Assessment of quality of spring waters of Valdai District of Novgorod Region by chemical indices

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Abstract. The article presents data on the chemical composition of water from springs of Valdai District of Novgorod Oblast. In twelve, the most known and frequently visited, sources concentrations of main ions, values of indices characterizing the pollution of springs with organic substances and mineral forms of nitrogen, as well as the content of ions of heavy metals were determined. Water from nine examined sources corresponds to sanitary and hygienic standards.

1. Introduction

Compared with surface waters, groundwater is better protected from pollution, usually clear and colorless, possesses a constant chemical composition, and is found everywhere.

However, today the quality of groundwater, including that of springs, is deteriorating due to antropogenic impact on the environment [1–7]. Pollution of groundwater is observed at a depth of less than 30 m [8].

In 2018, in Novgorod Oblast, 35.4% of water samples taken from sources of non-centralized water supply (wells and springs) did not meet the requirements of hygienic standards for chemical composition, and 70.6% did not meet them for the results of microbiological analysis [9].

The part of the Valdai Hills where many rivers take their origin is situated on the territory of Valdai District of Novgorod Oblast. Almost all of the most important water bodies of the Valdai National Park, such as Valdai, Uzhin, Velje, Borovno lakes, the Polomet, Lonitsa, Shegrinka rivers, are located on the territory of Valdai District. An important part of the hydrologic systems of Valdai lakes and rivers are springs. Local residents use water from equipped springs for drinking and household needs. Springs as the objects of recreational and religious tourism cause a growing interest. Therefore it seems necessary to clarify sanitary and chemical indices of spring water quality in this area.

The purpose of this work is to assess the quality of spring waters of Valdai District by chemical indices.

2. Objects and methods of research

On the territory of Valdai District the water samples were taken from 12 of the most famous and frequently visited springs: №1 – the Tekunok spring, the village of Uzhin; №2 – the Sokolovskiye klyuchi spring, the settlement of Roshchino; №3 – the Pyatnitskiy spring, the village of Bor; №4 – the spring of Saints Kosmas and Damian on the Bogomolnaya Gora, the town of Valdai; №5 – the Zhivonosnyy spring, the town of Valdai; №6 – the holy spring of Kazanskoy ikony Bozhiey Materi, the village of Izhitsy; №7 – a spring in the village of Varintsy; №8 – a spring at Sputnik camp, the village...
of Varnitsy; №9 – the holy spring of Paraskev Pyatnitsey, the village of Edrovo; №10 - a spring in the village of Plotichno; №12 – a spring in the village of Korotsko.

Samples were taken in November 2019. Capillary electrophoresis (main ions and mineral forms of nitrogen), fluorimetry (oil products), inductively coupled plasma atomic emission spectroscopy (heavy metal ions), redoximetric titration (biochemical oxygen consumption and permanganate oxidizability) were used as research methods.

3. Results and discussion

The results of determining the chemical composition of the spring water of Valdai District are given in Table 1.

| Spring | HCO₃⁻ | SO₄²⁻ | Cl⁻ | K⁺ | Na⁺ | Ca²⁺ | Mg²⁺ | Fe_total | pH | HCO₃⁻ | mg/dm³ | SO₄²⁻ | mg/dm³ | Cl⁻ | mg/dm³ | K⁺ | mg/dm³ | Na⁺ | mg/dm³ | Ca²⁺ | mg/dm³ | Mg²⁺ | mg/dm³ | Fe_total | mg/dm³ | 1-1.5 | 6-9 | 0.30 |
|--------|-------|-------|-----|----|-----|------|------|---------|----|-------|-------|-------|-------|-----|-------|----|-------|-----|-------|------|-------|------|-------|---------|-------|-------|-----|-----|
| №1    | 103.7 | 4.51  | 0.50| 0.87| 2.28| 10.0 | 2.50 | 0.12    | 7.53| 0.021 |
| №2    | 143.4 | 5.26  | 21.9| 1.28| 15.5| 10.5 | 4.38 | 0.20    | 7.60| 0.007 |
| №3    | 122.0 | 4.26  | 0.11| 0.74| 1.67| 10.0 | 2.90 | 0.14    | 7.20| 0.032 |
| №4    | 283.7 | 10.3  | 38.9| 2.25| 19.0| 13.0 | 9.93 | 0.40    | 7.10| 0.009 |
| №5    | 323.4 | 28.0  | 17.2| 8.15| 27.4| 12.5 | 8.74 | 0.43    | 6.90| 0.032 |
| №6    | 164.8 | 8.35  | 94.5| 1.55| 42.4| 11.6 | 4.44 | 0.33    | 7.80| 0.013 |
| №7    | 112.9 | 10.4  | 15.6| 2.56| 11.9| 10.4 | 3.62 | 0.17    | 6.64| 0.029 |
| №8    | 259.3 | 10.8  | 14.9| 6.04| 13.7| 12.9 | 6.55 | 0.32    | 7.28| 0.007 |
| №9    | 253.2 | 6.75  | 3.58| 1.23| 3.54| 13.2 | 6.02 | 0.29    | 6.98| 0.224 |
| №10   | 265.4 | 13.1  | 218 | 28.6| 81.3| 13.3 | 6.25 | 0.66    | 6.50| 0.015 |
| №11   | 219.7 | 5.33  | 9.59| 1.89| 5.23| 13.0 | 6.45 | 0.26    | 7.14| 0.001 |
| №12   | 180.0 | 2.02  | 0.50| 0.71| 1.14| 12.4 | 3.91 | 0.20    | 7.23| 0.011 |

90-99% of all mineral substances dissolved in natural water are composed of main ions: chloride, sulfate and bicarbonate ions, and sodium, magnesium, calcium and potassium cations. The relationship between the concentrations of main ions and the value of water mineralization is shown in the scheme [10]:

![Increasing vs. Decreasing of Mineralization](image)

The scheme shows that in low-mineralized water there is a predominance of bicarbonate ions and calcium cations, while in high-mineralized waters there is a predominance of chloride ions and sodium cations. Due to the low solubility of calcite (the polymorphic form of calcium carbonate prevalent in temperate latitudes), the concentrations of bicarbonate and carbonate ions do not reach high values. Due to the high solubility of chlorides of alkaline metals, the concentrations of chloride ions in groundwater can be quite significant.

Bicarbonate ions enter groundwater as a result of dissolution of carbonate rocks (calcite or magnesite) in carbonic acid.

Carbon dioxide dissolved in water, carbonic acid, bicarbonate and carbonate ions together form a carbonate system. In the range of 6.0 < pH < 10.0 values (almost corresponding to the values interval regulated for natural water) bicarbonate ions are the prevailing component of the carbonate system, their
maximum proportion corresponding to \( pH \approx 8.34 \). The quantitative composition of the carbonate system determines \( pH \) value in most natural waters. Examined waters have a reaction close to neutral one. The concentration of bicarbonate ions in the sources of non-centralized water supply is not regulated.

The concentration of sulfate ions is limited by the presence of calcium cations and the formation of low-soluble gypsum and anhydrates [11]. The source of chloride ions in natural waters are water-soluble chlorites minerals (halite, sylvinite, carnallite, bischofite, etc.). The content of sulfate and chloride ions in all sources is lower than maximum permissible concentration (MPC) [12].

Calcium and magnesium enter groundwater in the leaching of carbonate rocks (gypsum, anhydrite, limestone, dolomite, and magnesite). The concentration of calcium cations in waters of the sources examined is higher than that of magnesium cations which is the characteristic of groundwater. This may be due to the lying of carbonate rocks with the predominance of calcite at the locations of the examined springs. Another cause may be the binding of magnesium cations according to the equation:

\[
2 \text{CaCO}_3 + \text{Mg}^{2+} \leftrightarrow \text{CaMg(CO}_3)_2 + \text{Ca}^{2+}.
\]

As it was noted earlier, there is a close relationship between the mineralization value and the concentration of sodium cations. For this reason, in the water of spring №1 with the lowest mineralization the concentration of sodium cations is the lowest. The water from source №10 is characterized by the highest mineralization and the highest concentration of sodium cations. A similar ratio is also observed for chloride ions, which corresponds to the dependence between the content of main components and the water mineralization value shown in the scheme.

The content of \( K^+ \), \( Ca^{2+} \) and \( Mg^{2+} \) cations in the water sources of non-centralized water supply is not regulated. Water hardness that is determined by the presence of calcium and magnesium ions is regulated. Its value should not exceed 7.0 mmol / dm\(^3\) [12]. Hardness in all examined sources does not exceed 1.5 mmol/dm\(^3\), which allows them to be referred to as very soft [13].

Total concentration of inorganic substances dissolved in water is usually expressed in the form of mineralization \( M \) in g/dm\(^3\). Mineralization is calculated as the sum of mass concentrations of main ions. The waters of all the sources examined can be referred to fresh waters with mineralization to 1.0 g/dm\(^3\) [13]. Mineralization value does not exceed 1.0-1.5 g/dm\(^3\), which complies with established sanitary standards [12].

In addition to the classification of natural waters by mineralization and hardness, there are other classifications by chemical composition [10, 14]. O. A. Alekin proposed a classification according to prevailing anions and cations. By the predominant anion all natural waters are referred to one of three classes: bicarbonate, sulfate, chloride; by the predominant cation – to one of three groups: calcium, magnesium, sodium [10]. For the exception of source №10, the waters of all sources belong to bicarbonate class and calcium group, or sodium group, or mixed groups, and only the water of source №10 with higher mineralization belongs to chloride class and sodium group.

Total concentration of all iron forms in groundwater is frequently comparable with the concentrations of main ions. In underground water, iron (II) is present, mainly in the form of bicarbonate Fe(HCO\(_3\))\(_2\), which, when water exits to the surface, forms iron hydroxide (III) determining water coloration. In the analyzed waters the iron concentration is significantly lower than the maximum permissible concentration (MPC).

The indices characterizing the pollution of the examined sources with nitrogen mineral forms and organic matters are presented in table 2.

Concentrations of nitrogen mineral forms in natural waters are interconnected. Oxidation of ammonium ion in natural water follows the scheme: \( \text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^- \), corresponding to the sequential reaction of the first order. In the examined springs the concentration of ammonium ions is lower than the maximum permissible concentration (MPC).

The concentration of nitrite ions is frequently below the detection limit, since the rate constant of the second stage is greater than that of the first stage, and nitrite ions are rapidly oxidized to nitrate ions. In eight sources the content of nitrite ions was detected, which is the evidence of constant superficial pollution, and is likely to be the consequence of their regular use.
Nitrate ions are the final product of the mineralization of nitrogen-containing organic matters, their presence in natural water resulting from complete oxidizability of this group of pollutions. The content of nitrite ions and nitrate ions does not exceed the MPC (maximum permissible concentration) in the waters of the sources examined [12].

Table 2. Indices characterizing water pollution of the examined sources with nitrogen mineral forms and organic matters.

| Spring | NH₄⁺, mg/dm³ | NO₂⁻, mg/dm³ | NO₃⁻, mg/dm³ | BPK₅ (biochemical oxygen consumption), mgO₂/dm³ | PO (permanganate oxidizability), mgO/dm³ | Oil products, mg/dm³ |
|--------|--------------|--------------|--------------|---------------------------------|---------------------------------|-------------------|
| MPC    | 2.00         | 3.00         | 45.00        | 5.0-7.0                         | 0.100                           |
| №1    | 0.06         | n/d          | 16.50        | 1.22                            | 4.35                            | 0.014             |
| №2    | 0.09         | 0.003        | 0.60         | 2.92                            | 2.94                            | 0.029             |
| №3    | 0.07         | n/d          | 0.46         | 0.82                            | 3.66                            | 0.018             |
| №4    | 0.31         | n/d          | 4.56         | 0.82                            | 1.82                            | 0.012             |
| №5    | 0.26         | 0.110        | 4.78         | 0.36                            | 2.74                            | 0.019             |
| №6    | 0.28         | 0.003        | 8.25         | 0.73                            | 2.43                            | 0.010             |
| №7    | 0.05         | 0.002        | 31.57        | 0.90                            | 2.92                            | 0.008             |
| №8    | 0.10         | 0.008        | 9.88         | 0.58                            | 2.76                            | 0.015             |
| №9    | 0.06         | 0.034        | 6.49         | 0.65                            | 9.52                            | 0.010             |
| №10   | 0.12         | 0.003        | 8.81         | 0.82                            | 3.66                            | 0.010             |
| №11   | 0.05         | n/d          | 8.98         | 0.41                            | 1.15                            | 0.007             |
| №12   | 0.06         | 0.001        | 5.76         | 0.95                            | 1.38                            | 0.010             |

In the examined spring waters the indices were determined that characterize their pollution with dissolved organic matters: biochemical oxygen consumption (BPK₅) and permanganate oxidizability (PO), as well as the concentration of oil products.

Biochemical oxygen consumption used to assess the degree of natural water pollution with dissolved organic matters is determined by aerobic metabolism of heterotrophic microorganisms. In the examined waters, the values of biochemical oxygen consumption are expectedly low (more low than the biochemical oxygen consumption in surface water). Biochemical oxygen consumption for sources of non-centralized water supply is not regulated. In according to the values of the biochemical oxygen consumption only water in spring №2 is moderately polluted, in source №1 it is clean, in other springs it is very clean [13].

The value of permanganate water oxidizability in spring №9 is medium, in spring №1 it is small, in other springs it is very small [13]. Permanganate oxidizability is within the norm in all sources, except for source №9.

The widespread flow of oil products into groundwater is due to their losses and leaks. The concentration of oil products in the analyzed waters is significantly lower than the MPC.

In the spring waters of Valdai District the concentrations of the following heavy metals were determined: copper, manganese, nickel, zinc, cadmium, chrome, lead. All they have the ability for bioaccumulation and refer to the most toxic heavy metals. Cadmium and lead compounds are xenobiotics.

The content of heavy metals compounds in the spring waters of Valdai District is shown in table 3. Natural sources of heavy metals compounds in groundwater are mountain rocks and minerals. The concentrations of heavy metals ions in the waters of the analyzed springs except manganese are lower than the established standards [12]. Manganese compounds enter the water bodies during the leaching of clay minerals containing manganese. In the waters of springs №№ 5, 8 and 9 the content of Mn(total)
exceeds the MPC. The negative impact of manganese compounds on the central nervous system, blood-making processes, osseous tissue structure, kidneys was found [15].

Table 3. Concentrations of heavy metals compounds in the waters of the examined sources.

| Source | Cu(total), mg/dm³ | Mn(total), mg/dm³ | Ni²⁺, mg/dm³ | Zn²⁺, mg/dm³ | Cd(total), mg/dm³ | Cr(total), mg/dm³ | Pb(total), mg/dm³ |
|--------|-------------------|------------------|--------------|--------------|------------------|------------------|------------------|
| MPC    | 1.000             | 0.100            | 0.100        | 5.000        | 0.001            | 0.05             | 0.03             |
| №1     | 0.002             | 0.018            | 0.002        | 0.003        | 0.0005           | 0.0004           | 0.001            |
| №2     | 0.001             | 0.021            | 0.001        | 0.005        | 0.0003           | n/d              | 0.003            |
| №3     | 0.002             | 0.044            | 0.002        | 0.005        | 0.0002           | 0.0002           | n/d              |
| №4     | 0.002             | 0.025            | 0.001        | 0.004        | 0.0001           | 0.0003           | 0.001            |
| №5     | 0.003             | 0.752            | 0.002        | 0.007        | 0.0003           | 0.0002           | 0.001            |
| №6     | 0.002             | 0.026            | 0.001        | 0.005        | 0.0002           | 0.0001           | n/d              |
| №7     | n/d              | 0.010            | n/d          | 0.004        | n/d              | n/d              | 0.011            |
| №8     | n/d              | 0.104            | n/d          | 0.007        | n/d              | n/d              | n/d              |
| №9     | n/d              | 0.178            | n/d          | 0.002        | n/d              | n/d              | n/d              |
| №10    | 0.002             | 0.007            | n/d          | 0.034        | n/d              | n/d              | 0.004            |
| №11    | n/d              | 0.004            | n/d          | 0.004        | n/d              | n/d              | n/d              |
| №12    | n/d              | 0.017            | 0.001        | 0.001        | n/d              | n/d              | 0.002            |

4. Conclusion

Based on the research, we can conclude the following:

In all sources examined the water is fresh and very soft.

In all springs the water belongs to the bicarbonate class and calcium, or sodium, or mixed group, with the exception of the water of spring №10 belonging to the chloride class and sodium group.

The water from all springs meets the requirements of sanitary standards and regulations for chemical indices, with the exception of the water from springs №№ 5, 8 (excess of the MPC of manganese ions) and №9 (excess of the MPC of manganese ions and PO).

The content of heavy metals except manganese is below the MPC, and it is safe for the health of rural population using the water from the springs for drinking purposes.

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