Preliminary Study on Assessment of Mineralization Degree and Nutrient Content of Groundwater Bodies in Gorj County

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The research study performed aims to assess the degree of mineralization and nutrient contents of groundwater bodies in Gorj County in the period 2014-2015 based on the monitoring indicators such as: pH value, electrical conductivity, chlorides content, sulphates, nitrates, nitrites, phosphates, ammonium, sodium and potassium ions. Samples of waters were taken from eight wells located in depth groundwater bodies, code ROJi05 and ROJi08 in order to determine the mineral and nutrient contents. All the indicators monitored were taken into account for assessing the mineralization degree of groundwater. The values of monitored indicators of groundwater were within the allowed limits for drinking water according to Law 458/2002 amended by Law no. 311/2004 regarding the drinking water quality with the exception of sulfur content. The values of nutrient content exceeded the allowed limits for sulphates, nitrate, nitrite and ammonium.

Keywords: mineralization, nutrients, groundwater quality indicators, drinking water

The evidence of groundwater water resources at the territorial units for water management was imposed by the need to achieve their management combined with those of surface and to adopt a policy of preferential assignment [1]. According to Directive 60/2000/EC regarding establishing an action framework for Community in the field of water policy, zoning of free level aquifers systems and those of pressure level in the groundwater bodies represented by different groundwater volumes from an aquifer or aquifers it was carried out [2]. The aquifer is referred to a layer or multiple layers of geological rock with sufficient porosity and permeability to allow either a significant flow of groundwater or the tapping of significant quantities of groundwater.

Groundwater contamination hydrology includes a number of very complex issues related to hydrodynamic flow of water, the behavior of dissolved salts in it, the processes taking place in water passing through a porous medium, and the problems of aquatic hydrochemistry and hydrogeology. The geological and hydrogeological structure of the area is an important factor which can favor the penetration of pollutants in groundwater and their storage in aquifer [3].

The main sources of groundwater pollution can be atmospheric deposition, discharges from septic tanks, rocks weathering, organic matter decomposition, seepage from landfills, leaking sewers, spreading of sewage sludge to land [4].

Transport processes of pollutants in the form of dissolved salts in water can be divided into two categories: single-phase flows and multiphase flows. In the first case of the transport processes all fluids have densities and fluidity equal and they are completely miscible and soluble. The second case is related to immiscible fluids. In terms of the porous environment and aquifer is considered that they are homogeneous and isotropic or it is envisaged that they are granular and fragmented media. Equations for the transport of pollutants in solution can be established and dimensional, two-dimensional or three-dimensional estimations of groundwater contamination evolution based on these considerations. If porous media are considered, the problems are easy to be solved because it is considered that they are homogeneous. If they are granular media, they have effects on the infiltration processes as a result of sensitive changes of spatial characteristics of layer considered. In this case, the layer cannot be considered homogeneous. In case of fractured layers, we are dealing with different layers with different permeability and fractures. The fractures are usually the primary route of groundwater movement. Transport of pollutants from soil in depth is carried out in four stages: introduction of the pollutant in the soil as a result of pollution, migration of pollutant in unsaturated area - phenomenon being limited by mechanisms of self-purification, transport of pollutant in the aquifer, the process being accompanied by decreasing of pollutant's concentration and persistence.

Groundwater has long been called *clean water*, they naturally responding drinking water standards and being less affected by accidental pollution. The free level groundwater fueled by all above the soil surface, are more sensitive to pollution than the captive waters. When groundwater is polluted, it is very difficult to regain its initial purity due to the fact that pollutants are present not only in water, but they are at the same time fix and adsorbed on rocks and soil minerals [5-14].

Constraints imposed by quality of different water uses, the increasing water needs and the growing significance of pollution as a result of natural and anthropogenic activities makes it more necessary to consider aquifers as components of water resources system to increase dependable water supplies and to preserve water quality [15].

Preventing groundwater contamination is necessary for effective groundwater bodies management [16]. The first step to implement sustainable groundwater bodies management is understanding their quality and processes of mineralization [16]. Consequently, the aim of this paper is to present the preliminary study regarding the assessment of mineralization degree and nutrient content of groundwater bodies, exemplified by a case study of Jiu river and its tributary, in Gorj county.

Experimental part

Six wells belonging to groundwater bodies from the terraces and meadows of Jou and its tributaries (code ROJi05), namely Ceplea – W1, W2; Vidin – W3; Hurezani –

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W4, Turburea – W5; Stoinea W6, and two wells belonging to depth groundwater bodies from meotine formations (code ROJi08), namely Tg-Jiu – W7, and Sadu – W8 were monitored in this research study.

Water sampling from thse eight deep wells located within Gorj County was performed by the use of standardized methods for groundwater sampling.

Body of groundwater from terraces and meadows of Jiu and its tributaries (code ROJi05) is the most important hydrogeological unit in terms of spread of ground deposits and water resources. The length of this unit that develops in the plain is about 80 km and its average width is about 5 km. This unit has an important role in providing significant reserves of groundwater exploited by numerous capture fronts. Hydrogeological feature of this unit is the discontinuity of morphological slope and of aquifers deposits in boundaries areas between terrace levels and between terraces and meadows.

The second groundwater body monitored (code ROJi08) taped in the north of Targu Jiu city has drinkable water with low total mineralization. This water has been used in water supply of Targu Jiu city. This water source is currently conserved.

Assessment of water quality indicators monitored has been conducted by the use of standard methods. *p*H and conductivity level were performed by electrochemical methods. A multiparameter for water quality analysis Multi 3320 model was used for this purpose. The chlorides content in water sampled from these eight wells has been determined by the volumetric method by precipitation with silver nitrate. The contents of sulfates, nitrates, nitrites, phosphates and ammonia were determined by molecular absorption spectrometry using a UV-Vis spectrophotometer CINTRA 101 GBC. The content of sodium and potassium ions was determined by atomic absorption spectrometry using an atomic absorption spectrophotometer AA 500FGPC.

Results and discussions

Assessment of mineralization level and nutrients content was carried out by measuring the following indicators: *p*H, electrical conductivity, chlorides, sulfates, nitrates, nitrites, phosphates, ammonium ions, sodium and potassium.

Table 1 presents the results of measurements for these indicators for well drillings W1 and W2 from Ceplea recorded in 2014 – 2015.

No.	Quality indicators	W1		W2	
		2014	2015	2014	2015
1.	pH (pH units)	7.45	7.29	7.33	7.26
2.	Electrical conductivity (μS/cm)	1458	1537	1529	1543
3.	Cl^- (mg/L)	26.04	24.11	94.02	35.45
4.	SO_4^{2-} (mg/L)	435.8	478.2	50.74	101.45
5.	N-NO_3^- (mg/L)	2.48	8.02	51.15	72.25
6.	N-NO_2^- (mg/L)	0.15	0.25	0.19	0.16
7.	P - PO_4^{3-} (mg/L)	1.55	1.66	1.75	1.14
8.	N-NH_4^+ (mg/L)	1.06	0.72	0.65	0.21
9.	Na^+ (mg/L)	28.96	32.65	31.42	49.35
10.	K^+ (mg/L)	3.82	6.35	1.74	1.51

Table 1
AVERAGE VALUES RECORDED FOR WELL DRILLING W1 AND W2 FROM CEPLEA

No.	Quality indicators	W3		W4	
		2014	2015	2014	2015
1.	pH (pH units)	7.61	7.29	7.13	6,87
2.	Electrical conductivity (μS/cm)	1250	1236	685	668
3.	Cl^- (mg/L)	75.58	73.03	27.36	28.25
4.	SO_4^{2-} (mg/L)	63.1	29.98	49.92	28.67
5.	N-NO_3^- (mg/L)	57.73	39.77	6.66	10.76
6.	N-NO_2^- (mg/L)	0.17	0.22	0.73	0.52
7.	P - PO_4^{3-} (mg/L)	0.19	0.18	0.20	0.27
8.	N-NH_4^+ (mg/L)	0.37	0.94	0.34	0.36
9.	Na^+ (mg/L)	29.83	43.21	26.07	21.89
10.	K^+ (mg/L)	2.02	1.59	0.91	0.96

Table 2
AVERAGE VALUES RECORDED FOR WELL DRILLING W3 - Vidin and W4 - HUREZANI

No.	Quality indicators	W5		W6	
		2014	2015	2014	2015
1.	pH (pH units)	7.41	7.33	7.20	7.00
2.	Electrical conductivity (μS/cm)	817	881	1209	1268
3.	Cl^- (mg/L)	23.83	20.64	44.84	44.93
4.	SO_4^{2-} (mg/L)	88.1	30.4	170.4	195.5
5.	N-NO_3^- (mg/L)	8.9	4.52	3.14	4.92
6.	N-NO_2^- (mg/L)	0.29	0.24	0.43	0.16
7.	P - PO_4^{3-} (mg/L)	0.14	0.30	0.39	1.19
8.	N-NH_4^+ (mg/L)	0.29	0.27	0.26	0.28
9.	Na^+ (mg/L)	16.61	8.34	33.34	29.06
10.	K^+ (mg/L)	1.08	1.9	1.12	1.67

Table 3
AVERAGE VALUES RECORDED FOR WELL DRILLING W5-TURBUREA AND W6 - STOINA

Table 4
AVERAGE VALUES RECORDED FOR WELL DRILLING W7-TG. JIU AND W8 - SADU

No.	Quality indicators	W7		W8	
		2014	2015	2014	2015
1.	pH (pH units)	8.36	8.28	7.91	8.1
2.	Electrical conductivity (µS/cm)	271	283	358	347
3.	Cl^- (mg/L)	26.87	27.37	20.25	29.13
4.	SO_4^{2-} (mg/L)	24.21	25.3	39.24	40.26
5.	N-NO_3^- (mg/L)	9.52	10.48	9.83	10.98
6.	N-NO_2^- (mg/L)	0.38	0.30	0.35	0.15
7.	P - PO_4^{3-} (mg/L)	0.38	0.23	0.3	0.17
8.	N-NH_4^+ (mg/L)	0.57	0.35	0.39	0.25
9.	Na^+ (mg/L)	28.78	27.27	20.99	20.15
10.	K^+ (mg/L)	1.46	1.53	1.65	1.59

Table 5
MAXIMUM ADMISSIBLE VALUE ACCORDING LAW No. 458/2002, AMENDED BY LAW No. 311/2004 REGARDING THE DRINKING WATER QUALITY

No.	Quality indicators	Measurement units	Maximum admissible value
1.	pH	pH units	≥ 6.5; ≤ 9.5
2.	Electrical conductivity	µS/cm	2,500
3.	Cl^-	mg/L	250
4.	SO_4^{2-}	mg/L	250
5.	N-NO_3^-	mg/L	50
6.	N-NO_2^-	mg/L	0.5
7.	P - PO_4^{3-}	mg/L	5
8.	N-NH_4^+	mg/L	0.5
9.	Na^+	mg/L	150
10.	K^+	mg/L	12

The results for W3and W4 well drilling - Vidin and Hurezani recorded in the period 2014-2015 are presented in table 2.

The values of quality indicators for samples from drilling wells W5 and W6 are depicted in table 3.

The results recorded in the period 2014-2015, for W7-drilling wells that is supply drinking water for Targu Jiu city and for W8 Tg Jiu - Sadu drilling are shown in table 4.

In table 5 are shown the maximum admissible value according to romanian legislation (Law no 458/2002, amended by Law no. 311/2004 regarding the drinking water quality) for monitored indicators [17, 18].

Variation of mineralization level and nutrient content in groundwater monitored in the period 2014-2015, expressed by following indicators: *p*H, electrical conductivity, chloride, sulphate, ammonium content, Na^+ and K^+ are shown in figures 1-8.

By analysing the data presented in figure 1, it can be observed that for the *p*H indicator all the samples from drilling well monitored can be included in drinking water quality. The *p*H ranges between 6.87 to 8.36 *p*H units. The highest values are recorded for well drilling W7 and W8.

The variation of values for electrical conductivity shown in figure 2 revealed that the values for this indicator are in narrow limits of values for each well drilling, but they present a sinuous variation for all the 8 wells. The lowest values of conductivity were recorded for W7 and W8 well drillings, and the highest values were registered for W1 and W2 (Ceplea area).

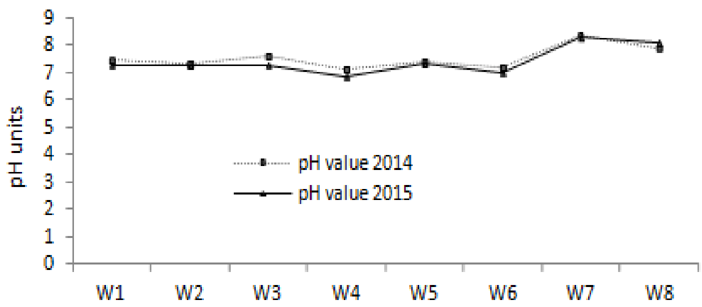

Fig.1. Variation of groundwater *p*H

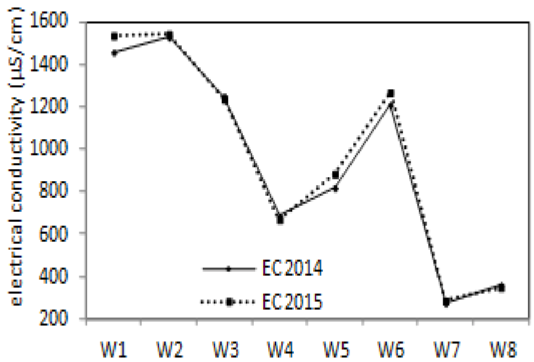

Fig. 2. Variation of electrical conductivity of groundwater

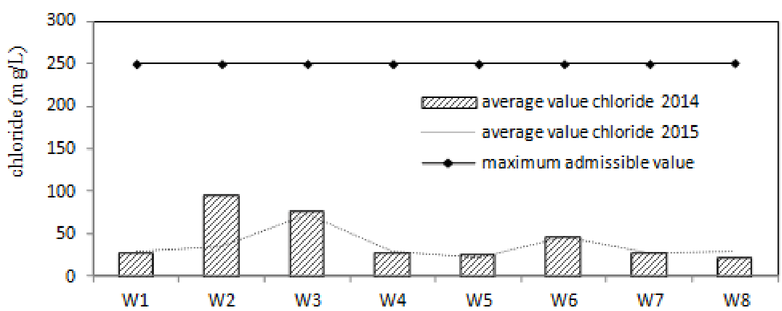

Fig. 3. Variation of average level of chloride

The mineralization level is specific to groundwater aquifers with values of the conductivity ranging between 271-1,543 μS/cm.

The high values are due to the existence of one ash and slag deposit of Turceni Thermal Power Plant in the area where those two wells are located. The area experiences significant changes of the content of dissolved salts as a result of infiltration of wastewater from ash and slag deposit into groundwater. The values recorded during those two years not exceeding the maximum admissible value for electrical conductivity indicator stipulated by Law 311/ 2004.

Regarding the chlorides content, the values recorded for all wells monitored in period 2014-2015 are far below the admissible limits stipulated in Law 311/2004. Based on the data presented in figure 3, it can be said that all the samples have drinking water quality, the range of this indicator being between 10.63 and 94.02 mg/L. In case of W2 well driling, a big difference between the average values recorded in both years has been observed. The average content of chlorides in 2014 was 2.65 times higher than in 2015.

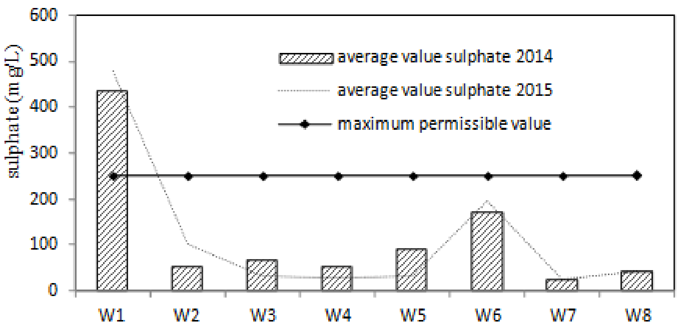

Fig. 4. Variation of average level of sulphate

The variation of values for sulphate content, shown in Figure 4 shows significant exceedings of the maximum permissible value (table 5) for drilling W1, both in 2014 and 2015. The average values recorded for W1 exceeding 1.74 times the admitted limit in 2014 and 1.91 times in 2015. These exceedings are due to changes in composition of groundwater in the area where it is located W1 Ceplea drilling that is characterized by an increased content of sulphates coming from infiltration of wastewater from ash and slag deposit of Turceni Thermal Power Plant.

In period 2014-2015, the average values of sodium and potassium content for all wells monitored are far below the admissible limits stipulated in 458/2002 Law amended by Law no. 311/2004 regarding the drinking water quality. Figure 5 reveals that all wells monitored have drinking water quality regarding sodium and potassium quality indicators. The variation range for sodium is between 8.34 mg/L (W5 well in 2015) and 49.35 mg/L (W2 well in 2015). In case of potassium, the variation range is between 0.91 mg/L (W4 in 2014) and 6.35 mg/L (W1 well in 2015).

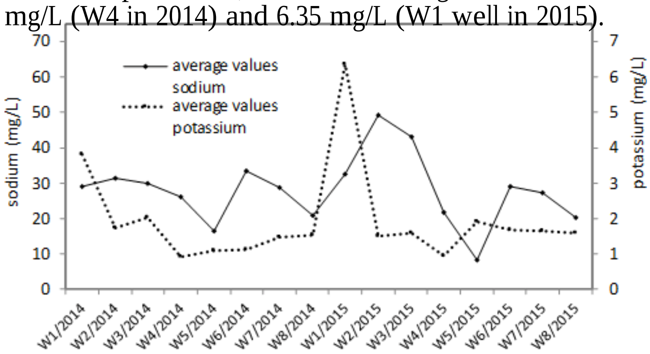

Fig. 5. Variation of Na^+ and K^+ content

Variation of nitrate content in the eight wells monitored in the period 2014-2015 is shown in figure 6. It indicates exceeded of the maximum allowed limit (50 mg/L N-NO_3^-) stipulated by Law 458/2002 amended by Law 311/2004 for three wells. Thus, in case of W2 well drilling (Ceplea), the average value registered was 1.023 times higher than the admitted limit, and for W3 Vidin well the average value recorded was 1.15 times higher than the admitted limit. The highest value was recorded in 2015 for W2 (Ceplea) being 1.44 higher than the admitted limit. High concentrations of nitrate are mainly attributed to the agricultural activities in the areas monitored.

The values recorded for phosphate content are within the limits admitted (5 mg/L) for this indicator according to Law 458/2002 amended by Law 311/2004 as it can be seen in figure 6.

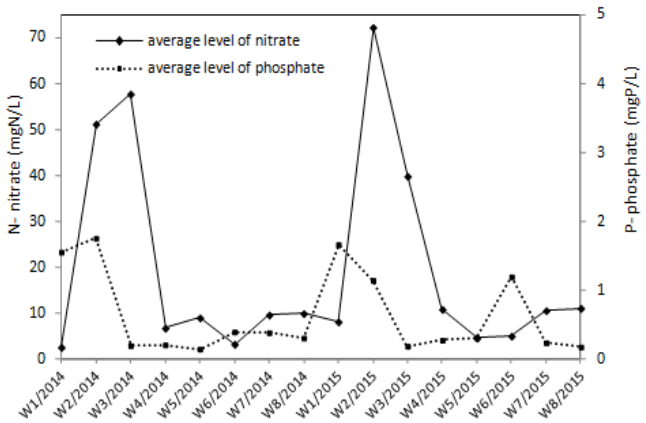

Fig. 6. Variation of average level of nitrate and phosphate

Variation of nitrite level of groundwater sampled from monitored wells is depicted in figure 7.

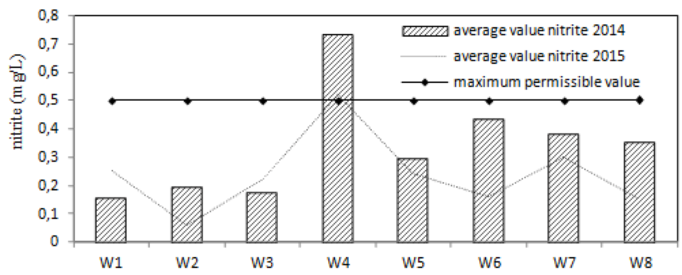

Fig. 7. Variation of average level of nitrite

The average values of nitrite content of monitored wells in period 2014-2015 are below the admissible limit (Law 458/2002 amended by Law 311/2004) with the exception of W4 well from Hurezani area (fig. 7). From the analysis of the data registered for this indicator leads the conclusion that the values recorded are 1.46 higher than the admitted value in 2014, and 1.04 higher than the admitted value in 2015.

The variation of ammonia content in the eight wells monitored in the period 2014-2015 is shown in figure 8. This variation indicates exceeded of the maximum allowed limit (0.5 mg/L) stipulated by Law 458/2002 amended by Law 311/2004 for drillings W1, W2, W3 and W7. Thus, for W1 Ceplea drilling, the average value registered in 2014 was 2.12 higher than the maximum allowed limit, and 1.44 higher than the maximum allowed limit in 2015. For W2 Ceplea drilling the average value for ammonium content was 1.3 higher than the maximum allowed limit in 2014, for W3 Vidin drilling was 1.88 higher than the maximum allowed limit, and for W7 Targu-Jiu was 1.14 higher than the maximum allowed limit.

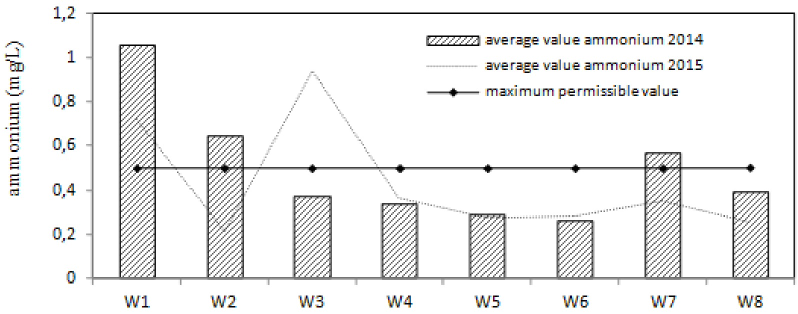

Fig. 8. Variation of ammonium content

Conclusions

The purpose of the present study conducted was to assess the level of mineralization and nutrient content of groundwater bodies in Gorj county. The following indicators: pH, electrical conductivity, chlorides, sulfates, nitrates, nitrites, phosphates, ammonium ions, sodium and potassium were monitored from collected samples from eight deep drills placed in groundwater bodies, code ROJi05 and ROJi08 in 2014 -2015. Results obtained were compared to the admissible limits stipulated by 458/2002 Law amended by 311/2004 Law. The average values for pH, electrical conductivity, chloride, sodium and potassium ions indicators were in the admissible limits for the period monitored. The mineralization degree is characteristic for groundwater bodies being mainly determined by leaching of metal salts from slag and ash deposit.

The variation of sulphate content has significant exceeding of admissible limit for W1 drilling due to the leaching from ash and slag deposit situated in Ceplea area.

The nutrient content has been assessed by monitoring the nitrate, nitrite, phosphate and ammonium content in period 2014-2015. Data registered indicated values higher than the admissible limits according to 458/2002 Law amended by 311/2004 Law for nitrate for three wells from those eight wells monitored. Groundwater nitrate exceeding the maximum allowable concentration can be an indicative of natural groundwater contamination as a result of human activities. The average values for phosphate content are lower than the admissible limit. The values recorded for nitrite ion content exceeded the permissible limit for water samples from W4 drilling Hurezani area both in 2014 and 2015. Ammonium content variation for wells monitored indicated exceeding for W1, W2, W3 and W7 wells.

Thus, it can be concluded that the nutrient content in the area monitored is higher than the admissible limits mainly due to human activities which influence the chemical composition of the two groundwater bodies monitored. The data collected is helpful to evaluate the effects of human activities on groundwater and to characterize the chemical quality of water.

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