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The Chemical Composition Patterns of the Izhora Groundwater Field (Leningrad Region)

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Abstract—The quality of drinking water is determined by its chemical composition and is regulated by sanitary legislation. The Izhora groundwater Field, the largest in the Leningrad Region, is located to the south of St. Petersburg on the Izhora Plateau. The water-bearing rocks are composed of fractured and karst limestone and dolomite (O_{1-3}). The priority substances for estimation of the quality of groundwater in the Ordovician aquifer were identified and analyzed: total hardness, Fe, Mn, Ba, and nitrates. A map of nitrate pollution of groundwater on the Izhora Plateau was constructed.

Keywords: quality of drinking water, Izhora groundwater field, nitrate contamination, transport forms

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INTRODUCTION

Surface water is the main source of water supply for St. Petersburg and a number of settlements in the Leningrad Region. Groundwater is a strategic resource serving as an alternative and reserve source of water supply. In some cities of the St. Petersburg Region with favorable hydrogeological conditions, such as Pushkin, Gatchina, Lomonosov, Krasnoe Selo, etc., groundwater is used for centralized water supply. Four areas of groundwater of the Ordovician horizon of the Izhora deposit are exploited to the south of St. Petersburg: Krasnosel'skii, Varvarinskii, Gostilitskii, and Vil'povitskii. Anthropogenic contamination of groundwater may occur, since the territory is located in a zone of increased agricultural load.

The Izhora groundwater field with an area of 2300 km^2 is the largest deposit in the Leningrad Region. There are many water intake wells, spring catchments, and single wells with a water withdrawal of ~200000 m^3/day on the territory of the Izhora Upland (Kurilenko and Zhdanov, 2013). The aim of our work was to study the chemical composition of groundwater of the Izhora Field, assess the possibility of its use for domestic and drinking purposes, and identify the areas where some physicochemical parameters of groundwater do not meet modern sanitary standards. Our paper reports the data of geochemical sampling of groundwater of the Izhora Plateau, the results of geochemical modeling of transport forms, and analysis of their toxicity; a map of nitrate contamination on the studied territory is constructed based on the authors' original and literature data.

AREA OF THE STUDY

Physical and Geographic Conditions

The formation of the modern relief of the southwestern part of the Leningrad Region is associated with the accumulative denudation activity of ancient glaciers and their meltwater. The Ordovician Plateau is confined to the poorly and unevenly drained Baltic Lowland. The Izhora Upland located in the western part of the plateau is characterized by a hilly–moraine relief of the sheet–denudation type. The surface is flat and fairly uniform, with a downward trend from the center to the periphery. The highest absolute marks are noted on the Duderhof Heights near the Mozhayskaya Station: Mt Voron'ya (175.9 m) and Mt Orekhovaya (146.9 m) with a slope steepness up to 30°.

Karst is developed on the Izhora Plateau, in Ordovician carbonate rocks underlying boulder loam. The rate of karst denudation is ~15.5 m^3/year. The most karstified areas are related to tectonic fault zones. The karst density is ~0.5–1 sinkholes per 1 km^2 on the watersheds of the Izhora Plateau; 4–10 sinkholes per 1 km^2 in the river valleys; and up to 150 sinkholes per

1 km^2 in some areas of the Volosovskii District (*Informatsionnyi*..., 2023). The diameter of karst sinkholes is from 0.5 to 30 m; the depth is 0.5–15 m. The flow rate of karst springs varies during the year (up to 100 times or more). The extensive development of karst forms promotes the recharge of atmospheric precipitation, therefore the hydrographic network in the inner part of the Izhora Plateau is completely absent.

The Izhora Plateau is a watershed for the right tributaries of the Luga River and a number of small rivers flowing into the Gulf of Finland. All these rivers are genetically related to the karst springs of the plateau; their discharge occurs in the marginal parts of the plateau (e.g., springs near the Mozhaiskaya Station).

Administratively, the territory of the Izhora Plateau includes the Volosovskii, Gatchinskii, southern part of the Lomonosovskii, eastern Kingiseppskii, and northwestern part of the Slantsevskii regions.

The climate of the territory is moderately cold, transitional from continental to maritime, with excessive moisture. It is formed under the influence of maritime Atlantic and continental air masses, periodic intrusions of Arctic air, and active cyclonic activity. SW winds predominate, carrying humid air of the Atlantic origin. Most of the precipitation falls from April to October.

As was shown by (Greyser, 1991), the average long-term precipitation on the Izhora Plateau for the period of 1951–1988 was 684 mm; 362 mm was evaporation, i.e., the amount of precipitation exceeded evaporation. According to the data from the weather station in Volosovo (Weather and Climate (Accessed August 28, 2023)), the average annual surface air temperatures over the past 20 years were 4.9°C (varying within the range of 1.2–6.7°C). The average annual amounts of precipitation in the 21st century varied within the range of 189–887 mm, with an average of 659 mm. The end of the past century saw lower amounts of precipitation and a greater spread of average annual surface air temperatures. At the same time, a tendency towards an increase in the amount of precipitation with increasing surface air temperatures emerged and persisted.

Currently, the precipitation on the Izhora Plateau is ~660 mm/year, with snow up to 50-cm thick lying approximately 125 days a year. Up to 50% of this incoming water is consumed for the formation of subsurface runoff (there is no surface runoff); the rest is evaporation or feeds deeper aquifers.

Geological and Hydrogeological Conditions

In the northern part of the Izhora Plateau, the crystalline basement, which is composed of granite, gneiss-granite, and granodiorite (AR–PR), occurs at a depth of 200 m; in the southern part it is 400 m. The basement is monoclinally overlain by a sedimentary cover, which in the lower part consists of Vendian deposits (V_2st–vr) with a total thickness of 150–170 m. This is sandstone with interlayers of argillite, siltstone, and thin-bedded dense shale in the upper part: from the Starorusskaya Formation of the Redkinskii Horizon to the Voronkovskaya and Vasileostrovskaya formations of the Kotlinskii Horizon. These are overlain by a thin (2–10 m) layer of Lower Cambrian Lomonosov sandstone ($Є_1$lm). A thick layer (~80–120 m) of Lower Cambrian Siverskii ($Є_1$sv) hydrous blue shale isolates this sandstone from the Ordovician carbonate deposits (O_{1-3}) (Verbitsky et al., 2012a, 2012b).

A thin marker layer of Lower Ordovician Dictyonema shale (O_1kp) and the underlying Obolus sandstone (O_1ts) form a horizon with a thickness from 0.2 to 5 m. The layer contains many organic substances and is black. The presence of U, V, Mo, and a number of other elements distinguish this shale.

Ordovician carbonate deposits are distributed to the south from glint in the form of a latitudinal stripe (from 3 to 50 km). They overly Cambrian rocks transgressively with an uneven stratigraphic break. The Ordovician deposits are represented in three sections. The thickness of the Lower Ordovician rocks varies from 5 to 15 m; the Middle Ordovician, from 70 m to 140 m; and the Upper Ordovician, from 0 to 50 m. This is a homogeneous unit of limestone dolomitized to various degrees and dolomite, which is strong, fractured, and sometimes karstified. Karst is developed in the Ordovician limestone in the western part of the Silurian Plateau on the Izhora Upland. There are interlayers of shale and marl with a thickness of 1–2 to 20–50 cm in the limestone unit. The lower section consists of sand, sandstone, and shale. The thickness increases in the southern direction from 0.1–0.2 to 10 m (*Gidrogeologiya SSSR*..., 1967).

The following Ordovician sections are distinguished on the geological map of pre-Quaternary formations for the Izhora Plateau (Verbitsky et al., 2012b) (Fig. 1): the combined Volkhov and Obukhov formations (O_2vl + ob), Mednikovskaya Formation (O_2md), Seletskaya Formation (O_3sl), Gryaznovskaya Formation (O_3gr), Shundorovskaya Formation (O_3sn), Khrevitskaya Formation (O_3hr), Elizavetinskaya Formation (O_3el), Vrudskaya Formation (O_3vr), and Izvarskaya Formation (O_3ir).

The Quaternary deposits are thin, uneven, and quite permeable.

According to the hydrogeological zoning, the Izhora Plateau is a part of the Izhora–Volkhov subregion, adjoining the Predglintovyi subregion from the south in the form of a sublatitudinal band of irregular shape, outlining the Ordovician deposits on the pre-Quaternary surface. The Izhora–Volkhov subregion is a part of the third-order structure of the Baltic–Ladoga hydrogeological region. Together with the Latvian and West Moscow regions, it is located within the Moscow artesian basin (second order), occupying

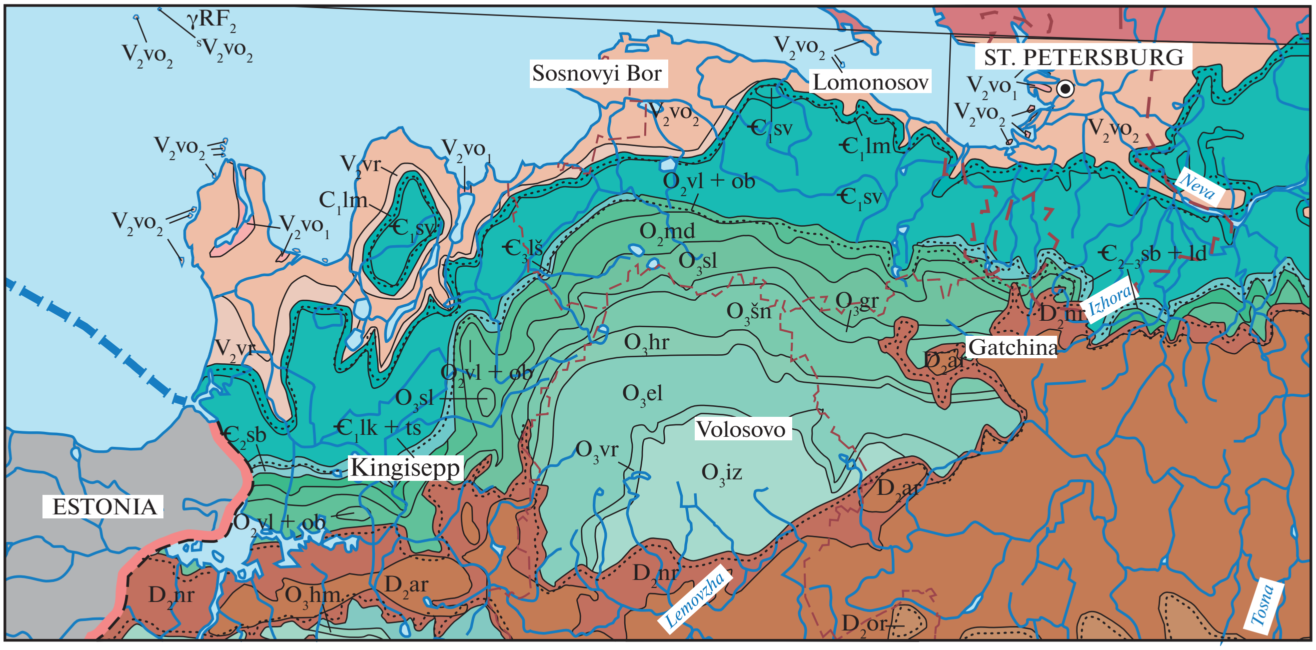

Fig. 1. A geological map of the Izhora Plateau (Verbitskii et al., 2012b).

the northwestern part of the Russian (Eastern European) complex artesian basin of the first order.

The hydrogeological conditions and stratification are considered based on the materials of the Russian Geological Research Institute (Verbitsky et al., 2012a) and using (*Gidrogeologiya SSSR*..., 1967).

Depending on the geology and lithology of the water-bearing rocks, there are various types of water on the territory: porous, fissure, fissure-porous, pore–stratal, (pore-)fissured, karstic, fissure–karstic, and other types. A number of aquifers with their own characteristics are formed under the conditions of excessive moisture there.

The shale layer of the Upper Vendian (V_2) is the regional aquifer. The Lower Cambrian rocks (Є$_1$sv) play the role of another confined aquifer. Thus, the following hydrogeological units are distinguished in the hydrogeological section of the Izhora Plateau: Quaternary aquifer complex, Ordovician–Silurian aquifer, Cambrian–Ordovician aquifer, Lower Cambrian impermeable layer, Upper Vendian–Lower Cambrian aquifer, Upper Vendian impermeable layer, and Vendian aquifer complex.

The Quaternary aquifer complex (Q) is thin and consists of Quaternary sediments, glacial boulder loam, and clayey varieties. These are aeolian, marine, alluvial, peat-bog, glacial–lacustrine, and other deposits.

The Ordovician–Silurian aquifer (O–S) occurs beneath the Quaternary deposits at a depth of >30 m or less (Fig. 2). It is confined to limestone and dolomite of the Middle and Upper Ordovician (from the Volkhov to the Porkunis layer) and has a unconfined character. The horizon is fed over the unconfined area of the plateau by recharge of atmospheric precipitation.

The carbonate section of the Izhora Plateau is characterized by fracturing of various genesis and karstification, which is the most intense in the near-surface zone (to a depth of 40 m), where both ancient and modern karst is developed. The main water resources of the Izhora Plateau are associated with these deposits.

The aquifer is absent in the pre-glint stripe. The Ordovician–Silurian aquifer is drained along the glint; there are a large number of springs and formational outcrops of groundwater with flow rates of up to 20–35 L/s. The springs give rise to many streams and rivers flowing along the Pre-glint Lowland (the Chernaya, Izhora, Duderhofka, and other rivers).

The transmissivity of the Ordovician complex is not uniform over the area. Descending discharge occurs along the glint stripe, while the confined discharge occurs along the rivers in the eastern confined and southern parts of the plateau. There are numerous bedded outlets and springs; the latter include the springs of the settlement of Mozhaiskii. According to the chemical composition, groundwater is usually fresh Mg–Ca or Ca–Mg hydrocarbonate, moderately hard, with pH ~ 7.5.

Groundwater from the Ordovician–Silurian aquifer is the main source of domestic and drinking water supply on the Izhora Plateau; in addition, it is transported over significant distances through water pipe-

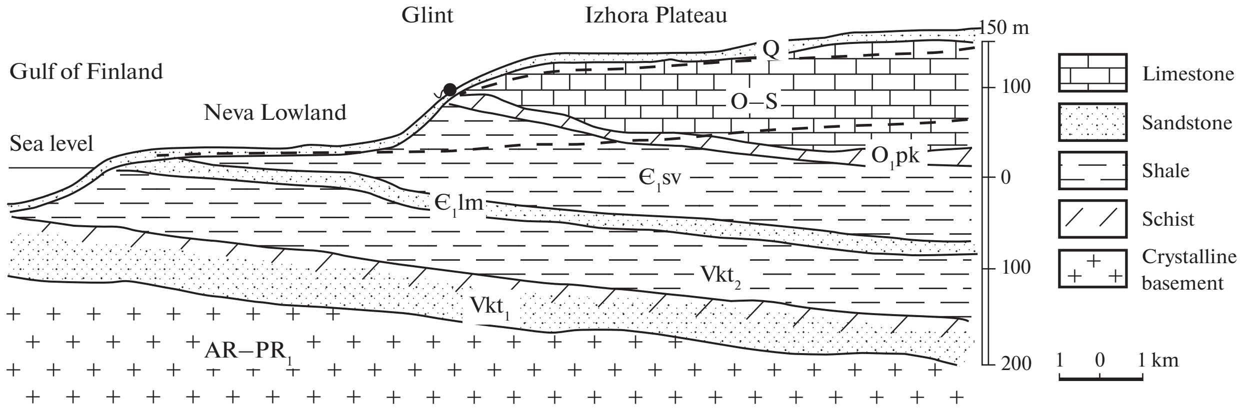

Fig. 2. The hydrogeological cross-section of the Izhora Plateau.

lines to the cities of Lomonosov, Peterhof, Kronstadt, etc.

METHODS

The data on the chemical composition of groundwater, including the results of sampling in 2005–2012, are used in our study. The temperature, pH, Eh, and specific electrical conductivity (SEC) were measured using portable devices from HANNA directly at the sampling site. Water samples for major components analysis were collected in 1-l plastic bottles; for trace element analysis, in 10–20-ml test tubes and acidified with nitric acid (2%) for preservation. The detection limits (mg/L) for cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) are 0.001, 0.005, 0.005, and 0.0001, respectively. The concentration of nitrates was analyzed by the electrochemical method on an I-500 portable ion meter using an ion-selective electrode (the limit of the permissible relative error of concentration measurement is 2 units pX) at the laboratory of the Department of Hydrogeology, St. Petersburg State University. Rn and Ra concentrations in groundwater were analyzed at the Radiation Monitoring Laboratory, Department of Hydrogeology, St. Petersburg State University, on a Radek scintillation analytical complex by the activity of γ-emitting radionuclides.

Hydrochemical modeling (calculation of transport forms of chemical elements dissolved in water) was carried out using the Geochemist's Workbench software package. The initial data for hydrochemical modeling were the results of testing of the chemical composition of groundwater. The standard dependencies of the software (Bethke et al., 2022) were applied for modeling of transport forms.

The construction of a scheme of nitrate contamination of groundwater on the Izhora Plateau was performed using the Surfer v. 15.0 software product. The construction of isolines of nitrate concentration in groundwater was performed using the Kriging interpolation method (*Surfer*..., 2023).

RESULTS AND DISCUSSION

A total of 20 groundwater samples from the Izhora Plateau were studied for major components and trace elements; 13 samples were obtained during well testing, and the others were from springs. Some data on the chemical composition of groundwater (about 70 samples) were obtained from published materials (Stepanyan et al., 2022a, 2022b). These data were used to assess anthropogenic contamination. Tables 1 and 2 present the data on the chemical composition of the studied groundwater. Fig. 3 shows the location of field sampling points, as well as cyclograms of the chemical composition of water. Kurlov's formulas were obtained as a result of the analysis of hydrochemical data. For the wells of the Izhora Plateau (13 samples):

$$M(0.5\text{–}0.7)\frac{HCO_3(81\text{–}97)SO_4(12\text{–}14)Cl(1\text{–}7)}{Ca(49\text{–}66)Mg(26\text{–}47)Na(1\text{–}10)}\quad pH(7.3\text{–}7.8),$$

for the sources (7 samples):

$$M(0.5\text{–}0.8)\frac{HCO_3(75\text{–}96)SO_4(2\text{–}13)Cl(2\text{–}14)}{Ca(40\text{–}53)Mg(31\text{–}45)Na(2\text{–}13)}\quad pH(7.2\text{–}7.6).$$

According to the data (Table 1), all the studied groundwater is hard or very hard, more than half of the samples do not meet modern standards for hardness. There are individual samples with excess Mg. Nevertheless, the composition of the major components is quite stable (Fig. 4). Analysis of the trace elements showed excess of the MPCs for Fe and Al (according to *GOST* (State Standard) *1.2.3685–21*). The data we obtained are quite consistent with previously conducted studies (Schwartz, 2005), according to which 57% (41 samples) did not meet sanitary standards for Fe. There are areas with fairly high concentrations of Ba (in 3 samples of 21) at the Izhora Field, which is explained by the presence of Ba-bearing minerals (Schwartz, 2005).

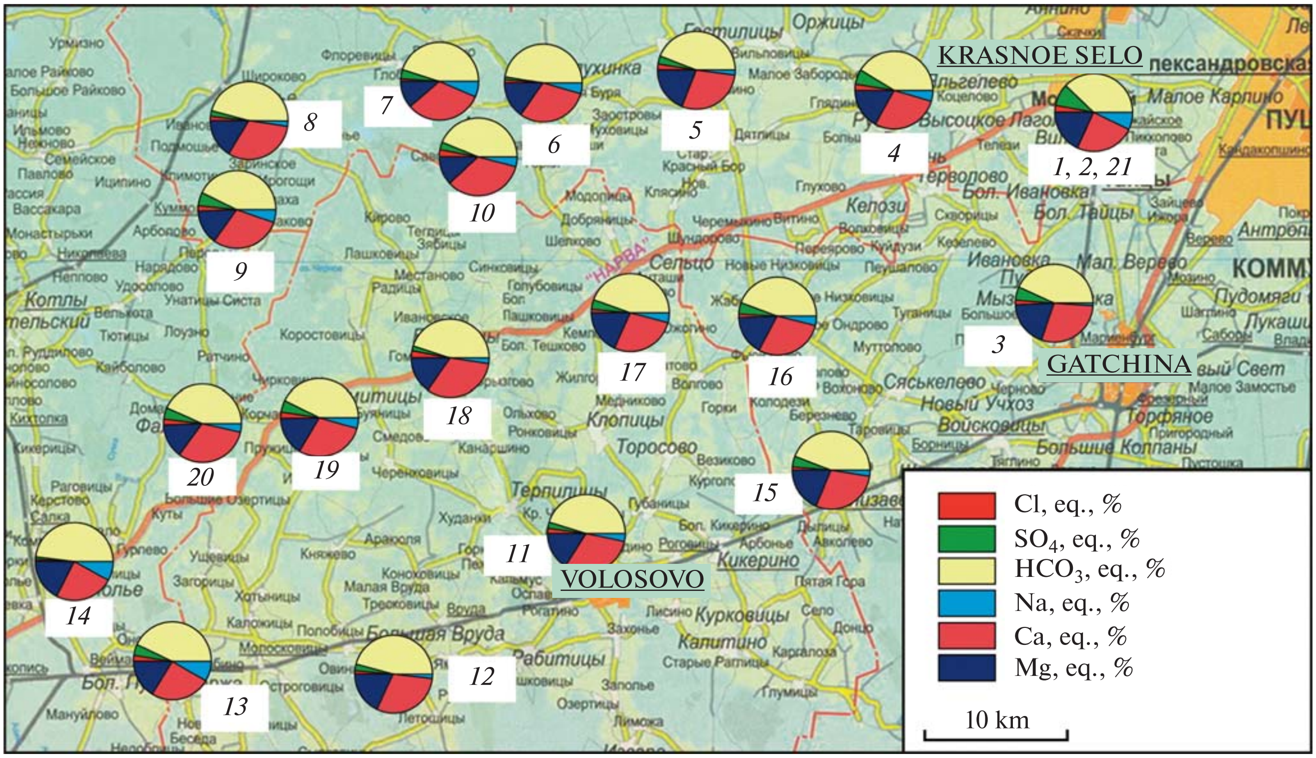

Fig. 3. A map of the actual material with chemical composition cyclograms.

The natural radioactivity of groundwater in the region was studied. The Klyuch spring, which is actively used by the population for drinking purposes, was studied especially thoroughly. As a result, it was found that the groundwater of most springs in the Mozhaisky Village did not meet the radiation safety standards for Rn (Zhdanov and Kayukova, 2006; Kayukova, 2018), with Klyuch turning out to be the most unfavorable in this regard. High levels of Rn impact are explained by the influx of groundwater saturated with Rn from emanating uraniferous Dictyonema shale. The average U content in the rock is 240 ppm (in 20% of samples, the U content exceeds 300 ppm) (Lebedev et al., 2018).

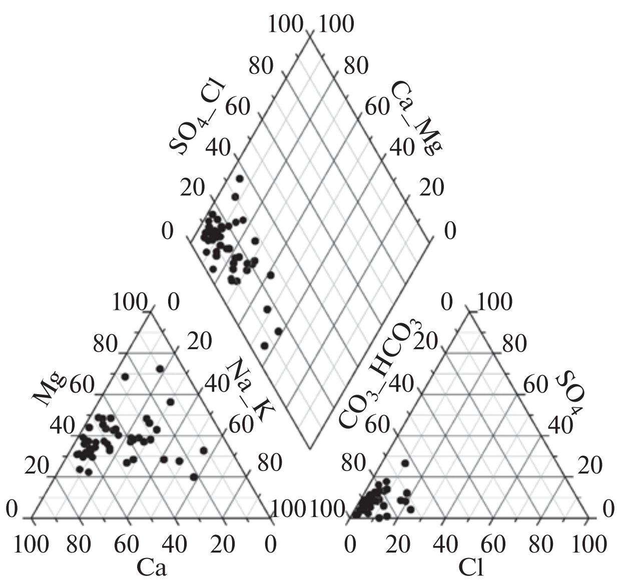

Fig. 4. The chemical composition of groundwater of the Izhora Field on the Piper diagram.

According to the standards (*GOST* (State Standard) *1.2.3685–21*) and NRB 99/2009, no ≤ 60 Bq/L is allowed. High radon activities were detected in the Klyuch spring (Table 3) (Kayukova, 2018). At the Duderhof station, purified Neva water and groundwater from the Ordovician aquifer are mixed to ensure that the quality of tap water in Krasnoe Selo complies with the standards for hardness and radiation safety.

Assessment of the quality of drinking water in the Russian Federation is based on *GOST* (State Standard) *1.2.3685–21* Hygienic standards and requirements for ensuring the safety and (or) harmlessness of environmental factors for humans, which presents the maximum permissible concentrations (MPCs) of the regulated components.

One natural pattern of the Ordovician horizon waters is their increased hardness (a median is 7.3 mg-eq/L), with a MAC of 7 mg-eq/L (*GOST* (State Standard) *1.2.3685–21*).

The higher values of TDS, Cl, sulfates, and nitrates were revealed relative to background indicators. In some areas, nitrate content exceeds the MPC (45 mg/L). Figure 5 shows a diagram of nitrate con-

Table 1. Major components and some indicators (temperature, pH, Eh) in groundwater of the Ordovician aquifer of the Izhora Plateau

Locality	Object type	Depth, m	No. on the map (Fig. 3)	T, °C	pH, units	Eh, mV	H*, mg-eq/L	TDS**, g/L	Na	K	Ca	Mg	HCO_3	Cl	SO_4
									mg/L / mg-eq/L						
Klyuch***	Spring	–	1	7.8	7.3	168	8.4	0.8	31.0 / 1.35	13.0 / 0.33	80.0 / 4.0	54.0 / 4.44	498.0 / 8.7	57.5 / 1.62	60.0 / 1.25
Vilozi***	Spring	–	2	8.8	7.2	128	7.2	0.7	15.0 / 0.65	3.8 / 0.1	75.0 / 3.75	42.0 / 3.45	457.5 / 7.5	37.6 / 1.06	38.4 / 0.8
Pudost'	Spring	–	3	7.7	7.4	109	8.0	0.62	5.4 / 0.23	3.3 / 0.09	86.8 / 4.34	44.0 / 3.64	429.4 / 7.04	8.5 / 0.24	38.4 / 0.80
Ropsha	Spring	–	4	9.8	7.4	179	7.5	0.60	11.0 / 0.48	7.5 / 0.19	79.3 / 3.97	42.0 / 3.49	405.0 / 6.64	11.6 / 0.33	48.0 / 1.00
Gostilitsy	Well	24	5	7.6	7.4	179	6.1	0.53	15.0 / 0.65	15.0 / 0.38	74.0 / 3.70	28.8 / 2.37	341.6 / 5.60	11.4 / 0.32	47.7 / 0.99
Verkhnie Ruditsy	Spring	–	6	7.0	7.5	223	6.2	0.49	3.8 / 0.17	3.2 / 0.08	67.7 / 3.38	34.0 / 2.80	370.9 / 6.08	5.7 / 0.16	5.8 / 0.12
Voronino	Spring	–	7	7.6	7.6	195	6.3	0.58	8.0 / 0.35	44.0 / 1.13	78.4 / 3.92	29.0 / 2.41	395.3 / 6.48	4.3 / 0.12	24.5 / 0.51
Kopor'e	Well	25	8	10.0	7.5	164	7.8	0.60	6.5 / 0.28	4.9 / 0.12	93.5 / 4.68	38.0 / 3.09	439.2 / 7.20	8.8 / 0.25	14.4 / 0.30
Lomakha	Well	23	9	11.1	7.3	206	8.9	0.71	16.0 / 0.70	6.6 / 0.17	102.2 / 5.11	46.0 / 3.77	483.1 / 7.92	8.5 / 0.24	50.4 / 1.05
Savol'shchina	Well	31	10	10.2	7.5	158	7.0	0.55	1.8 / 0.08	1.2 / 0.03	93.8 / 4.69	28.0 / 2.29	390.4 / 6.40	14.2 / 0.40	19.7 / 0.41
Sumino	Well	27	11	8.3	7.6	72	6.4	0.60	16.0 / 0.68	49.0 / 1.26	84.0 / 4.20	26.4 / 2.17	385.5 / 6.32	8.5 / 0.24	29.2 / 0.61
Bolshaya Vruda	Draw-well	5	12	10.1	7.8	158	6.1	0.47	8.2 / 0.36	3.7 / 0.10	65.2 / 3.26	35.0 / 2.87	336.7 / 5.52	6.0 / 0.17	12.5 / 0.26
Kalozhnitsy	Spring	–	13	7.5	7.6	203	6.8	0.55	3.3 / 0.14	1.4 / 0.04	73.2 / 3.66	38.0 / 3.10	390.4 / 6.40	11.4 / 0.32	33.6 / 0.70
Fedorovka	Well	31	14	11.7	7.6	181	8.0	0.71	3.6 / 0.16	1.3 / 0.03	95.2 / 4.76	38.9 / 3.20	561.2 / 9.20	5.1 / 0.14	7.2 / 0.15
Alekseevka	Well	29	15	11.1	7.8	134	6.2	0.49	3.3 / 0.15	1.5 / 0.04	65.6 / 3.28	36.0 / 2.97	351.4 / 5.76	5.7 / 0.16	25.0 / 0.52
Starye Nizkovitsy	Well	27	16	7.8	7.5	143	8.3	0.65	6.4 / 0.28	3.1 / 0.08	94.1 / 4.71	43.0 / 3.56	458.7 / 7.52	5.4 / 0.15	36.5 / 0.76
Rutelitsy	Well	36	17	11.4	7.7	177	7.4	0.58	2.2 / 0.09	1.8 / 0.04	77.5 / 3.88	43.0 / 3.56	419.7 / 6.88	5.7 / 0.16	29.3 / 0.61
Begunits	Well	21	18	10.7	7.6	165	7.5	0.58	19.0 / 0.83	5.6 / 0.14	87.1 / 4.35	38.0 / 3.10	405.0 / 6.64	17.0 / 0.48	7.7 / 0.16
Zimititsy	Well	27	19	9.3	7.7	154	7.2	0.56	5.7 / 0.25	2.0 / 0.05	79.3 / 3.96	39.0 / 3.19	390.4 / 6.40	13.9 / 0.39	31.7 / 0.66
Domoshovo	Well	24	20	8.1	7.7	134	6.7	0.50	5.3 / 0.25	2.0 / 0.05	76.8 / 3.84	34.0 / 2.81	341.6 / 5.60	9.4 / 0.26	27.9 / 0.58
MPC	–	–	–	–	6–9	–	7.0	1.0	200	–	–	50	–	350	500

* Hardness; ** Mineralization; ***Springs in the Mozhaiskii Village.
MPC, maximum permissible concentrations, according to *GOST* (State Standard) *1.2.3685–21.*

Table 2. The trace element composition of groundwater of the Izhora Plateau, mg/L

Sample no. (Fig. 3, Table 2)	Si	Sr	Fe	Al	B	Ba	Mn	Zn	Li	Ti	Rb	As	Pb	V	Cr	Cu	Mo	Se	U
1	5.3	0.09	0.01	0.01	0.03	0.16	<	0.003	0.004	<	0.002	0.0002	<	0.0001	0.0006	0.0005	0.0003	0.0005	0.003
2	5.3	0.19	0.04	0.02	0.08	0.18	<	0.007	0.010	0.001	0.002	0.0003	<	0.0002	0.0029	0.0009	0.0009	0.0009	0.012
3	4.6	0.08	0.03	0.01	0.04	0.096	<	0.010	0.004	<	0.002	0.0003	<	0.0002	0.0022	0.0010	0.0005	0.0001	0.001
4	5.1	0.08	0.03	0.01	0.03	0.082	<	0.046	0.004	0.001	0.002	0.0004	<	0.0004	0.0029	0.0020	0.0008	0.0003	0.002
5	4.6	0.09	0.14	0.08	0.04	0.10	0.0005	0.040	0.007	0.003	0.003	0.0004	0.0004	0.0003	0.0024	0.0044	0.0007	0.0005	0.002
6	4.7	0.08	0.19	0.12	0.02	0.078	0.0081	0.193	0.005	0.005	0.002	0.0002	0.0004	0.0005	0.0026	0.0015	0.0000	0.0004	0.002
7	5.1	0.09	0.09	0.05	0.05	0.077	0.0004	0.045	0.003	0.003	0.006	0.0008	0.0001	0.0006	0.0030	0.0029	0.0028	0.0003	0.002
8	4.2	0.08	0.11	0.03	0.02	0.029	0.0035	0.162	0.002	0.002	0.001	0.0002	0.0030	0.0003	0.0032	0.1125	0.0003	0.0001	0.001
9	4.5	0.07	0.00	0.01	0.03	0.28	<	0.040	0.001	<	0.002	0.0001	0.0006	0.0001	<	0.0282	0.0009	0.0008	0.012
10	3.7	0.07	0.06	0.01	0.02	0.042	<	0.366	0.002	<	0.001	0.0001	0.0003	0.0001	0.0018	0.0035	0.0003	0.0000	0.001
11	8.2	0.09	0.74	0.07	0.05	0.040	0.0053	0.026	0.003	0.004	0.006	0.0004	0.0003	0.0005	0.0027	0.0030	0.0005	0.0001	0.001
12	5.2	0.05	0.17	0.02	0.02	0.063	0.0090	0.079	0.002	0.001	0.002	0.0002	0.0002	0.0003	0.0017	0.0020	0.0002	<	0.001
13	4.7	0.04	0.02	0.02	<	0.051	<	0.014	0.001	0.001	0.001	0.0002	<	0.0003	<	<	<	0.0001	0.001
14	4.3	0.06	0.05	0.01	0.01	0.068	<	0.005	0.002	<	0.001	<	0.0002	0.0001	0.0026	0.0053	0.0004	0.0002	0.001
15	4.4	0.03	0.18	0.10	0.01	0.054	0.0022	0.095	0.001	0.047	0.001	0.0001	0.0011	0.0004	0.0017	0.0011	0.0001	0.0001	0.001
16	4.6	0.09	0.05	0.02	0.04	0.077	<	0.318	0.003	0.001	0.001	0.0002	0.0001	0.0001	0.0027	0.0026	0.0005	0.0000	0.001
17	3.9	0.03	0.04	0.02	0.01	0.017	<	0.126	<	0.001	0.000	0.0004	0.0013	0.0001	0.0014	0.0624	0.0001	<	0.001
18	4.2	0.06	0.06	0.01	0.02	0.037	<	0.030	0.002	0.001	0.003	0.0001	0.0003	<	0.0010	0.0067	0.0000	0.0001	0.001
19	4.3	0.04	0.02	0.01	0.01	0.037	<	0.033	0.002	<	0.001	<	<	0.0001	0.0006	0.0009	<	0.0000	0.001
20	5.0	0.05	1.18	0.44	0.01	0.064	0.0475	0.074	0.002	0.011	0.002	0.0006	0.0013	0.0008	0.0021	0.0015	0.0006	0.0001	0.001
MPC	20	7	0.3	0.2	0.5	0.7	0.1	5	0.03	0.1	0.1	0.1	0.01	0.1	0.05	1.0	0.07	0.01	0.015

MPC, maximum permissible concentrations, according to *GOST* (State Standard) *1.2.3685–21*; (<) less than the detection limit.

Table 3. The contents of Rn and Ra (Bq/L) in springs of the Mozhaisky Village (2003–2005)

^{222}Rn, Bq/L					Level of impact**
sample no.	number of analyses	average	min	max	Bq/L
21. Klyuch (ul. 25 Oktyabrya)	22	120 ± 15	103	130	60
22. Vilozi	2	72 ± 12	70	73	

* Level of impact (LI) is the level of the radiation factor, above which certain protective measures should be taken (*GOST* (State Standard) *2.6.1.2523–09*).

tamination, constructed according to the authors' and literature data (Stepanyan et al., 2022a, 2022b). Anthropogenic contamination is associated mainly with the influence of agriculture.

The study of the transport forms of chemical elements is of great importance for investigation of the chemical composition and quality assessment of drinking water, since different forms of transport of the same element can have different effects on the human body due to their different toxicity. These issues were addressed in (Kraynov et al., 2004; Linnik et al., 2007; Kayukova and Filimonova, 2022).

Toxicity is determined by the state in which the metal usually transports rather than by the total concentration of metal in water. The more toxic form is the one that corresponds to the greater biological and chemical activity of the metal. Hydrated (free) metal ions are toxic (Linnik et al., 2007). The toxicity of water-soluble substances has a greater reactivity and, therefore, is more proportional to their solubility. For example, soluble Ba salts (especially $BaCl_2$) are very toxic; insoluble $BaSO_4$ is completely nontoxic.

A number of heavy metals (Hg, Pb, Sn, Cd, etc.) are toxic to humans. It has been shown that their organometallic compounds are the most toxic and are even more toxic than their free (hydrated) ions (Kraynov et al., 2004; Linnik et al., 2007).

Calculation of the transport forms of chemical elements in water (in the Geochemist's Workbench program) showed the predominant forms. Thus, 80–82% of the transport forms of Ca and Mg occur in an aqueous solution in the form of free cations Ca^{2+} and Mg^{2+} (not bound in complex compounds); 10–13% are $CaHCO_3^+$ and $MgHCO_3^+$ hydrocarbonate complexes. The predominant transport forms of Na and K are Na^+ (96–97%) and K^+ (97%). The predominant transport forms of the major anions are the following: SO_4^{2-} (70%), Cl^- (98%), and HCO_3^- (96%).

Such metals as Ba^{2+} (93%), Li^+ (99%), Mn^{2+} (80%), Sr^{2+} (90%), and Zn^{2+} (96%) transport in

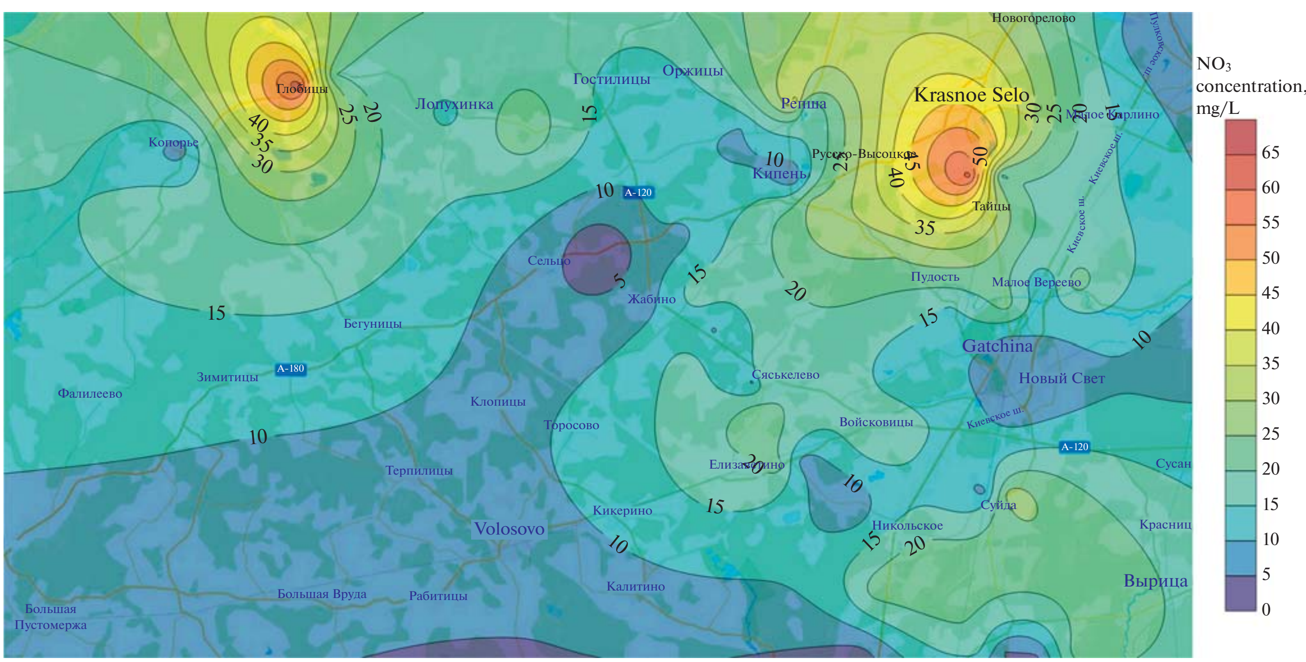

Fig. 5. A scheme of the nitrate contamination of groundwater of the Izhora Plateau.

groundwater mainly in the form of free cations. These forms are toxic, but in the case of low weight concentrations, the effects of these forms on the human body are insignificant. Since excesses of the MPC for Ba and Mn are likely in some areas in the Ordovician aqifer, it is necessary to remember that the transport forms for these elements will have a toxic effect on human health.

CONCLUSIONS

In terms of the chemical composition, the groundwater of the Ordovician aqifer of the Izhora Plateau is mainly fresh alkaline Mg–Ca hydrocarbonate of an meteoric origin. The hardness of 60% of the studied water samples did not meet modern sanitary standards.

The general chemical composition and the content of trace elements in the water generally meet the requirements of SanPiN 1.2.3685-21, except for the contents of some trace elements, primarily Fe, as well as Al and Ba. Higher values of TDS, Cl, sulfates, and nitrates relative to background were detected, which is associated with anthropogenic activity, mainly due to agriculture. The detected centers of nitrate contamination (with concentrations of more than45 mg/L) showed that they were confined to the areas of agriculture and livestock farming as well.

The predominant transport forms of the major elements in groundwater are mainly presented by free ones; this is true for both anions and cations. The metal cations Ba^{2+}, Li^{+}, Mn^{2+}, Sr^{2+}, and Zn^{2+} are not complexed. In the case of high weight concentrations of these elements in drinking water they will have a toxic effect on the human body.

The waters of the Duderhof springs, which are actively used in decentralized water supply, have natural radioactivity due to the contact of groundwater with the Dictyonema shale. This makes their use dangerous to human health. Unlike other areas, the groundwater of the Krasnoe Selo section of the Izhora Field has increased radioactivity. At the water treatment stage, it is diluted with water from the Neva River, so that the water meets modern quality standards for hardness and radiation indicators.

Fresh groundwater of Ordovician deposits is a real treasure of the St. Petersburg region and its strategic reserve. Groundwater has good drinking qualities; however, constant monitoring of the chemical composition of the waters of the Izhora Field is necessary for the timely detection of probable sources of contamination.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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