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Various Features of Nitrate Pollution of Spring Water of the Kaluga Urban District

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***Abstract*—A simple assessment of nitrate pollution of spring water of the Kaluga urban district using the threshold limit value showed that the decrease in the average concentration of nitrates in groundwater of 30 springs from 2001 to 2016 is almost 25%, but this assessment does not allow solving a number of environmental problems. According to the proposed criterion for not exceeding the margin of error standard for the determining nitrates methods and the total hardness of water, the standard deviation values show that there is stable nitrate content in spring water of only 4 sources and this indicates lack of significant impacts of natural and anthropogenic factors on these springs. At the same time, the effect of prolonged rains on the quality of groundwater was quantitatively confirmed for some springs: on average, the nitrate content increased by almost 2.3 times after rains in June 2004.**

***Keywords*—*groundwater pollution, nitrates, water hardness, spring water, pollution assessment methodology*.**

I. Introduction

Spring water pollution can be considered as a process of changing the chemical composition of groundwater as a result of the input of nitrogen-containing pollutants, leading to a deterioration in the quality of water consumption or water use, due to anthropogenic factors (human activities) or natural factors (drought, heavy rains). Groundwater pollution is usually expressed through the excess of nitrate concentration over the threshold limit values (TLV), although for solving many environmental problems it is important to exceed the long-term natural (background) average (within its extreme values) nitrate concentration.

The objective is to establish the patterns and influence of natural factors on the nitrate content in spring water of the Kaluga urban district territory according to the results of many years of research.

Spring water, as an alternative to centralized drinking water supply, is constantly examined, as a rule, at the regional level for chemical and biological pollution or for establishment of background concentrations of chemicals [1-9]. According to these works, it follows that the general qualitative laws are:

- high and very high variation in the content of nitrates in spring water according to the seasons of the year, as well as significant differences in years;
- increase in mineralization and general hardness of spring water is regional in nature, associated with the modern regional hydrogeochemical background;
- relationship between concentrations of nitrates in groundwater and amount of precipitation for most of the studied springs.

The quantitative characteristics of the indicated patterns of spring water in the Kaluga territory were not fully reflected in the works [10-11].

II. Research methodology

The object of the study was groundwater from 34 springs located in the Kaluga urban district territory. During the studies, 4 springs have dried up; therefore, statistical processing was carried out according to the chemical analysis of water from 30 sources. The subject of research is the level of nitrate concentration and the total hardness of spring water.

Single samples were taken in the spring-summer period of 2001-2004 and 2011-2016. In order to determine the concentration of nitrates in the studied water, we used GOST 18826-73 “Drinking water. Methods for determining the content of nitrates”, and to determine the total hardness – GOST 4151-72 “Drinking water. Method for determining the total stiffness”.

Practical significance of this study is about to obtain statistically reliable data on “environmentally friendly” and contaminated springs of the Kaluga urban district in terms of nitrate content and total spring water hardness in the period of 2001-2016.

III. Research results and discussion

The results of statistical processing of data from a chemical analysis of spring water for the content of nitrates are presented in Table I.

TABLE I. RESULTS OF STATISTICAL PROCESSING OF DATA ON THE CONTENT OF NITRATES IN SPRING WATER (MG/DM^3), SELECTED DURING THE STUDY PERIOD

Spring No.	Year									$C_{average}$	S_r, %
	2001	*2002*	*2003*	*2011*	*2012*	*2013*	*2014*	*2015*	*2016*		
1	97.8	43.0	97.8	67.4	60.2	45.7	14.4	38.7	39.0	56.0	49.9
4	69.6	60.0	63.0	65.0	58.0	51.6	48.3	38.8	39.0	54.8	20.3
5	54.7	58.0	92.8	145	36.6	36.7	48.7	35.0	40.4	60.9	59.7
6	145	146	118	38.5	140	124	187	115	101	124	32.7
8	215	143	198	166	169	201	116	88.4	130	158	26.9
9	9.9	5.0	3.1	0.1	0.1	7.2	4.3	6.7	0.1	4.1	87.2
10	193	189	6.6	91.7	87.3	85.4	71.2	57.0	53.6	92.8	66.2
11	53.0	30.0	41.4	40.7	43.3	46.4	37.8	32.2	39.5	40.5	17.2
12	29.8	35.0	32.3	25.1	27.5	30.9	36.3	32.4	27.6	30.8	11.9
13	64.6	65.0	76.2	63.0	52.8	56.1	61.7	51.2	56.9	60.8	12.6
14	44.7	43.0	54.7	21.0	32.2	44.4	55.6	52.2	46.9	43.9	25.4
15	69.6	83.0	74.6	88.2	55.9	62.0	66.5	54.8	56.4	67.9	17.8
16	64.6	83.0	78.8	52.2	51.7	63.3	63.3	59.6	65.0	66.2	15.1
17	67.9	66.0	78.7	80.0	53.1	54.8	51.2	43.6	55.3	61.2	20.7
18	12.6	19.2	23.1	23.5	38.5	27.3	27.3	20.6	29.0	24.6	29.5
19	31.5	15.0	21.5	18.2	1.2	22.0	22.0	16.7	14.3	18.0	45.2
20	24.8	18.0	17.9	18.8	31.7	66.2	46.6	13.7	20.3	28.7	60.1
21	43.8	20.0	56.3	45.1	51.1	45.0	46.8	29.1	38.0	41.7	26.8
22	61.3	31.0	99.4	59.2	65.3	57.7	57.7	44.0	49.8	58.4	31.9
23	28.6	23.0	25.0	32.0	40.9	23.4	49.3	26.5	26.8	30.6	29.1
24	17.4	43.0	24.9	15.2	34.3	22.0	19.5	20.2	19.9	24.0	37.3
25	19.3	26.0	0.6	13.1	13.8	19.2	101	68.4	8.8	30.0	109
26	14.0	19.0	0.5	20.3	17.9	11.6	104	32.4	9.9	25.5	120
27	53.0	45.0	0.6	33.0	42.0	39.1	19.9	24.6	19.4	30.7	52.7
28	14.9	35.0	0.4	9.1	9.9	11.7	14.5	12.7	7.0	12.8	73.6
29	111	31.3	0.6	82.7	3.0	26.2	15.5	13.8	23.8	34.3	110
30	122	166	75.4	78.7	57.3	79.3	80.7	68.4	55.6	87.0	40.6
32	60.0	65.0	14.9	155	108	31.9	41.4	36.8	37.4	61.2	72.1
33	63.0	52.0	63.3	58.1	50.5	34.8	40.2	38.2	38.4	48.7	23.0
34	92.4	89.0	0.1	21.7	83.9	53.8	2.7	10.2	78.8	48.1	81.9
$C_{average}$	65.0	58.2	48.0	54.3	50.5	49.4	51.7	39.4	40.9		
C_{max}	215	189	198	166	169	201	187	115	130		
C_{min}	9.9	5.0	0.1	0.1	0.1	7.2	2.7	6.7	0.1		
S_r, %	78.0	80.3	95.7	79.0	76.3	76.6	73.9	61.4	68.0		

The average concentration of nitrates in the groundwater of 30 springs in the period from 2001 to 2016 significantly decreased from 65 to 40 mg/dm^3 (almost by 25%). In 2001 in 18 springs underground water contained nitrates higher than the TLV, and in 2016 this indicator decreased to 10 sources.

There is a very high variation in the nitrate content in groundwater from different springs, as well as significant differences in years: from the practical absence (below the limit of determination of the analytical methodology) to 200 mg/dm^3 or more, which coincides with published data [4], [7].

Averaged data on the nitrate content over 9 years of observation and the calculated standard deviation (S_r) show that S_r is less than 15% only in three springs (margin of error for methods for determining nitrates in water [12]). This gives reason to believe that only in these three sources there is a stable nitrate content in spring waters during the study period and, as a result, in the formation area of springs No. 12, No. 13 and No. 16 there was no significant influence of natural and technogenic factors during the study period. This list also includes spring No. 9, the water of which contains small concentrations of nitrates during the study period from 2001 to 2016, an average of 4 mg/dm^3, which is a rather rare phenomenon.

The literature data [3], [6], [8] indicated the influence of rains on the quality of spring water, but the degree of this influence was rarely quantified. Table II shows the nitrate content in spring water before and after heavy rains in June 2004 (according to the meteorological center, 160 mm of precipitation fell this month). As follows from the presented data, the average nitrate content after rains increased from 72.9 to 169 mg/dm^3, i.e. increased by almost 2.3 times. Moreover, for spring No. 17, such an increase occurred almost by 9 times.

TABLE II. THE NITRATE CONTENT IN SPRING WATER BEFORE AND AFTER HEAVY RAINS IN JUNE 2004

Spring No.	Before rainfalls, mg/dm^3	After rainfalls, mg/dm^3	Increase, mg/dm^3	Increase, %
3	103	252	149	143
4	58.0	105	47.1	81.1
5	35.2	84.0	48.8	138
6	59.7	246	187	313
7	205	285	80.3	39.1
8	159	346	187	117
10	153	252	98.8	64.4
11	24.9	68.3	43.5	174
12	27.4	53.8	26.4	96.6
13	59.7	89.3	29.6	49.6
14	31.5	73.5	42.0	133
15	59.7	110	50.6	84.8
16	48.9	99.8	50.9	104
17	43.1	372	329	763
19	23.2	94.6	71.4	307
$C_{average}$	72.9	169	96.1	174
C_{max}	205	372	329	763
C_{min}	23.2	53.8	26.4	39.1
S_r, %	55.3	102	76.9	151

To confirm the absence of significant impacts of natural and anthropogenic factors on the territory of formation of springs No. 9, No. 12, No. 13 and No. 16 during the formation of groundwater quality during the study period, we consider the results of statistical processing of the obtained data on the total spring water hardness (Table III).

TABLE III. RESULTS OF STATISTICAL PROCESSING OF THE TOTAL HARDNESS OF SPRING WATER (MMOL/DM^3), SELECTED DURING THE STUDY PERIOD

Spring No.	**Year**									$C_{average}$	S_r, %
	2001	***2002***	***2003***	***2011***	***2012***	***2013***	***2014***	***2015***	***2016***		
1	10.7	10.6	11.2	10.2	7.9	9.5	8.2	8.3	8.3	9.4	13.5
4	7.6	7.5	9.0	9.8	4.5	6.3	6.4	8.8	8.3	7.6	21.6
5	7.5	7.4	8.7	7.9	10.0	8.1	6.9	9.8	9.0	8.4	13.0
6	8.2	9.0	11.1	11.0	11.0	7.8	9.9	7.6	6.1	9.1	19.7
8	8.3	8.7	9.6	11.1	5.0	6.5	4.9	5.8	5.8	7.3	30.2
9	3.5	3.6	3.9	4.3	4.4	4.3	4.1	4.0	4.1	4.0	7.8
10	5.8	6.1	0.7	6.0	5.9	5.0	5.1	4.9	4.6	4.9	34.0
11	6.0	6.5	6.7	7.5	7.7	6.6	6.6	6.5	5.2	6.6	11.2
12	7.1	6.5	6.7	8.5	8.0	6.8	7.8	6.5	5.2	7.0	14.1
13	7.3	7.0	6.8	8.0	7.4	7.7	7.7	6.5	6.8	7.2	6.9
14	4.8	5.6	5.7	6.7	6.6	6.2	6.4	7.2	5.7	6.1	12.0
15	6.9	7.0	7.2	7.2	7.7	7.7	7.7	7.2	7.8	7.4	4.7
16	6.4	7.2	6.3	7.4	8.3	7.3	7.0	7.0	7.6	7.2	8.5
17	5.6	6.0	7.4	7.3	7.4	7.4	7.1	7.0	6.7	6.9	9.5
18	4.7	4.5	5.0	5.8	5.7	5.2	5.2	4.9	6.8	5.3	13.5
19	2.8	2.3	2.6	3.0	3.2	2.3	3.7	3.0	3.5	2.9	16.7
20	4.8	5.2	6.3	7.6	7.7	6.5	5.1	6.1	8.1	6.4	19.2
21	6.3	4.7	5.8	8.0	8.4	5.0	4.7	11.2	8.4	6.9	32.0
22	8.9	5.5	8.4	8.4	8.4	9.4	9.4	9.4	8.8	8.5	14.4
23	7.2	3.3	5.8	11.0	9.6	7.4	7.3	9.6	7.7	7.7	29.9
24	6.7	5.6	8.1	7.6	6.5	5.6	7.0	5.4	6.8	6.6	14.2
25	5.5	4.3	5.5	6.4	5.9	6.0	6.4	6.2	5.2	5.7	11.9
26	5.4	3.9	5.8	5.8	5.9	5.7	5.7	5.5	5.2	5.4	11.4
27	5.7	5.7	7.2	8.0	7.2	6.5	5.7	5.4	6.8	6.5	13.9
28	4.9	5.1	6.9	6.8	7.3	6.4	5.1	5.8	5.6	6.0	15.0
29	6.1	5.6	5.5	8.0	6.1	6.0	4.8	12.0	12.2	7.4	38.3
30	6.0	4.8	8.2	9.3	9.3	6.1	7.8	7.1	5.5	7.1	23.2
32	2.7	2.8	1.4	3.7	5.8	6.7	6.5	6.5	6.3	4.7	43.5
33	5.8	5.3	6.5	7.1	7.2	5.9	6.4	6.2	7.2	6.4	10.8
34	6.6	4.0	7.2	5.7	8.6	4.4	4.7	4.5	4.0	5.5	29.4
$C_{average}$	6.2	5.7	6.6	7.5	7.2	6.4	6.4	6.9	6.6		
C_{max}	10.7	10.6	11.2	11.1	11.0	9.5	9.9	12.0	12.2		
C_{min}	2.73	2.3	0.7	3.0	3.2	2.3	3.7	3.0	3.5		
S_r. %	27.6	32.6	36.1	26.6	24.3	22.9	23.4	29.8	27.4		

The average total hardness of groundwater in all springs during the study period varied within rather narrow limits of 5.7-7.5 mmol/dm^3, and the maximum concentrations reached 11-12 mmol/dm^3.

The averaged data on the total hardness for 9 years of observations and the calculated standard deviations (S_r) show that the S_r value was less than 15% in 17 springs (margin of error for the methods for determining the total hardness in water [12]), among which only 4 springs (No. 9, No. 12, No. 13 and No. 16) noted in the assessment of nitrate pollution. This indicates a weak relationship between factors affecting the formation of nitrate content in spring water and its general hardness.

IV. CONCLUSION

Methodology for assessing the natural and anthropogenic impacts on nitrate pollution of groundwater in the territory of the city of Kaluga was supplemented by using the criterion for not exceeding the margin of error for determining nitrates methods and the total hardness in spring water for the standard deviation.

The discovered decrease in the average concentration of nitrates in the underground water of 30 springs from 2001 to 2016 from 65 to 40 mg/dm^3 (by almost 25%) is possibly associated with a significant decrease in the area of arable land over this period.

An almost 2.3-fold increase (from 72.9 to 169 mg/dm^3) of the average nitrate content in spring water after heavy rains in June 2004 can serve as a basis for predicting the natural impact on the spring water quality.

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REFERENCES

[1] G.A. Orekhova, L.L. Novykh and A.B. Soloviev, “Nitrate contamination of spring waters of the Yakovlevsky district of the Belgorod region,” Problemy regionalnoj ekologii (Regional Environmental Issues), No. 2, pp. 55-57, 2012. (in russ.)

[2] S.G. Skugoreva, L.I. Domracheva, A.I. Fokina and I. A. Domracheev, “Study of the chemical composition and content of microorganisms in spring water,” Water. Chemistry and ecology, No. 10-12, pp. 23-29, 2018. https://doi.org/10.18334/watchemec.11.10-12.23-29

[3] S.N. Elokhina and A.S. Yurkin, “The present-day state of spring runoff in the territory of the Ural hydrogeological massif (Middle Urals),” Vodnye resursy (Water Resources), Vol. 34, No. 5, pp. 631-640, 2007. (in russ.)

[4] P.M. Mazurkin and E.I. Tarasova, “Factor analysis of pollution of springs,” Usrpehi sovremennogo estestvoznaniya (Advances in current natural sciences), No. 2, pp.65-72, 2013. (in russ.)

[5] V.I. Badelin, S.A. Buymova, V.V. Kostrov and A.P. Kupriyanovskaya, “On the quality of spring waters of the Ivanovo region,” Ekologiya i promyshlennost Rossii (Ecology and Industry of Russia), No. 4, pp. 38-40, 2005. (in russ.)

[6] S.A. Buymova and V.V. Kostrov, “Changes in Spring Water Quality in the Towns of Ivanovo and Kokhma of Ivanovo Region,” Teoreticheskaya i prikladnaya ekologiya (Theoretical and Applied Ecology), No. 2, pp. 38-42, 2008. (in russ.)

[7] O.Yu. Tarasov, I.I. Shakirova, F.M. Abdullina and R.Ch. Yuranets-Luzhayev, “Nitrate pollution of groundwater in the Republic of Tatarstan,” Zhurnal ekologii i promyshlennoj bezopasnosti (Journal of Ecology and Industrial Safety), No. 1-2, pp. 33-35, 2015. (in russ.)

[8] A.A. Kiseleva, “Springs of the Iva River Basin, Territory of the City of Perm,” Vodnoe hozyajstvo Rossii: Problemy, Tehnologii, Upravlenie (Water sector of Russia: problems, technologies, management), No. 6, pp. 70-78. 2010. (in russ.)

[9] K.T. Crabtree, “Nitrate and nitrite variation in ground water,” The technical bulletin from the Wisconsin department of natural resources, No. 58, 1972.

[10] I.N. Lykov and L.V. Golenkova, “The results of ecological and sanitation monitoring of the springs of Kaluga,” Vestnik Kaluzhskogo universiteta (Bulletin of the Kaluga University), No. 2, pp. 58-61, 2018. (in russ.)

[11] I.V. Semenova, I.N. Lykov and M.N. Katkova, “Assessment of environmental condition and the risk from using of water springs on the urbanized territories,” Problemy regionalnoj ekologii (Regional Environmetal Issues), No. 6, pp. 29-33, 2012. (in russ.)

[12] GOST 27384-02. Water. Rates of measurement error of characteristics of composition and properties. (in russ.)