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Original Research

Peculiarities of Statistical Water Quality Assessment in an Industrial Region

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Abstract

The aim of the work is to investigate water quality in the industrial region of the Ural (Russia) according to the main parameters. The study was conducted in 2021 in 10 cities of the Sverdlovsk region. Water samples were taken from artesian wells and centralized water supply systems. Water samples were tested for pH value, hardness, mineralization, nitrate concentration, and the content of heavy metals (voltammetry method). A high content of nitrates was established for 2 towns: Verkhnyaya Pyshma ($p\leq0.05$ to the norm) and Degtyarsk (3 times more than the norm, $p\leq0.01$). In terms of cadmium concentration, water samples from Nizhny Tagil and Degtyarsk are 8 times the norm ($p\leq0.01$), from Bogdanovich - 4 times ($p\leq0.05$), from Serov - 6 times ($p\leq0.01$), from Kamensk-Uralsky - 10 times ($p\leq0.001$). In terms of lead concentration, samples from 5 cities are 1.2-1.5 times higher than the norm ($p\leq0.05$), from Serov - 7 times higher ($p\leq0.01$), and from Yekaterinburg - 2.5 times higher ($p\leq0.05$). Most (6 of 10) cities have shown high levels of water pollution by heavy metals.

Keywords: cadmium, heavy metals, lead, industrial region, water

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Introduction

Water is one of the necessary conditions for life on Earth. Water is a component of the hydrosphere and is among the most important abiotic factors on the planet, providing the environment for living organisms, as well as the opportunity for metabolic processes and chemical reactions. In the last half-century, there has been an increasing human impact on the environment, including the hydrosphere [1]. The consequence of this is the critical state of the biosphere according to several experts [2, 3]. At the same time, most of the water bodies cannot be restored. This is typical not only for developed industrialized countries, as the processes occurring in the biosphere are global and interconnected [4]. Russia is no exception, which has one of the largest reserves of fresh water in the world. About 70% of the studied water bodies are not suitable for use as drinking water resources. It is worth noting that in industrialized areas the effect of pollution is manifested to the greatest extent, affecting both public health and the biosphere [5]. This is shown in the examples of developed industrial regions of Asia, America, and Europe [6-8]. When industrial regions are properly restored, as was done in the Ruhr coal basin, Germany, ecosystems as well as water purity indicators come back to normal. To meet these conditions a combination of several factors is required: the absence of active industrial facilities and properly organized recreational and ecological activities [9]. In those regions where industrial activity continues, the load from enterprises, transport, as well as mineral development is a determinant of the negative changes in the hydrosphere at the local level. The same factors include agricultural waste (fertilizers, organic matter, etc.) [10]. In addition, a considerable share of pollution is due to domestic waste (sewage, etc.). In developing countries, this factor becomes particularly relevant, because often the sewerage network is represented by worn-out pipes [4, 5].

Among the most significant agents of pollution that can cause severe pathological diseases in humans are heavy metals, as well as various compounds of organic origin. They also include nitrates and radionuclides. Pathogenic bacteria, which are dangerous pathogens of infectious diseases, may be present in groundwater [11]. Therefore, when drinking water that contains contaminants and pathogenic microorganisms for a long time, diseases and even epidemics are possible.

In the work [12] authors showed that the number of pathogenic bacteria increases in industrial waters. The author of the work [13] showed the number of pathogens in wastewater [L^{-1}] in different countries (Table 1).

Table 1. Reported numbers of pathogens in wastewater [L^{-1}].

Pathogen	Range	Country
Bacteria		
Salmonella spp.	930-110,000 8,900-290,000	Finland Germany
Campylobacter spp.	500-4,4·10^6 16,300	Germany Italy
Enteric viruses		
Enteroviruses	100-10,000	Italy
Rotavirus	<1-10,000	Netherlands
Norovirus	<1,000-1,6·10^6	Germany
Adenovirus	250-250,000	Spain
Protozoa		
Giardia cysts	1,100-52,000 100-9,200	Scotland Canada
Cryptosporidium oocysts	<20-400 1-560	Scotland Canada

We can conclude that number of pathogens varies from <1 to 1.6·10^6 L^{-1}.

It follows from the above that directed and unregulated discharge of pollutants into waters and on the surface of landscapes can significantly worsen their sanitary condition [14]. In particular, as shown in several studies, enterprises of the mining and industrial complex may be the main factor of pollution in some regions [8, 9]. This is exacerbated by the fact that often the main source of drinking water for the local population is artesian wells, which receive pollutants from groundwater. As for surface water, most often it is used by the population both for domestic needs and for recreation (bathing) or fish breeding. Because in such regions heavy metals act as the main pollutants, they can enter the human body directly from water, or the tissues of animals consumed in food [15].

HPI (heavy metal pollution index) is one of the water quality index methods that provide insight into the composite influence of heavy metals on the total water quality which is based on the unit-weighted arithmetic mean method [16].

$$HPI = \frac{\sum_{i=1}^{n} w_i Q_i}{w_i} \quad (1)$$

Unit weight (w_i) for each parameter is calculated as a value inversely proportional to the standard value (s_i) prescribed by BIS [17] of the corresponding parameter [18].

$$Q_i = 100\left(\frac{v_i - v_0}{s_i - v_0}\right) \quad (2)$$

Where v_i – monitored the value of the i-th parameter in the water sample, v_0 – the ideal value of the parameter, and s_i – the recommended value of the i-th parameter. The standard and ideal values given by BIS are taken as s_i and v_0 values respectively (Table 2).

W_i is the unit weight for each parameter is calculated by the formula:

Table 2. Standard values used for the calculation of HPI.

Metals	Standard value s_i	Ideal value I_i	Unit weigh w_i
Pb	0.01	-	100
Co	0.009	-	111.11
Zn	15	5	0.0666
Cu	1.5	0.05	0.0666
Ni	0.02	-	50
Cr	0.05	-	20
Cd	0.003	-	333.33

$$w_i = \frac{1}{s_i} \quad (3)$$

Based on the HPI values, the water source can be classified as low (<15 HPI), medium (15-30 HPI, high (>30-100 HPI) and critical (>100 HPI) pollution class [19].

Further, along the trophic chains, heavy metal ions enter the human body. It is known that there are more food levels in the aquatic trophic chain compared to land trophic chains. One of the key elements of the trophic chain in aquatic ecosystems is macrophytes. In particular, macrophytes are the basis for feeding various hydrobionts, which form the basis for the diet of fish as well as birds that feed in water bodies. In addition, macrophytes can form the basis of the diet of some fish species, which are fed by predatory fish. Getting into the tissues of fish, ions of heavy metals and their compounds, enter the cycle and move through the trophic chains to people who feed on fish. The danger is exacerbated by the fact that during the transition to a new trophic level, the concentration values of pollutants increase by 1-2 orders of magnitude [20].

The above-mentioned factors determine the level of health not of individuals, but entire population groups living in industrial regions [21]. Therefore, the issues of studying water quality and ways of pollutants penetration into surface and ground waters remain extremely important. The direction of monitoring the state of water and its quality in such regions is also relevant. There are many works devoted to the problem of studying water quality [1-4], but for the region, under study (Sverdlovsk region of Russia) they are absent or presented fragmentarily. At the same time, a comparison of data on water quality from different regions of the planet will allow one to create a database, by which it will be possible to establish general patterns of movement of pollutants in the hydrosphere.

The purpose of the work was to study the quality of drinking water in one of the most industrialized regions of Russia – the Sverdlovsk region. The study objectives were a) to study indicators of pH, hardness, and acidity of water; b) to analyze the concentration of heavy metal ions and nitrates in tap water in water used from sources; c) to compare the indicators of water analyses with each other and draw conclusions about their possible toxicity.

Material and Methods

Research Region

The study was conducted in 2021 in the Sverdlovsk region of the Russian Federation. For the experiment, the authors selected 100 samples of water belonging to two types: water from the centralized water supply system and water used by people individually (i.e., from sources). Water was sampled from 5 locations, namely Yekaterinburg (the largest city of the region), and cities of regional importance - Nizhny Tagil, Kamyshlov, as well as Sukhoy Log and Kamensk-Uralsky. All cities are located in the industrial impact zone (in the Ural region for more than 200 years there is an active industrial activity (mining companies and metallurgical plants)). Five sites - Serov, Bogdanovich, Sysert, as well as Degtyarsk and Verkhnyaya Pyshma - were also selected as natural sources. The water extracted from these sources lay in aquifers at a depth of 30-50 meters.

Research Methods

For a complete assessment of water quality, the authors used the following parameters: a) pH; b) water hardness; c) water acidity parameter; d) nitrate concentration level; e) heavy metal (Pb, Cu, Cd) concentration level. The samples were studied at the analytical chemistry laboratory. The following standard methods were used: titrimetry, potentiometry, and inversion voltammetry. The first of the methods are designed to establish the exact concentration of a substance that reacts with the analyzed compound. Registration of the signal is established visually when a change in the coloring of the reagent indicator is manifested. The parameters of hardness and acidity were established using this method. Each determination was performed in parallel with three samples. The potentiometric method is based on the relationship between the potential of the electrode, which is the indicator, and the concentration of ions of the nitrates to be determined. For potentiometry, the authors used an ionometer (model PX 150) equipped with ion-selective electrodes. This method was used to determine the pH level as well as the concentration of nitrate anions.

To establish the level of concentration of heavy metal ions, the authors used the third method. It is based on the possibility of metal ions accumulation using deposition on the surface of a stationary type of electrode. Then, during polarization on the anode and the subsequent dissolution of the formed precipitate, the peak of the anode current indicators will be registered as an analytical signal. The higher the concentration level of heavy metal ions, the greater the signal parameters. As an analyzer, the authors used the Yves model, together with which a personal computer was connected, as well as an electrochemical cell of three electrodes. In addition, samples of the state standard showing components of aqueous solutions of heavy metals under study were used. The error at 0.95, in this case, was not more than 1 per cent, at a concentration level of 1 milligram per 1 cm^3. The authors chose the following steady-state conditions for the determination: -0.8 V (copper), -1.2 V (cadmium and lead) - concentration potential. The concentration-time was -1.0 V at 1 second. Each registration was performed two to three times. The analytical signal of the sample with the additive was recorded in the same way as the analytical signal of the sample.

Statistical Analysis

Statistical processing of the data was performed using the program Statistica, version 10.0. The authors calculated the arithmetic mean for each of the studied parameters, and plotted the dependencies of electrode potentials and differential voltammetry. The obtained values for the parameters from different points were tested using Student's t-test for independent samples. The obtained differences are reliable at $p \leq 0.05$.

Results

To establish the level of nitrate anions in the studied samples, the authors used the measurement of potential values at the electrodes in several standard analytical solutions of potassium nitrate. The obtained data series became the basis for plotting the dependence E = f (1 g **C** KNO_3). This is shown in Fig. 1.

As the concentration of the standard solution increases, the electrode potentials decrease (Fig. 1). More detailed results on the characteristics of water are given in Table 3.

According to the data in Table 3, in all selected samples reaction indicators were within the norm

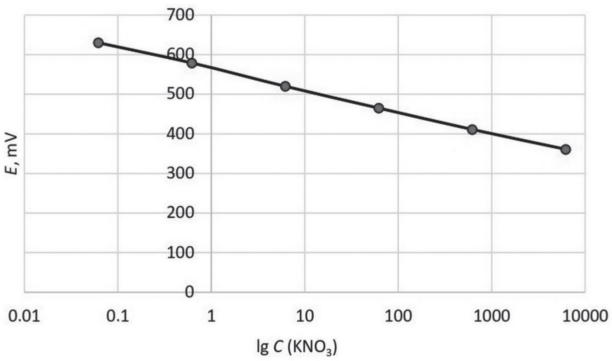

Fig. 1. Correlation between the value of the electrode potential and the concentration of nitrate anions in potassium nitrate solution of different concentrations.

($p \geq 0.05$, obtained values with the norm). At the same time, at least two points recorded elevated levels of nitrate anions, these are Verkhnyaya Pyshma ($p \leq 0.05$ with the norm) and Degtyarsk (exceeds the normal values 3 times, $p \leq 0.01$). This may be a consequence of the constant contamination of groundwater with nitrate anions because there is a migration from the overlying layers of fertilizers containing nitrogen in the soil. Such fertilizers are applied at dacha plots close to settlements as well as at agricultural fields. The average depth of a well in the Degtyarsk location is 30 meters, so there is insufficient protection of the aquifer from penetration of nitrogen fertilizers from the surface and near-surface layers. In addition, a significant role in the ingress and accumulation of nitrate anions belongs to acidic precipitates, which contain nitric acid. The latter readily dissolves salts formed by weaker acids, such as carbonates or sulfites.

Elevated values were established for the parameter of hardness in the same location (1.1-1.5 times higher than normal, $p \leq 0.05$, Table 3). This is the norm for waters that belong to the class of hydrocarbonate, with calcium and magnesium impurities. The presence of the latter is associated with the features of soil-forming rock composition, located in the places of drilling artesian wells. Limestone rocks make the main contribution to the hardness.

According to the indicators from the Kamyshlov location, temporary hardness is 2 times higher than permanent (Table 3, $p \leq 0.05$). However, the concentration values of hydroxide anions are the same as those of calcium and magnesium. The authors believe that the high concentration of hydroxide anions is associated with the presence of softener substances in the water, which contain hydroxyl groups, when reacting with water, passing into the solution as OH ions. From this one can conclude that the study of the parameter of temporary water hardness in samples from the centralized water supply is not always adequate, and a more appropriate parameter can be general hardness.

In terms of acidity, the studied water samples corresponded to normal levels (Table 3). The exception was the samples from Nizhny Tagil, where an extremely unfavorable situation is recorded. In most of the samples, there were organic pollutants in the water, which could have entered there as a result of an accidental inflow of sewage into the water intake point or the high level of organic contamination of the water body itself. Another reason could be the high degree of wear and tear of the wastewater treatment plant. For Nizhny Tagil, due to the high degree of industrialization, the presence of petroleum products, surfactants, various phenols, and heavy metals is recorded.

Fig. 2 indicates that the recording of the analytical response of Pb falls at a potential value of -0.42 V when an aliquot of the sample is added to the electrolyte serving as the background. An interesting feature is that there is no signal from cadmium when the standardized additive is applied and appears only when a solution

Table 3. pH values, temporary and permanent hardness values, nitrate concentrations and acidity in the studied water samples.

Sample location	pH values	Norm	Concentration of nitrate anions, mg per 1 dm^3	Norm	Temporal hardness, mmol/dm^3	Total hardness, mmol/dm^3	Norm	Acidification, mg/dm^3	Norm
1	7.30	6.0–9.0	5.60	45.0	1.36	2.48	7.0	5.57	5.0
2	6.92		3.18		0.91	1.45		**7.88**	
3	7.35		**46.7**		1.03	1.67		1.09	
4	7.25		15.8		1.11	3.85		4.28	
5	7.90		**155.2**		1.22	**7.59**		4.97	
6	7.46		1.26		**7.05**	**10.27**		3.19	
7	7.18		40.1		1.27	2.19		1.78	
8	7.43		15.9		1.88	2.54		5.74	
9	7.17		9.2		**6.29**	2.81		3.07	
10	7.67		3.0		1.64	2.43		4.79	

Symbols. 1 - Sysert, 2 - Nizhny Tagil, 3 - Verkhnyaya Pyshma, 4 - Sukhoy Log, 5 - Degtyarsk, 6 - Bogdanovich, 7 - Serov, 8 - Kamensk-Uralsky, 9 - Kamyshlov, 10 - Ekaterinburg. The values that do not correspond to the norm are highlighted in bold.

of ions of this metal is applied. Table 4 shows the results of studying the concentration of heavy metals in selected water samples.

According to the data obtained, the concentration of copper cations in the water samples corresponds to the standards included in the drinking water characteristics (Table 4, $p \geq 0.05$). On the other hand, a number of samples taken from locations contain concentrations of lead and cadmium that exceed the norm. For lead, such exceedance was fixed in 6 locations out of 10, for cadmium - in 5 (Table 4). This is characteristic for both water samples taken from artesian wells and for water samples taken from centralized water supply systems. Among centralized water supply systems, samples from the following locations are the most contaminated with heavy metals: Kamensk-Uralsky, Nizhny Tagil, Yekaterinburg, and Kamyshlov. Among the samples taken from artesian wells, Degtyarsk, Serov, and Bogdanovich were the most contaminated with heavy metals. As for cadmium content, water from Nizhny Tagil and Degtyarsk exceeded the norm 8 times ($p \leq 0.01$), from Bogdanovich - 4 times ($p \leq 0.05$), from Serov - 6 times ($p \leq 0.01$), and from Kamensk-Uralsky - 10 times ($p \leq 0.001$). Samples from Nizhny Tagil, Kamensk-Uralsky, Kamyshlov, Bogdanovich, and Degtyarsk were 1.2-1.5 times ($p \leq 0.05$) higher than

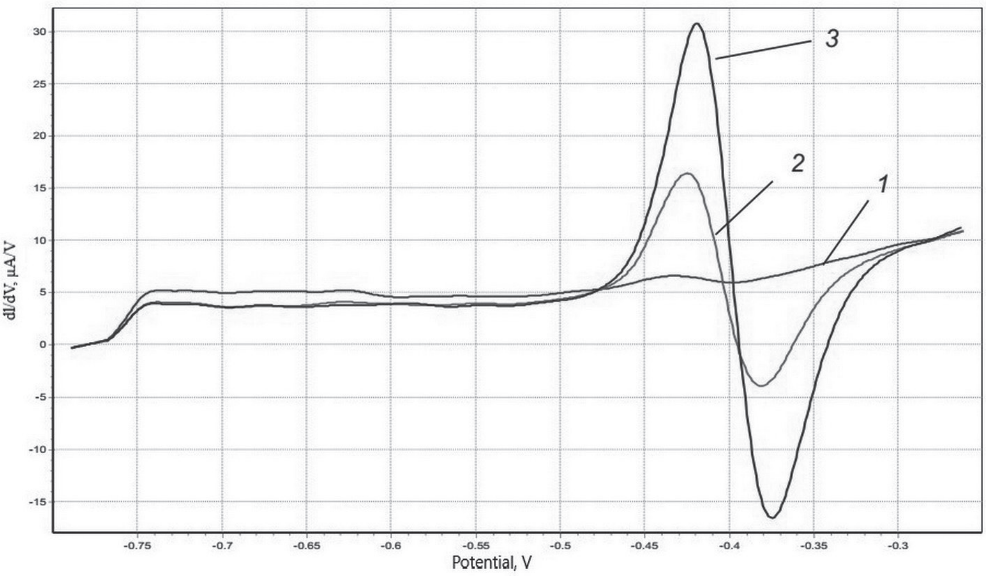

Fig. 2. Example of anodic voltammetry of Pb. Notes: 1 - background (hydrochloric acid, concentration 0.1 mole per 1 dm^3); 2 - 2 cm^3 of the studied water sample, Kamensk-Uralsky location; 3 - standardized additive of divalent lead ions (20 micrograms per 1 dm^3).

Table 4. Concentrations of heavy metals (Cu, Pb, Cd) in selected water samples from different locations.

Sampling location	Copper	Norm	Lead	Norm	Cadmium	Norm
1	0.039	1.000	0.008	0.030	none	0.001
2	0.009		**0.049**		**0.008**	
3	0.025		0.014		none	
4	0.016		0.008		none	
5	0.008		0.018		**0.008**	
6	0.018		**0.047**		**0.004**	
7	0.006		**0.207**		**0.006**	
8	0.013		**0.056**		**0.010**	
9	0.009		**0.039**		none	
10	0.056		**0.081**		none	

Note. Locations are numbered as in Table 3. Bold font indicates values that do not correspond to the norm.

the norm for lead content, from Serov - nearly 7 times ($p \le 0.01$), from Yekaterinburg - 2.5 times ($p \le 0.05$).

Discussion

In most agricultural regions of the world where there is no heavy industry, the main pollutants are nitrate anions, which are formed due to the application of nitrogen fertilizers to the soil [22]. These pollutants are major not only in surface water but also in groundwater. Agricultural waste collectors can also be a source of pollution to a no lesser extent [23]. In the studied region, agricultural sources of pollution are not the main, ones as was shown by the concentration of nitrate anions and heavy metal cations. It is the latter (cadmium and lead) that dominated among pollutants.

Both lead and cadmium, according to some reports, are the main sources of pollution among metals [24, 25]. Their accumulation in the body can lead to irreversible pathological processes, which are expressed in disorders of the functioning of organ systems, as well as in the violation of the entire homeostasis of the body [26].

Industrial plants, such as Uralvagonzavod, metallurgical plants, and non-ferrous metal production plants, are located on the territory of these settlements. In addition, Degtyarsk has many waste heaps, which are sources of pollution with heavy metals and radionuclides. Pollution occurs due to the formation of mine water, which has an acidic reaction. This leads to an ecological catastrophe on local scale. Pollution by industrial emissions leads to the accumulation of heavy metals in the soil, resulting in the formation of local anomalies affecting the geochemical processes in the soil, the result of which is the pollution of both surface and groundwater. Heavy metal ions from slag dumps and spoil tips are dissolved in precipitation water, which has an acidic reaction, and then through rock layers enter groundwater [27, 28]. Secondary pollution occurs due to heavy metal ions from groundwater through upward filtration flows back into surface water [29]. Industrial wastes in developed Western countries are usually discharged into special settling tanks with high-quality filters, wastewater undergoes multistage treatment and filtration [30]. In the Ural region under study, the discharge is often direct, straight into water bodies, from which water is withdrawn. Another option is the use of already used or obsolete filters, which do not adequately treat the wastewater from factories and plants. Therefore, as a recommendation, priority should be given to the replacement of existing filters, this will significantly reduce the burden on the environment. The main mass of groundwater in the Ural does not belong to the artesian, passing in cracks and veins of rocks. Therefore, they have a close connection with waters coming from the surface, including precipitation from the atmosphere. The chemical composition of such waters depends on anthropogenic influence and is associated with plowing and agricultural land, with a decrease in the forest area.

Table 5. Maximum concentration limit of heavy metals.

Heavy metals	Maximum concentration limit (mg/l)
Arsenic (As)	0.01
Lead (Pb)	0.015
Copper (Cu)	1.30
Mercury (Hg)	0.002
Chromium (Cr)	0.01
Zinc (Zn)	5.00
Nickel (Ni)	0.01
Cadmium (Cd)	0.005

We can conclude that number of heavy metals in investigated industrial wastes is similar to those in foreign countries [31]. In Table 5 there is a maximum concentration limit of heavy metals in foreign countries.

As is known, pH determines the normal homeostasis of the organism [32]. In the locations studied, no significant deviation was found for these indicators. On the other hand, such deviations were found for water hardness indicators, in particular for the concentration of potassium and magnesium salts. In the case of high concentrations of these salts, serious problems with the digestive and excretory systems of the body may arise [33, 34]. Still, the most significant factor present in many of the investigated locations is the increased concentration of heavy metals, which are characterized by increased toxicity, which has already been shown earlier [35]. This pollution is caused by industrial activities in the Ural region.

Conclusions

As a result of the analysis, it was found that most of the water samples from the industrial region of the Ural do not meet drinking water standards.

The main result of the impact of industrial enterprises in the Ural region is a high concentration of heavy metals, particularly lead and cadmium. Increased concentrations of these metals were found in the waters of 7 locations, in 6 of them these concentrations exceeded the norm 2 or more times. This may be a consequence of increased soil contamination, as a result of the activities of metallurgical and machine-building plants. Both solid and liquid wastes enter the soil. In water samples taken from centralized water supply systems, the contamination present was due to the heavy wear and tear of the pipes. An average assessment of the quality of artesian and tap water samples in the Sverdlovsk region led to the conclusion about the unsatisfactory condition of drinking water in this industrial region. The present study data can be used as a basis for recommendations to improve the situation in the region, which is close to an ecological disaster. Undoubtedly, poor water quality can lead to an increasing number of diseases among the population. The practical value of this study is the possibility of determining the patterns of pollution by heavy metals in the inefficient operation of sewage treatment plants. The results can be used to create a database of regions with a similar level of industrial load and level of development of sewage treatment plants. This will help give a more detailed picture of how pollution occurs, its main objects, and which elements are the most toxic to the environment (biota). The data obtained can help a comprehensive analysis of the causes of pollution, as well as to develop ways to prevent or further pollution. For more detailed results, it is necessary to focus on pollution causes.

Conflict of Interest

The authors declare no conflict of interest.

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