Static and dynamic approach to estimation of spring water hardness cation content as a natural factor of groundwater formation

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Abstract. To assess the degree of influence of natural factors on the groundwater mineralization, it is proposed to simultaneously consider in a static and dynamic position the results of titrimetric determination of the total mineralization and concentration of calcium and magnesium ions in spring water. This is shown by the example of four springs located in the territory of Kaluga. The study made it possible to establish: the average annual background concentrations, as well as to justify the relative variable for groundwater in springs No. 1, No. 3 and No. 4 and the influence of the natural factor on the formation of the total hardness and concentration of calcium and magnesium ions in the study period, relatively stable for groundwater in spring No. 2 by the value of the molar ratio of the concentrations of calcium and magnesium ions.

1. Introduction

Spring waters are a natural product of the natural discharge of groundwater. They have physiological usefulness in the content of mineral substances, among which calcium and magnesium ions that determine water hardness appear in the list of pollutants when assessing damage to public health [1, 2]. Long-term studies of the quality of groundwater in the three springs revealed some patterns in their formation, as well as distinguish between natural (natural) and anthropogenic factors in the influx of pollutants into spring waters. According to the authors of [3], the general hardness of spring waters is controlled not by anthropogenic, but by natural factors, which are directly related to the physicochemical properties of the underlying rocks of the aquifers. Since the natural conditions for each spring are individual, the variety of underlying rocks forms a unique chemical composition of spring waters, therefore, the obtained regularities of its formation for one source should not be copied to another source without further research. To prevent spring water from pollution and depletion, it is necessary to monitor the groundwater of each spring, which is a system of observation, assessment and prediction of changes in the state of groundwater under the influence of anthropogenic and natural factors. The specified monitoring should satisfy certain requirements. It has to be carried out with a monitoring frequency of at least 1 time per month. When analyzing the results of monitoring, it is necessary to take into account the dynamics of the levels of monitored indicators relative to the background values. Therefore, one of the environmental tasks of studying spring water is to establish the average annual background concentrations of chemical indicators of water quality, including hardness ions and total hardness.
The total hardness of the groundwater in the springs varies widely. For example, for the city of Stavropol [4] it is 7 ÷ 20 mmol/l, for the city of Saratov [5] it is 4 ÷ 10 mmol/l, for the Ulyanovsk region [6] it is 0.73 ÷ 10 mmol/l. Not only the intra-annual changes in the total hardness is of particular interest from the point of view of assessing the formation and stability of the mineral composition of spring water, but also the intra-annual patterns of the content of calcium and magnesium ions in groundwater, including the molar ratio of calcium and magnesium concentrations attract the attention of researchers.

The content of calcium ions is usually 2-4 times higher than the magnesium ions in the aquifers contained in sedimentary rocks, and in the waters of igneous rocks this ratio can change in the direction of an increase in the amount of magnesium. In most natural waters, magnesium plays a subordinate role and, participating in the formation of energetically favorable crystal lattices of secondary silicates and dolomites, leaves the solution [7]. Thus, according to the laws of change in the ratio of molar concentrations of calcium and magnesium ions in the annual cycle (under dynamic conditions), it is possible to judge the features of the influence of natural factors on the total hardness of the underground water of the studied spring.

General ideas about the ratio of the molar concentrations of calcium and magnesium ions (MCa/Mg) under static conditions can be obtained by statistical processing of the results of single determinations of mineralization, total hardness, and the content of calcium and magnesium ions in underground water from 48 springs [6]. According to the data of statistical processing, it can be accepted (figure 1) that the total hardness of spring water and the content of calcium ions in it increase in proportion to the increase in water salinity, and the dependence of the concentration of magnesium ions on water salinity is more close to a power function, i.e. with an increase in mineralization, (MCa/Mg) changes toward an increase in the content of calcium ions. It should be noted that the found dependence does not lead to a significant change in the MCa/Mg, since the value of the MCa/Mg for the studied spring waters varies over a wide range of 5.1 ± 2.0.

The aim of the work is to develop methodological approaches to assess the content of hardness cations and the total hardness of spring waters in an annual cycle using a static and dynamic approach.

![Figure 1](image.png)

**Figure 1.** Dependence of total hardness and content of calcium and magnesium ions on mineralization of spring water according to the data [6].

2. Research objects and methods

The research objects were the groundwater of four springs (figure 2): spring No. 1 - Berezuevsky ravine, down from the Stone Bridge, turn st. Cosmonaut Komarov; Spring No. 2 - a site near the St. Lavrentievsky Monastery at the intersection of Sadovaya and Shirokaya Streets; spring No. 3 - the intersection of Vygonnaya and Sadovaya streets; spring number 4 - Azarov district, the right side of the river. Terepets, country cooperative "Progress". Spring waters were taken monthly from October 2017 to October 2018.
Determination of the concentrations of calcium and magnesium ions in spring water was carried out according to GOST 4151-72.

3. Results and discussion
The static approach. The statistically processed results of determining the total hardness, calcium and magnesium ions in the studied underground waters of the four springs, selected from October 2017 to October 2018, are presented in tables 1-4, which makes it possible to obtain background average annual hardness values under static conditions and average annual concentration of calcium and magnesium ions.

![Map-scheme of the location of the studied springs.](image)

Table 1. Results of determination of total and ions hardness of groundwater spring No 1 (n=3).

| Month | $H_{av}$ | $S_r$ % | $C(Ca)_{av}$ | $S_r$ % | $C(Mg)_{av}$ | $S_r$ % |
|-------|---------|--------|--------------|--------|--------------|--------|
| Oct 17 | 8.75    | 1.98   | 4.50         | 2.22   | 4.25         | 2.35   |
| Nov 17 | 6.58    | 2.32   | 4.92         | 1.17   | 1.67         | 12.49  |
| Dec 17 | 7.83    | 2.95   | 6.25         | 1.60   | 1.58         | 20.30  |
| Jan 18 | 8.00    | 2.17   | 5.00         | 2.00   | 3.00         | 8.82   |
| Feb 18 | 9.33    | 1.64   | 6.67         | 0.87   | 2.67         | 5.73   |
| Mar 18 | 10.33   | 1.48   | 6.83         | 1.69   | 3.50         | 2.86   |
| Apr 18 | 8.00    | 5.73   | 4.75         | 0.00   | 3.25         | 14.10  |
| May 18 | 10.33   | 1.48   | 6.42         | 0.90   | 3.92         | 3.90   |
| Jun 18 | 8.25    | 2.10   | 6.83         | 0.84   | 1.42         | 8.15   |
| Jul 18 | 8.17    | 1.87   | 6.92         | 0.83   | 1.25         | 13.86  |
| Aug 18 | 8.42    | 0.69   | 6.83         | 0.84   | 1.58         | 3.65   |
| Sep 18 | 8.25    | 2.10   | 6.92         | 0.83   | 1.33         | 15.61  |
| Oct 18 | 7.58    | 2.01   | 6.75         | 1.48   | 0.83         | 22.71  |
| Max    | 10.33   | 5.37   | 6.92         | 2.22   | 4.25         | 22.71  |
| Min    | 6.58    | 0.69   | 4.50         | 0.00   | 0.83         | 2.35   |
| Average| 8.45    | 2.1    | 6.12         | 1.2    | 2.33         | 10.1   |
| $S_r$, mmol/l | 0.76 | - | 0.82 | - | 1.02 | - |
| $S_r$, % | 9.0 | - | 13.3 | - | 43.7 | - |

Spring No. 1. Fluctuations in the total hardness and concentration of calcium and magnesium ions during the year were in the range of 8.45 ± 0.76 mmol/l; 6.12 ± 0.82 mmol/l and 2.33 ± 1.02 mmol/l, respectively. In this case, the standard deviation ($S_r$), respectively, was 9.0%, 13.3%, and 43.7%. Since the obtained $S_r$ values exceed the error of the titrimetric method (2% [6]) by 3 or more times, the obtained average values of the total hardness and concentrations of calcium and magnesium ions can...
be taken as the background average values from October 2017 to October 2018 with a note that during the study period there were significant deviations of the total hardness and concentration of calcium and magnesium ions from the average annual values.

Table 2. Results of determination of total and ions hardness of groundwater spring No 3 (n=3).

| Month | H$_{av}$ | S$_r$ % | C(Ca)$_{av}$ | S$_r$ % | C(Mg)$_{av}$ | S$_r$ % |
|-------|---------|--------|--------------|--------|--------------|--------|
| Nov17 | 9.50    | 1.82   | 5.83         | 0.99   | 3.67         | 4.17   |
| Dec 17| 7.58    | 2.01   | 6.58         | 1.75   | 1.00         | 26.46  |
| Jan 18| 9.67    | 2.15   | 6.83         | 0.84   | 2.83         | 8.15   |
| Feb 18| 8.08    | 1.89   | 6.75         | 1.48   | 1.33         | 11.46  |
| Mar 18| 6.50    | 3.08   | 4.58         | 2.52   | 1.92         | 6.02   |
| Apr 18| 7.08    | 2.94   | 5.92         | 0.98   | 1.17         | 13.09  |
| May 18| 9.00    | 1.11   | 7.17         | 0.81   | 1.83         | 8.33   |
| Jun 18| 8.67    | 2.40   | 7.08         | 0.82   | 1.58         | 14.59  |
| Jul 18| 8.67    | 2.40   | 7.58         | 0.76   | 1.08         | 21.32  |
| Aug 18| 9.67    | 0.60   | 7.67         | 0.75   | 2.00         | 5.00   |
| Sep 18| 9.42    | 0.61   | 7.42         | 0.78   | 2.00         | 5.00   |
| Oct 18| 8.17    | 1.87   | 7.25         | 0.00   | 0.92         | 16.66  |
| Max   | 9.67    | 3.08   | 7.67         | 2.52   | 3.67         | 26.46  |
| Min   | 6.50    | 0.60   | 4.58         | 0.00   | 0.92         | 4.17   |
| Average| 8.50  | 1.9    | 6.72         | 1.0    | 1.78         | 11.7   |
| S$_r$. mmol/l | 0.85 | -  | 0.66         | -      | 0.60         | -      |
| S$_r$. % | 9.9  | -  | 9.8          | -      | 33.6         | -      |

Spring No. 3. The characteristics of the underground waters of spring No. 3 and spring No. 1 are fairly close. Fluctuations in the values of the total hardness and concentrations of calcium and magnesium ions in the underground water of spring No. 3 during the year were in the range of 8.50 ± 0.85 mmol/l; 6.72 ± 0.66 mmol/L and 1.78 ± 0.60 mmol/L, respectively. Moreover, $S_r$, respectively, had a value of 9.9%, 9.8%, and 33.6%. The average annual values of the total hardness and concentration of calcium and magnesium ions of groundwater in springs No. 1 and No. 3 practically do not differ. Therefore, the same as for spring No. 1, the obtained average values of the total hardness and concentration of calcium and magnesium ions of groundwater in spring No. 3 can be taken as background average annual values from October 2017 to October 2018 with a note that during the study period there were significant deviations of the total hardness and concentration of calcium and magnesium ions from the average annual values.

Table 3. Results of determination of total and ions hardness of groundwater spring No 2 (n=3).

| Month | H$_{av}$ | S$_r$ % | C(Ca)$_{av}$ | S$_r$ % | C(Mg)$_{av}$ | S$_r$ % |
|-------|---------|--------|--------------|--------|--------------|--------|
| Dec 17| 10.00   | 1.0    | 7.08         | 0.8    | 2.92         | 1.98   |
| Jan 18| 9.17    | 0.6    | 7.42         | 2.1    | 1.75         | 11.43  |
| Feb 18| 9.25    | 1.1    | 7.58         | 0.8    | 1.67         | 3.46   |
| Mar 18| 9.00    | 0.0    | 7.08         | 0.8    | 1.92         | 3.01   |
| Apr 18| 9.00    | 3.3    | 7.50         | 0.0    | 1.50         | 20.00  |
| May 18| 9.17    | 1.7    | 7.50         | 0.0    | 1.67         | 9.17   |
| Jun 18| 9.17    | 1.7    | 7.50         | 0.0    | 1.67         | 9.17   |
| Jul 18| 9.00    | 1.9    | 7.42         | 0.8    | 1.58         | 13.15  |
| Aug 18| 8.17    | 0.7    | 6.17         | 0.9    | 2.00         | 5.00   |
| Sep 18| 8.33    | 1.8    | 7.42         | 0.8    | 0.92         | 12.60  |
Fluctuations in the values of total hardness and concentrations of calcium and magnesium ions in groundwater during the year were in the range of 8.97 ± 0.36 mmol/l; 7.20 ± 0.35 mmol/l and 1.77 ± 0.29 mmol/l, respectively.

Table 4. Results of determination of total and ions hardness of groundwater spring No 4 (n=3).

| Month   | H_av | S_r, % | C(Ca)_av | S_r, % | C(Mg)_av | S_r, % |
|---------|------|-------|----------|-------|----------|-------|
| Nov 17 | 6.17 | 1.87  | 3.58     | 1.61  | 2.58     | 5.91  |
| Dec 17 | 7.00 | 2.47  | 5.00     | 0.00  | 2.00     | 8.66  |
| Jan 18 | 6.58 | 0.88  | 4.42     | 1.31  | 2.17     | 5.33  |
| Feb 18 | 6.83 | 2.24  | 4.83     | 1.19  | 2.00     | 8.66  |
| Mar 18 | 4.92 | 1.17  | 3.00     | 3.33  | 1.92     | 7.97  |
| Apr 18 | 6.08 | 1.90  | 5.17     | 1.12  | 0.92     | 16.66 |
| May 18 | 6.67 | 2.29  | 5.50     | 0.00  | 1.17     | 13.09 |
| Jun 18 | 5.08 | 1.14  | 3.67     | 1.57  | 1.42     | 8.15  |
| Jul 18 | 6.25 | 1.60  | 5.08     | 1.14  | 1.17     | 4.95  |
| Aug 18 | 6.08 | 0.95  | 5.50     | 0.00  | 0.58     | 9.90  |
| Sep 18 | 6.00 | 1.67  | 5.42     | 1.07  | 0.58     | 9.90  |
| Oct 18 | 6.08 | 0.95  | 5.42     | 1.07  | 0.67     | 8.66  |
| Max    | 7.00 | 2.47  | 5.50     | 3.33  | 2.58     | 16.66 |
| Min    | 4.92 | 0.88  | 3.00     | 0.00  | 0.58     | 4.95  |
| Average| 6.15 | 1.6   | 4.72     | 1.1   | 1.43     | 8.9   |
| S_r, mmol/l | 0.44 | -    | 0.70    | -     | 0.59    | -    |
| S_r, %  | 7.1  | -    | 14.8    | -     | 40.9    | -    |

Moreover, Sr, respectively, had a value of 4.0%, 4.8%, and 16.5%. As it follows from figure 1, springs No. 2 and No. 3 are located at a distance of about 300 meters from each other and at the same time on one straight line towards the reservoir. The average annual values of the total hardness and concentration of calcium and magnesium ions in the underground waters of springs No. 3 and No. 2 are practically the same, but the Sr, 4.0% and 4.8% obtained for the annual cycle for the total hardness and concentration of calcium ions (less than 6%) indicate that during the study period there are insignificant deviations of the total hardness and concentration of calcium and magnesium ions in the underground waters of springs No. 3 and No. 2 are practically the same, but are different from those for spring No. 4. Fluctuations in the values of total hardness and concentrations of calcium and magnesium ions in groundwater during the year were in the range of 6.15 ± 0.44 mmol/l; 4.72 ± 0.70 mmol/l and 1.43 ± 0.59 mmol/l, respectively. Moreover, S_r, respectively, had a value of 7.1%, 14.9%, and 40.9%, which are quite close to the S_r values obtained by statistical processing of the results of a chemical analysis of groundwater in springs No. 1 and No. 3 (see table 1 and 2).

Thus, the static approach to assessing the results of chemical analysis of spring waters made it possible to obtain the average annual background values of the total hardness and concentrations of calcium and magnesium ions from October 2017 to October 2018 for the underground water of the studied springs with a note that significant deviations occurred during the study period total hardness.
and concentration of calcium and magnesium ions from the average annual values in the underground water of springs No. 1, No. 3 and No. 4.

Dynamic approach. Spring No. 1. From the graph shown in figure No. 2 it follows that the total hardness of the underground water changed significantly and differently during the study period, but the average annual tendency to increase or decrease is clearly not expressed.

![Figure 3. Dynamics of total hardness and concentration of calcium and magnesium ions in underground water of spring No 1.](image)

At the same time, with a relatively constant value of the total hardness of groundwater during the study period, there is an increase in the concentration of calcium ions and a proportional decrease in the concentration of magnesium ions on average by 0.2 mmol per month. This leads to the fact that MCa/Mg in the first months of the studies was about 1. Then at the end of the studies it increased to 4. The replacement of magnesium ions with calcium ions in groundwater indicates the active occurrence of metabolic processes in the underground horizons of spring No. 1 during the study period.

Spring No. 2. From the graph presented in figure 3 it follows that the total hardness of groundwater decreases during the study period by 1.5 mmol/l and this decrease occurs by 75% due to a decrease in the concentration of magnesium ions and by 25% due to reduce the concentration of calcium ions.

![Figure 4. Dynamics of total hardness and concentration of calcium and magnesium ions in underground water of spring No 2.](image)

A distinctive feature of the underground water of spring No. 2 is the relative constancy of MCa/Mg during the entire period of research at the level of 3.3 ÷ 3.5. Such constancy of MCa/Mg does not
indicate a variable nature, but rather a relatively stable occurrence of metabolic processes in the underground horizons of spring No. 2 during the study period, i.e. we can talk about relative stability, the influence of the natural factor on the formation of the total hardness and concentration of calcium and magnesium ions in the underground water of spring No. 2.

Spring No. 3. Figure 4 shows that, the same as in the case with groundwater of Spring No. 1, the total hardness of the groundwater of Spring No. 3 changed significantly and differently during the study period, but the average annual increase in total hardness was 0.5 mmol/l which should be attributed more to the error of the analytical methodology than to a certain trend.

Figure 5. Dynamics of total hardness and concentration of calcium and magnesium ions in underground water of spring No 3.

At the same time, with a relatively constant value of the total hardness of groundwater during the study period, an increase in the concentration of calcium ions and a decrease in the concentration of magnesium ions are observed. This leads to the fact that the M Ca/Mg in the first months of the studies was about 3, then at the end of the studies it increased to 7. The replacement of magnesium ions with calcium ions in groundwater indicates a variable nature of the exchange processes in the underground horizons of spring No. 3 in the studied period i.e. we can talk about the relative variable influence of the natural factor on the formation of the total hardness and concentration of calcium and magnesium ions in the underground water of spring No. 3.

Spring No. 4. From the graph presented in figure 5, it follows that, the same as in the case with groundwater of Spring No. 1, the total hardness of the groundwater of Spring No. 3 changed significantly and differently during the study period, and the average annual decrease in total hardness was 1.0 mmol/l which should most likely be attributed to a certain trend.

At the same time, during the study period, there is a significant increase in the concentration of calcium ions and a decrease in the concentration of magnesium ions. This leads to the fact that the M Ca/Mg in the first months of the research was about 2, then at the end of the research it increased to 10, which gives reason to talk about the relative variable influence of the natural factor on the formation of the total hardness and concentration of calcium and magnesium ions in the underground water of the Spring No 4.
Figure 6. Dynamics of total hardness and concentration of calcium and magnesium ions in underground water of spring No 4.

4. Conclusion
The methodology for assessing the degree of influence of natural factors on the quality of groundwater throughout the year was expanded by examining in a static and dynamic position the results of titrimetric determination of the total hardness and concentration of calcium and magnesium ions in the groundwater of four springs, which made it possible to establish:

- the level of average annual background values of the total hardness and concentration of calcium and magnesium ions in the underground water of the four springs;
- significant deviations of the total hardness and concentration of calcium and magnesium ions during the study period from the average annual values in the underground water of springs No. 1, No. 3 and No. 4;
- the relative variable for the groundwater of springs No. 1, No. 3 and No. 4 and the influence of the natural factor on the formation of the total hardness and concentration of calcium and magnesium ions during the study period according to the value of Mca/Mg, relatively stable for the underground water of spring No. 2.
- the most resistant to the influence of the natural factor on the formation of the total hardness and concentration of calcium and magnesium ions in the studied period should be recognized as the groundwater of spring No. 2.

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