RESEARCH PAPER

SEASONAL STREAM WATER CHEMISTRY RESPONSE TO LONG-TERM FORESTRY DRAINAGE AND WILDFIRE: A CASE STUDY IN A PART OF THE GREAT VASYUGAN MIRE

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ABSTRACT. Recent research suggests that climate change is contributing to rising solute concentrations in streams. This study focuses on assessing the concentrations of major elements, nutrients, and dissolved organic carbon (DOC), and their release through the bog-river system in the taiga zone of Western Siberia. The research was carried out in the northeastern part of the Great Vasyugan Mire (GVM), the largest mire system that impacts the quality of river water in the Ob River basin. By using PCA and cluster analysis, we examined the long-term dynamics of the chemical composition of headwater streams of the GVM affected by drainage and wildfires. Our data from 2015-2022 revealed that the concentrations of Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, and HCO_{3-} in stream water from the drained area of the GVM were, on average, 1.3 times lower than those at the pristine site. Conversely, the concentrations of NH^{+}_{4}, Fe_{total}, Cl^{-}, SO_4^{2-}, NO^{-}_{3}, DOC, and COD were higher, indicating the influence of forestry drainage and the pyrogenic factor. Our findings also demonstrated that the GVM significantly impacts the water chemical composition of small rivers. We observed a close correlation in the concentrations of K^{+}, Na^{+}, Cl^{-}, Fe_{total}, NH^{+}_{4}, HCO_{3-}, and COD between the GVM and the Gavrilovka River waters. PCA analysis revealed that air temperature influences the concentrations of Ca^{2+}, Mg^{2+}, NH_4^{+}, NO_{3-}, HCO_{3-}, Fe_{total}, and DOC in the studied streams, with an inverse correlation with river discharge. The removal of major elements, nutrients, and DOC from the drained area of the GVM was most pronounced in April, being twice as high as in the pristine area. However, the total export from the drainage area of the Gavrilovka in April-September 2022 was 1.3 times lower than in the pristine area, amounting to 8487 kg/km^2, with DOC removal at 42%.

KEYWORDS: water chemistry, mire, drainage, wildfire, Western Siberia

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INTRODUCTION

Western Siberia is a large peatland-dominated region in the northern hemisphere (Neishtadt 1971; Liss et al. 2001). Peatlands occupy vast areas on terraces and interfluves, playing an important role in the region's temperature and water balance. These peatlands also influence the water quality of the Ob River and its tributaries, thereby affecting the overall flow of mineral and organic substances into the Arctic Ocean (Kirpotin et al. 2009; Evseeva et al. 2012; Berezin et al. 2014; Pokrovsky et al. 2015; Terentiev et al. 2016; Savichev et al. 2016; Krickov et al. 2019; Dyukarev et al. 2019). Siberia experiences the highest rate of temperature change in the surface layers of the atmosphere (1.39°C/100 years), surpassing the average rate for Northern Eurasia and Northern Asia, the Arctic, and the entire northern hemisphere (Groisman et al. 2013). According to (Third Assessment Report of Roshydromet 2022), Western Siberia has seen a positive trend in average annual air temperature, with an increase of +0.42 °C/decade between 1976 and 2020. The region also experiences a growth in atmospheric precipitation with changes in its patterns, i.e. an increase in extremely heavy rainfall during summer and autumn (Kharyutkina et al. 2019).

The rise in air temperature, atmospheric precipitation, and the prevalence of wildfires can enhance the mobilization of mineral and organic substances from peatlands and accelerate their transport into surface waters and the Arctic Ocean (Frey 2005; Pokrovsky et al. 2015). Studies of river water chemistry in Western Siberia across climatic gradients (Krickov et al. 2019) revealed that under conditions of climate change, the greatest increase in dissolved organic carbon (DOC) occurs in streams with a catchment area of less than 1,000 km^2, particularly during summer and autumn.

Temperature rise contributes to more frequent wildfires in Siberia and other regions (Kharuk et al. 2021; Nelson et al. 2021), often associated with dry conditions in the summer period. Drained peatlands are particularly vulnerable to climate change and wildfires, as lower water table levels make them prone to burning, negatively impacting water quality. Various peatland use practices, such as forestry, agriculture, peat extraction, and peat fires, as well as their impact on water pollution, have been extensively studied (Nieminen et al. 2017; Marttila et al. 2018; Sulwiński et al. 2020, etc.). Peatlands drainage and fires lead to increased erosion, water pollution, eutrophication, and brownification, especially in headwater catchments (Broder, Biester 2017; Marttila et al. 2018; Ackley et al. 2021; Finér et al. 2021; Nieminen et al. 2020, 2021). Although water chemistry and substance removal from the medium-size river basins in the Middle Ob basin have been well-studied (Savichev 2007; Dubrovskaya and Brezhneva 2010; Savichev et al. 2016; Savichev et al. 2018), and some data on peatland-dominated streams are summarized in (Peatlands of Western Siberia 1976), there is a lack of detailed data on the effect of drainage and the pyrogenic factor on stream water chemistry in Western Siberia. Therefore, this study aims to assess the concentrations of major elements, nutrients, and DOC, as well as their release through the bog-river system in the taiga zone of Western Siberia.

MATERIALS AND METHODS

The study was carried out within the Gavrilovka River basin, a left-bank tributary of the Iksa River in the Middle Ob River basin (Fig. 1). Covering an area of 81 km^2, the Gavrilovka River basin is located in the drained area of the northeastern part of the Great Vasyugan Mire (GVM). The drainage network covers 39 km^2, while the peatlands account for approximately 75 km^2 or 93% of the catchment area. The bog was drained in the 1980s through a network of open ditches spaced 160–180 m apart (Maloletko et al. 2018). Currently, due to ditch overgrowth, self-restoration has been observed (Sinyutkina 2021). In 2016, a fire burned an area of 3.10 km^2 in the Gavrilovka River basin, with a burnt layer thickness of 5-15 cm (Sinyutkina et al. 2020). A similar pristine area of the GVM, located 3 km to the north within the 76 km^2 catchment area of the Klyuch River, a right-bank tributary of the Bakchar River, was selected as a background area. Peatlands in the Klyuch River basin cover around 60 km^2 or approximately 79% of the catchment area. The study area is characterized by poor infrastructure development, with the primary sources of pollution (industry, thermal power plants, etc.) located 200 km away.

River water sampling was conducted monthly from March to September between 2015 and 2022. In 2022, to assess spatial variation in water chemistry within the drained part of the GVM, simultaneous sampling was carried out at 6 key sites in the Gavrilovka River basin: pine dwarf-shrub *Sphagnum*, sedge *Sphagnum* communities, and the hummock-hollow complex. In the background watershed of the Klyuch River (a pristine part of the GVM), sampling was carried out in similar plant communities (Table 1). We measured water temperature, pH, O_2, and CO_2 immediately after sampling. Samples were preserved to determine Fe_{total}, NO^-_3, and NH^+_4. Dissolved O_2 was measured using a HI 9146-04 HANNA Instruments (Germany), pH was measured using a pH-200 field device from HM Digital (South Korea), and redox potential (Eh) was determined using ORP-200 from HM Digital (South Korea). The electrical conductivity (EC) was measured using a HI 8733 from HANNA Instruments (Germany) (Table 2). Dissolved carbon dioxide was measured by titrating samples with NaOH solution in the presence of Rochelle salt and the phenolphthalein indicator (FR.1.31.2005.01580).

The chemical analysis of water samples was carried out at the analytical laboratory of the Siberian Research Institute of Agriculture and Peat. Prior to analysis, water samples were filtered through a paper filter with a pore diameter of 1.0-2.5 µm. The concentrations of Ca^{2+}, Mg^{2+}, HCO_3^-, and Cl^- were determined using the titrimetric method, while Fetotal, NO^-_3, NH^+_4, and SO_4^{2-} were analyzed using the spectrophotometric method (Specol-1300, Analytik Jena AG, Germany). The concentrations of K^+ and Na^+ ions were determined using flame photometry (PFA-378, Russia). Chemical oxygen demand (COD) was estimated with potassium dichromate, and DOC was determined using the Tyurin method with potassium dichromate, along with photometric termination according to (STP 0493925-008-93) (Table 3). Total dissolved solids (TDS) were estimated by summing the concentrations of ions.

Statistical analysis of the chemical composition of water was performed using principal component analysis (PCA) and cluster analysis in Statistica 10. The chemical composition of water was analyzed using a cluster analysis with the classification of water samples based on homogeneity within classes (hierarchical method). The cluster analysis was carried out using the calculation of the Euclidean distance and the Ward method. Factor analysis was carried out using the principal component method (PCA), which is based on the calculation of vectors and eigenvalues of the covariance matrix of the initial data, along with the construction of a scree plot to determine the leading factors and the assessment of the factor loading matrix.

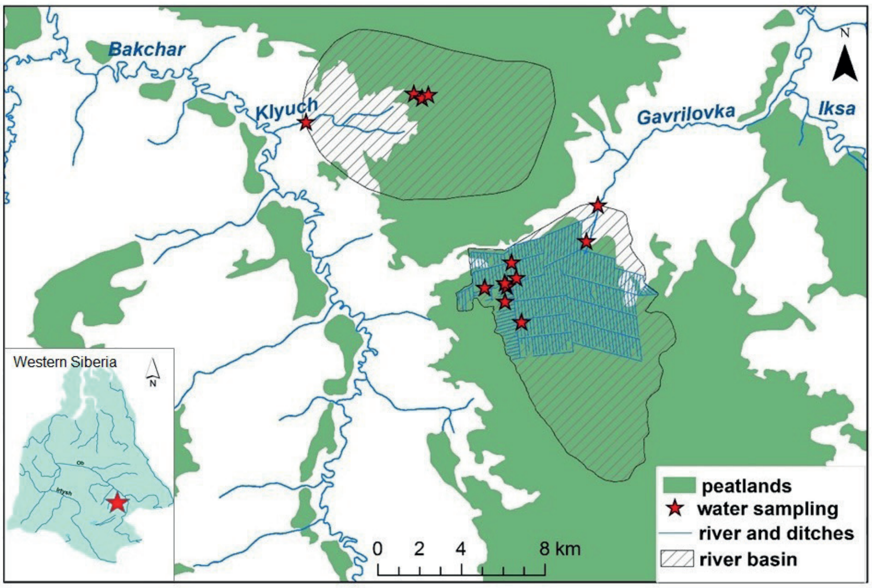

Fig. 1. Study area with sampling points in the Gavrilovka and Klyuch River basins

Table 1. Location, vegetation type, and water table level in the key sites of the Great Vasyugan Mire in March-September 2022

№	Vegetation type	Coordinates	Catchment	Land use type	Water table level, cm
1	Pine dwarf-shrub *Sphagnum* (RG)	N56°53’25,8”, E82°40’50,5”	Gavrilovka	Forestry drainage	-13
2	Pine dwarf-shrub *Sphagnum* (RG2)	N56°53’57,10» E82°41’05,95»	Gavrilovka	Forestry drainage	-41
3	Pine dwarf-shrub *Sphagnum* (RG3)	N56°53’32,7” E82°41’19”	Gavrilovka	Forestry drainage	-18
4	Pine dwarf-shrub *Sphagnum* (PG2)	N56°53’18,6” E82°40’36,7”	Gavrilovka	Forestry drainage and fire event area	-27
5	Sedge *Sphagnum* lagg (TG)	N56°52’23,6”, E82°41’30,1”	Gavrilovka	Forestry drainage	-10
6	Hummock-hollow complex (D2)	N56°53'18,8'' E82°39’48,6”	Gavrilovka	Forestry drainage	-29
7	Pine dwarf-shrub *Sphagnum* (P3)	N56°58'24, 3'', E82°36'41,2''	Klyuch	Forestry drainage	-13
8	Sedge *Sphagnum* lagg (P5)	N56°58'17, 3'' E82°37'04,5”	Klyuch	Forestry drainage	-10
9	Hummock-hollow complex (D1)	N56°58’22,1» E82°37’22,4»	Klyuch	Forestry drainage	-8

Table 2. Instrument accuracy

№	Component	Instrument	Accuracy
1	O_2	HANNA 9146-04, Germany	±5 %
2	pH/T	PH200, HM Digital, South Korea	±0.1 ºC ±0.02pH
3	Eh	ORP200 HM Digital, South Korea	± 2мВ
4	EC	HANNA HI 8733, Germany	±1%

Water levels in Klyuch and Gavrilovka headwater streams were measured using Micro-Diver loggers (Eijkelkamp, Netherlands) every hour throughout the year. Discharge measurements were made using an acoustic current meter OTT Hydromet (Germany) at gauging stations set up at the Klyuch and Gavrilovka rivers, with measurements carried out every 5-10 days during typical water content periods in 2015-2022. The release of major elements, nutrients, and DOC was calculated in 2022 as the product of the total volume of river runoff and the concentrations of components in the Klyuch and Gavrilovka rivers obtained from the results of laboratory analysis of river water samples. On average, during spring flood and summer-autumn low water in 2022 (April-September), water flow was 0.35 m^3/s in the Klyuch River, and 0.24 m^3/s in the Gavrilovka River.

The average annual air temperature for the study period was 1.04 °C. Among the 8 years, 2015 and 2020 were the warmest, with average annual air temperatures of 2.05 and 3.03 °C, respectively (Table 4), marking the absolute maximum for the observation period from 1970 to 2022 at the Bakchar weather station. Throughout the study period, the annual precipitation averaged 537 mm, with decreases to 431-486 mm observed in 2016, 2019, and 2020. In 2018, the annual precipitation reached 677 mm, the highest value for a long period.

RESULTS AND DISCUSSION

Stream water chemistry

The pH values and concentrations of Ca^{2+}, Mg^{2+}, K^+, Na^+, and HCO_{3-} in the waters of the Gavrilovka River, were 1.3 times lower than in the Klyuch River, which drains the pristine area of the GVM. Conversely, the waters of the Gavrilovka River exhibited high concentrations of NH^+_4, Fe_{total}, Cl^-, SO_4^{2-}, and NO^-_3, as well as DOC, COD, and CO_2 were revealed as indicators of forestry drainage. The increased concentrations of major elements in the Klyuch River are probably determined by the smaller peatland-dominated area (about 77%) and the removal of substances from the catchment area occupied by mineral soils or ion-rich groundwater supply. Similar findings were made by (Tokareva et al. 2022), whose research in the Yenisei River basin demonstrated that streams draining basins with a higher number of pristine ombrotrophic bogs (atmosphere-fed bogs) receive more atmospheric precipitation and have ion-poor runoff.

Analysis of the data revealed that, similar to previous studies (Kharanzhevskaya 2022a, b), the chemistry of river waters in the drained and pristine areas of the GVM may be similar in certain periods. Studies conducted in drained raised bogs in Canada also showed a slight effect of drainage on mire water chemistry. The differences in the

Table 3. Analytical methods

№	Component	Method	Standart	Accuracy,%
1	Ca^{2+}, Mg^{2+}	Titrometry	PNDF 14.1:2.98-97	±15
2	K^+	Flame photometry (PFA-378, Russia)	PNDF 14.1:2:4.138-98	±12
3	Na^+	Flame photometry (PFA-378, Russia)		±17
4	SO_4^{2-}	Spectrophotometry (Specol-1300, Analytik Jena, Germany)	PNDF 14.1:2.159-2000	±20
5	Cl^-	Titrometry	PNDF 14.1:2:4.111-97	±12
6	NH^+_4	Spectrophotometry (Specol-1300, Analytik Jena, Germany)	PNDF 14.1:2.1-95	±10
7	Fe_{total}	Spectrophotometry (Specol-1300, Analytik Jena, Germany)	PNDF 14.1:2:4.50-96	±15
8	HCO_{3-}	Titrometry	PNDF 14.2.99-97	±25
9	NO^-_3	Spectrophotometry (Specol-1300, Analytik Jena, Germany)	PNDF 14.1:2:4.4-95	±10
10	DOC	Spectrophotometry (Specol-1500, Analytik Jena, Germany)	STP 0493925-008-93	±10
11	COD	Titrometry	(Lurie, 1973)	±10
12	CO_2	Titrometry	FR.1.31.2005.01580	±10

Table 4. Hydrometeorological conditions according to the weather station near Bakchar village

Year	Annual precipitation, mm	Precipitation in April-September, mm	Average annual air temperature, ^{0}C	Sum
2015	616	382	2.05	T>10 ^{0}C
2016	486	347	0.72	
2017	566	419	1.30	1972
2018	677	495	-0.80	2162
2019	431	284	0.88	1891
2020	477	293	3.03	1781
2021	497	311	0.29	1860
2022	545	376	0.86	2136

Source: (http://meteo.ru/)

water chemistry between pristine and drained peatlands are influenced by the rate of decomposition of organic residues and biogeochemical processes in the region, which are largely dependent on the average annual air temperature (Harris et al. 2020).

Comparison of long-term data on Gavrilovka and Klyuch river waters using the nonparametric Mann-Whitney test revealed significant differences in the pH value (Z=-2.94, p=0.003), as well as in the concentrations of K^+ (Z=-2.26, p=0.024), Mg^{2+} (Z=-2.21, p=0.027), Fe_{total} (Z=2.63, p=0.009), NH^+_4 (Z=2.31, p=0.021), NO^-_3 (Z=2.52, p=0.012), HCO_{3-} (Z=-2.31, p=0.021), COD (Z=2.10, p=0.036), CO_2 (Z=2.10, p=0.036), and DOC (Z=3.05, p=0.002). These findings partially align with the results obtained in 62 small peatland-dominated watersheds in Finland (Marttila et al. 2018), which indicated increased concentrations, particularly of nitrogen and phosphorus, in headwater streams where peat extraction and peatland forestry were the main types of land use. While DOC, COD, and Fe concentrations in stream waters in Finland were at similar levels with near pristine sites, those sites exhibited lower pH levels in comparison to areas affected by peatland drainage (Marttila et al. 2018). However, our studies showed higher DOC content and concentrations of NO^-_3 and NH^+_4 in stream water of the GVM compared to data from Finland. On the contrary, the stream water pH in the drained part of the GVM was lower, which is determined by higher concentrations of DOC resulting from the decomposition of peat layers due to intensive drainage. Studies conducted in the Yenisei River basin (Tokareva et al. 2022) also showed lower pH values and elevated concentrations of NH^+_4 in stream water chemistry due to the input of highly acidic organic-rich solutes from a pristine peatland area within the basin and specific biogeochemical processes occurring directly in the stream channel.

Our data showed that differences in water chemistry between the Klyuch and Gavrilovka rivers varied from year to year, with no significant differences found in 2021. Differences were observed in the content of Fe_{total} (Z=2.56, p=0.011) in 2015, and of K^+ (Z=-2.04, p=0.041) and CO_2 (Z=2.87, p= 0.004) in 2016. In 2017 and 2018, there were differences in the content of NO_{-3} (Z=2.30, p=0.021), and also COD (Z=2.87, p=0.004) in 2018. In 2019, there were significant differences in SO_4^{2-} (Z=2.17, p=0.030) and DOC (Z=2.68, p=0.007). In 2020, significant differences were observed only in the pH value (Z=-2.30, p=0.021). Finally, in 2022 differences were found in the concentrations of DOC (Z=2.24, p<0.05), NO_{3-} (Z=-2.68, p<0.05), and Cl^- (Z=-2.81, p<0.05).

Cluster analysis showed that all the samples taken in the Klyuch River, except the ones from 2019 and 2022, and the samples taken in the Gavrilovka River in 2017, 2020, and 2021 belonged to the first cluster. The water samples taken in 2017 and 2021 stood out as a separate subcluster, as an indicator of the pyrogenic factor and the temperature regime. The second cluster included samples taken in 2015, 2016, 2018, 2019, and 2022. The first subcluster included the samples taken in the Gavrilovka River during high water in 2018 and low water in 2019, as well as in 2016 and 2022. The second subcluster included the water samples from the Gavrilovka River taken in 2015, as well as the samples from the Klyuch River taken in 2019 and 2022. Thus, under drought conditions, an increase in major element content was observed in the Gavrilovka River, and, as a result, water chemistry became comparable to the Klyuch River (Fig. 2).

Seasonal dynamics in stream water chemistry is characterized by an increase in pH, K^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, Fe_{total}, Cl^-, and HCO_{3-} in March after the winter low water period, by 1.3-3 times. In winter, an increase in total dissolved solids is observed due to the displacement of ions during the formation of the ice cover on the river. The second maximum of ion content is achieved during the flood period (SO_4^{2-}, NO_{3-}, DOC, NH_4^+, Cl^-) and at the end of the summer-autumn low water period (K^+, Na^+, Ca^{2+}, Mg^{2+}, HCO_{3-}).

Differences are also observed in the long-term dynamics of river water chemistry. Our studies have shown that in the Gavrilovka River, it is determined by hydrometeorological conditions, forestry drainage, and the pyrogenic factor. The pH value of the Gavrilovka River waters was highest in 2016-2017 and 2022 (pH=6.53), with a decrease to the minimum values (pH=6.07) in the high-water year 2018 due to water supply from the GVM with high DOC content. In 2015, there was an increase in pH (6.93) in the Klyuch River due to high air temperature, while the minimum pH value (6.41) was observed in the dry year 2019. The Klyuch River catchment differs from the Gavrilovka River by a larger proportion of peatland area and regular groundwater discharge, factors contributing to higher content of main ions and pH in the Klyuch River.

Our data demonstrated that in 2017, following the fire, the waters of the Gavrilovka River showed an increase in the concentrations of K^+, Na^+, Ca^{2+}, Mg^{2+}, Fe_{total}, Cl^-, SO_4^{2-}, NO^-_3, and HCO_3^-, consistent with the results obtained for the GVM (Kharanzhevskaya and Sinyutkina 2021). In the high-water year 2018, there was a sharp decrease in concentrations of these elements due to dilution by atmospheric precipitation. Subsequent years saw an increase in the content of Ca^{2+}, Cl^-, NO_3^-, and HCO_3^- in 1.2-3 times in the Gavrilovka River, attributed to increased air temperatures in 2020 and further degradation of the pyrogenic layer. Studies (Lydersen et al. 2014; Rust et al. 2018; Stirling et al. 2019; Wu et al. 2022) showed that after a fire, there is an increase in pH and the concentrations of the main cations (Ca^{2+}, Mg^{2+}, Na^+, K^+), anions of strong acids (SO_4^{2-}, Cl^-, NO_3^-), ammonium ions, total nitrogen, phosphorus, and DOC. The greatest changes occur within three years after the fire, but the influence of the pyrogenic factor can persist for about 12 years (Sulwiński et al. 2020).

The water chemistry of the Klyuch River, draining the pristine part of the GVM, is mainly influenced by changing climatic conditions. As a result, in 2020, which was characterized by an absolute maximum of the average annual temperature, the Klyuch River waters showed increased concentrations of Ca^{2+}, Mg^{2+}, K^+, Na^+, HCO_3^-, and NO^-_3, except for Fe_{total}, NH^+_4, SO_4^{2-}, and Cl^-. In the dry year 2019, the content of Ca^{2+}, Mg^{2+}, K^+, SO_4^{2-}, Cl-, and HCO_3^- decreased due to the decomposition of organic matter in the active layer above the water table level. Its dissolution in water occurs when the water table level rises during precipitation events. Peatland drainage leads to increased leaching of nutrients over time because of the decomposition and degradation of peat deposits (Nieminen et al. 2017).

On the contrary, our studies have shown that, as a result of ditches' overgrowth, the river water chemistry of the drained area of the GVM becomes closer to the natural site. For example, in 2021, we did not find significant differences in major element, nutrient, and DOC concentrations. However, fires and elevated air temperatures impacted this trend. As a result, in 2020, with an absolute maximum air temperature over a long period, there was a sharp increase in major element and DOC content (Table 5). Similar results obtained in Finland showed positive correlations of organic matter (TOC, DOC, COD, LOI) and Fe with air temperature (Marttila et al. 2018). Additionally, a positive correlation between increasing nitrogen concentrations in waters discharging from drained boreal peatland forests in Finland and Sweden and temperature was noted (Nieminen et al. 2021). River waters exhibit concentrations of K^+, NH_4^+, Fe_{total}, Cl^-, SO_4^{2-}, and DOC similar to those in the waters of the GVM, with higher pH values of Na^+, Ca^{2+}, Mg^{2+}, NO_{3-}, and HCO_{3-}.

Mire water chemistry

Water samples taken in 2022 from the drained area (RG, RG2, RG3, PG2, TG, D2) of the GVM are characterized by a 1.5-3 times higher content of almost all components in comparison with the pristine area (P3, P5, D1). Conversely,

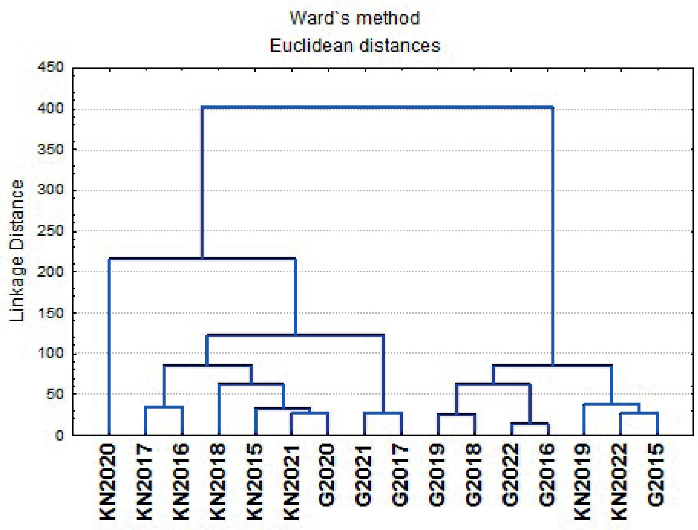

Fig. 2. Dendrogram of river water chemistry in March-September 2015-2022 of the Gavrilovka River (G) and the Klyuch River (KN)

Table 5. Long-term dynamics of the average concentrations in river waters (March-September 2015-2022)

		EC	pH	K^+	Na^+	Ca^{2+}	Mg^{2+}	NH_4^+	Fe_{total}	Cl^-	SO_4^{2-}	NO_{3-}	HCO_{3-}	DOC	TDS
2015	K	186	6.93	0.82	4.75	24.3	8.94	4.05	1.87	3.93	4.26	1.14	120.0	59.8	174
	G	138	6.25	0.48	4.44	19.2	7.56	5.07	4.21	3.31	3.87	1.55	87.6	69.8	137
2016	K	188	6.82	0.65	6.53	27.19	10.81	5.38	2.93	4.29	4.09	2.14	139.81	54.0	204
	G	113	6.53	0.31	4.49	18.6	6.93	6.64	4.88	3.98	5.16	2.07	76.4	65.0	129
2017	K	201	6.85	0.67	8.80	28.8	10.9	3.61	5.43	5.25	2.80	1.57	141.7	61.4	210
	G	151	6.53	0.79	7.96	27.3	9.14	4.29	8.27	4.71	7.71	3.61	110.4	71.4	184
2018	K	144	6.57	0.91	6.52	24.00	9.40	3.27	2.83	3.66	2.28	1.36	119.4	51.4	174
	G	125	6.07	0.57	5.71	21.4	7.62	4.28	8.48	4.28	3.60	3.50	85.7	74.6	145
2019	K	138	6.41	0.63	5.16	20.72	8.73	2.41	2.97	3.29	1.41	1.67	93.3	52.4	140
	G	143	6.23	0.48	5.77	23.3	8.07	3.57	4.58	4.11	2.22	2.19	91.1	71.7	145
2020	K	221	6.88	0.94	9.11	39.41	19.25	3.41	3.71	3.61	2.55	2.82	199.6	45.9	284
	G	182	6.44	0.66	7.46	28.9	7.37	4.85	4.49	4.48	2.91	3.65	117	60.4	182
2021	K	170	6.70	0.66	6.50	27.16	10.91	3.87	3.76	4.52	3.13	2.06	113.9	67.5	177
	G	165	6.37	0.65	6.13	26.9	8.88	4.90	7.48	5.16	4.07	4.54	108	79.3	177
2022	K	117	6.70	0.63	6.00	20.87	6.34	3.83	2.50	5.08	3.62	1.39	81.8	57.6	132
	G	113	6.56	0.57	6.21	21.34	6.86	5.18	3.53	6.79	5.07	3.81	70.50	75.9	130

there is a lower pH due to high organic substance content and minimal concentrations of HCO_3-. Spatially, samples from the pine dwarf-shrub *Sphagnum* communities of the drained part of the GVM taken in 2022 (RG, RG2, RG3, PG2) had low pH and higher concentrations of K^+, Na^+, NH_4^+, Fe_{total}, Cl^-, NO_3^-, and DOC compared to the sedge *Sphagnum* community (TG) and the hummock-hollow complex (D2). At the same time, in the waters of the sedge *Sphagnum* community (TG), there was an increase in the content of Ca^{2+}, Mg^{2+}, HCO_{3-}, and pH, indicating deep groundwater supply. We also saw an increase in SO_4^{2-} and DOC in the waters of the hummock-hollow complex, indicating high peat decomposition rates due to a significant water level decrease (Table 6).

Principal component analysis (PCA) showed similarity in weather condition impact on the Klyuch and Gavrilovka rivers water chemistry. Air temperature (-0.42) and water temperature (-0.40) significantly affect the content of Ca^{2+} (-0,93), Mg^{2+} (-0,75), Na^+ (-0,78), HCO_{3-} (-0,96), and Fetotal (-0.78) in the Gavrilovka River (Fig.3). We see a direct correlation with the concentrations of NO_{3-} (0.42) and Gavrilovka River discharges (0.60). The second component is less significant, but it also reflects an increase of NH^+_4 (0.59) and DOC (0.51) in river waters with an increase in air (0.64) and water (0.81) temperatures. Similarly, the leading factors determining the concentrations of NO_{3-} (0.54), NH^+_4 (0.69), Fetotal (0.59), and DOC (0.65) in the Klyuch River are air (0.70) and water (0.79) temperatures. Klyuch River discharges (-0.63) are inversely correlated with nutrient content, indicating a dilution effect (Fig. 3). Thus, factor 1 characterizes the increase in the content of chemical substances in river waters as a result of an increase in air and water temperatures. Factor 2 mainly characterizes the dilution effect of river waters by precipitation.

Table 6. Spatial patterns in water chemistry of the drained (RG, RG2, RG3, TG, PG2, D2) and pristine (P3, P5, D1) areas of the GVM in April-September 2022, mg/l

	EC	pH	K^+	Na^+	Ca^{2+}	Mg^{2+}	NH_4^+	Fe_{total}	Cl^-	SO_4^{2-}	NO_{3-}	HCO_{3-}	DOC	TDS
RG	56	3.55	0.43	1.43	3.88	1.53	7.52	2.27	4.74	3.87	2.84	0.46	75.3	29.0
PG2	48	3.46	0.95	1.02	4.06	1.29	7.53	2.12	4.66	3.29	2.36	1.86	74.5	29
RG2	65	3.21	0.92	1.78	5.12	1.51	8.69	2.31	5.22	5.52	2.83	0.00	91.2	33.9
RG3	64	3.31	0.48	1.10	5.58	1.89	9.25	2.55	5.43	5.16	3.12	1.25	94.4	35.8
P3	47	3.46	0.47	0.90	2.33	0.76	6.11	1.83	4.39	3.16	1.86	0.56	52.7	22.4
TG	39	3.82	0.47	1.15	6.15	2.26	4.95	1.68	3.94	2.61	1.86	9.11	61.5	34.2
P5	29	3.70	0.57	0.92	2.71	1.15	3.55	1.03	3.05	1.28	1.18	4.75	41.6	20.2
D2	50	3.60	0.63	1.33	4.78	1.99	7.22	1.95	4.77	5.41	2.87	2.72	81.3	33.7
D1	31	3.92	0.55	1.30	3.70	1.43	4.28	1.45	3.30	2.81	1.42	7.76	53.0	28.0

To assess which key site of the drained part of the GVM had the most significant impact on the water chemistry of the Gavrilovka River, a correlation analysis was performed, which showed the closest positive relationship for the content of K^+, HCO_{3-}, NH^+_4, COD, and TDS in the Gavrilovka River and the GVM, and to a lesser extent for pH, Na^+, Cl^-, Fe_{total}, SO_4^{2-}, NO_{3-}, and DOC (Table 7). The pH value and the content of SO_4^{2-}, NO_{3-}, and DOC in the Gavrilovka River and the GVM were predominantly in an inverse relationship, which characterizes dry periods when river discharges are the lowest and the correlation in water chemistry is violated due to low hydrological connectivity of the river and the bog. The highest correlations in water chemistry were found between the Gavrilovka River and the sedge *Sphagnum* lagg (TG), where the river bed is formed. We also noticed that even 6 years after the fire, the pyrogenic factor still influences river water chemistry, with the highest correlation coefficients in the content of K^+, NH^+_4, HCO_{3-}, COD, DOC, and TDS in the waters of the Gavrilovka River and the post-fire area (PG2).

Our data showed that there was primarily an inverse correlation between the content of Na^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_{3-}, and SO_4^{2-} in the waters of the Gavrilovka River and river discharges, which indicates dilution and a subsequent decrease in the concentration of substances during the spring flood. In certain periods, there was a significant positive correlation between water discharges in the river and the content of K^+, NO_{3-} in April and June, DOC in June-July, and NH_{4+} in September (Table 8). The total removal of substances from the Gavrilovka River catchment area in April-September 2022 was 8487 kg/km^2, with DOC release equal to 42% or 3603 kg/km^2. Removal from the pristine part of the GVM was 1.3 times higher, totaling 11385 kg/km^2 in April-September 2022, with DOC flux at 37% (4243 kg/km^2). Generally, the higher removal of mineral components from the Klyuch River basin may be due to groundwater inflow into the river bed and the removal of substances from the part of the catchment area with mineral soils.

Export of major elements, nutrients, and DOC

The seasonal dynamics of major elements, nutrients, and DOC release from the studied watersheds is determined by differences in the hydrological regime. Thus, the largest flux of mineral and organic substances in the Gavrilovka River during the studied period was observed in April-May, coinciding with the spring flood. In June-September, substances removal decreased to 270-382 kg/km^2. The total flux of mineral and organic substances from the drained area of the GVM in April 2022 was 1.2-22.0 times higher than from the pristine area. Similar trends were observed in May, while in other months, removal from the pristine area was 3-5 times higher (Fig. 4). This aligns with findings from previous studies (Lepistö et al. 2014; Finstad et al. 2016) which link the leaching of nutrients and organic carbon to changes in seasonal weather conditions.

PCA indicates that with increasing precipitation and river water levels, the concentration of chemical components decreases. However, the total removal of major elements, nutrients, and DOC is greatest during periods of

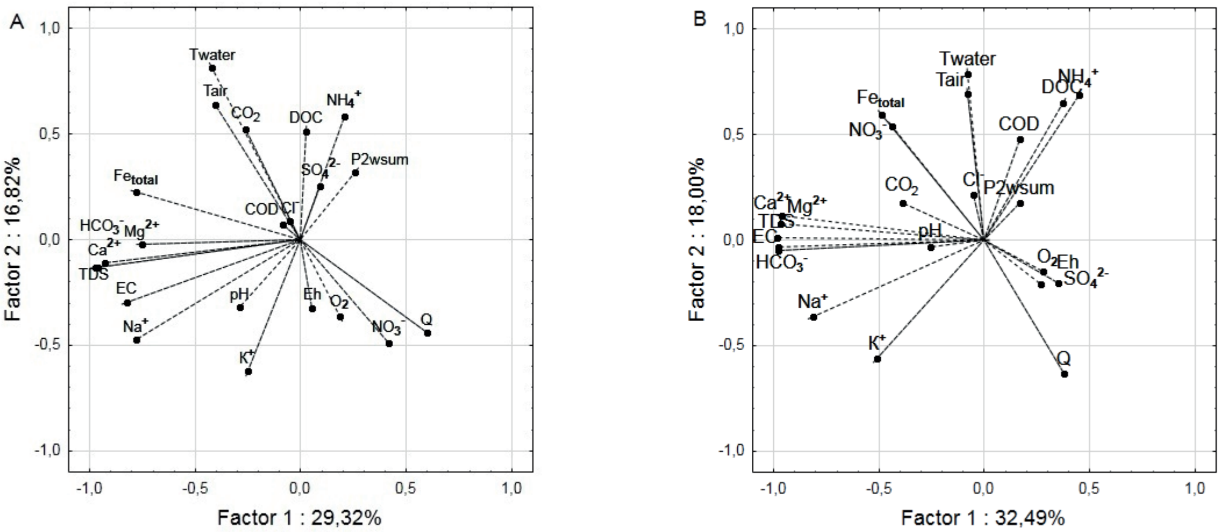

Fig. 3. PCA diagrams of the chemical composition of the waters of the Gavrilovka (A) and the Klyuch (B) rivers in April-September 2015-2022

(P_{2wsum} – total precipitation during 2 weeks before sampling, mm; T_{air} – air temperature at the sampling date, °C; T_{water} – water temperature at the sampling date, °C; Q – river discharge, m^3/s)

Table 7. Pearson correlation of the GVM and the Gavrilovka River water chemistry in 2022 (significance level p<5 %)

		Gavrilovka River														
Great Vasyugan Mire	Key site	EC	pH	K^+	Na^+	Ca^{2+}	Mg^{2+}	NH4$^+$	Fe_{total}	Cl^-	SO_4^{2-}	NO_{3-}	HCO_{3-}	COD	DOC	TDS
	RG	-0.57	-0.48	0.51	-0.21	-0.02	0.05	0.85	-0.43	0.11	0.56	-0.11	0.98	0.76	-0.50	0.62
	PG2	0.10	-0.29	0.79	-0.16	0.46	0.24	0.84	-0.60	0.01	-0.09	-0.44	0.53	0.79	0.62	0.67
	RG2	-0.62	-0.18	0.53	0.43	0.02	0.27	0.75	0.59	0.18	-0.44	-0.54	0.93	0.61	-0.40	0.94
	RG3	-0.28	-0.03	0.48	0.88	-0.05	-0.12	0.81	0.25	-0.09	-0.53	-0.71	0.51	0.64	-0.15	0.92
	TG	0.33	-0.65	0.82	-0.25	-0.28	-0.13	0.65	0.69	0.74	-0.81	-0.64	-0.35	0.50	-0.44	0.27
	D2	-0.18	-0.10	0.50	0.11	-0.52	-0.14	0.81	0.35	0.90	0.44	-0.68	-0.66	0.64	0.47	-0.70

Table 8. Pearson correlation of Gavrilovka River water chemistry and river discharges in 2015-2022 (significance level p<5 %)

	Month	EC	pH	K^+	Na^+	Ca^{2+}	Mg^{2+}	NH_{4+}	Fe_{total}	Cl^-	SO_4^{2-}	NO_{3-}	HCO_{3-}	DOC	TDS
Gavrilovka River discharges	Apr	-0.32	0.39	0.54	-0.72	-0.89	-0.36	-0.55	-0.02	-0.43	-0.74	-0.28	-0.61	-0.54	-0.82
	May	-0.19	0.00	-0.34	0.18	-0.49	-0.32	-0.27	-0.31	-0.48	-0.13	0.24	-0.43	-0.07	-0.51
	Jun	-0.23	-0.64	0.59	-0.37	-0.06	0.11	0.14	0.46	-0.20	0.11	0.62	-0.29	0.72	-0.16
	Jul	-0.13	0.21	0.10	-0.14	-0.20	0.12	0.41	0.34	-0.45	-0.18	-0.05	-0.34	0.63	-0.28
	Aug	-0.45	-0.79	-0.48	-0.58	-0.65	-0.37	0.18	-0.70	0.29	-0.05	-0.01	-0.74	0.37	-0.73
	Sep	-0.64	-0.54	-0.31	-0.64	-0.70	-0.52	0.78	-0.57	-0.50	0.38	0.20	-0.59	-0.26	-0.62
	All data	-0.25	-0.08	0.31	-0.26	-0.48	-0.44	-0.15	-0.47	-0.21	0.01	0.58	-0.50	-0.13	-0.49

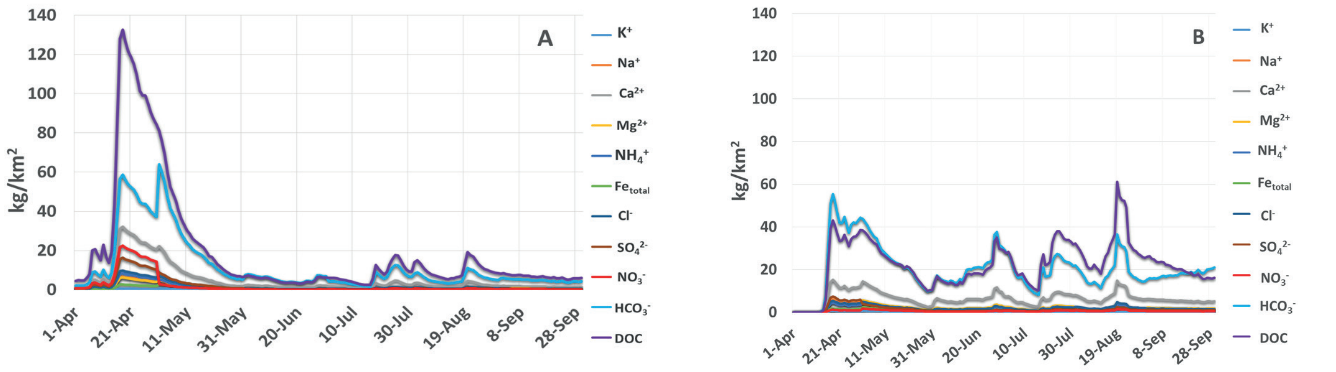

Fig. 4. Export of major elements, nutrients, and DOC by the Gavrilovka (A) and Klyuch (B) rivers in April-September 2022

high water levels, suggesting that a combination of high air temperatures and increased precipitation contributes to substance removal from river catchment areas.

CONCLUSIONS

The analysis revealed increased concentrations of NH^+_4, Fe_{total}, Cl^-, SO_4^{2-}, NO_{-3}, DOC, COD, and CO_2 in the waters of the Gavrilovka River, attributed to long-term forestry drainage. Additionally, a fire-related increase in pH, Ca^{2+}, Mg^{2+}, K^+, Na^+, Fe_{total}, SO_4^{2-}, and NO_{-3} was observed in the first year after the fire, with minimum concentrations of major elements registered mainly in 2015-2016, before the fire. Changes in water chemistry of the Gavrilovka River after the fire had a pulsating character, with extreme increase in air temperature in 2020 and the decomposition of the peat deposit's burnt layer leading to a repeated increase in Ca^{2+}, Na^+, and HCO_{3-}, and nearly a threefold increase in NO_{3-} concentration over the studied period. PCA analysis showed that air and water temperature affect the content of Ca^{2+}, Mg^{2+}, Na^+, Fe_{total}, NH_{4+}, NO_{3-}, and DOC in the studied streams and that there is an inverse correlation between them and river discharges.

Correlation analysis revealed the closest positive relationship between the content of K^+, HCO_{3-}, NH^+_4, COD, TDS in the Great Vasyugan Mire and the Gavrilovka River waters. There is an inverse correlation between the content of Na^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_{3-}, SO_4^{2-} in the waters of the Gavrilovka River and river discharges, which is a sign of dilution during spring floods. However, a significant positive correlation with river discharges was noted for K^+, NO_{3-} in April and June, DOC in June-July, and NH_{4+} in September.

The total export of major elements, nutrients, and DOC from the drained area of the Great Vasyugan Mire was 1.3 times lower in comparison to the pristine area, amounting to 8487 kg/km^2, with DOC flux at 42% or 3603 kg/km^2. Overall, our study suggests that climate change, alongside increased air temperature and precipitation in the region, will likely contribute to the removal of nutrients and organic substances from peatlands.

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