CORRELATIVE STUDIES REGARDING THE VALUE OF CERTAIN WATER POLLUTION-INDICATING PARAMETERS AND THE TYPE OF ANTHROPOGENIC POLLUTION

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Abstract

Monitoring groundwater requires taking several water samples which are subjected to numerous analyses. As regards the identification of the types of pollution sources, a correlative analysis of parameters may be useful. In this study, we have analyzed the relationship between industrial and agricultural pollution sources and the correlation between three parameters: fixed residue, sulfates and nitrates, for one of the areas of Oradea municipality that has been subject to industrialization and deindustrialization, in the course of time.

Key words: anthropogenic pollution, chemical status, quality parameters combination

INTRODUCTION

In the western part of Oradea municipality, considered an industrial area before 1989, during approximately 25 years, several industrial, as well as agricultural enterprises were developed. They were built without an environmental strategy and without a coherent approach as regards the location of objectives, which is understandable in the contxt of the respective period. This is how a thermal power station emerged, as well as an alumina factory, a chemical product plant, a furniture factory, a sugar factory, greenhouses, a chicken rearing enterprise, etc. All these have become sources of pollution of the environment with organic compounds (solvents, lacquers, pharmaceuticals, plant protection products, phenols) and inorganic compounds (pigments, metal oxides, slag, ash, nitrates, synthetic fertilizers, etc.) (Oneț C, Oneț A., 2011; Pantea E et. Al., 2010). While industrial activity has significantly decreased in intensity, the underground water in the area under study has a poor chemical status, or is even non-potable (Dumitru M. et al., 2010; Dumitru M., Botău O., 2010)

Our study only takes into account underground water pollution with inorganic compounds, which confer water a certain degree of mineralization, trying to establish a correlation between anthropogenic pollution (from industrial and agricultural sources), the content of sulphates, nitrates and the degree of water mineralization.

MATERIAL AND METHOD

The assessment of the chemical status of a body of underground water is done by relating determined parameter values to threshold values (TV) set in MM (Minister of the Environment) Order no. 137/2009. In setting targets regarding water quality status, one must take into account the natural background values (NBL), which refers to the specific geological substratum.

The area on which this study focuses is part of the body of water ROCR01 located in Crișul Repede hydrographic basin. For this body of water, the threshold value of 250 mg/l was set for the sulfate ion, as well as the natural background values for both sulphate ion and nitrate ion, namely 75 mg/l and 7 mg/l. Law 311/2004 regarding drinking water quality imposes as maximum permissible values: 250 mg/l for sulphate, 50 mg/l for nitrate and between 100 and 800 mg/L for fixed residue.

From a lithological point of view, aquifers in the aforementioned body of water consist of boulders and gravel in the eastern area and formations of decreasing grain size in the western area, where they turn into medium and fine sands (Sabău N.C., 2008). Deposits in the western area are between 5 and 15 m thick and have characteristics favourable to the formation of underground water whose hydrostatic level displays seasonal fluctuations (Moza A., 2009; Pereș A., Koteles N., 2010). Covering layers have a high permeability and allow for groundwater infiltration and circulation. As a result, pollutants can penetrate quite easily, being circulated in the water flow direction, which is generally the East-West direction. (Oneț A., Oneț C., 2010; Șerban E., Mut. C., 2013; Șerban E., Romocea T., 2008)

In order to characterize undergroundwater quality and track the variability in time and space of underground water pollution from the former industrial Western area, as of 1977 a hydrogeological drilling system has been developed, arranged in two alignments: the first one oriented on the East-West direction (P_1,P_3, P_5, P_6, P_9) and the other one perpendicular to the first (P_7, P_{11}, P_{12}, P_{14}).

In order to characterize water chemistry, a number of parameters were determined. Our study focuses only on the variance and interdependence of three of them: fixed residue, concentration of sulphates and nitrates.

High values of fixed residue were determined in drillings P_9, P_6, P_5, P_3, P_1. This is the reason why we have chosen as a subject of our study only these 5 drillings. These drillings are located as follows:

P_1 – Borș customs,
P_3 – Borș field
P_5 - Sântion,
P_6 - S.C. Sinteza S.A. precinct,

P_9 - S.C. Zahărul S.A., sludge fields

Our study takes into account 16 analyses of each parameter analyzed. The data processed in this paper are included in the Water Basin Administration (ABA) Crişuri Oradea archive. The processing of the data in order to highlight any interdependencies was done with the IBM SPSS Statistics v. 20 software (Jaba E., Grama A., 2004). The correlation study for the three selected parameters was done for the 5 wells separately and for the 5 wells combined, in order to achieve a picture of the interdependencies at well level, but also at the level of the underground water for a larger area of the aquifer.

RESULTS AND DISCUSSIONS

In Tables 1, 2 and 3, the determined values of the three indicators are shown: fixed residue, sulfates and nitrates, for drillings P_9, P_6, P_5, P_3, P_1, during the period between 1997 and 2007. The values were determined by using standardized physical-chemical methods, valid during the respective period.

Table 1

Fixed residue values (mg/l)

Nr. crt	P_1	P_3	P_5	P_6	P_9
1.	762	526	370	1898	1565
2.	744	524	388	1434	1098
3.	1214	460	356	1438	708
4.	1308	631	405	2270	1258
5.	972	828	716	668	280
6.	744	86	740	404	184
7.	1214	818	720	932	180
8.	1308	776	806	572	266
9.	1340	1053	844	782	478
10.	1350	1710	1040	790	496
11.	1214	892	1058	794	272
12.	1430	1238	760	890	592
13.	1389	1420	2461	1557	208
14.	1245	1414	1337	1666	341
15.	1202	1491	1170	1596	358
16.	1280	1204	900	1259	252

Table 2

Sulfate ion concentration values (mg/l)

Nr.crt.	P_1	P_3	P_5	P_6	P_9
1.	144,44	85,83	49,45	717,16	62,84
2.	134,05	98,57	80,69	93,82	126,63
3.	75,05	54,48	58,76	373,29	86,74
4.	98,07	69,46	79,66	424,99	115,56
5.	136,00	128,00	124,00	-	20,00
6.	90,00	152,00	144,00	-	25,00
7.	120,00	150,00	116,00	-	33,00
8.	270,00	148,00	152,00	-	12,00
9.	633,00	380,00	170,00	120,00	84,00
10.	460,00	260,00	160,00	104,00	70,00
11.	460,00	143,00	200,00	100,00	12,00
12.	520,00	290,00	220,00	84,00	55,00
13.	674,65	225,30	173,20	385,80	9,17
14.	161,60	280,34	264,60	171,16	30,13
15.	362,80	192,00	177,00	173,90	54,78
16.	600,00	217,05	206,2	233,54	7,75

Table 3

Nitrate ion concentration values (mg/l)

Nr.crt.	P_1	P_3	P_5	P_6	P_9
1.	7,93	8,23	8,51	0,73	0,22
2.	7,30	10,29	8,01	0,47	0,74
3.	6,92	29,67	30,42	1,25	1,75
4.	17,21	20,92	31,28	1,92	0,01
5.	86,42	28,81	41,15	1,23	14,98
6.	33,10	3,70	64,19	3,36	6,16
7.	57,61	4,61	50,21	2,96	2,88
8.	36,87	30,29	28,79	3,78	27,16
9.	45,40	24,75	4,45	0,62	8,72
10.	20,02	67,65	68,75	1,07	2,40
11.	40,05	51,62	69,42	6,36	5,78
12.	20,47	13,35	32,04	0,89	14,24
13.	73,50	36,90	42,84	6,98	6,09
14.	75,18	83,27	114,14	8,19	3,20
15.	65,45	78,01	59,69	6,59	6,63
16.	67,37	39,05	141,75	17,36	0,79

Underground waters in the studied area are significantly mineralized. The values of fixed residue exceed the maximum permissible value according to Law 311/2004 regarding drinking water quality in 55% of the tests. Natural background values were established for this parameter.

In the case of sulphates, the threshold value, which is the same as the maximum permissible value according to the Law regarding drinking water quality, is surpassed in 50% of the tests, for well P_1, and in 25% of the tests, for well P_3. In the case of wells P_5, P_6, P_9, exceedance is only sporadic. Natural background value, set at 75 mg/l, is exceeded in 96% of the tests performed on wells P_1, P_3, P_5, P_6. In the case of well P_9, no exceedance was recorded.

In terms of water content in nitrates, the following remarks can be made: the background value, set at 7 mg/l, is only sporadically exceeded in wells P_6 and P_9. By contrast, in the other wells, the threshold value is exceeded in 96.05% of the analyses. The maximum value allowable under the Law on drinking water quality (50 mg/l) is exceeded in 37.5% of the tests on well P_1, 31.25% for well P_3, 43.75% of the P_5 well tests.

Data processing in order to highlight possible associations was performed with regard to two situations:

A. Analysis of the association between fixed residue and sulfate ion values, respectively between fixed residue and nitrate ion values for the 5 wells separately.

B. Analysis of the association between fixed residue and sulfate ion values, respectively between fixed residue and nitrate ion values, for their pooled (combined) data (Eblin et. al., 2014; Filik I. et al., 2007)

A. Distribution normality in the 5 x 3 samples was verified by means of the Kolmogorov-Smirnov and Shapiro-Wilk Tests. Because the samples are small (smaller than 50) the Shapiro-Wilk test results were taken into consideration, being presented in the column Distribution Type of Summarizing Table 4. In Figure 1 you can see the Fixed Residue Histogram for well P_1, which illustrates a deviation from normal distribution.

Table 4

Summary of results for the 5 wells analyzed

Well	Type of distribution Residue (Rz) Sulfate Ion Nitrate Ion	Correlation Fixed Residue (Rf) with Sulfate Ion	Correlation Fixed Residue (Rf) with Nitrate Ion
P1	No No Yes	Yes [rho= 0.647; p<0.05]	No [rho= 0.137; p>0.05]
P3	Yes Yes Yes	Yes [r= 0.680; p<0.05]	Yes [r= 0.743; p<0.05]
P5	No Yes Yes	Yes [rho= 0.847; p<0.05]	Yes [rho= 0.612; p<0.05]
P6	Yes No No	Yes [rho= 0.706; p<0.05]	No [rho= 0.147; p>0.05]
P9	No Yes No	Yes [rho= 0.805; p<0.05]	Yes [rho= -0.447; p<0.05]

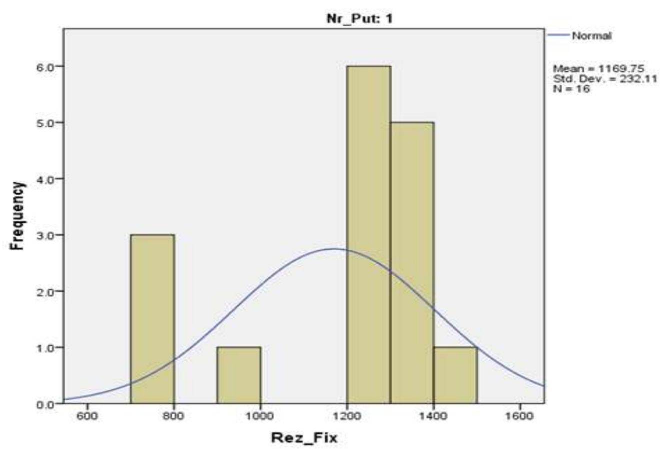

Fig. 1. Fixed Residue Distribution Histogram for well P_1

B. Because the 3 pooled samples are normal in volume (more than 50 measurements), the correlations were made by means of the Pearson parametric test [16]. As shown in Tables 5 and 6, test results indicate the presence of correlations, more strongly in the case of the sulfate ion (higher coefficient, 0.625 higher than 0.263); same difference of intensity is found in the case of wells taken individually. In Fig. 2, the “Point Cloud” Graph for the Sulfate Ion and Fixed Residue Correlation shows a very clear linear correlation, especially for smaller values of the samples [1],[6].

Table 5

Correlation between Fixed Residue and Sulfate Ion

		Rez_Fix	Ion_Sulfat
Rez_Fix	Pearson Correlation	1	.625**
	Sig. (2-tailed)		.000
	N	80	76
Ion_Sulfat	Pearson Correlation	.625**	1
	Sig. (2-tailed)	.000	
	N	76	76

**. Correlation is significant at the 0.01 level (2-tailed).

Table 6,

Correlation between Fixed Residue and Nitrat Ion

		Rez_Fix	Ion_Nitrat
Rez_Fix	Pearson Correlation	1	.263*
	Sig. (2-tailed)		.018
	N	80	80
Ion_Nitrat	Pearson Correlation	.263*	1
	Sig. (2-tailed)	.018	
	N	80	80

*. Correlation is significant at the 0.05 level (2-tailed).

Table 7

Summary of results for the cumulative samples

Well	Type of distribution Residue (Rz) Sulfate Ion Nitrate Ion	Correlation Fixed Residue (Rf) with Sulfate Ion	Correlation Fixed Residue (Rf) with Nitrate Ion
Cumulative sample (80 samples)	no verification is necessary	Yes [r=0.625; p<0.05]	Yes [r=0.263; p<0.05]

The strong correlation that exists between the parameters fixed residue and sulfates, both for wells considered individually and as a whole, highlights the fact that, with the movement of underground waters in the South East – North West direction, waters become rich in sulphate and other minerals, through simple dissolution and the anthropogenic contribution from industrial sources adjacent to thee wells studied [13].

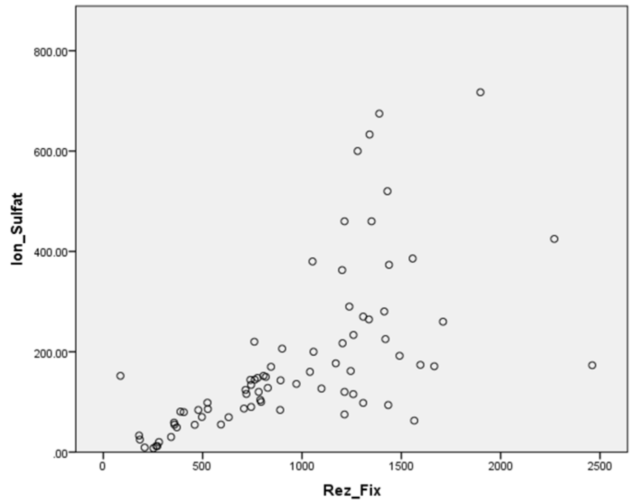

Fig. 2, “Point Cloud” Graph for the Correlation between Fixed Residue and Sulfate Ion

Significant correlations between fixed residue and nitrate are only present in the case of wells P_3, P_5, The first two are located in rural areas where repeated operations of soil fertilization take place. Both the use of natural fetilizers and of chemical fertilizers result in the pollution of underground water with nitrates. They are mineralized over time, eventually turning into nitrates. The lack of correlation between fixed residue and nitrate in the case of wells P_1 and P_6, areas without anthropogenic nitrate input, is therefore perfectly understandable.

CONCLUSIONS

The variability of underground water quality in the studied area can be attributed to the geochemical characteristics of the covering layer of the aquifer, the industrial and agricultural polluting sources in the area and the undergound water flow direction. The study of possible correlations between some chemical parameters (fixed residue – sulphates, fixed residue – nitrates, possibly other combinations, as well) can identify the nature of anthropogenic pollution sources. A strong fixed residue – sulfate correlation highlights the existence of industrial pollution sources and also reveals the underground water flow direction. The existence of a significant fixed residue – nitrate correlation highlights the existence of agricultural pollution sources or of food industry objectives.

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