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EVALUATION OF A RURAL SETTLEMENT WELL WATERS BASED ON THE QUANTIFICATION OF SOME PHYSICAL AND CHEMICAL PARAMETERS. A CASE STUDY

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ABSTRACT. Water samples from 30 wells from Remetea Oaşului village (Satu Mare county, Romania) have been characterized by the determination of 2 physical parameters (temperature and electrical conductivity) and of 19 chemicals (the Na, K, Li, Rb, Ca, Mg, Zn, Cu, Fe, Pb, Cd, Cl^{-}, NO_3^{-}, NH_4^{+}, SO_4^{2-} content, pH, total hardness (D,°G), alkalinity (Alk.) and chemical oxygen demand (COD). The chemical composition of the waters shows their suitability for household and agriculture purposes. Among the determined constituents only the Cd, Cu and NO_3^{-} content exceed the concentration limits for drinking water, being inappropriate for human and animal consumption. The hierarchical cluster analysis shows that the water samples are classified best based on the Pb, Cd, Zn, Cu, COD content, the well waters are grouped in 5 clusters. The waters can be only partially classified; wells from different zones are not separated. Considering the most eight significant variables, they are grouped in two factors, which cover 90.78 % of the total variance.

Keywords: *well water, chemical composition, pollution, cluster analysis, factor analysis*

INTRODUCTION

The freshwater plays a vital role in our life and in the everyday (industrial, agronomical and household) activity. In our days, the water consumption exhibits an increasing trend worldwide; being obtained from surface and underground sources. For rural and remote settlements the driven or sunken wells assure the water for everyday use, including for human and animal consumption. The quality and the quantity of the available drinking water from healthcare point of view are considered as one of the measure of the wellbeing and civilization [1]. From this point of view the drinking water must fulfill the most restrictive conditions, including the physical, chemical and biological parameters. The United Nations World Health Organization (WHO), the European Union's as well as the Romanian legislations set exactly the quality of the drinking water, the nature and the quantity of different substances that could be contained [2]. The characteristics of well waters are diverse,

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depending on many factors, such as: geological structure of the rocks and their chemical composition, the position of the aquifer layer, the environmental temperature, the geochemical reactions, meteorological conditions and on the mode of water extraction, human activity, etc. Usually, the water brought to the surface is used for different purposes without any further treatment, despite of its physical, chemical and biological characteristics. For the unequivocal characterization of the waters a series of standardized determinations must be carried out [3-5]. From the data one can predict the utility of the water, the effect on the health, the chemical composition of the rocks, including the aquifers, the origin of the water source, etc.

In order to reveal of the hidden relationships among the data statistical and chemometrical methods are employed efficiently in large scale [6]. The cluster-, factor- and principal component analysis, as well as the linear discriminant analysis allow the classification of the waters based on the physical and chemical data; to establish the similarity among the water sources; to get the main parameters on which the classification is performed; to identify the aquifer layers, the pollutants, etc. [7-13].

The aim of this work is to evaluate the well water quality of a rural settlement, to identify the most frequent inorganic pollutants by the quantification of the inorganic components and to estimate the structure of the aquifer layers. In order to reveal the hidden relationships the chemometric approach of the data has been proposed.

RESULTS AND DISCUSSION

The results of the quantification data are summarized in the Tables 1-3.

Water samples exhibit medium hardness and salinity, with low organic matter content. The NH_4^+-ion is present only in 4 samples (noted 9, 11, 26 and 27) probably due to infiltration of manure liquor. The NO_3^--ion is present in all samples, exceeding many times the maximum allowable quantity of 44.2 mg/L sets by WHO for drinking water. The infiltration of the long term used ammonium nitrate as fertilizer could be responsible for this fact. The Cd content of the waters is also too high for drinking water, exceeding with about two orders of magnitude the WHO set value (0.003 mg/L). The abnormal high Cd-content is the consequence of the corrosion of the galvanized iron pipes and buckets used for water outtake. Taking into account the high Cd and NO_3^--ion content it is not recommended to use these waters for human and animal consumption.

In order to reveal the hidden relationships among the parameters, and to classify the wells, first the cluster analyses have been performed. Three of the parameters were excluded from the calculations (T, Rb and NH_4^+ content), being irrelevant. The tree diagram (the Euclidean distance as similarity measure and complete linkage) is presented in the Figure 1.

Table 1. The physical data of the well water samples

Sample	Zone	T (°C)	pH	D (°G)	TDS	Alk.	COD
					(mg / L)		
1	**A1**	1	7.24	13.0	188	4.04	1.62
2	**A1**	3	6.94	5.8	68	2.10	1.75
3	**A1**	1	7.10	12.7	160	3.90	3.24
4	**A1**	1	7.12	27.3	402	6.20	3.16
5	**A1**	0	7.03	8.4	150	2.74	3.00
6	**B**	4	6.97	18.4	206	5.16	0
7	**B**	5	6.36	6.47	82	1.50	1.22
8	**B**	1	6.54	22.3	355	3.70	1.00
9	**B**	1	6.71	9.3	142	1.88	4.05
10	**B**	1	6.74	28.0	355	5.13	1.62
11	**B**	4	7.01	26.3	316	6.65	1.75
12	**B**	5	7.03	14.4	159	4.33	1.38
13	**B**	3	6.62	13.0	211	2.03	1.75
14	**C1**	1	6.81	11.5	203	2.91	1.46
15	**C1**	3	6.90	13.0	308	4.14	3.73
16	**C2**	0	5.90	1.9	23	0.34	2.19
17	**C2**	2	7.10	14.8	164	4.68	1.21
18	**C2**	1	6.53	18.0	329	1.80	2.03
19	**C2**	2	6.90	23.2	340	4.97	3.80
20	**C2**	2	6.47	13.0	247	3.13	2.43
21	**C2**	2	7.26	22.5	297	5.55	2.84
22	**C2**	1	7.26	9.6	157	2.86	2.35
23	**A2**	3	6.72	15.8	281	4.00	2.02
24	**A2**	1	6.83	11.0	149	2.89	4.05
25	**A2**	5	6.90	17.8	267	3.46	1.05
26	**A2**	3	7.05	8.6	115	1.20	3.80
27	**A2**	2	7.37	26.3	363	3.12	3.32
28	**A2**	1	7.41	31.3	490	7.24	4.21
29	**A2**	3	7.44	14.3	148	3.84	2.68
30	**A2**	3	6.44	35.0	491	2.64	2.84

Table 2. The metal content of the well water samples

Sample	Zone	Concentration (mg / L)					
		Na	K	Rb	Mg	Ca	Cu
1	**A1**	29	3.1	0	26.2	27.4	1.4
2	**A1**	7.4	2.5	0	4.5	7.9	1.4
3	**A1**	15.8	6.8	0	26.2	43.3	1.5
4	**A1**	90.3	4.3	0	36.2	66.5	1.4
5	**A1**	38.5	14.6	0	12.7	27.0	1.4
6	**B**	20.0	1.4	0	28.4	57.0	1.5
7	**B**	12.0	0.8	0	8.5	16.0	1.4
8	**B**	72.5	0.7	0	26.8	62.4	1.5
9	**B**	19.8	6.0	0	12.4	34.7	1.6

Sample	Zone	Concentration (mg / L)					
		Na	K	Rb	Mg	Ca	Cu
10	**B**	34.2	4.8	0	38.8	67.4	1.5
11	**B**	44.6	2.7	0	40.9	59.7	1.5
12	**B**	14.2	0.5	0	18.8	48.8	1.6
13	**B**	39.1	17.9	0	15.4	16.0	1.6
14	**C1**	31.1	49.5	0.1	15.4	19.7	1.5
15	**C1**	45.3	113	0.1	21.3	19.2	1.6
16	**C2**	2.5	2.2	0	4.6	3.8	1.5
17	**C2**	20.4	24.8	0	25.4	37.0	1.5
18	**C2**	80.5	13.6	0	21.2	14.7	1.6
19	**C2**	48.5	22.2	0	30.5	42.9	1.6
20	**C2**	29.2	67.7	0.1	18.5	14.7	1.7
21	**C2**	43.2	36.9	0	33.0	43.3	1.7
22	**C2**	28.7	32.2	0	13.0	16.0	1.7
23	**A2**	52.3	57.6	0.1	19.5	30.6	1.6
24	**A2**	31.5	15.7	0	14.3	9.2	1.7
25	**A2**	31.2	31.1	0	27.0	34.7	1.7
26	**A2**	5.6	6.3	0	11.6	33.8	1.8
27	**A2**	46.8	14.2	0	40.5	65.1	1.7
28	**A2**	84.6	3.3	0.1	56.5	72.9	1.8
29	**A2**	16.2	2.0	0	24.3	42.9	1.9
30	**A2**	73.2	1.6	0	55.1	78.3	1.7

Table 3. The metal and the anion content of the well water samples (cont.)

Sample	Zone	Concentration (mg / L)						
		Zn	Pb	Cd	NH_4^+	Cl^-	SO_4^{2-}	NO_3^-
1	**A1**	0.48	0.0001	0.42	0	33.0	20.0	119.3
2	**A1**	0.52	0.0002	0.04	0	2.2	0.0	25.7
3	**A1**	0.52	0.0002	0.04	0	12.7	17.7	64.8
4	**A1**	0.52	0.0002	0.39	0	128.8	27.6	445.2
5	**A1**	3.41	0.0002	0.45	0	27.7	10.0	172.7
6	**B**	0.65	0.0002	0.39	0	12.5	0.0	209.1
7	**B**	0.45	0.0001	0.55	0	6.8	8.8	106.1
8	**B**	0.45	0.0002	0.36	0	146	10.0	589.2
9	**B**	0.45	0.0002	0.33	0.1	35.5	14.6	201.6
10	**B**	0.45	0.0002	0.42	0	111.0	29.7	342.5
11	**B**	0.45	0.0001	0.80	0.1	47.7	27.4	57.0
12	**B**	0.68	0.0002	0.17	0	6.0	0.0	48.7
13	**B**	0.45	0.0002	0.33	0	62.0	14.1	973.4
14	**C1**	0.62	0.0003	0.61	0	38.5	18.2	524.2
15	**C1**	0.68	0.0002	0.77	0	73.2	29.4	682.8
16	**C2**	0.62	0.0003	0.77	0	2.1	16.7	114.5
17	**C2**	0.62	0.0002	1.27	0	3.6	0.0	212.6
18	**C2**	0.68	0.0019	0.61	0	154.0	29.2	831.7
19	**C2**	0.68	0.0003	0.30	0	73.4	29.4	837.3
20	**C2**	0.65	0.0001	0.30	0	62.0	25.2	640.8

Sample	Zone	Concentration (mg / L)						
		Zn	Pb	Cd	NH_4^+	Cl^-	SO_4^{2-}	NO_3^-
21	**C2**	0.68	0.0001	1.14	0	71.8	20.9	44.3
22	**C2**	0.75	0.0002	0.52	0	24.6	0.0	328.5
23	**A2**	0.91	0.0002	0.64	0	80.2	9.4	690.0
24	**A2**	0.75	0.0002	0.83	0	35.6	0.0	108.6
25	**A2**	1.34	0.0002	0.42	0	77.6	2.7	643.5
26	**A2**	1.11	0.0002	0.04	0.2	47.0	1.2	368.3
27	**A2**	0.94	0.0002	0.39	0.1	182.4	29.3	290.8
28	**A2**	0.81	0.0003	0.39	0	192.4	20.9	235.7
29	**A2**	0.75	0.0000	0.23	0	7.7	0.0	481.7
30	**A2**	1.27	0.0002	0.26	0	260	30.1	1060

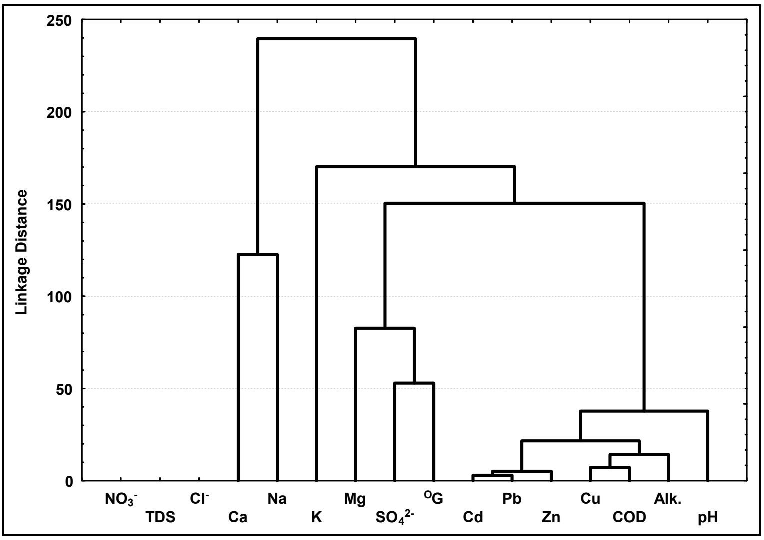

Figure 1. The tree diagram for the 16 variables considered

The variables are grouped in 5 groups, according to linkage distances, the greatest distances being for NO_3^-, TDS and Cl^- (in descending order), variables, less proper for classification. The most suitable variables for this purpose are Cd, Pb, Zn, Cu and COD content of the water samples. Significant correlation exists between the variables Na and Cl^--ion content ($r = 0.83$) and Mg and Ca content ($r = 0.87$), respectively. Using all the 16 variables the classification of the wells (cases) is represented in the Figure 2.

The diagram shows that the wells have close similar chemical composition, being grouped in 4 main groups. Wells from different zones, some of them situated at 200-300 m distance to each other, take part close, in the same subgroup. This suggests that the wells are feed by the same aquifer layers, they communicate between each other (an important feature of public health aspect). The differences seem to appear mainly due to the distinct mode of exploitation by the owners, such as the distinct frequency and water withdrawal quantity from the well.

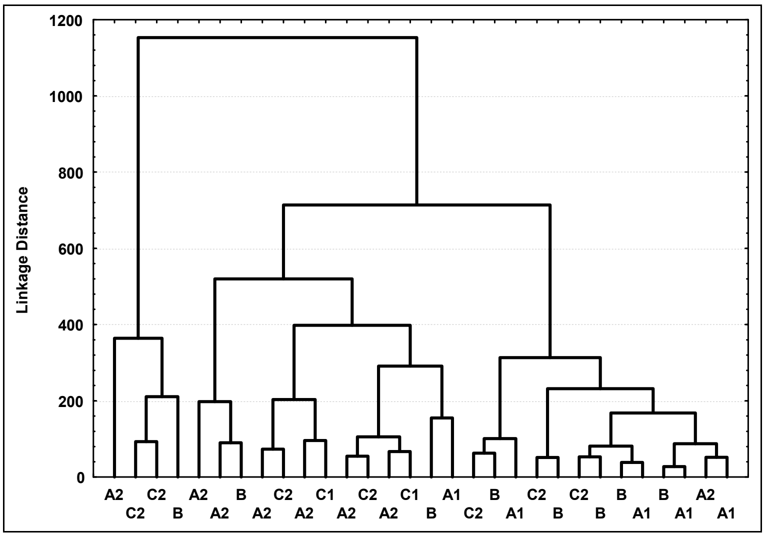

Figure 2. The tree diagram for the 30 well water samples

In the next step the factor analysis was carried out. Based on the scree plot data, 5 factors were retained, also the first three factors cover 95.77 % of the variance. The factor loadings for each variable are synthesized in the Table 4.

Table 4. Factor Loadings (Varimax normalized)

	Factor 1	**Factor 2**	**Factor 3**	**Factor 4**	**Factor 5**
pH	0.207563	**0.770780**	0.236369	0.008961	0.215662
Alk.	**0.667291**	0.598495	-0.112624	0.233278	-0.110554
COD	0.129281	0.072931	0.638477	0.075670	0.412815
^{O}G	**0.971984**	0.103140	0.060046	-0.081636	-0.079986
TDS	**0.967382**	-0.101480	0.175258	0.079374	-0.009263
Na	**0.851140**	-0.277206	0.051300	0.138125	0.179426
K	-0.083540	-0.149300	0.398450	**0.790085**	-0.068063
Mg	**0.933271**	0.231893	0.086673	-0.073718	-0.042683
Ca	**0.816476**	0.351372	-0.022124	-0.344708	-0.048337
Cu	0.106008	0.113988	**0.859824**	-0.067920	-0.055023
Zn	-0.045120	-0.004045	0.063097	-0.053661	**0.882874**

	Factor 1	**Factor 2**	**Factor 3**	**Factor 4**	**Factor 5**
Pb	-0.163514	0.647606	0.126985	-0.072130	-0.196369
Cd	0.043922	0.085520	-0.274024	**0.798977**	0.005318
Cl^-	**0.842973**	-0.339580	0.244909	-0.119279	0.098616
SO_4^{2-}	0.659487	-0.349934	0.023661	0.244843	0.002926
NO_3^-	-0.346795	0.651629	-0.433585	-0.044882	0.139131

highlighted loadings > 0.700

The first factor (covering 62.08 %, includes the variables Alk., D(^{O}G), TDS, Na, Mg, Ca and Cl^-, the main components of the waters; the second one includes only the pH (covering 28.68 % of total variance), the followings each includes only one variable: Cu, Cd, and Zn, respectively.

CONCLUSIONS

The well waters take part of medium mineralized and hardness waters, being suitable for household and agriculture purposes. The high Cd and NO_3^- - ion content make the waters unsuitable for human and animal consumption. The well waters have similar chemical composition, the wells being fed by the same aquifer layers. The hierarchical cluster analysis shows that the waters could be classified best based on the Pb, Cd, Zn, Cu, COD content; the wells being grouped in 5 clusters. They can be only partially classified; wells from different zones could not be separated. 8 variables could be grouped in two factors, which cover 90.78 % of the total variance.

EXPERIMENTAL SECTION

Selection of the settlement

In order to get representative results, the followings were taken into account in the selection of the sampling site: to have a population greater than 500 inhabitants, the freshwater water supply realized by wells, constant everyday water consumption. All these conditions were fulfilled by Remetea Oaşului village (Satu Mare county), located in the north-western part of Romania with the following geographic coordinates: Latitude - 47° 52' 60 N, Longitude - 23° 19' 0 E, altitude: 200 m above the sea level. The village lies in the Tur-stream valley, surrounded by 50-100 m high hills, with about 600 habitants. The people deal with animal breeding, plant cultivation; the well waters are used for agricultural, stock-raising, household purposes, including human and animal consumption. The wells are placed usually in the farmyards, and are covered with lids; the water is brought to the surface using metal buckets or immersion pumps.

Sampling and sample handling

Waters of 30 private wells from village were sampled. Three different zones of the settlement were selected, situated evenly along the main- and the neighboring side roads plots. There were collected 13 samples from the southern zone (labeled A), 8 samples from the northern zone (labeled B) and 9 samples from the central zone (labeled C) of the village. The samples were collected during November 2007 period in according to the EPA prescriptions: collected in 500 mL PET bottles, conserved on the spot with 1 mL of conc. HNO_3 and kept at 4 °C.

Instrumentation

The quantification of the metals was carried out with a Perkin Elmer 373 (Waltham, MA, USA) flame atomic absorption spectrophotometer. The original burner head for C_2H_2 – air flame was replaced with a home made one for CH_4 – air flame [14]. The instrumental parameters for each element were optimal, set as indicated in the manufacturer's prospect. The chloride-ion content, the alkalinity (Alk.) and the total hardness (D) were determined by potentiometric titration (670 Titroprocessor, Mettler, Herisau, Swiss). The electric conductivity was quantified by using an OK – 102/1 (Radelkis, Budapest, Hungary) conductometer. The total dissolved salts (TDS) values were calculated by converting the conductivity data. The chemical oxygen demand (COD) has been determined by using the Kubelka method. The quantification of the SO_4^{2-}, NO_3^- and NH_4^+ ions were performed in molecular absorption mode, at λ = 490 nm, 210 nm and 401 nm respectively, using a double beam UV-Vis spectrophotometer (T80+, PG Instruments Ltd., UK) [3, 4].

Chemicals

All stock standard solutions were of 1000 mg/L, prepared from RbCl, CsCl, Li_2CO_3 (Merck, Darmstadt, Germany), NaCl, KCl, KNO_3, NH_4Cl (Reactivul, Bucuresti, Romania), $CaCO_3$, Cd, Fe, Cu, Zn and Mg (Specpure, Johnson Matthey Chemicals Limited, England), HCl, H_2SO_4, HNO_3 (analytical grade, Merck, Darmstadt, Germany)), respectively. The calibration solutions were obtained by diluting a given volume of stock solution with double distilled water. The diluted solutions were prepared just before measurements. $KMnO_4$, $C_2H_2O_4.2H_2O$, $AgNO_3$ and EDTA 0.1 N solutions are all manufacturer-made volumetric solutions and were used as received (Reactivul, Bucharest, Romania).

Procedure

The temperature, electric conductivity and the pH values were determined in the field; the other parameters were quantified in the laboratory. For the flame AES, AAS and spectrophotometric quantifications the standard calibration method was used in all cases. The titrations were carried out in the dynamic automatic titration mode, using appropriate potentiometric sensors. Three parallel measurements were made, the mean, and the SD were calculated. The statistical and chemometrical processing of the data was carried out by using the Statistica software program, version 6, (StatSoft.Inc., OK, USA).

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