PERIÓDICO TCHÊ QUÍMICA
ARTIGO ORIGINAL

ÍON SULFATO EM ÁGUAS SUBTERRÂNEAS DA BACIA DO RIO MAYMA (ALTÁI DO NORTE, RÚSSIA)

SULFATE ION IN THE GROUNDWATER IN THE BASIN OF MAYMA RIVER (NORTHERN ALTAI, RUSSIA)

СУЛЬФАТ-ИОН В ПОДЗЕМНЫХ ВОДАХ БАССЕЙНА Р. МАЙМА (СЕВЕРНЫЙ АЛТАЙ, РОССИЯ)

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RESUMO

A relevância do problema investigado é que a maioria da população mundial sofre com a falta de água potável. Uma parte significativa da água na superfície da Terra é caracterizada por baixa qualidade e não é adequada para uso doméstico. É por isso que é importante investigar as causas das mudanças na composição qualitativa da água e encontrar maneiras de influenciá-la. O objetivo do artigo é estudar o conteúdo de íons sulfato nas águas do norte de Altái pelo exemplo da bacia do rio Mayma. Os dados foram analisados de duas fontes diferentes em dois laboratórios para obter resultados mais precisos. O estudo mostrou que o conteúdo de íons sulfato na água é influenciado por fatores como precipitação, características geológicas, características da paisagem. Diferentes condições de temperatura e umidade em diferentes épocas do ano também afetam esse indicador. Gelo e neve congelados podem acumular íons sulfato criados por fatores antropogênicos e, consequentemente, durante o derretimento, os íons sulfato caem nas águas subterrâneas e nas águas dos rios. O indicador estudado também é afetado pela temperatura do ar e da água subterrânea, cujo aumento pode ser causado por terremotos. Devido ao grande número de fatores que afetam o conteúdo do íon sulfato na água, é bastante difícil determinar a causa exata de flutuações significativas. Portanto, o trabalho comprova a importância de uma análise abrangente dos materiais factuais e do estudo de todos os fatores acima. Os materiais de artigos podem ser úteis no estudo adicional da composição qualitativa das águas de Altái do Norte, bem como em sua aplicação prática para melhorar a composição da água potável.

Palavras-chave: *composição qualitativa da água, precipitação atmosférica, água potável, terremotos nas montanhas, fator antropogênico.*

ABSTRACT

The relevance of the investigated problem is that the majority of the world's population suffers from a lack of drinking water. A significant part of the water on the surface of the Earth is characterized by low quality and is not suitable for home use. That is why it is important to investigate the causes of changes in the qualitative composition of water and find ways to influence it. The aim of the article is to study the content of sulfate ion in the waters of Northern Altai by the example of the Maima river basin. The data was analyzed from two different sources in two laboratories for more accurate results. The study showed that the content of sulfate ions in water is influenced by such factors as precipitation, geological features, landscape features. Different temperature and humidity conditions at different times of the year also affect this indicator. Ice and snow can accumulate sulfate ions created by anthropogenic factors, and, accordingly, during melting, sulfate ions get into groundwater and river waters. The studied indicator is also affected by air temperature and groundwater temperature, the increase of which can be caused by earthquakes. Due to the large number of factors affecting the content of sulfate ion in water, it is rather difficult to determine the exact cause of significant fluctuations. Therefore, the work proves the importance of a comprehensive analysis of factual materials and the study of all

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of the above factors. Article materials can be useful in further studying the qualitative composition of the waters of the Northern Altai, as well as for their practical application to improve the composition of drinking water.

***Keywords**: qualitative composition of water, precipitation, drinking water, mountain earthquakes, anthropogenic factor.*

АНОТАЦИЯ

Актуальность исследованной проблемы состоит в том, что большинство населения планеты страдает от недостатка питьевой воды. Значительная часть воды на поверхности Земли характеризуется низким качеством и не подходит для домашнего употребления. Именно поэтому важно исследовать причины изменения качественного состава воды и найти способы влияния на него. Цель статьи заключается в исследовании содержимости сульфат иона в водах Северного Алтая на примере бассейна реки Майма. Был произведен анализ данных из двух разных источников в двух лабораториях для большей точности результатов. Исследование показало, что на содержание сульфат ионов в воде влияют такие факторы, как атмосферные осадки, геологические особенности, особенности ландшафта. Разный режим температуры и влажности в разные времена года также влияют на данный показатель. Замерзший лед и снег могут аккумулировать сульфат ионы, создавшиеся антропогенными факторами, и, соответственно, во время таяния, сульфат ионы попадают в подземные воды и воды рек. На изучаемый показатель влияет также температура воздуха и температура подземных вод, повышение которой может быть связано с активизацией сейсмической деятельности. В связи с большим количеством факторов, влияющих на содержание сульфат иона в воде, определить точную причину значительных колебаний достаточно сложно. Поэтому работа доказывает важность комплексного анализа фактических материалов и исследования всех вышеперечисленных факторов. Материалы статьи могут быть полезными при дальнейшем изучении качественного состава вод Северного Алтая, а также для практического их применения для улучшения состава питьевой воды.

***Ключевые слова**: качественный состав воды, атмосферные осадки, питьевая вода, горные землетрясения, антропогенный фактор.*

1. INTRODUCTION

As noted by V. I. Vernadsky: "Throughout the geological history, we observe a very close connection between water and life, both in the aquatic environment and on land" (Vernadsky, 2003). Natural waters (underground and surface) are needed in various sectors of the national economy and the industrial sector. Up to 68% of surface and 32% of GW are used for household purposes (Danilov-Danilyan *et al*., 2005). According to some American scientists, in 2015, almost half of the world's population (3 billion people) will live in countries experiencing water shortages (Danilov-Danilyan *et al*., 2005; Trofimov *et al*., 2000; Yazvin, 2003). Therefore, today much attention is paid to the study of the quality of water suitable for household purposes.

Noteworthy is the statement of some researchers (Jaramillo and Destouni, 2014) that "the individual and cumulative effects of various factors of changing water resources are still difficult to distinguish and are largely unknown, especially on a global scale." In this paper (Jaramillo and Destouni, 2014), data of 859 hydrological basins for the period 1901-2008 were analyzed. The world spectrum of various sizes and directions of changes in the Budyko space (Budyko, 1980) was studied, from which climatic and landscape drivers are pointed out, for example, changes in land use and water use, which are necessary to explain at least in 74% of the basins studied (Kiryukhin *et al*., 1998). The impact of such landscape factors on the change in water resources is basically the opposite of the effects of atmospheric climate change, according to the authors of the work (Jaramillo and Destouni, 2014). An important component of the study of natural waters is their chemical composition.

Mountains are an important component of the nature of the Earth. Most often, they are a gravity drain area for adjacent aligned spaces, which leads to the study and monitoring of the dynamics and composition of the natural waters of mountainous countries. The work (Tague and Grant, 2009) considers the dynamics of GW in the Alps due to climate change. Landscape and climatic features in the Alps determine the patterns of snow cover formation, which affects the hydrological and hydrogeological regime of natural waters.

The relationship of land use, topography, composition of rocks and composition of PS was considered in the work (Schot and Van der Wal, 1992), where it was pointed out that intensive anthropogenic impact provokes oxygen depletion and subsequent low oxidation-reduction potentials that lead to denitrification, dissolution of manganese and iron oxides and changes in the content of sulfates. Thus, the study of the dynamics and composition of the GW is today conducted in different regions and at different levels (Robertus, 2010). The Republic of Altai is no exception.

In the Republic of Altai, almost one third of the exploited natural water provides drinking needs (Roldugin *et al*., 2018; Report on the stat, 2016). The largest consumer of this type of water is the city of Gorno-Altaisk and two large villages (Mayma and Kyzyl-Ozek). These settlements are located in the valley of Mayma river which is the right tributary of Katun river (Figure 1). The purpose of this work is to study the content of sulfate ion in the natural waters of Northern Altai (using the example of the Mayma river basin).

2. MATERIALS AND METHODS

The paper presents the results of the analysis of data on the content of sulfate ion in natural waters, groundwater temperature and air temperature, as well as a seismic activity over the period 1999-2016. The use of a data complex from different sources and the results of the analysis of two laboratories makes it possible to compare and monitor the results obtained, which increases the reliability of the study.

The distance in a straight line between the outermost OP is about 20 km (Figure 1). The height of the study area varies from 260 to 450 m above sea level, which determines 190 m difference in elevation on the territory of 20 km. Modern research tools and graphics allow to visualize the main geomorphological features of the study area and get a general idea of the relief and the hydrological and transport network.

A long study of the geological structure of Gorny Altai revealed its main laws and features, which include a sharp transition from the mountains to the plains of Western Siberia – the "face" of Altai (Ryabchikov and Gvozdetsky, 1978). Maps (geological, minerals, etc.) of the new generation reflect minerogenic subdivisions identified on the basis of various types of geological analysis. The published materials indicate that the "ore cluster" assumed in the study area is "confined to terrigenous-carbonate and siliceous-terrigenous-carbonate formations of the Eskong Formation and the Barotal series. As a rule, ore minerals are associated with a fine impregnation of pyrite and cord-like excretions of organic material, indicating hydrogen sulphide contamination of sedimentation pools" (Fedak *et al*., 2011).

In the northern part of the study area (OP in Novaya St.), alluvial sediments of the r. Katun are water-bearing minerals (Figure 2, Table 1), which overlap the bedrock. The thickness of water-bearing deposits varies widely – from 10 meters on the slopes of the terraces to 42 meters in the coastal zone (Katz *et al.,* 1996). In the southern part, alluvial deposits of the Mayma river are the water-bearing minerals, whose power varies widely. The basin of the Mayma river, like the whole Northern Altai, is located in a zone of sharply continental climate. The average long-term air temperature in January is minus 13.8 ºC, in July it is 18.7 ºC according to the Gorno-Altai CHEM (Gorno-Altai Center for Hydrometeorology and Environmental Monitoring) (average for the period 1971-2000). During the same period, the average rainfall over the winter is 153 mm, during the spring it is 137 mm, the contribution of summer is 310 mm, and that of autumn is 140 mm.

The landscape diversity of the Maima District is relatively small. In total, 4 geoms are distinguished: bald peaks and subbald peaks; mountain taiga South Siberian; subtaiga South Siberian; forest-steppe south-siberian. On the territory of the region, groups of facies of the mountain-taiga South-Siberian group of geoms sharply predominate, among which the class of middle-mountain slope cedar and birch-larch middle-mountain and low-mountain facies is distinguished (Zhuravleva *et al.,* 2016), which are characteristic of the slopes of the ridges bounding Mayma river Landscape structure of the basin of Mayma river is reflected on the map, published in work by Zolotov (2012). The length of the river is 60 km (Ryabchikov and Gvozdetsky, 1978), almost half of which runs through residential areas.

3. RESULTS AND DISCUSSION:

3.1. The condition of ion sulfate in water nowadays

Sulfate ions are present in almost all surface and GW, belonging to the most important anions that determine the quality and class of water in all regions of the World (Peristaya *et al*., 2011; Kiryukin *et al*., 1988; Shvartsev and

Savichev, 2006). The content of this component in natural waters is not constant and varies under the influence of various factors (Report on the state…, 2016): from geographic location to the activation of seismic processes. Today, one of the most comprehensive lists of published results of hydrogeological and hydrochemical works performed in the Republic of Altai is given in (Katz *et al.,* 1996). The number of works devoted to various aspects of the chemical composition of natural waters increased after the strong earthquake of 2003.

The data on OP in Novaya street show that the difference between the minimum and maximum content of sulfate ion is 38%, which is not surprising as the number of samples is small (Figure 2). However, this number is still significant and should have a justification. The following factors were considered as environmental factors that may affect the content of sulfate ion: precipitation (Tague and Grant, 2009); geological features (Tague and Grant, 2004); landscape features (Jaramillo and Destouni, 2013; Jaramillo and Destouni, 2014). The correlation of precipitation in the year of testing with the content of sulfate ion was-0.4 (Spearman's correlation coefficient). The indicator of non-parametric statistics was used because of the small amount of data, which makes it impossible to use parametric analysis methods. According to these data, it is possible to talk about the tendency to reduce the sulfate ion content.

3.2. The influence of temperature

Features of the temperature and humidity regime of the study area consist of uneven precipitation at different periods of the year (Sukhova, 2009). This preconditions the analysis of precipitation during the winter (Figure 2) and the summer period of the year.

The relationship between the content of sulfate ion and the external environment consists of reducing the sulfate ion content in the years of high snow cover, which causes a smaller depth of soil freezing and a greater amount of melt water that penetrates to different depths in different parts of the basin. At this point of observation, no correlation was recorded between the amount of precipitation in the summer period and the content of sulfate ion in the groundwater. In the course of the work, there was a tendency of a closer connection of the sulfate-ion content with the amount of winter precipitation compared to the air temperature. This does not contradict the basic laws of the behavior of meltwater and GW in the conditions of Siberian mountains, as well as the results of the analysis of data of another OP – a well in Severnaya street. It is located at the foot of Tugaya mountain in the city of Gorno-Altaisk. The well section is illustrated in Table 1.

The monitoring of chemical elements content, water temperature and radon activity were adjusted here. This OP is characterized by the largest amount of data compared to the rest of the network. Regime observations were started in January 2004. Using the entire array of accumulated data, the correlation coefficients were calculated (Table 2).

3.3. Seismic and radon activity

Correlation coefficients were obtained between: the content of sulfate ion and the amount of precipitation – minus 0.18; sulfate ion content and radon activity of 0.14; sulfate ion content and seismic activity of 0.39. The latter provided a basis for studying the relationship between the content of sulfate ion and seismic activity in the time interval immediately following the strong earthquake of 2003 with the epicenter in the South-East Altai – for the period 2004-2006. The correlation coefficient for this period of time showed a higher value – 0.42. The result obtained is consistent with the data from a study of the hydrochemical effects of the earthquake on December 23, 2003 in the south-eastern part of Iran (Malakootian and Nouri, 2010). Standard statistical methods established the most significant reaction of chemical compounds in the first year after the earthquake (Malakootian and Nouri, 2010).

The authors could not ignore the study of the relationship between seismic and radon activity according to the data from Severnaya street OP for the entire observation period. The authors of this work confirmed the trends identified in the course of the earlier study (Peristaya *et al.,* 2011; Katz *et al.,* 2015) and obtained a statistically significant correlation coefficient between these characteristics equal to 0.93.

The obtained data of the correlation analysis determined the interest in the water temperature dynamics in the well in Severnaya street (Figures 3, 4). The average water temperature in the well in 2004 was 35.7 ° C, in 2017 – 13.4 ° C. Dispersion analysis allows you to demonstrate the identified differences and prove their significance. Two peaks in the graph (Figure 4) indicate an abnormal temperature increase. The analysis showed the statistical significance of the first of them, which was conducted in 2004-2006.

To verify the significance of the peak temperature in the period 2011-2012 the temperature dispersion analysis was performed for the period 2007–2018. It is established that 2007 is also included in the period of an abnormal increase in water temperature. Its anomalous decrease in 2010 also draws attention. Perhaps this decrease in water temperature is due to the weather conditions. To test this hypothesis, the data of HMS (hydrometeorological station) Kyzyl-Ozek on the air temperature for ten years 2006-2015 were analyzed. It was in 2010 that the lowest average temperature of the year in the period under study was recorded. Perhaps here is one of the reasons for lowering the temperature of groundwater. This idea is consistent with another result, which consists in the fact that throughout the study period, the temperature of the GW in Severnaya street fell to the minimum at the end of winter – in early spring. The same trend is scheduled for OP in Novaya street.

In 2007, the highest air temperature was noted, which perhaps affected the temperature of the groundwater. It should be noted that the seismic activity in 2007 and 2010 was at the minimum level, which suggests a significant role for geographical conditions in the supply of sulfates in GW and during its temperature. However, it does not contradict the idea that seismic activation leads to an increase in the temperature of the groundwater. An indirect confirmation of this idea are the features of the geological structure of the OP in Novaya street (Table 1) and Severnaya street.

OP data in Severnaya street provide the opportunity for a multilateral study of the status and dynamics of the quality of GW in this area. The results obtained by the authors of this work are consistent with the results for other mountain areas (Guseva *et al*., 2013).

3.4. A connection between various factors

A significant fluctuation of the sulfate-ion content in the water of wells was revealed, the causes of which are difficult to establish for some sites. These difficulties are determined by the nature of the object of the study and a small amount of data. Unfortunately, these conditions today are the norm and are characteristic of most OPs (Yazikov and Shatilov, 2004), which leads to incomplete hydrogeological and hydrochemical information. With this type of testing, it is possible to talk only about trends (Novaya Street, Monday), and in some cases only about introducing new data into use. To convincingly explain the dynamics of sulfate ion and other components, it is necessary to continue monitoring with the study of the landscape features of the territory.

A large data array (for example, the OP Severnaya street) makes it possible to establish patterns and confirm them by quantitative methods. A tendency has been revealed towards the connection of the studied component, sulfate ion, with environmental factors: water and air temperature, as well as with the amount of precipitation. Mathematical indicators of this connection are different and often do not reach high values. The authors suggest that the mechanism of this relationship is more complex than the direct dependence of one indicator on another. The combination of factors is the most possible variant. The conditions of the mountainous area create some balance, which is easily broken when activating, for example, the technogenic factor. An example is the OP in Novaya street. At the same time, high-speed, energy-intensive natural processes, such as earthquakes, are capable of interfering with the "traditional" fluctuations of the state of its components for the given territory. An example is the OP in Severnaya street.

Analysis of our data shows that the minimum content of sulfate ion is typical for precipitation. This suggests that snow and rain are not a source of sulfate ion in the GW. At the same time, in the snow that had lain all winter, more sulfates are accumulated than in the snow that just fell. The reason may be the anthropogenic effect on snow cover, for example, aerosols from motor vehicle emissions. In the rivers and streams of the Maima river basin sulfate ion content is lower than in well water and also does not reach the TLV value.

The processes of atmospheric portage of anthropogenic and natural anthropogenic substances from economically developed regions can be an important factor in the formation of the chemical composition of natural waters. Nevertheless, according to hydrochemical indicators, surface and groundwater in the basin of Maima river is generally characterized as "clean", and the ecological and geochemical state of the basin of the study area can be assessed as satisfactory.

The temperature of groundwater rises during the earthquake. This increase can be considered instantaneous compared with the time it takes to return to its average values. The greatest increase in the temperature of the groundwater and the longest period of its return to the mean value is observed for the aquifer confined to the deposits of the Vendian-Cambrian age. This is important to note due to the fact that the depth of observation wells drilled in ancient and Quaternary sediments is comparable (Table 1).

4. CONCLUSIONS:

In this paper, only the sulfate ion content was considered, but the chemical composition of natural water was analyzed over a large spectrum of components. It needs to be emphasized that all the components in the natural waters of the study area do not exceed the TLV for fishery and cultural and community water use. There can be different reasons for this phenomenon. The fact that the snow that had lain all winter contained more sulfates than the snow that just fell proves a possibility of anthropogenic influence. Also there is no correlation in the amount of precipitation in the summer period and the content of sulfate ion in the groundwater. The causes of significant fluctuation of the sulfate-ion content in the water of wells are difficult to establish. Because the investigation fully depends on the nature of the object of the study, on external conditions and as result of this dependence there is small amount of data.

The work done has shown that at all observation points of the monitoring network of the TLV sulfate ion are not exceeded and the condition of the groundwater is satisfactory for this component. The study revealed a very close relationship between the seismic activity and radon activity (correlation coefficient 0.93), which determines the relationship between the sulfate ion content and the radon activity.

The authors consider the complex of factual material and the results obtained as a unique phenomenological array, which can serve as a basis for assessing the ecological status of the Mayma river and identify factors affecting the formation of the composition of the natural waters of the territory. Practical investigation and learning of data showed that earthquakes, processes of atmospheric portage of anthropogenic and natural anthropogenic substances, time of year can be among these factors. In addition, our study demonstrates the importance of spatial analysis of the current state of natural waters for understanding the context of hydrological changes, within which any sustainable water management plan should be located.

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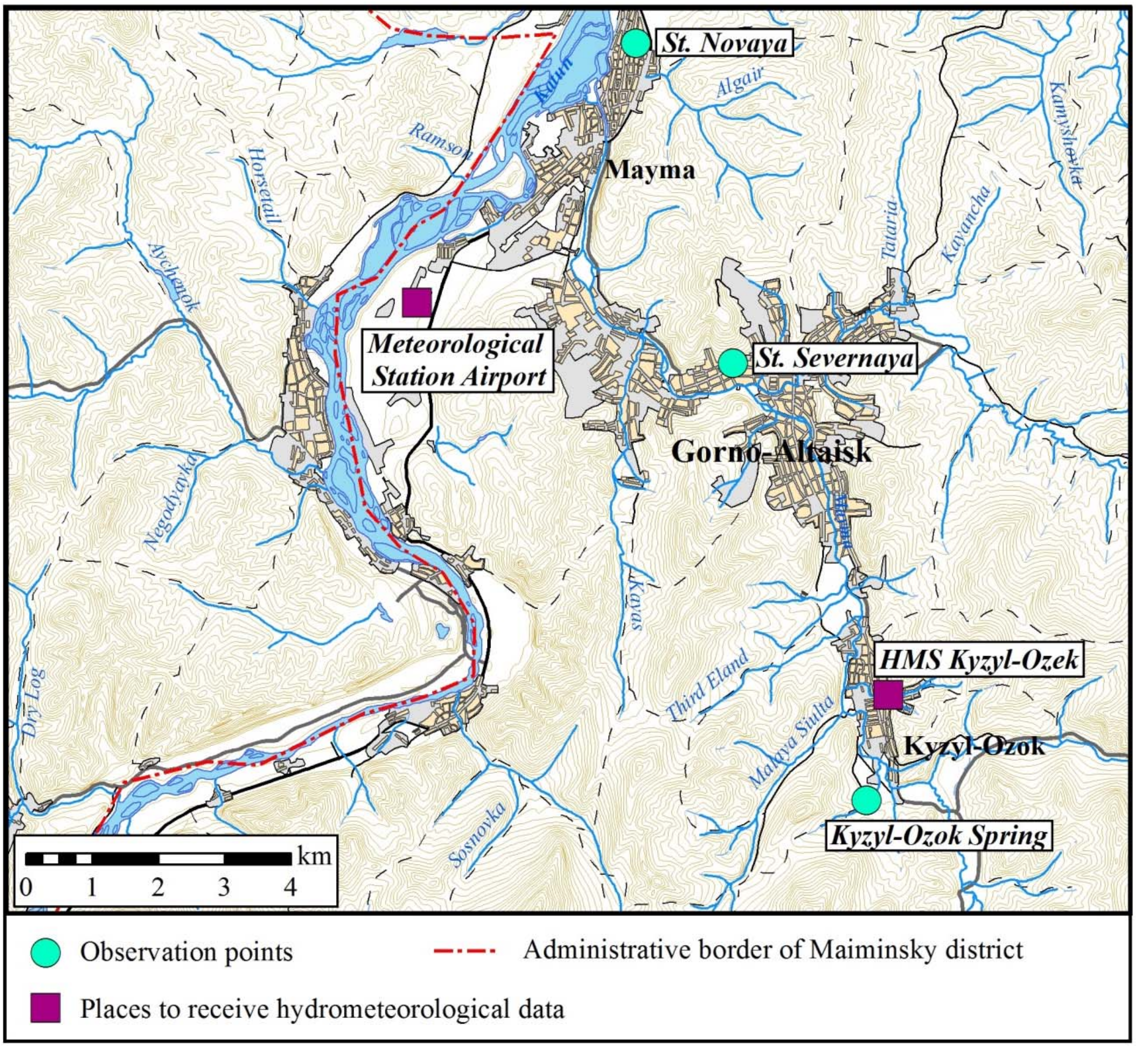

Figure 1. *Scheme of observation points (compiled by V. V. Roldugin) (Roldugin, 2018)*

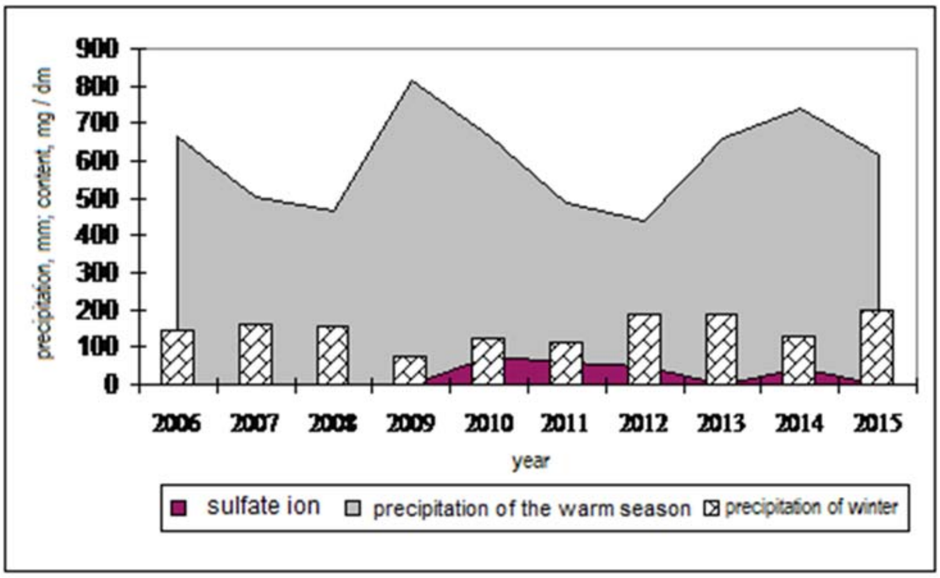

Figure 2. *The amount of precipitation and the content of sulfate ion in the water well in Novaya Street*

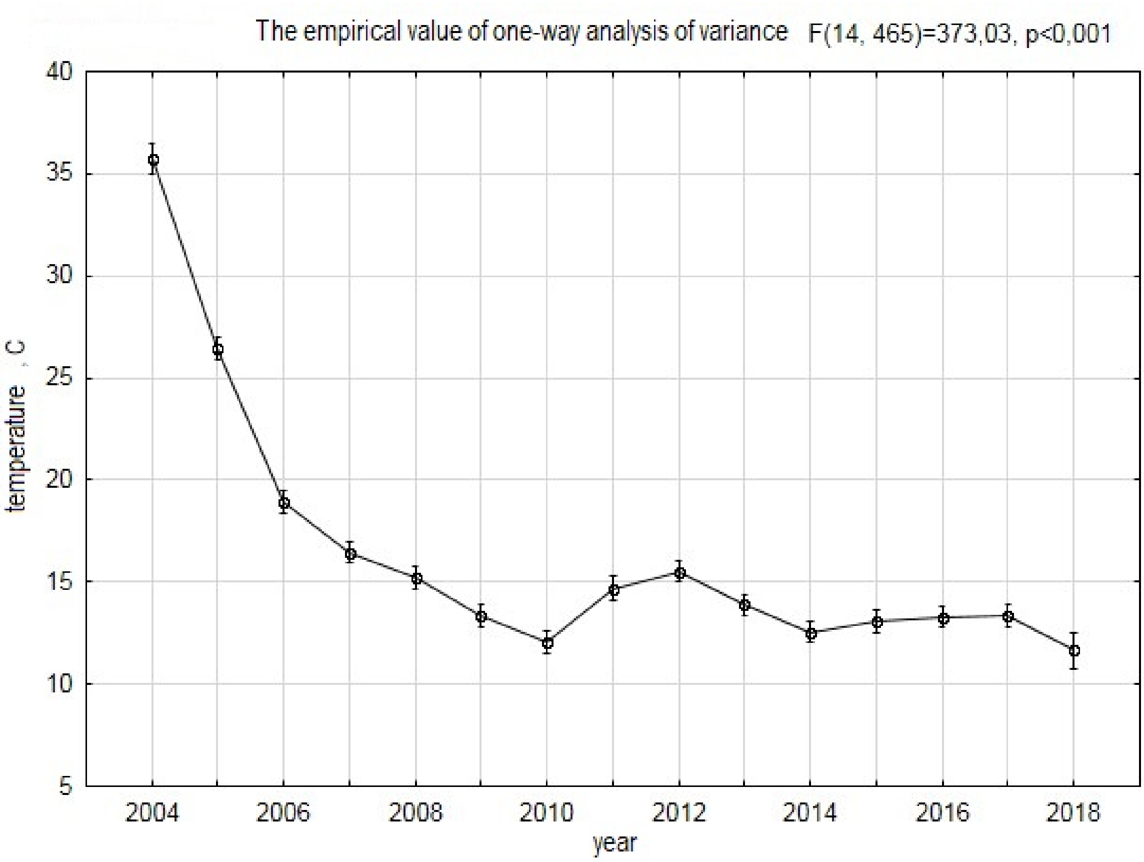

***Figure 3.** Dispersion analysis of the well water temperature in Severnaya Street for the period 2004-2018*

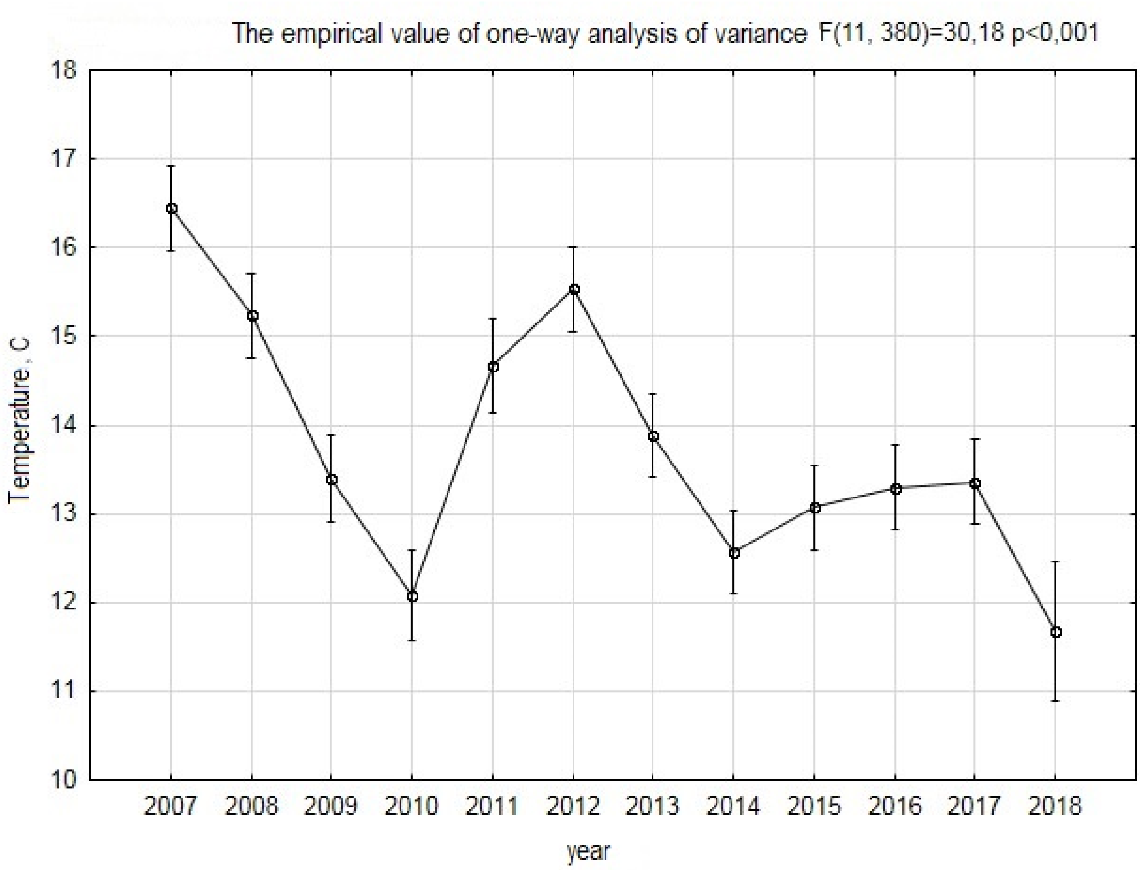

***Figure 4.** Dispersion analysis of the well water temperature in Severnaya Street for the period 2007-2018*

Table 1. *Well cut in Severnaya Street.*

Geological index	Lithological composition of reservoirs	Depth, м	Layer thickness, м	Go-technical cut	Well casing	
					diametr, мм	depth, м
Q_{III-IV}	Rubble deposits	9	9		100	10
V-Є	Shale rock	10	1			

Table 2. *Correlation of hydrochemical indicators and characteristics of the environment according to OP in Severnaya Street (Gorno-Altaisk)*

	Content of fluorine	Water temperature,ºC
Content of radon	-0.6	0.0
Seismic activities	-0.2	- 0.27
SO_4/Cl	0.3	-0.3