The influence of natural geochemical provinces on the drinking water quality and the public health risk formation

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Abstract. The high content of chemical elements in the sources of drinking water in addition to anthropogenic contamination may be due to the presence of the source in a particular geochemical province, creating the initially high background levels of chemicals of concern in water. It was found that among 14 geochemical provinces of Perm region in 4 there was the excess of the maximum allowable concentrations in water sources: the manganese to 2.3 MAC and strontium to 17.0 MAC. It is shown that, despite the use of modern methods of water treatment used in the economic activity and for the purpose of drinking water, in drinking water after treatment manganese, fluorine, strontium, beryllium and Nickel exceeding to 20.0 MPC, substance characteristic water sources within the boundaries of the geochemical provinces, are recorded. The event production control does not always include a program of sampling on the specific geochemical provinces of the substance, such as boron, bromine, barium, etc. In the course of the assessment of health risk from consumption of drinking water from sources located within the boundaries of geochemical provinces obtained that the coefficients of the danger (HQ) exceeded the acceptable level to 2.2 times for a number of substances, and the hazard index (HI) of health disorders exceeded the permissible level up to 2.5 times. The total contribution of the typical geochemical provinces of substances has reached 100,0 % for some organs and target systems.

1. Introduction

The concentration of chemicals in the soil directly affects the ecological condition of the territories. The lithosphere, and in particular the pedosphere, is the main factor in several processes: it is the initial link in the food chain, it can be an indirect indicator of air and water pollution, and it is also an integral indicator of the ecological state of the environment. Saturation of the soil cover with toxic elements as a result of anthropogenic activity or during geodynamic processes can lead to different consequences. Heavy metals can in some cases act as a leading environmental factor that determines the nature and direction of the development of biogeocenosis. At the same time, intense environmental pollution by heavy metals in some cases can lead to catastrophic toxicosis of plants, animals, and humans [1, 2]. The short-term effects of low concentrations of heavy metals may not cause serious environmental damage, but in situations of prolonged exposure or high levels of exposure to heavy metals, serious shifts in biological equilibrium can occur. In this regard, geochemical mapping of territories and assessment of the situation within the boundaries of geochemical provinces is an important environmental tool that allows us to predict the possible outcomes of the migration of chemical compounds from the soil.
From a historical point of view, a major factor in the founding settlements often were favourable landscape of the area, which fulfils at least one of the elements: the terrain, hydro geographical features, type of soil, climatic conditions or species diversity of the biocenosis. Of the following symptoms the presence of a water body was determined as the basis of the settlement (from lakes and rivers to the sea and the ocean) most frequently. At the time of settlement and the founding of new cities and settlements there was not the influence of the chemical composition of the soil understanding. For this reason, the plants, the animals and the people who settled in the territories of geochemical provinces with initially high or low contents of certain chemicals were involved in the processes of migration of these substances. The high level of bioaccumulation or rather the lacking essential element eventually leads to the formation of the endemic areas [3]. The soil is only the initial stage of these processes, and a water object acts as one of the factors in the direct transport of substances.

The task of providing the population with quality drinking water was one of the most important factors in the survival and development of companies. In the twentieth century with the advent of the technology of manufacturing high-quality and durable tubing the development of modern plumbing systems began. Centralized potable water supply involves the provision of water resource of a huge number of the population, so the safety, quality and security of water are the priority requirements of the feed resource (drinking water), and sufficient flow rate of water is a prerequisite for adequate resource consumption. Along with the development of the water supply system, water treatment methods begin to appear, be tested and improved, because in most cases the original quality of water, especially from surface water sources is unsuitable for use without prior preparatory measures.

Currently, despite well-established process of water disinfection and special water conditioning methods, trace element composition and organoleptic properties of water are largely dependent on geochemical province, which is the source of water supply. In addition, the surface water sources types are influenced by anthropogenic factors: wastewater of industrial enterprises and settlements, agricultural activities, water transport, etc. The combination of these factors creates preconditions for occurrence of health disorders of population using for drinking water source with inherently low water quality.

At the moment, in the Russian Federation, ensuring a safe environment and the health of the population are the priority tasks of the national projects “Ecology”, “Demography”, “Healthcare”, and increasing the proportion of the population provided with quality drinking water is one of the main tasks of the federal project “Clean water” [4].

A study evaluating the negative impact of drinking water in several Bangladesh rivers showed that the hazard index (HI) exceeded the acceptable limit (> 1.0) for both adults and children. The risk existed both when administered orally and in case of contact with the skin, especially in relation to endemic substances: arsenic, cadmium, chromium, lead [5]. In the works of L. Maurice et al. it is shown that despite the existing risk in drinking water (oil, microbiological pollution) and the knowledge about it among the population, socio-economic factors (quality and standard of living) will play a decisive role as at their low value, the population will be forced to use obviously low-quality (not purified) water [6].

In a study of B. Gao et al., which assesses the risk to public health from the microelement composition of drinking water from the five largest river basins in China, it was found that HI values for both adults and children were within safe limits (<1, 0). However, for the children's population, the values of the HI and HQ indices and hazard coefficients were higher than for the adults, which indicates both a greater relative volume of consumption per 1 kg of body weight and a greater sensitivity of the child's body to the microelement composition of water. The greatest danger, according to researchers, can be arsenic when administered orally, despite the values falling within the recommended range of the US EPA (1.0 * 10^-6-1.0 * 10^-4), but exceeding the limits set by the Chinese government [7]. According to Abdulmutalimova T.O. and Revich B.A. high arsenic content in drinking water from artesian sources can increase individual carcinogenic risk and lead to an additional number of cases of malignant neoplasms (from 1.0 to 94.8 cases per year) [8]. In the study of T. Sisay et al. on the topic of drinking water quality in Ethiopia, it has been shown that with the current success in the field of drinking water supply for the population, the risk for a large number of people still remains for a number of reasons. A
high incidence rate remains, especially among children, both in urban and rural settlements; high HI values have been established with respect to exposure to fluorine and the development of fluorosis in the population [9]. A number of studies report that, despite the negligible or acceptable risk existing in the territories and coming from drinking water supply, it can lead to an increase in the incidence and mortality from cancer, especially in combination with other factors [10, 11, 12, 13].

The results of foreign and domestic studies indicate that currently serious risks to public health remain for developing countries, where insufficient measures are taken for water treatment and water purification of the water resource while at the same time intensifying the processes of industrial production, the agricultural industry and urbanization. At the same time, the socio-economic situation of the population of these countries is aggravated by the fact that the population either does not have sufficient information about the possible risks or does not have alternative options for drinking water consumption. For economically developed countries, strict requirements for the drinking water quality, as well as the use of a modern set of measures for water treatment and water purification, allow us to maintain a good quality of the supplied drinking water. In the Russian Federation, despite more stringent hygienic standards regarding the quality of drinking water than in several Western countries, as well as high quality standards among resource-supplying organizations, there are problems with the distribution network. The problem of positional hydrogeochemical provinces is highly relevant to all countries. The problem is the high content of minerals in the source of drinking water. It is frequently found among underground sources, the reason for this are the features of the aquifer. For this reason, this type of water is characterized by high degree of mineralization, hardness, specific organoleptic properties. Small flow rates, the high cost and complexity of special methods of water treatment do not give wide dissemination of this type of water sources as the main sources of centralized drinking water supply. Surface water sources often have problems of high salinity, but under certain hydrogeological conditions of their location, these sources are saturated with chemical elements to high levels of acceptable content. The use of such drinking water to the population capable of microelementoses, toxic effects, formation of carcinogenic and non-carcinogenic risks.

2. Purpose of study
The purpose of this study was to assess the natural geochemical provinces impact of the Perm Territory (RF) on the water quality in water sources used for drinking water, as well as to assess the potential risk of health problems among the population from the use of this drinking water.

3. Material and methods
In the Perm region, there are 14 geochemical provinces [14] with their own peculiarities of occurrence of rocks and soils, each of which, to a certain extent, forms the chemical composition of drinking water lying on their territories (figure 1). A number of chemicals and compounds (bromine, boron, barium, manganese, cadmium, nickel and others), which form the basis of the formation of a geochemical province, can affect public health.

The spatial boundaries of geochemical provinces in the form of vector layers of the GIS ArcView 3.2 format, scale 1: 1,000,000, were established using data from the atlas of the Geogart map. The location of water sources obtained from the Office of the Federal Service for the Protection of Consumer Rights and Human Welfare in the Perm region, and the spatial intersection of the points of water intake and geochemical provinces were performed in the GIS ArcView 3.2 GIS (ESRI, USA).

Assessment of the drinking water quality and water sources within the boundaries of the water intake located in geochemical provinces was carried out according to the Federal State Health Institution “Center for Hygiene and Epidemiology in the Perm region”, obtained in the course of socio-hygienic monitoring and control measures for the observation period of 2014-2019. The analysis included 32 substances, including 17 substances characteristic of geochemical provinces capable of exerting a non-carcinogenic and carcinogenic effect on the health of the population of the Perm region living in selected geochemical provinces.
Figure 1. Perm region geochemical provinces.

The non-carcinogenic risk assessment was carried out in accordance with Guidelines P 2.1.10.1920-04 [15], taking into account the parameters set for assessment, and negative health effects (table 1).

**Table 1.** Parameters for assessing non-carcinogenic health risks when drinking a number of chemical impurities typical for geochemical provinces.

| Element    | RfD, (mg / kg·day) | Critical organs and systems                                      |
|------------|-------------------|-----------------------------------------------------------------|
| Boron      | 0.2               | reproductive system, gastrointestinal tract                     |
| Barium     | 0.07              | kidneys, cardiovascular system                                  |
| Beryllium  | 0.002             | gastrointestinal tract, body weight                            |
| Cadmium    | 0.0005            | kidneys, endocrine system                                      |
| Chromium   | 0.005             | liver, gastrointestinal tract, mucous membranes                |
| Fluoride   | 0.06              | teeth, skeletal system                                          |
| Manganese  | 0.14              | central nervous system, blood                                  |
| Nickel     | 0.02              | liver, cardiovascular system, gastrointestinal tract, blood, body weight |
| Lead       | 0.0035            | central nervous system, peripheral nervous system, blood, development, reproductive system, endocrine system |
| Strontium  | 0.6               | skeletal system                                                |

Zinc, Bromine, Cobalt, Phosphorus, Antimony, Titanium, Vanadium

They are not included in the program of social and hygienic monitoring and in the plan of control and supervision measures. The critical organs and systems for these substances are: liver, kidneys, gastrointestinal tract, blood, reproductive system, etc.
4. Results

During the study period of observation (2014-2019) in the Perm region, 72 058 studies were performed on 32 chemical compounds at 182 sampling points. Within the boundaries of geochemical provinces, there are 101 sampling points for 11 substances, the total number of studies in which was 15 549, including sampling in water sources and drinking water. Six chemicals (Zn, Br, Co, P, Sb, Ti, Va) were not included in the program of socio-hygienic monitoring and the plan of control and supervision measures, although these substances are widespread within the boundaries of geochemical provinces. In particular, in some provinces the Clarke number for manganese was up to 23.0, for cadmium - up to 25.0.

It was found that the excess of MAC for the monitored components for the analysed period in water samples of water sources located within the boundaries of 14 geochemical provinces was recorded for manganese (up to 17.0 MPC) and strontium (2.3 MPC). In addition, the excess of MAC for iron (up to 8.3 MAC) and nitrates (up to 1.1 MAC) was established in the water of water sources. Registration of these substances in water sources indicates natural (geochemical) and anthropogenic pollution. Exceeding the standards in water samples of water sources is characteristic of the Chusovskaya, Sylvenskaya, Srednekkamskaya and Obvinskaya geochemical provinces. The largest settlements are concentrated in these provinces and more than half the population of the Perm region lives.

Samples of drinking water from these water sources exceed the standards for 5 substances characteristic of geochemical provinces. Thus, excess MAC was recorded for beryllium (2.5 MAC), fluoride (up to 1.5 MAC), manganese (up to 20 MAC), nickel (up to 1.3 MAC) and strontium (up to 2.5 MAC). In addition, other components with excess MAC were also recorded in drinking water samples: aluminum (up to 6.0 MAC), petroleum products (up to 1.6 MAC), nitrates (up to 1.6 MAC), iron (up to 9.0 MAC) and chloroform (up to 9.8 MAC), the source of which is economic activity and water treatment processes. The excess of MAC in drinking water samples was characteristic of the Sylven, Srednekkamsk, Obvinskaya, Kosvinsky, Yayvinsky provinces for substances typical for these provinces. In drinking water from the water sources of the Chusovskaya, Kosinskaya, Tulva and Severokamsk geochemical provinces, only nitrates (up to 1.6 MAC), iron (up to 3.2 MAC), oil products (up to 1.5 MAC) and chloroform (up to 1.6 MAC). However, in these provinces there is no monitoring of bromine, barium and boron, which are widely distributed substances in the soil of these provinces.

The most common cause of violations of hygienic standards in water sources in the territory of the region is the mismatch of water samples according to sanitary and chemical indicators, the highest proportion of non-standard samples was recorded in surface water sources, while the dynamics shows a decrease (by 19.3%) of this indicator in recent years (table 2) [16, 17].

**Table 2.** The proportion of water samples in centralized water sources that do not meet sanitary requirements, (%).

| Indicators                  | Source type | 2014 | 2015 | 2016 | 2017 | 2018 | 2019 |
|-----------------------------|-------------|------|------|------|------|------|------|
| Sanitary and chemical       | total       | 16.4 | 19.0 | 21.2 | 18.1 | 12.75| 13.9 |
|                            | superficial | 58.2 | 57.5 | 49.3 | 48.9 | 43.6 | 38.9 |
|                            | underground | 11.6 | 14.7 | 17.4 | 15.2 | 9.9  | 11.1 |
|                            | total       | 4.2  | 4.7  | 3.7  | 3.8  | 3.1  | 4.7  |
| Microbiological             | superficial | 7.2  | 7.4  | 7.9  | 6.0  | 4.3  | 12.5 |
|                            | underground | 3.8  | 4.4  | 3.0  | 3.5  | 3.0  | 4    |
| Parasitological             | total       | 0.0  | 0.0  | 0.0  | 0.46 | 0    | 0    |
|                            | superficial | 0.0  | 0.0  | 0.0  | 0.46 | 0    | 0    |

Excessive concentrations of manganese (to 20.0 MAC), strontium (to 2.5 MAC), fluoride (up to 1.6 MAC), nickel (up to 1.3 MAC) and beryllium (up to 2.5 MAC) in drinking water samples on the territory of the Perm region is stipulated by its high background level due to the influence of geochemical provinces on water sources and characteristics of soil and rocks, leading to migration of these substances into the water. The high content of these elements, and iron, without the use of special methods of water...
treatment will lead to disruption of water treatment systems and water supply systems, and deterioration of the properties of water when using it for the purpose of drinking water. Corrosion of pipe material for water distribution networks and external factors can further increase the content of these substances in the water.

Relevant and additional influencing factor in the province and the country in general, is the halogenated compounds excess content in drinking water (chloroform, dichlorobromomethane, dichloromethane, etc.), formed as a result of water disinfection.

In addition to the economic costs in industry and agriculture associated with the application of additional measures for water treatment, in order to obtain water of the right quality, these compounds can affect the state of human health.

In the course of assessing the risk to public health, which is generated, among other things, by the increased background content of a number of chemical compounds in drinking water, it was found that when these chemicals are ingested with water, a hazard coefficient (HQ) above an acceptable level (HQ > 1) is formed for fluorides (HQ 1.6), nitrates (HQ 2.1), chloroform (HQ 2.2) among children. For the adult population, hazard coefficients did not exceed an acceptable level; the highest hazard coefficient values were formed with respect to nitrates (HQ 0.9) and chloroform (HQ 0.9).

Hazard indexes (HI) in the case of additive oral intake of substances with drinking water in the child population exceeded the acceptable level (HI > 1) by 1.6-2.5 times, in the adult population by 1.1 times. In particular, for the children's population, increased hazard indices were formed in relation to diseases of the blood system (HI up to 2.5; total contribution of substances from the geochemical provinces - up to 3.2%), central nervous system (HI up to 2.4; total contribution of substances from the geochemical provinces - up to 4.6%), kidneys (HI up to 2.3; total contribution of substances from the geochemical provinces - up to 5.2%), liver (HI up to 2.3), cardiovascular system (HI up to 2.2; total contribution substances of the geochemical provinces - up to 22.8%), endocrine system (HI up to 2.2; total contribution of substances from the geochemical provinces - up to 1.5%), skeletal system (HI up to 1.6 total contribution of substances from the geochemical provinces - 100.0 %) and teeth (HI up to 1.6; the total contribution of substances from the geochemical provinces is 100.0%). Increased hazard indices were formed in the territories of Srednekamsk, Obvinsk, Chusovsk and Tulvinsk geochemical provinces. The results obtained are consistent with data on excess of the MAC of chemical compounds in water sources and drinking water in these territories.

5. Conclusion

Based on the study, the following conclusions can be drawn:

- on the territory of the Perm region, due to hydrogeological features, conditions have been created for the increased content (up to 17.0 MAC) of manganese and strontium in water bodies of 5 geochemical provinces (Sylven, Srednekamskaya, Obvinsk, Yayvinskaya, Kosvinskaya);
- when monitoring the quality of water bodies - sources of water supply and drinking water from these sources located within the boundaries of the geochemical provinces of the studied territory, the priority substances for geochemical provinces (Zn, Br, Co, P, Sb, Ti, Va) are not included in instrumental research programs;
- the most significant excess of MAC (up to 20.0 MAC) in drinking water samples for substances characteristic of geochemical provinces were recorded in Sylven, Srednekamsk, Obvinsk, Kosvinsky and Yayvinsky provinces. Additional pollution of drinking water (up to 9.0 MAC) from substances (aluminum, chloroform, iron) that fall during water treatment and water transportation, except for the above-mentioned provinces, is also characteristic of the territories of the Chusovskaya, Tulvinskaya, Kosinskaya, Severokamskiy provinces;
- the highest maximum permissible concentration in samples of drinking water were recorded in respect of aluminium, manganese, iron, nitrate, and chloroform (up to 6.0; 20.0; 9.0; 1.3; of 9.8 MAC, respectively). High concentrations of these compounds in water is caused by
their high content in rocks and soil (manganese), corrosion of plumbing system and the insufficient application of special methods of water treatment (iron), the disinfection process (chloroform) and coagulation (aluminum), as well as anthropogenic activity in the form of sewage and runoff water from agricultural land (nitrates);

• exceeding the maximum allowable concentrations of several chemical compounds, including geochemical origin, creates the risk of increased morbidity among the population, especially children as the most vulnerable to the impact of pollutants. Thus, the risk factors for children after oral intake of substances with drinking water were exceeded in respect of fluorides (HQ of 1.6), nitrate (HQ 2.1), chloroform (HQ 2.2), the hazard indices exceeded the acceptable level of 2.5 times. The highest levels of risk were formed on the territories Sredneekamsky, Obminsks, the Chusovoy and Tolwinski geochemical provinces. The aggregate contribution of a typical geochemical provinces of substances has reached 100.0 % for some organs and targets systems.

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