Static and dynamic approach to estimation of spring water mineralization stability as a factor of groundwater ecological safety

A E Vasyukov, A P Korzhavyi and S N Nikulina
The Tsiolkovsky Kaluga State University, Kaluga branch of Bauman Moscow State Technical University

E-mail: Voinsveta579@mail.ru

Abstract. To assess the degree of influence of technogenic factors on the groundwater mineralization, it is proposed to consider simultaneously in a static and dynamic position the results of conductometric determination in spring water of generalized indicators, such as electrical conductivity and the coefficient of identification of the mineral composition of water. This is shown by the example of four springs located in the territory of Kaluga. This made it possible to establish the average annual background values of electrical conductivity and the coefficient of identification of the mineral composition of water, as well as to justify the permissible or weakly expressed degree of influence of technogenic factors on the quality of groundwater in the period from November 2017 to October 2018 by the criterion of exceeding the error of the conductometric method (2%) by 3 or more times.

1. Introduction
The conclusion about changes in the quality of groundwater and the development of necessary measures to prevent pollution and depletion is based on reliable results of groundwater monitoring, which is a system of monitoring, evaluating and predicting changes in the state of groundwater under the influence of anthropogenic and natural factors. One of the most accessible areas for such monitoring is the monitoring of spring water in urban areas [1-7]. The main disadvantages of monitoring spring waters at the determining stage of observations include one-time or random sampling of groundwater for a short observation time, which makes it impossible to detect dynamic intra-annual trends in the composition and properties of groundwater. These shortcomings are also characteristic of sanitary-hygienic studies of spring waters in Kaluga, which were obtained as a result of chemical analysis of single samples taken in the spring-summer period [8-10].

It should be noted that according to the requirements of, in order to obtain reliable information, the frequency of control should be at least 1 time per month, and when analyzing the results of the control, it is necessary to take into account the dynamics of the levels of controlled indicators relative to the background values. The background concentration of the pollutant is the base or reference point for assessing the pollution of the studied environmental object [11-13]. Since pollution is a process occurring in space and time, the background concentration should be associated with the average concentration of the pollutant over a certain period, obtained as a result of statistical processing of a sufficient amount of the results of chemical analysis of samples of the studied environmental object. With this approach, the results of the analysis of single samples for the content of chemicals, including
the content of the main ions that determine the salinity of groundwater, cannot serve as background concentrations.

Mineralization of groundwater varies widely. To obtain data on the mineral composition of natural waters, various physicochemical methods are used, among which it is necessary to distinguish a conductometric method as a fairly accurate and simple, meeting the requirements of "green" chemistry [14]. It allows indirectly evaluate both the mineralization of water by specific electrical conductivity (SEC, μS/cm) [15] and by the constancy of the ratio of the main ions in the studied natural water [16].

The aim of the work is to develop methodological approaches to assess the stability of the mineral composition of spring water as an environmental safety factor of groundwater in urban areas according to the results of determining SEC of spring water by the conductometric method.

2. Research objects and methods
The objects of study were the groundwater of four springs (figure 1): spring No. 1 - Berezuevsky ravine, down from the Stone Bridge, turn st. Cosmonaut Komarov on the street Ryleyev; spring No. 2 - the intersection of Vygonnaya and Sadovaya streets; spring No. 3 - Azarov district, the right side of the river. Terepets, summer house "Progress"; spring No. 4 - a site near the St. Lavrentievsky Monastery at the intersection of Sadovaya and Shirokaya Streets. Spring waters were taken monthly from November 2017 to October 2018.

The conductivity measurements of spring water were carried out using a conductivity meter - anion analyzer of the laboratory series Anion 4100 model A4155 (K-A4155). The operability of the measuring channels was checked in accordance with the K-A4155 operating manual [15] during the course of the current comparisons and analysis of the results of measurements of the electric conductivity of distilled water and standard KCl solutions.

To control the constancy of the mineral composition of spring water, we used a generalized indicator of water quality — the coefficient of identification of the mineral composition (C_{id}, cm/μSm), which is equal to the tangent of the angle of inverse SEC of water depending on the degree of dilution of the studied water with distilled water [14]. In its physical meaning, C_{id} reflects the sum
of the dependences of the SEC of the main cations and anions on the degree of dilution and has a strictly defined value for a given mineral composition of the studied one.

3. Results and discussion

The statistically processed results of the determination of SEC in the studied groundwater of the four springs selected from November 2017 to October 2018 are presented in Table 1.

The data of Table 1 show that the found values of the standard deviations (S_r) of the results of determining the conductivity of three parallel samples range from: for spring No. 1 - 0.09 ± 0.77 %, for spring No. 2 - 0.11 ± 2.12 %, for spring No. 3 - 0.31 ± 1.65 %, for spring No. 4 - 0.11 ± 2.03 %. They do not exceed the certified error of the conductometric method, because this method is one of the most accurate analytical control methods and the error in determining the UEP of aqueous solutions is in the range of 1.2 %.

Table 1. Results of determination of SEC (μS/cm) of groundwater of four springs during the study period (n=3).

| Month | Spring No 1 | Spring No 2 | Spring No 3 | Spring No 4 |
|-------|-------------|-------------|-------------|-------------|
|       | SEC_{av}    | S_r, %      | SEC_{av}    | S_r, %      | SEC_{av}    | S_r, %      | SEC_{av}    | S_r, %      |
| Nov 17 | 1008.0      | 0.40        | 842.0       | 0.36        | 950.0       | 0.63        | 542.0       | 2.03        |
| Dec 17 | 1033.0      | 0.39        | 864.0       | 0.35        | 941.0       | 0.32        | 561.0       | 1.60        |
| Jan 18 | 1020.0      | 0.59        | 873.0       | 0.34        | 947.0       | 0.42        | 562.8       | 0.11        |
| Feb 18 | 1043.0      | 0.48        | 896.0       | 0.78        | 965.0       | 0.31        | 573.5       | 0.19        |
| Mar 18 | 1048.0      | 0.38        | 899.0       | 1.33        | 965.0       | 0.41        | 569.0       | 0.70        |
| Apr 18 | 1054.0      | 0.09        | 917.0       | 1.31        | 972.0       | 1.65        | 578.0       | 0.52        |
| May 18 | 1062.0      | 0.47        | 929.0       | 2.12        | 972.0       | 0.93        | 572.0       | 0.35        |
| Jun 18 | 1042.0      | 0.38        | 950.0       | 1.05        | 973.0       | 0.41        | 578.1       | 0.17        |
| Jul 18 | 1034.0      | 0.10        | 954.0       | 0.21        | 972.0       | 0.41        | 579.0       | 0.52        |
| Aug 18 | 1033.0      | 0.77        | 952.0       | 0.74        | 971.0       | 0.31        | 578.0       | 0.35        |
| Sep 18 | 1009.0      | 0.20        | 922.0       | 0.33        | 941.0       | 0.53        | 560.0       | 0.54        |
| Oct 18 | 1016.0      | 0.30        | 918.0       | 0.11        | 961.0       | 0.52        | 571.0       | 0.35        |
| Max    | 1062.0      | 0.77        | 954.0       | 2.12        | 973.0       | 1.65        | 579.0       | 2.03        |
| Min    | 1008.0      | 0.09        | 842.0       | 0.11        | 941.0       | 0.31        | 542.0       | 0.11        |
| SEC_{av} | 1033.5      | -           | 909.7       | -           | 960.8       | -           | 568.7       | -           |
| S_r    | 13.7        | -           | 29.1        | -           | 10.7        | -           | 8.2         | -           |
| S_r, % | 1.3         | -           | 3.2         | -           | 1.1         | -           | 1.4         | -           |

The results of statistical processing showed that the SEC fluctuations during the year were within: for spring No. 1 - 1033.5 ± 13.7 μS/cm, for spring No. 2 - (909.7 ± 29.1 μS / cm, for spring No. 3 - 960.8 ± 10.7 μS/cm and for spring No. 4 - 568.7 ± 8.2 μS / cm. In this case, Sr, respectively, had a value of 1.3%, 3.2%, 1%, 1% and 1.4%. Since the calculated Sr values do not exceed the error of the conductometric method (2%) by 3 or more times, the average values of SEC for spring No. 1 are 1034 μS / cm, for spring No. 2 - 910 μS / cm, for spring No. 3 - 961 μS / cm and for spring No. 4 - 569 μS / cm can be accepted as background average annual values of UEP in the period from November 2017 to October 2018.

The results of numerous studies that show that the average coefficient of proportionality between SEC and total mineralization is 0.65, it can be used to switch from SEC to general water mineralization. In this case, the background average annual values of the total mineralization of spring waters were 672, 591, 625, and 370 mg/l, respectively.

Total mineralization is a general indicator of water quality, having a hygienic standard for water quality of 1000 mg/l. In this case, the norm of the error in measuring total mineralization by dry residue is set at the level δn = ± 10% [20]. If we compare the two methods for determining the total...
mineralization by SEC and solids in terms of efficiency, metrological characteristics, financial costs and the requirements of "green" chemistry, then clearly the method for determining the total mineralization by SEC should be put in first place for all of these indicators.

Taking into account the background average annual values of the total mineralization of spring waters, respectively, 672, 591, 625 and 370 mg/l, the calculated \( S_r \) values and the hygienic norm of water quality 1000 mg/l, the degree of influence of technogenic factors on the groundwater quality according to the hygienic classification can be considered on this permissible research stage, because periodic excess of background indicators at their maximum levels throughout the year is below hygienic standards.

A slightly different conclusion about the degree of influence of technogenic factors on the groundwater quality can be made in the process of further research with a graphical review of the results (figure 2).

**Figure 2.** Dynamics of SEC of spring waters in the studied period.

The graphs of SEC of groundwater in springs No. 1, No. 3 and No. 4 are practically parallel to each other and have no significant kinks, which visually confirms the permissible degree of influence of technogenic factors on the quality of underground waters. At the same time, three sections can be distinguished on the SEC chart of groundwater of spring No. 2: SEC has been increasing since November 2017 to June 2018. Stabilization has been observed from June to August 2018 and a decrease has been seen from August to October 2018.

The increase of SEC in the first section occurs from 842 to 954 \( \mu \text{S/cm} \), i.e. by 112 \( \mu \text{S/cm} \) or 13.3%, which cannot be connected with the error of the conductometric method. In this case, we can talk for spring No. 2 about the presence of a weakly expressed degree of influence on the quality of groundwater of technogenic factors throughout the year.

Thus, to assess the degree of influence of technogenic factors on the quality of groundwater throughout the year, it is necessary to analyze the results of chemical analysis of the studied waters in two positions simultaneously: static (tabular) according to the results of statistical processing and the error of the used method of chemical analysis, and dynamic - according to changes in the graphs in the studied period.

According to the proposed scheme, we will analyze the results of the monthly determination of groundwater \( C_{id} \) of four springs (table 2).
The results of statistical processing showed that $C_{id}$ fluctuations during the year were within the following values: for spring No. 1 - $0.909 \pm 0.034$ cm/$\mu$S, for spring No. 2 - $1.056 \pm 0.042$ cm/$\mu$S, for spring No. 3 - $0.991 \pm 0.019$ cm/$\mu$S and for spring No. 4 $1.565 \pm 0.019$ cm/$\mu$S.

**Table 2.** Results of determination of groundwater $C_{id}$ (cm/MSM) of four springs in the period from November 2017 to October 2018 ($n=3$-4).

| Month | Spring No 1 | | Spring No 2 | | Spring No 3 | | Spring No 4 | |
|-------|-------------|------|-------------|------|-------------|------|-------------|------|
|       | $C_{id ave}$ | $S_r, \%$ | $C_{id ave}$ | $S_r, \%$ | $C_{id ave}$ | $S_r, \%$ | $C_{id ave}$ | $S_r, \%$ |
| Nov17 | 0.963       | 0.11  | 1.139       | 0.44  | 0.990       | 0.81  | 1.540       | 1.95  |
| Dec17 | 0.934       | 0.54  | 1.131       | 0.53  | 1.028       | 0.39  | 1.570       | 1.91  |
| Jan18 | 0.907       | 0.22  | 1.114       | 0.63  | 1.000       | 0.00  | 1.587       | 0.03  |
| Feb18 | 0.925       | 1.30  | 1.090       | 1.83  | 1.010       | 0.99  | 1.530       | 2.61  |
| Mar18 | 0.870       | 0.34  | 1.050       | 1.90  | 0.970       | 1.24  | 1.600       | 1.88  |
| Apr18 | 0.878       | 0.34  | 1.060       | 0.94  | 0.960       | 1.04  | 1.538       | 0.78  |
| May18 | 0.890       | 1.12  | 1.050       | 2.86  | 0.988       | 2.02  | 1.547       | 0.13  |
| Jun18 | 0.870       | 1.15  | 0.990       | 0.61  | 0.978       | 0.31  | 1.580       | 1.27  |
| Jul18 | 0.840       | 0.60  | 1.007       | 0.99  | 0.961       | 0.52  | 1.560       | 1.28  |
| Aug18 | 0.918       | 0.65  | 0.962       | 0.83  | 0.975       | 0.51  | 1.601       | 0.31  |
| Sep18 | 0.957       | 1.04  | 1.029       | 1.07  | 1.009       | 0.62  | 1.566       | 0.08  |
| Oct18 | 0.962       | 1.25  | 1.050       | 0.76  | 1.021       | 0.49  | 1.566       | 0.08  |
| Nov18 | 0.963       | 1.30  | 1.139       | 2.86  | 1.028       | 2.02  | 1.601       | 2.61  |
| Min   | 0.840       | 0.11  | 0.962       | 0.44  | 0.960       | 0.00  | 1.530       | 0.03  |
| SECav | 0.909       | -     | 1.056       | -     | 0.991       | -     | 1.565       | -     |
| $S_r$ | 0.034       | -     | 0.042       | -     | 0.019       | -     | 0.019       | -     |
| $S_r, \%$ | 3.7 | -     | 4.0         | -     | 1.9         | -     | 1.2         | -     |

Moreover, $S_r$, respectively, had a value of 3.7%, 4.0%, 1.9% and 1.2%, which do not exceed the error of the conductometric method (2%) by 3 or more times. Based on this, the average values of the groundwater $C_{id}$ for the spring No. 1 are as follows: $0.909$ cm/$\mu$S, for the spring No. 2 - $1.056$ cm/$\mu$S, for the spring No. 3 - $0.991$ cm/$\mu$S and for the spring No. 4 - $1.565$ cm/$\mu$S, they can be taken as background average annual $C_{id}$ values between November 2017 and October 2018.

The same as in the case of SEC, a graphical examination of the obtained results makes it possible to obtain additional information on the intra-annual features of the change in the quality of the studied groundwater (figure 3).
Figure 3. Dynamics of $C_{id}$ of spring water in the studied period.

The graphs of $C_{id}$ groundwater values of springs No. 3 and No. 4 are practically parallel to each other and have no significant kinks, which visually confirms the permissible degree of influence of technogenic factors on the groundwater quality. At the same time, on the graph of the $C_{id}$ value of the underground water of spring No. 1 and No. 2, two sections can be distinguished: a decrease in the Kidd value from November 2017 to July 2018 increase from August to October 2018.

The largest decrease in the $C_{id}$ value from 1.139 to 0.962 cm/μS, i.e. by 0.177 cm/μS or 15.5%, observed for groundwater of spring No. 2 in the first section, which suggests that there is a slightly pronounced degree of influence on the quality of groundwater of spring No. 2 of technogenic factors throughout the year and coincides with the above conclusions on the degree of influence on the quality of groundwater of spring No. 2 according to the results of determining SEC of underground water of spring No. 2.

A significant decrease in the $C_{id}$ value of groundwater in the first section from 0.963 to 0.840 cm/μS, i.e. by 0.123 cm/μS or 12.7%, it was noted for spring No. 1, while according to the schedule of changes in underground water conductivity of spring No. 1 (figure 2), it is difficult to unequivocally state that there are significant changes in underground conductivity of underground water in the study period. Such a significant decrease in the $C_{id}$ value of groundwater, which exceeds the error of the conductometric method by 6 times, makes it possible to talk about the presence of a weakly pronounced degree of influence of technogenic factors on the quality of groundwater throughout the year and for spring No. 1.

Thus, the simultaneous consideration in a static and dynamic position of the results of determining the SEC and $C_{id}$ underground waters of the studied springs allows us to establish the background values of indicators and speak for the groundwater of springs No. 3 and No. 4 about the permissible degree, and for underground water of springs No. 1 and No. 2 about weak pronounced degree of influence on the quality of groundwater of technogenic factors in the period from November 2017 to October 2018.

4. Conclusions

The methodology for assessing the degree of influence of technogenic factors on the groundwater quality throughout the year has been expanded by simultaneously examining the results of conductometric determination of SEC and $C_{id}$ on the example of groundwater of four springs in a static and dynamic position, which made it possible to establish:
the level of background SEC values (μS/cm) during the year: for spring No. 1 - 1033.5 ± 13.7, for spring No. 2 - 909.7 ± 29.1, for spring No. 3 - 960.8 ± 10.7 and for spring No. 4 - 568.7 ± 8.2.

- the level of background Cid values (cm/μSm) during the year: for spring No. 1 - 0.909 ± 0.034, for spring No. 2 - 1.056 ± 0.042, for spring No. 3 - 0.991 ± 0.019 and for spring No. 4 - 1.565 ± 0.019.

- the permissible degree for the underground water of springs No. 3 and No. 4, and a weakly pronounced degree of influence of technogenic factors on the groundwater quality in spring water from springs No. 1 and No. 2 from November 2017 to October 2018.

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