Changes in the Concentration and Flux of Dissolved Biogenic Elements in the Yenisei River

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Abstract—The spatiotemporal variability of concentrations and export of inorganic dissolved biogenic elements (nitrogen and phosphorus) in the Yenisei River runoff is assessed. The analysis of changes in phosphate, nitrate, nitrite, and ammonium concentrations in the river water was carried out from the Krasnoyarsk hydroelectric power station tailwater (56 N) to the outlet near Igarka (68 N). The enrichment of the Yenisei water with biogenic substances flowing from the Krasnoyarsk Reservoir was found. Among the largest tributaries, the Angara River has the greatest effect on the concentration of inorganic nitrogen and phosphorus in the Yenisei runoff. The spring flood makes the maximum contribution to the annual flux of biogenic elements. The summer-autumn period, despite its duration and significant water consumption, is characterized by the low flows of dissolved inorganic nitrogen and phosphorus, which indicates an active participation of biogenic elements in the biogeochemical processes in the Yenisei.

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INTRODUCTION

The increase in average annual air temperature in the basins of the largest Arctic rivers in the recent decades has been equal to 1°C and, according to projections, will increase by 4–7 C more during the next century [15]. Climate change has significant consequences for the permafrost extent [23], river runoff value [24, 26], and watercourse biogeochemistry, especially in the permafrost zone [18, 27]. In particular, the transport of such biogenic elements as nitrogen and phosphorus to the Kara Sea as a terminal basin intensifies [22].

The Yenisei is the largest river flowing into the Arctic Ocean not only in the volume of incoming water but also in the value of annual carbon and nitrogen flux [14]. Despite the fact that extensive data on the concentration of carbon and biogenic elements in the Yenisei channel runoff have been accumulated in the recent years [1, 4, 8, 13, 17, 19, 21, 22, 25], most studies were episodic: they were performed mainly in summer, during one year, and not all of them, along the river. So, they did not provide a full idea about variations in the concentration of biogenic elements along the river and on the dynamics of their content during a year.

The objective of the present study was to assess the spatiotemporal variability of concentrations of biogenic elements in the Yenisei River runoff based on route and stationary studies. The key tasks of the studies were as follows: the analysis of changes in the concentration of mineral forms of nitrogen (nitrates, nitrites, and ammonium) and phosphorus (orthophosphate ion) in the Yenisei channel flow along the latitu-

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dinal gradient from 56 to 68° N during the main hydrological periods; the determination of high-frequency variability of their concentrations at observation stations; the estimation of the seasonal and annual hydrological flow of biogenic elements from the Yenisei basin to the Arctic Ocean.

DATA AND METHODS

The multiyear mean Yenisei runoff is 593 km³/year, the catchment basin area is 2589 10 km², the length is 4092 km [5]. In the present study, the Yenisei was divided into four segments distinguished according to the influx of the largest right-bank tributaries and corresponding to certain types of permafrost: I is from the Krasnoyarsk hydroelectric power station (HPS) tailwater to the influx of the Angara River (mainly no permafrost or insular permafrost); II is from the Angara River mouth to the Podkamennaya Tunguska River mouth (mainly insular permafrost); III is from the Podkamennaya Tunguska River mouth to the Nizhnyaya Tunguska River mouth (mainly sporadic permafrost); IV is from the Nizhnyaya Tunguska River mouth to the city of Igarka (mainly continuous permafrost).

The concentration of dissolved biogenic elements (nitrogen and phosphorus compounds) in the Yenisei channel flow was analyzed using route and stationary studies. The route studies were carried out in the zone from 56.0 to 68.25 N during the spring flood and summer low water, and expeditionary works to Bor settlement were performed during the winter low-water period. Additionally, the samples were taken in the areas of Bakhta, Verkhneimbatsk, and Turukhansk. The total number of the samples is 49.

Water flows at 16 Yenisei cross-sections were measured with the Rio Grande 600 kHz acoustic Doppler current profiler using the WinRiver II software during the route studies in the 2016 summer low-water period. The validation of the flow data was based on their comparison with the daily values presented for the Central Siberian Administration for Hydrometeorology and Environmental Monitoring (AHEM) stations (Bazaikha, Yeniseisk, Podkamennaya Tunguska, and Igarka) for the corresponding dates (two dates for each station). The resulting linear dependence $Q_{IL} = 0.9275Q_{AHEM}$ has a high degree of confidence (the coefficient of determination $R_2 = 0.979$, p < 0.001). The value of the flux of biogenic elements was computed by multiplying their concentration by the water flow at the corresponding cross-section.

Data on average daily water flows in the Yenisei from the following Central Siberian AHEM stations were used: Bazaikha, Podkamennaya Tunguska (Bor), and Igarka. The values for 2015–2018 and average long-term values of runoff according to the yearbooks [9] were used to calculate mean flows over hydrological periods. For Igarka gaging station, water flow data for 2019 and 2020 were taken from the Arc-tic-GRO website (https://arcticgreatrivers.org/discharge/).

Stationary studies at the Yenisei outlet (Igarka station) have been performed since 2015 on the basis of the Igarka Geocryological Laboratory (Mel'nikov Permafrost Institute, Siberian Branch, Russian Academy of Sciences). The channel runoff water sampling is carried out every 5 days in the middle part of the channel from the depth of 20–30 cm. In total, 193 samples were taken.

Immediately after the sampling the water samples were filtered using Millipore cellulose filters (0.22 m), were frozen and stored at -18 C until the analysis in the laboratory. The concentrations of phosphates (P-PO₄), nitrates (N-NO₃), nitrites (N-NO₂), and ammonium (N-NH₄) were analyzed with the Lachat Quikchem 8500 flow injection analyzer (USA).

The statistical processing of the data was performed using the STATISTICA 10 software package.

RESULTS

According to long-term observations, there is a 6.7-fold increase in the Yenisei water flow from the border of Krasnoyarsk (Bazaikha station) to the outlet (Igarka station). In the latitudinal direction, the seasonal distribution of runoff considerably varies. Due to the runoff control, the contribution of the spring flood to the annual flow is about 19% in the upper reaches and 44% at the outlet. The observation period (2015–2018) was characterized by the decreased annual runoff, especially during the spring flood at the confluence of the Podkamennaya Tunguska (82% of the multiyear mean value) and at Igarka station (87%), as well as during the summer low-water period (86–88%).

The results of the route studies of the spatial variability of inorganic nitrogen and phosphorus concentrations point out an obvious impact of the Krasnoyarsk Reservoir and probably an inflow of wastewater from Krasnoyarsk. In segment I from the Krasnoyarsk HPS tailwater (55.98 N) to the influx of the Angara River (58.1 N), the Yenisei water is characterized by the highest concentration of biogenic substances (Fig. 1). The concentration of phosphates in the Krasnoyarsk HPS tailwater varied during the year from 99 to 25.1 g P/L. Downstream of Krasnoyarsk, their concentrations reached 50–63 g P/L during the spring

Fig. 1. The spatiotemporal variability of concentrations of biogenic elements: (a) $P-PO_4$, (b) $N-NO_3$, (c) $N-NO_2$, and (d) $N-NH_4$ in the Yenisei channel flow at the latitudinal transect from 56.0 to 67.4 N (68.3 N) during (*I*) the spring flood

(a) 12^{-1} (b) 12^{-1} (c) 12^{-1} (

flood and varied within 18–30 g P/L in summer and autumn (Fig. 1a). Further down the stream within segment I to the influx of the Angara River, the concentrations of phosphates decreased to 29-33 g P/L during the spring flood and 13-15 g P/L during the summer low water.

The similar dynamics in this segment is also observed for nitrate (Fig. 1b) and ammonium (Fig. 1d) nitrogen: a decrease in their concentrations from the HPS tailwater to the Angara River mouth made up from 140–200 to 50–70 g N/L and from 60–80 to 40 g N/L, respectively. During the summer low water, the content of ammonium nitrogen also has a decreasing trend in this segment, while nitrate nitrogen is maintained at an extremely high level (>150 g N/L) up to the Angara mouth. For nitrite nitrogen (Fig. 1c), there is a high concentration in the Yenisei runoff during the spring flood (9–18 g N/L), whereas nitrites in the Yenisei water in summer are at the level of the detection limit.

In segment II, the concentration of phosphates during the mixing of the Yenisei and Angara water both during the spring flood and the summer low water gradually decreases and remain at relatively constant levels in segment III. Quite considerable differences (p < 0.05) in the concentration of P-PO₄ should be noted between the spring flood and summer low water.

When the Angara water arrives, the concentration of nitrates dramatically drops to the values which are often below the sensitivity level of the method (<7~g N/L). During the summer-autumn period, the concentrations of nitrate nitrogen in segments II, III, as a rule, do not exceed 10 g N/L, and only when the Nizhnyaya Tunguska water flows in, its concentration increases.

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Fig. 2. The temporal variability of water flow and concentrations of (a) phosphates, (b) nitrate, (c) nitrite, and (d) ammonium nitrogen in the Yenisei runoff at the outlet (Igarka station) over the period of 2015–2020. The light green color highlights the spring flood, the green color marks the summer-autumn period, and the blue color, the winter period.

Such tendency toward a decrease in the concentration after the confluence of the Angara River was also found for ammonium. The concentrations of ammonium nitrogen in the Yenisei channel flow vary within 18–77 g N/L during the spring flood and 16–66 g N/L during the summer low-water period. At the same time, the N-NH₄ minima were recorded within segment II.

The stationary studies in the area of Igarka station during 2015-2020 allow a more detailed assessment of the temporal variability of concentrations of biogenic elements during the hydrological year (Fig. 2). The winter low-water period (November to May) is characterized by the gradual increase in the phosphate and nitrate nitrogen concentrations. The concentration of nitrate nitrogen remains at the level below 40 g N/L during the spring flood and the summer-autumn period, while increased concentrations of phosphates are registered both in July (for example, in 2017 and 2018) and in August and September (2015 and 2017). Nitrite nitrogen is characterized by the peak values (>10 g N/L) in the periods of maximum water content (during the spring flood).

According to the authors' calculations, with a more than six-fold increase in the average annual runoff of the Yenisei from Bazaikha station to Igarka station (from 2530 to 17287 m^3/s), the annual flux of phosphates and nitrates in this segment increased only by three times (from 2500 to 8100 t/year) for P-PO₄ and

Fig. 3. The spatial variability of (1) concentrations and (2) the flux of dissolved biogenic elements in the Yenisei channel flow in the zone from 56.00 to 68.25 N. Route survey data for the period from July 24 to August 3, 2016 are presented. (a) The regression equation for the flux y = 0.983x - 52.123, the coefficient of determination $R^2 = 0.8342$; (b) $y = 0.9735x^2 - 122.31x + 3849.7$, $R^2 = 0.746$; (c) y = 0.2914x - 13.486, $R^2 = 0.3411$; (d) y = 1.7837x - 86.626, $R^2 = 0.6783$.

by two times (from 13650 to 28240 t/year) for N-NO₃. The flux of nitrite and ammonium nitrogen grew considerably: by 7 and 10 times, respectively. The seasonal distribution of the flux of biogenic elements has slightly differing trends at different observation stations. For example, for Bazaikha station, which has the smallest duration as compared to the other observation stations, the contribution to the annual flux of all nitrogen and phosphate forms in winter is ~40% and >50%, respectively, while the respective values during the spring flood vary from 11 (nitrites) to 30% (ammonium nitrogen). For the downstream stations, the contribution of the spring flood to the annual flux of the elements plays a more significant role, which is especially noticeable for nitrite nitrogen (78% of the annual value at Igarka station) and phosphates, whose flux during this period reaches 51% in the area of Bor and 43% in Igarka. In the summer-autumn period, the flow of inorganic nitrogen and phosphorus, as a rule, is smaller than in the other periods of the hydrological year, despite its duration and significant water discharge.

To provide more detailed assessment of the formation of the flux of inorganic nitrogen and phosphorus in the Yenisei in the summer of 2016, their fluxes were computed for the zone from 56.00 to 68.25 N. The respective values of concentrations and water flows at the cross-section were used. The flux growth in the analyzed zone was from 4 to 15 t P/day for phosphates and from 9 to 35 t N/day for ammonium nitrogen. In both cases, the dependences are linear, which considerably differs from the variation pattern for the concentration of these compounds (Fig. 3). The 10-fold flux reduction for the nitrate form after the influx of the Angara (from 50 to 5 t N/day) and the further increase described by the power function to 44 t N/day at the northernmost observation point were revealed.

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DISCUSSION

The route studies of changes in the hydrochemical composition of river runoff demonstrated that before the influx of the Angara (segment I), the Yenisei water is quite rich in biogenic elements during all hydrological periods. Maximum concentrations obtained both in our and other studies [4, 8, 11] were recorded in this segment. According to [4], this indicates the river water pollution with domestic wastewater.

In addition, high concentrations of inorganic nitrogen are also observed directly in the reservoir. After the filling of the reservoir (1971–1974), the concentration of nitrates in it was equal to 1250 g N/L [2], it dropped to 170 20 g N/L in 1982 [3] and remained at a rather high level (130–170 g N/L) during 1990 to 2005 [3, 12]. According to literature data, the ammonium concentration in the reservoir is also significant: 590 190 g N/L in 1990–1992 [12], 150 30 g N/L in 2000 and 2005 [3]. In view of this, it may be assumed that the water enrichment in segment I is rather due to the runoff formation by the water from the deep layers of the reservoir enriched with biogenic elements than due to the wastewater, which is also shown in [11].

The concentration of biogenic elements considerably decreases in segment II in the area after the confluence of the Angara. For example, the concentration of phosphates drops from 15–60 to 10–20 g P/L. According to [10], the concentration of phosphates directly in the Angara water is 10–20 g P/L, which is comparable with the data obtained by the authors for the Yenisei. The amount of nitrates after the mixing of the Yenisei and Angara water also decreases from 145–186 to 5–39 g N/L. The authors of [13] noted a decreasing concentration of nitrates: from 80 to 20 g N/L.

The decreasing concentration of nitrogen and phosphorus, which are the main substrate factors determining the primary production increase, after the Angara confluence is most likely caused by the phytoplankton activity growth. The low phytoplankton productivity in the Yenisei upper reaches is caused by the low temperature of discharged deep water of the Krasnoyarsk Reservoir [13] and by the partly death of phytoplankton during the passage through the high-pressure HPS turbines [6]. However, the mixing of the warmer Angara water and the Yenisei water enriched with biogenic elements creates favorable conditions for the phytoplankton development and photosynthesis activation [11].

Extremely low concentrations of biogenic elements during the summer low-water period in the Yenisei channel flow were detected in segments II–IV, which implies limiting the production processes and finding the system in a hemostasis state [16]. The linear increase in the flux of biogenic elements (except for nitrates, Fig. 3) all along the river confirms the balance of exchange processes.

It was revealed for the integral segment in the area of Igarka, i.e., for the water flowing into the Arctic Ocean that the average concentration of phosphates during the summer low water is 13.9 1.6 g P/L, which is comparable with the previously presented values [1, 13]: 6–15 g P/L. However, the concentrations of the main forms of inorganic nitrogen obtained by the authors (28.5 ± 10.8 g N/L for NH₃, 28.3 18.5 g N/L or NO₃, 5.4 1.7 g N/L for NO₂) are smaller than those presented in the previously published papers [1, 13, 20] (270–1350 g N/L for NH₃, 40–130 g N/L for NO₃).

In winter, the concentrations of biogenic elements in the Yenisei channel runoff in the integral segment and all along the latitudinal transect are maximal, which indicates the inhibition of their consumption in biological processes. Thus, the consumption of mineral elements by microorganisms is an essential factor determining their dynamics during a year.

During the spring flood, the authors found increased concentrations of nitrites in the Yenisei runoff as compared to the summer and winter low-water periods. No due attention wasj paid to this parameter in literature before because of their insignificant concentrations [8]. However, it should be emphasized that the increase in the concentration of nitrites in river runoff is observed in the lower reaches of the river and, hence, is associated with their inflow from permafrost soils rich in organic matter in the cryolithozone.

The contribution of the Yenisei to the annual runoff of rivers flowing into the Kara Sea is up to 45%, hence, it is a significant source of biogenic elements arriving to the Arctic Ocean [7]. The studies showed that the annual flux of phosphates in the upper reaches (Bazaikha station) is about 2500 t P/year and the one for total mineral nitrogen (NO₃ + NO₂ + NH₄) is 16 630 t N/year, increasing at the outlet (Igarka) up to 8100 and 55550 t N/year, respectively. The close values (not taking into account nitrite nitrogen) were given in [22], but the value was determined mainly by the flux of nitrate nitrogen (96% of total nitrogen), while its contribution is much smaller (51%) according to the studies by the authors.

CONCLUSIONS

The analysis of the data revealed the spatiotemporal inhomogeneity of the concentration of inorganic nitrogen and phosphorus in the Yenisei River runoff depending on the geographic position of the river segment and the season. The water in the upper reach of the Yenisei is relatively rich in these biogenic elements during the whole hydrological year, indicating the impact of the Krasnoyarsk Reservoir and wastewater from the city of Krasnoyarsk, while the considerable decrease in their concentration occurs after the confluence of the Angara River both as a result of dilution and biological processes.

In the middle and lower reaches of the river, the most significant role in the annual flux of phosphates, nitrites, and ammonium is played by the spring flood. The summer low-water period is characterized by the low values of the flux of biogenic elements, despite its duration and significant water consumption. The winter low water plays the main role in the annual flux of nitrate nitrogen.

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