other studies [96–100]. In our case, this could indicate an existence of sizable underground sources of CO₂ (discharge of CO₂-rich fluids, especially pronounced during low water level period). These effects are visible for large rivers, which demonstrated strong positive impact of E.C., pH and DIC on fCO₂ (Table S1).

Overall, the differences on CO₂ emissions among different works may be due to the peculiarities inherent to our region, as well as due to differences in the methodologies used. It is interesting that the carbon uptake flux in the terrestrial Tyva steppe regions is estimated as $184 \pm 41 \text{ g C m}^{-2} \text{ yr}^{-1}$ [101]. This is fairly comparable with the CO₂ emission flux by the rivers of the region, assessed in the present study ($213 \text{ g C m}^{-2} \text{ yr}^{-1}$). Such a comparison is consistent with the importance of inland water bodies (rivers and lakes) in overall C balance of the terrestrial biomes, as also demonstrated in Western Siberia [102]. However, at the present status of research, straightforward comparison of the data on C pattern revealed in the Sayan-Altai region and that reported in the adjacent subarctic and mountain territories requires more thorough assessment of possible controlling factors such as local climate variation, productivity of the terrestrial compartments, underground influx, respiration of sediments and primary productivity in the river and lakes.

5. Conclusions

A thorough, first-time assessment of contemporary status of C biogeochemical cycle (concentration, emission from the water surfaces) was conducted in lakes and rivers of the Central Asian, Sayan-Altai mountain system in order to provide a background for judging possible future changes induced by a particulate climate instability in this region. Using a physio-geographical and climatic transect of inland water bodies, which comprised large variety of natural ecosystems and landscapes of the region, we found that permafrost exerts the largest impact on lake water hydrochemistry and C pattern including CO₂ exchange with atmosphere, whereas the size of the river watershed had relatively little impact on CO₂ pattern. In contrast, pCO₂ decreased with an increase in lake size which could be linked to a combination of factors, notably *i*) enhanced input of terrestrial, biolabile DOM in small lakes which served as a source of CO₂ production in the water column, *ii*) terrestrial input of CO₂-rich shallow groundwater and soil waters, more pronounced in small lakes, and *iii*) CO₂ uptake in large lakes due to macrophytes, periphyton and phytoplankton activity. Oxygen regime was found to be an important controlling factor of pCO₂ level in both rivers and lakes during specific seasons, likely due to sediment respiration processes. However, despite these qualitative features of possible CO₂ regime control in studied water bodies, a pairwise correlation analysis did not demonstrate statistically significant relationships between CO₂ flux and physico-geographical parameters of river watersheds, river and lake size and internal parameters of the water column, including basic hydrochemical characteristic, DOM concentration and quality and bacterial concentration. A likely reason is the complexity of the 'external' and 'internal' factors controlling CO₂ exchange between water surfaces and the atmosphere, and their often counter-action on CO₂ production/uptake in the water column, sediments and the watershed.

We argue that further assessment of possible controlling factors such as local climate variation, productivity of the terrestrial compartments, underground influx, respiration of sediments and primary productivity in the river and lakes, are necessary for comparison of the aquatic C pattern revealed in the Sayan-Altai region in this study to that reported in the adjacent subarctic and mountain territories.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org.

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