Methods of Statistical Control for Groundwater Quality Indicators

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Abstract. The article describes the results of conducted groundwater quality control. Controlled quality indicators included the following microelements – barium, manganese, iron, mercury, iodine, chromium, strontium, etc. Quality control charts – X-bar chart and R chart – were built. For the upper and the lower threshold limits, maximum permissible concentration of components in water and the lower limit of their biologically significant concentration, respectively, were selected. The charts analysis has shown that the levels of microelements content in water at the area of study are stable. Most elements in the underground water are contained in concentrations, significant for human organisms consuming the water. For example, such elements as Ba, Mn, Fe have concentrations that exceed maximum permissible levels for drinking water.

1. Introduction

Water quality control is an ongoing important task. Water quality: characteristics of water composition and properties, determining its suitability for specific types of water use. Quality indicators: a list of water properties, which numerical values are compared against the water quality standards. Quality standards: officially established values of water quality indicators for specific types of water use. When organizing the process of water quality assessment, there arises a task of monitoring the groundwater characteristics being within the limits, for the groundwater to be able to meet its intended usage purpose. In the process of monitoring, various parameters of groundwater quality are compared against benchmarks, established in standards, regulations and technical conditions [1].

On the one hand, excessive content of some microelements of natural origin in groundwater may exceed maximum permissible concentrations (MPC), thus making the water unsuitable for consumption by humans, and on the other hand, thanks to the presence of other microelements, drinking water may be more useful for health. To denote concentrations, at which elements entering a human body with water can affect its overall microelement balance, the term of biologically significant concentration (BSC) is used [2]. All microcomponents contained in groundwater can be divided into several groups. The first group – elements that do not produce a substantial impact on the microelement composition of human bodies; the second group – elements contained in biologically significant concentrations (BSC), and the third group – elements, which content in water exceeds the maximum permissible concentrations (MPC) and which are simply dangerous. Maximum permissible concentration of substance in water is such concentration of hazardous substance in water, that does not have direct or indirect impact on human organisms during their entire life and on the health of their future generations, and it does not affect the hygienic conditions of water use [3].

The purpose of the study is to perform control of water quality indicators and to determine the elements contained in underground water in biologically significant concentrations.

Statistical methods allow us to determine, with an accepted level of accuracy and reliability, the studied processes condition in the quality control system. Shewhart control charts are one of the main tools in the arsenal of statistical methods of control [4–5]. Quality control charts, or, shorter, control charts, are used for permanent monitoring of processes, to ensure that the process remains statistically under control from the statistic point of view. Practical application of control charts is mainly confined to using the charts of mean values (X-bar chart) and the charts of ranges (R-chart) [6]. X-bar chart and R-chart are designed to detect the process variations from the average values and the emergence of non-standard ranges in the sample.

2. Research object and method

We have examined the results of chemical analysis of underground water, selected from 343 wells of Ob-Tomsk river value (Russia) in 1962-2009 years. To assess the quality of groundwater, twenty indicators were selected: total iron (Fe), manganese (Mn), fluorine (F), aluminum (Al), arsenic (As), bor (B), barium (BA), strontium (SR), beryllium (Be), chromium (Cr), copper (Cu), cadmium (Cd), cobalt (Co), molybdenum (Mo), nickel (Ni), lead (Pb), mercury (Hg), iodine (I), titanium (Ti), zinc (Zn).

Data on the concentrations of each indicator were collected into samples. A sample includes the array of concentration values of one indicator measured by all wells during a single year. For each sample, the mean value and the range of the sample were calculated. For each indicator, overall average value (mean of the means) was calculated.

To monitor the water quality indicators, X-bar charts and R-charts were built in the "Statistica" system ("Quality Control Charts" module). The horizontal axis on both control charts contains the numbers of the relevant samples (year of sampling); while the vertical axis on the X-bar chart contains mean concentrations of studied indicators, and the vertical axis on the R-chart – the ranges of the relevant samples. Parameters of the charts were defined:

Central line of the X-bar chart corresponds to the mean concentration value for the given indicator, and central line on the R-chart corresponds to the acceptable range of concentration values in the samples.

Threshold limits of the process: MPC - the upper limit of biologically significant concentration, and LLBSC- the lower limit of biologically significant concentration. LLBSC is the amount of a microelement, at which its entry into a human body with drinking water makes 5% of its overall statistical intake [2].

3. Results and considerations

For a continued period of time, in order to conduct water quality analysis, water samples were taken from 343 wells several times a year. The collected water samples were analyzed using standard techniques in accredited laboratories [7].

For each water quality indicator, quality control chars were built. Such charts for some individual indicators are shown in the figures 1–3. The "Quality Control Charts" module of the "Statistica" system was used.

Table 1 contains the quality indicators, number of samples, the average content of microelements in underground water on the studied territory and the relevant standards.

Quality control charts have revealed the difference in behavior of water quality indicators. All average contents of such microelements as aluminum, zinc, cobalt are below the lower limits.

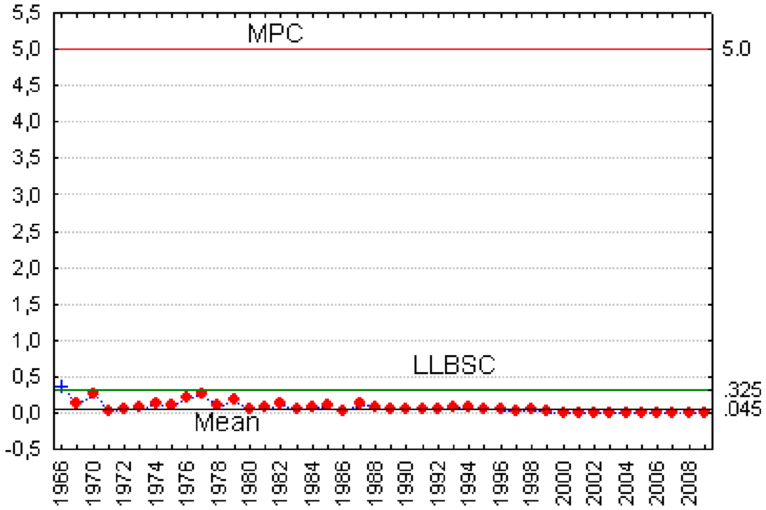

Figure 1. X-bar chart for zinc indicator.

All points of such elements as strontium, chromium and iodine lie within the established borders and their spread from the mean value can be considered as uniform. The substance concentration for them meets the requirements of statistical control for mean level and ranges.

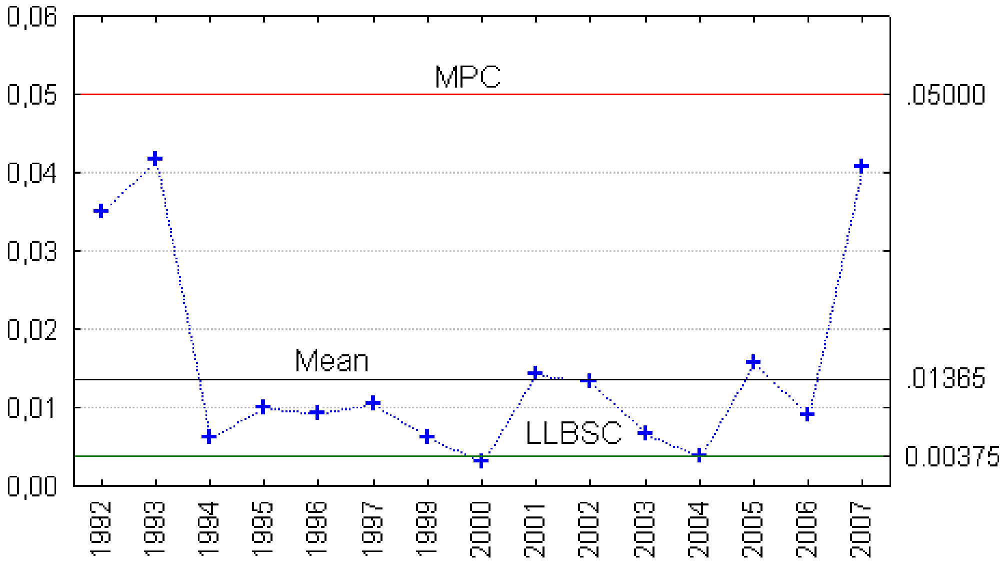

Figure 2. X-bar chart for chromium indicator.

Table 1. Structure of water quality indicators and the standards.

Indicators	Number of samples	Mean, mg/l	LLBSC, mg/l [2]	MPC , mg/l [3]
Al	861	0.14947	0.375	0.5
Ba	656	0.157622	0.02	0.1
Be	158	0.0003	0.00025	0.0002
B	122	0.1137	0.0325	0.5
Fe	10298	5.958	0.375	0.3
I	996	0.21	0.00375	
Cd	262	0.0022	0.0025	0.001
Co	238	0.0032	0.0075	0.1
Mn	5336	0.3980	0.0925	0.1
Cu	4658	0.0497	0.0875	1.0
Mo	412	0.02312	0.00625	0.25
As	530	0.01494	0.00125	0.05
Ni	405	0.0226	0.0075	0.1
Hg	243	0.00045	0.00037	0.0005
Pb	2326	0.01	0.01	0.03
Sr	491	0.51	0.05	7.0
Ti	218	0.07	0.02	
F	4413	0.27	0.05	1.5
Cr	349	0.01392	0.00375	0.05
Zn	4052	0.045	0.325	5.0

All points of average content of iron, manganese and barium are located above the upper limit. This allows us to draw a conclusion that the reason for their increased content is the same and most likely it is related to the geological structure of the territory.

The average contents of lead and mercury relative to the central line (mean of the means) vary on the control charts. In our case, there is a dispersion of mean values; therefore, there are wells with higher concentration levels of separate indicators, compared to other wells.

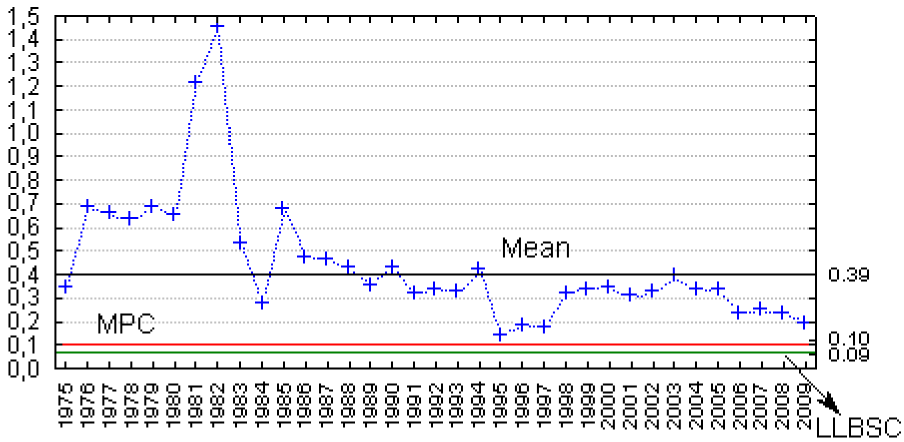

Figure 3. X-bar chart for manganese indicator.

As a result of analysis using the quality control charts, all studied microelements were divided into three groups: Al, Co, Zn, Cu – are contained in concentrations below LLBSC; (B, I, As, Ni, Mo, Hg, Pb, Sr, Ti, F Cr – are contained in concentrations within BSC; Ba, Be, Cd, Mn, Fe – are contained in concentrations above MPC.

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Also it is necessary to pay attention to the contents of such microelements as Cu, Mo, Ni, Pb, Hg, as in individual water samples their concentration values exceed maximum permissible concentrations.

4. Summary

The quality control charts analysis has shown that the levels of microelements content in water on the area of study are stable. Fifteen indicators (B, Be, I, As, Ni, Mo, Hg, Pb, Sr, Ti, F, Cr, Ba, Mn, Fe) from twenty are contained in underground water in biologically significant concentrations. Concentrations of five indicators (Ba, Mn, Fe, Be, Cd) exceed maximum permissible concentration (MPC) for drinking water. Such microelements as Al, Co, Zn, Cu are contained in concentrations below LLBSC.

Thus, the method of using the X-bar charts and R-charts allows us to improve quality control of underground water.

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