Major anion and cation fluxes from the Central Siberian Plateau watersheds with underlying permafrost

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Abstract. The subarctic rivers of the Central Siberian Plateau have specific fed-characteristics due to the permafrost distribution and the active layer thawing dynamics. Two watersheds with different types of permafrost (from insular to continuous) are studied. Different data sources (Roshydromet and our own observations) are used for receiving anions’ (HCO₃⁻, SO₄²⁻, Cl⁻) and cations’ (Ca²⁺, Mg²⁺) fluxes from the Nizhnyaya Tunguska river (1960-2011) and the Tembenchi river (1970-2011). The annual discharge of N. Tunguska for 1939-2011 is characterized by an increase of 0.3 km³/year/year, and for Tembenchi, 0.04 km³/year/year. The major part of the increase (about 60%) is due to spring flooding (May - June). The volume-weighted mean concentrations of major anions and cations in the N. Tunguska river water increased three times in the spring period (40.7 – 116.8 mg/l) and in the summer-fall period (74-212.9 mg/l). On the contrary, such concentrations decreased sharply during the winter mean water period. Due to these results, the total export of main anions and cations from the N. Tunguska river basin rose more than 4.5 times. Two possible reasons can be identified: 1) a water discharge increase of the Subarctic rivers (Peterson et al., 2002); 2) permafrost degradation induced by global climate warming (Frey and McClelland 2009).

1. Introduction

Chemical composition of rivers water of Central Siberian Plateau determined by permafrost underlying watersheds. Precisely, permafrost distribution on river basins and active layer thawing dynamics of soil define the fed-characteristics of Subarctic rivers. During the winter mean water period the greatest contribution in river feeding is made by ground water discharged through taliks, during the frost-free period – by precipitation, infiltrating in soil (Prokushkin et al 2011).

Climate data analysis indicates increase of average annual temperature, precipitation and water discharge in Central Siberia rivers since 1950. Concerning, study of chemical elements’ fluxes from Central Siberian Plateau watersheds can measure the changes in intensity of biogeochemical processes according to global climate changes.

Our purpose was to analyze main anions and cations export from Central Siberian Plateau watersheds, our objects of study – Nizhnyaya Tunguska and Tembenchi river basins, characterized by different distribution of permafrost beneath (figure 1).

2. Materials and methods

1.1. River water sampling and hydrochemical analysis

Hydrochemical composition of Nizhnyaya Tunguska and Tembenchi rivers investigated ourselves from 2004 and 2006, respectively (Evenki Station, Tura, Krasnoyarskii Kray, Russia). There are different methods of water sampling during each period of hydrological year: winter mean water (October – April) – sampling 1 time a month, spring flood (May – June) – 2-3 times a week, summer mean water
July–August) – 1 time a week. Collected samples are filtered immediately after sampling using 0.45 µm filters (Millipore).

Anions’ concentrations (Cl\(^{-}\), SO\(_{4}^{2-}\)) obtained by ion chromatography (Dionex ICS 2000), hydrocarbonate concentration analysis based on DIC content, measured on Vario TOC Elementar (conversion factor – 5.08). Cations concentration (Ca\(^{2+}\), Mg\(^{2+}\)) determined using spectrometer Perkin-Elmer 5100 PC, or by ICP-MS method (Agilent 7500).

**Figure 1.** Permafrost distribution on studied permafrost (Brown et al 2002 based).

1.2. Main anions and cations fluxes analysis

For hydrochemical composition and water discharges of Nizhnyaya Tunguska and Tembenchi rivers from 1960 archive data of ROSHYDROMET was used. There are two studied gauging stations: 1) #4008 Tura, river basin square – 268000 km\(^{2}\) (studied period – 1960-2011); 2) #4046 Tembenchi, 21600 km\(^{2}\) (1970-1993). Due to a few measuring during each year, Roshydromet archive data divided into decades for the analysis of studied anions and cations fluxes’ tendency (for N. Tunguska river – 1960-1969, 1970-1979, 1980-1989, 1990-1999, 2000-2009 and 2010-2011; for Tembenchi river – 1970-1979, 1980-1989, 1990-1993).

For calculating daily fluxes, we applied the following stages: 1) elements’ concentrations multiplied by water discharges for all available dates; 2) then, we analyzed fluxes (F) function on water discharges (Q) for each anion and cation and we found that this dependence could be described by the function \( F = a \times Q^b \) most significantly (\( a \) and \( b \) – coefficients). Confidence levels (p) for \( a \) and \( b \) obtained with using STATISTICA 10 and all coefficients for entire period and all anions had necessary reliability (\( p \leq 0.05 \), or \( p \geq 95\% \)). Then, using this function daily and annual (the sum of daily values) fluxes from N. Tunguska and Tembenchi watersheds calculated for the period 1960-2011.

1.3. Volume-weighted mean concentrations analysis

Studied time divided by periods (1955-1959, 1960-1964, 1965-1969 etc.). For volume-weighted mean concentrations calculated using the following method: 1) Main anions and cations concentrations (mg/l) multiplied by water discharge values (m\(^{3}\)/s); 2) Then, received values summed up and divided by summed water discharge values for each month, according to selected periods.

2. Results and their discussions
2.1. Water chemical composition
In general, investigated rivers water chemical composition is homogeneous. Such factor indicates similar geological structure of N. Tunguska and Tembenchi river basins. In winter mean water period Tembenchi river water is chloride-calcium, N. Tunguska river water is chloride-sodium. During the “open” water period Tembenchi river water becomes hydrocarbonate-calcium, N. Tunguska river water – hydrocarbonate-sodium-calcium. During dry years, N. Tunguska and Tembenchi refer to transitional types of chemical compositions – hydrocarbonate-chloride-calcium and hydrocarbonate-chloride-sodium-calcium types, respectively (by Alekin classification, 1946). Studied main anions and cations have inverse relationship to the flow of their concentration during annual cycle (Bagard et al. 2011, Prokushkin et al. 2011). During the spring flood period, caused by snowmelt, river water are weakly mineralized and belong to ultra fresh type. In summer-fall period, as soil stratum thawing, the outcome of basalt weathering has great significance in river flow (Bagard et al. 2011) and inorganic ions flux, naturally, increases. During winter period, inorganic ions concentrations increase as active layer thawing, and taliks become the main source for river water (Kadamtseva et al. 2005). The chemical compositions of taliks caused by evaporate occurrence and determine the great amount of chloride, sodium and calcium in river water (Kadamtseva et al. 2005).

The average annual mineralization of Tembenchi river significantly lower than N. Tunguska river (67-82 mg/l vs. 301-498 mg/l). It conditions by different types of permafrost distribution beneath studied watersheds. For “northern” part of Central Siberian Plateau (Tembenchi) permafrost is spread continuously, determining the less square of through taliks, which are the source of solutions from subpermafrost highly mineralized brines for river. Also, lower temperatures provide the slowdown of paedogenesis and parent rock (basalts) weathering processes. In “southern” part of Central Siberian Plateau (studied N. Tunguska watershed) continuous permafrost distribution has less than 60%, and average annual temperature is higher than Tembenchi watershed (-7.3 and -10.9 °C respectively). Thus, temperatures increase and taliks expansion by permafrost degradation may cause significant mineralization growth of Central Siberian Plateau rivers runoff.

A great increase of volume-weighted concentrations of main ions during the open water period (May – October) revealed by long-term analysis (1955-2015, May – October, Figure 2). Volume-weighted mean concentrations of chloride show a large growth (5.5 to 42.6 mg/l in spring flood time and 9.4 to 67.2 mg/l in summer-fall time). The same is for hydrocarbonate ion – 22.8 to 45.5 mg/l in spring flood time and 43.3 to 82.9 in summer-fall time. Such tendency observed for all studied ions. Wherein increase of chloride, calcium and sodium concentrations indicates increase of evaporate input, assuming permafrost degradation, and taliks expansion in N. Tunguska watershed. During winter mean water reverse pattern is obtained – significant decrease of inorganic ions concentration (April, figure 2). It supposed smaller depth of seasonally freezing part of soil stratum, which determines increase the amount of soil solutions with lower mineralization in winter runoff.

Archive data of main ions concentrations for Tembenchi River limited by period 1970-1993. Volume-weighted mean concentrations of main ions for each month have insignificant changes for entire period. It may be distinguished only two variations - increase of hydrocarbonate concentration (28.16 – 53.45 mg/l) in April and in October (18.21 – 29 mg/l). Such phenomenon may indicates higher intensity of weathering processes on Tembenchi watersheds.

Besides the concentrations increase, described previously, the river flow has the important effect on annual flux of main anions and cations. For the period 1939 – 2011 on N. Tunguska watershed flow increased of 0.31 km$^3$/year/year, on Tembenchi watershed – 0.04 km$^3$/year/year. The spring-flood time has the most important impact on flow growth – about 60%.

2.2. Annual fluxes of the main anions and cations
The increase of ions fluxes observed for N. Tunguska river basin from 1960 to 2011: hydrocarbonate – 2.92-12.77 Mg/km$^2$/year, chloride – 0.95 – 11.07 Mg/km$^2$/year, sulfate – 1.13-2.79 Mg/km$^2$/year, calcium – 1.48-4.64 Mg/km$^2$/year, magnesium – 0.4-1.44 Mg/km$^2$/year (figure 2). It was the most
substantial “jump” since 1980: rise of hydrocarbonate from 2.88 to 7.21 Mg/km$^2$/year, chloride – 3.79-7.45 Mg/km$^2$/year. Total flux of the main anions and cations from N. Tunguska watershed increased more than 4.5 times (6.88-32.72 Mg/km$^2$/year). But there was no reliable tendency for flux from Tembenchi watershed. It could be noticed some slight decrease of hydrocarbonate and chloride fluxes and increase of sulfate and calcium fluxes.

Figure 2. Volume-weighted mean concentrations for studied anions and cations in N. Tunguska.

Nevertheless, estimation of ions fluxes from N. Tunguska watershed based on our own investigations fit with estimation based on Roshydromet data. However, some differences in ions flux values observed. In particular, there are essential distinction in sulfate and calcium fluxes values. For Tembenchi, values measured on our instrumental base, have the significant increase of the main ions fluxes in comparison with values, based on Roshydromet. The only exception is sulfate, which flux is higher by Roshydromet data. Such discrepancy may be the result in different methods of sampling and hydrochemical analysis.
At the same time, according to our last observations, it was a significant increase of hydrocarbonate, calcium and magnesium fluxes from Tembenchi river basin for the last decade (2005-2015).

![Graphs showing changes in HCO₃⁻, Cl⁻, SO₄²⁻, Ca²⁺, and Mg²⁺ concentrations and fluxes over years 1955 to 2015.](image)

**Figure 3.** Cations and anions fluxes from N/Tunguska watershed.

In this way, as a result of comparative analysis of Central Siberian Plateau watersheds it can be concluded that the most clear evidence of permafrost degradation and taliks expansion are registered in the zone of discontinuous distribution of permafrost. Such processes, probably, are in initial stage on the central and northern parts of Central Siberian Plateau. Nevertheless, the growth of paedogenic ions (hydrocarbonate, calcium and magnesium) concentrations and fluxes form watersheds draining this territory indicates the increase of active layer and weathering processes intensification. Thus, the main
ions concentrations and fluxes analysis from other Central Siberian Plateau watersheds may be the indicators of permafrost degradation and weathering processes intensification.

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