Monitoring of the use of underground water of the Leningrad region for drinking water supply

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Abstract. How closely humans and the environment are related to each other is especially evident in the case of groundwater. The causes and extent of damage are difficult to determine in groundwater, processes are difficult to control, and remediation work is often tedious and successful only in the case of locally limited damage. This article examines the current state of groundwater monitoring in the Leningrad region in areas with a high population density and active use of land by humans. After all, almost any anthropogenic activity leads to a human impact on the environment. Intentional or accidental exposure can lead to groundwater contamination.

Six springs in the Vsevolozhsky district of the Leningrad region were analysed for ten indicators including chemical, organoleptic, and biochemical properties. Among them are pH, alkalinity, dissolved O₂, KMnO₄, nitrates, NH₄⁺, colour, smell, biochemical oxygen demand (BOD), and biotesting duckweed.

1. Introduction
Purification of contaminated groundwater is costly. Moreover, this water is a habitat for a previously unexplored diversity of organisms, the basis for the existence of wetlands, and an important part of the water cycle [1, 2].
Due to the replenishment of groundwater with rain, it is constantly reformed, but there is a layer of soil above it that protects it from pollution. But both are true only to a certain extent, and the amount and quality of groundwater are subject to constant pressure from outside [3, 4].

The purpose of this work is to draw as much attention as possible to the outlet points of underground water in the form of springs from which people take water, and do not think how pure this water is and how these objects are protected by the state.

2. Methods
During research work, six springs were selected in the Vsevolozhsky district of the Leningrad region for analysis for nine indicators including chemical, organoleptic, and biochemical properties. For the samples to be as representative as possible, two springs were selected in one settlement, so that water in both cases came from the same aquifer [5].

The pH of the acidity or alkalinity of water (the ratio in the water of H⁺ and OH⁻ ions formed during the dissociation of water) is quantitatively determined by the concentration of hydrogen ions. pH quantitatively characterizes the concentration of free hydrogen ions in water. pH was determined by the colorimetric method [6]. Alkalinity is the concentration of weak acid anions and hydroxyl ions in water (mmol/dm³). These anions react with hydrochloric or sulphuric acid to form sulphate salts or alkali and alkaline earth metals [7].
The release of oxygen into the reservoir occurs by dissolving it upon contact with air (absorption), as well as because of photosynthesis by water at atmospheric pressure, the degree of water turbulence, water salinity, etc. In surface waters, the content of dissolved oxygen can vary from 0 to 14 mg/dm$^3$. There is practically no oxygen in artesian water. The content of dissolved oxygen depends on temperature. The relative oxygen content in water, expressed as a percentage of its normal content, is called the degree of oxygen saturation. This parameter depends on the water temperature, atmospheric pressure, and salinity level and is calculated by the formula:

$$M = \frac{(a*0.1308+100)}{N*P}\ (1)$$

where $M$ – the degree of water saturation with oxygen, %; $a$ – oxygen concentration, mg/dm$^3$; $P$ – atmospheric pressure in a given area, MPa; $N$ – the normal oxygen concentration at a given temperature and a total pressure of 0.101308 MPa [8].

Oxidability is an indicator characterizing the content of organic and mineral substances in water, oxidized by a strong oxidizing agent. Oxidability is expressed in MgO$_2$ required for the oxidation of these substances, contained in 1 dm$^3$ of the investigated water [9].

Nitrogen compounds (ammonia, nitrites, and nitrates) arise mainly from protein compounds that enter the water along with wastewater. Ammonia present in water can be of organic or inorganic origin. Nitrite occurs mainly due to the oxidation of ammonia in water and can also penetrate it with rainwater due to the reduction of nitrates in the soil. Nitrates are a product of the biochemical oxidation of ammonia and nitrite, or they can be leached from the soil [10, 11].

Colour is primarily an indicator of water quality. The colour increases mainly due to the presence of humic and sulphuric acids in the water. Colour also depends on the number of iron compounds (Fe$^{3+}$). The amount of these substances depends on the geological conditions in the aquifers.

So, the highest colour is the surface waters of rivers and lakes located in the zones of peat bogs and swampy forests, the lowest is in the steppes and steppe zones. In winter, the content of organic matter in natural waters is minimal [12].

The smell is an indicator of the quality of water, determined by the organoleptic method using the sense of smell based on the odour strength scale. The smell of water is influenced by the composition of the dissolved substances, temperature, pH values, and many other factors. The intensity of the odour of water is determined by expert judgment at 20°C and 60°C and measured in points, according to the requirements [13].

Biochemical oxygen demand (BOD) is the amount of oxygen consumed for aerobic biochemical oxidation under the influence of microorganisms and the decomposition of unstable organic compounds contained in the test water [14].

The analysis determines the amount of oxygen that has gone in a set time (usually 5 days – BOD5) without access to light at 20°C for the oxidation of pollutants contained in a unit volume of water. The difference between the concentrations of dissolved oxygen in the water sample immediately after sampling and after incubation of the sample is calculated.

For bio testing, duckweed plants Lemna minor L are cultivated under constant light and temperature conditions and the composition of the growth mineral medium. The bio testing period is 7 days. The degree of toxicity is assessed through the average daily share of small duckweed growth and is calculated by the formula:

$$D = \frac{(B-A)}{A*t}\ (2)$$

where $A$ is the initial number of duckweed fronds in the sample, $B$ is a finite number of fronds, and $t$ is the growth time in days. The number of fronds in the samples is counted on the second, fifth, and seventh days of the test [15].
3. Results

3.1. Compounds of the nitrogen group

All measuring points show a nitrate concentration between 11.4 and 52 mg/dm$^3$, and therefore, 85% are not contaminated or slightly contaminated. In one of the two springs Toksovo No. 6, the content of nitrates was 52 mg/dm$^3$, in the neighbouring Toksovo No. 5 – 41 mg/l, which reveals some regularity. These measuring points are heavily contaminated with nitrates. With the content of ammonium cations, the same regularity was revealed at these points, the concentration for Toksovo No. 6 and Toksovo No. 5 was 3.45 and 2.43 mg/dm$^3$, respectively, which exceeds by 42 and 20% the maximum permissible concentration (MPC) according to SanPiN 2.1.4.1175-02 for drinking water [16]. Reasons for nitrogen infiltration into groundwater vary from point inlets, leaking sewers at Toksovo, and sludge and other storage tanks, through diffuse inlets from fertilizers. A comparison between the prevailing land use near the measuring point and the nitrate content of groundwater indicates where the main causes of penetration can be found [17].

The group of measurement points, near which forest dominates, usually has the lowest nitrate pollution. In two small settlements on the border of Rappolovo No. 3 and Sergi No. 4, nitrate concentrations are 13.7 and 20.6 mg/dm$^3$, and ammonium concentrations are 0.24 and 0.13 mg/dm$^3$, respectively. If forests dominate near the measuring points, the groundwater there is not affected by higher levels of nitrates. And if there are larger settlements near the measuring points, such as Toksovo or arable land, the proportion of measuring points with a nitrate content will more than double. It should be noted that in the springs Murino No. 1 and Novoe Devyatkin No. 2 the above-described indicators were not exceeded. It would seem that these two springs are close to St. Petersburg, but both points are protected from any anthropogenic influences, appropriate signs have been installed. Chemical indicators of points Murino No. 1 and Novoe Devyatkin No. 2 are presented in Table 1.

### Table 1. Chemical indicators of points Murino No. 1 and New Devyatkin No. 2.

|                      | pH  | Alkalinity, mg/dm$^3$ | O$_2$ dissolved, mg/dm$^3$ | KMnO$_4$, mg/dm$^3$ | Nitrates, mg/dm$^3$ | NH$_4^+$, mg/dm$^3$ | Colour, degrees | Smell, points | BOD, mg/dm$^3$ | Biotesting duckweed, toxicity criterion |
|----------------------|-----|-----------------------|-----------------------------|--------------------|---------------------|--------------------|----------------|--------------|----------------|------------------------------------------|
| Murino No. 1         | 7.1 | 0.9                   | 7.44                        | 1.44               | 11.4                | 0.39               | 8.67           | 0            | 1.84           | No, dead 0                                |
| Novoye Devyatkin No. 2 | 6.8 | 1.2                   | 8.62                        | 2.46               | 23.7                | 0.23               | 4.2            | 0            | 0.76           | No, dead 1                                |
| Threshold limit value | 6-9 | no standard           | 14                          | 5-7                | < 45                | < 30               | < 1-2           | 3            | < 20 %          |                                          |

3.2. Permanganate oxidisability

Organic and mineral substances are found naturally in groundwater. Usually, surface waters, in contrast to underground ones, contain significant concentrations of organic and mineral substances. Their composition can be formed by completely different properties, ranging from anthropogenic impact in the form of discharges from household and industrial enterprises, ending with the flow of surface water and precipitation. First of all, permanganate oxidisability is characterized by the total ratio of organic and mineral substances in the test water. This indicator is widely used in laboratories and potassium permanganate is used as a strong oxidant. In the already familiar springs Toksovo No. 6 and No. 5, the permanganate oxidisability indicators are also exceeded and are equal to 7.34 and 7.45, respectively. It can be concluded that both springs are not potable, because several indicators exceed the MPC according to SanPiN 2.1.4.1175-02 [7]. At the same time, it is worth mentioning that the BOD-5...
at both points does not go beyond the MPC, but in terms of indicators, this water is classified as “moderately polluted”. It should be noted that all 6 points were also tested for organoleptic indicators: colour, taste, and smell, and biochemical indicators: BOD-5 [14] and bio testing by Ryaska [15]. The excess of the MPC was not found, except for the bio testing indicator Ryaska [15]. For Toksovo No. 6, more than 10 % of the sheets died off per day.

Chemical indicators of points Syargi No. 3, Rappolovo No. 4, Toksovo No. 5, and Toksovo No. 6 are presented in Table 2.

Table 2. Chemical indicators of points Syargi No. 3, Rappolovo No. 4, Toksovo No. 5, and Toksovo No. 6.

|          | pH | Alkalinity, mg/dm³ | O₂ dissolved, mg/dm³ | KMnO₄, mg/dm³ | Nitrates, mg/dm³ | NH₄⁺, mg/dm³ | Chromatity, degrees | Smell, points | BOD, mg/dm³ | Biotesting duckweed, toxicity criterion |
|----------|----|--------------------|----------------------|--------------|----------------|--------------|--------------------|--------------|------------|----------------------------------------|
| Syargi No. 3 | 7.4 | 1.8                | 7.28                 | 1.76         | 13.7           | 0.24         | 8.7                | 0            | 1.27       | No, dead 2                               |
| Rappolovo No. 4 | 7.0 | 0.6                | 7                    | 0.96         | 20.6           | 0.13         | 4.3                | 0            | 1.44       | No, dead 0                               |
| Toksovo No. 5  | 8.2 | 1.1                | 7.34                 | 7.45         | 41             | 2.43         | 35                 | 2, earthy    | 2.39       | No, dead 4                               |
| Toksovo No. 6  | 7.5 | 1.4                | 6.22                 | 7.34         | 52             | 3.45         | 32.5               | 1            | 2.76       | Yes, dead 6                              |

4. Conclusion
The main identified groundwater pollutants in the Leningrad Region are nitrogenous compounds. The input of nitrogen compounds through agriculture affects the quality of water, this problem is encountered everywhere in the Leningrad region. The sources of groundwater pollution primarily include agricultural land, industry, and households. Organic farming aims to avoid the release of substances from agriculture into groundwater and surface water. This is achieved by banning the use of chemically synthetic pesticides. Even in your garden, the absence of chemical pesticides, biocides, and the economical use of fertilizers helps to avoid contamination of groundwater. The tendency is that the water from the springs within the city limits is cleaner in chemical indicators than in the settlements of the Leningrad region, where there are common houses with gardens and vegetable gardens, as well as pastures and industrial agricultural land. It is also worth mentioning that wastewater seeps into the soil and groundwater from leaking pipes and collecting pits if they are above the water table. Then there is a risk of groundwater contamination. For example, cracks in containers or pipes, ingrown roots, damaged and leaking pipes can cause leaks. It is important to remember that the proper operation of sewer pipes operating in a private area is the responsibility of the respective property owner.

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