QUANTIFICATION OF MAJOR IONS IN GROUNDWATERS USING ANALYTICAL TECHNIQUES AND STATISTICAL APPROACHES

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Abstract. Groundwaters are used for domestic consumption, including drinking water, commercial, industrial as well as for irrigation. It is well known that the water-related health problems are the result of microbial and chemical contamination of drinking water. The main objective of this study was to determine quantitatively the contributions of various ground-water nitrate pollution sources including chemical fertilizers and animal wastes applied to croplands using the statistical approaches of PCA. In this respect, 240 wells water samples were collected from pre-existing wells, situated mainly in rural agricultural area from Targoviste Plain, Romania, between September and November 2014. Sampling was performed in according with EPA Guide for Ground-Water Sampling. Dissolved cations including Ca, Mg, Na, K, Cr, Fe, and Mn, were analysed using an iCAP™ Q ICP-MS. Dissolved anions (i.e. SO₄²⁻, NO₃⁻ and Cl⁻) were determined using Dionex ICS-3000 Ion Chromatography system. Alkalinity of groundwater samples was measured by titration method to quantify the carbonate species (mainly HCO3). Quality control (QC) of chemical analyses was achieved by analyzing blanks duplicate samples. A statistical analysis of quantitative source apportionment for the chemical investigated elements was performed. The chemical parameters were interpreted with Principal Component Analysis (PCA). Pearson correlation coefficient matrix using a Student's t distribution in MatLab is used to determine the linear dependence between the analysed parameters. Schoeller diagram achieved with the RockWare AqQA program is presented for analysed ions $(SO_4^{2^-}, HCO_3^-, Cl^-, Ca^{2+}, Mg^{2+})$ behavior interpretation. Durov Diagram is achieved as well, for a real interpretation of obtained data.

Key words: ICP-MS, ion chromatography, statistical approach.

1. INTRODUCTION

Rural areas from Romania are characterized by the existence of sites with common and important contaminations of water from the wells with nitrogenous substances and exceeded concentrations of metals. For example, beginning with 1955, the methemoglobinemia was recognized as public health problem in rural areas [1]. Responsible with this disease are the nitrogenous substances, especially nitrates and nitrites, which are considered minor constituents of water. Usually, nitrates in public-supply wells occur from residential and agricultural fertilizers, or seepage from a septic system. The natural nitrate in groundwater is normally less

than 10 mg/L, according with international legislation [2]. The major ions in wells water are: calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}) and potassium (K^{+}), as cations, and bicarbonate (HCO_3^{-}) / carbonate (CO_3^{-2}) , sulphate (SO_4^{-2}) , and chloride (CI), as anions. Mainly, the rains are responsible with the presence of these ions in wells. Many chemical substances are dissolved by rain water which passes through the air and through and over the land. The gases from air, including nitrogen, oxygen and carbon dioxide are dissolved by the rain water, pass through the atmosphere and reach in wells water. The carbon dioxide dissolution from the air is important, because the resulted carbonic acid enhances the water's capacity to dissolve certain chemical salts contained in rocks and soil. When rain passing through polluted atmosphere, the water dissolves the gases associated with pollution, including sulphur and nitrogen oxides. These dissolved gases increase the acidity of water, as well as the water's capacity to dissolve the salts. In present, the existing information about the occurrence and distribution of major, minor ions and trace metals in wells water from studied area (i.e. Targoviste Plain) are insufficient. In this respect, this study aims to achieve a water-quality data set by using the consistent methods of sampling and analysis, and statistical approach as well, to provide a data base with which can compare data obtained in future sampling campaign. In the past few years numerous studies on the spatial distribution of environmental components [3-5] or wells water quality using interpolation methods for the flow of nitrates [6, 7] have been achieved. The spatial distribution of the ions concentrations in wells water were achieved in this study.

2. EXPERIMENTAL

1.1 Description of study area

The analysis of hydrochemical parameters is focused to the groundwater from a piedmont area (i.e. Targoviste Plain, with terraces and alluvial cones in steps). In figure 1 is presented the use of land in Targoviste Plain, achieved by using CORINE Land Cover CLC/2001.



Figure 1 - The use of land in Targoviste Plain.

With an area of 1061 km², the region includes floodplains and large terraces of the Ialomita and Dambovita rivers, composed by a complex of gravel and sands, covered by loess. Elevations decrease from north to south from 400 m to 200 m. Shallow groundwater from Targoviste Plain is influenced by climatic and anthropogenic factors due to its circulation at shallow depths, phreatic layer being situated at depths of 1-3 m in the floodplain, 4-6 m in the lower terraces of rivers Ialomita and Dambovita and maximum 25 to 26 m in the high terraces of Dambovita river. The areas where the groundwater is near the topographical surface or in close proximity of Dambovita and Ialomita rivers are most exposed to contamination by various pollutants. Groundwater is well represented in studied area, being used mainly for household. Groundwaters are quartered at different depths (1-5 m in the space of floodplains, to the Southwest and the Southeast region; 5-10 m in the Northern part of the Targoviste Plain and Dambovita-Ialomita interfluve; 10-20 m in the area Băleni-Dobra). With a population of 200,000 habitants, the region has a predominantly agricultural character (53%) arable land, pasture and meadow 9%), forest areas representing only 25% (figure 1). Targoviste Plain is famous for vegetable crops (6% of arable land, especially in area Băleni, Sălcioara, Targoviste, Bucșani, Văcărești).

1.2 Sampling and sample analysis

In this study 80 wells were selected to provide a better spatial distribution across the studied land (figure 1), having variable depths hydrostatic level (3.0 -27.5 m) and placed in households or near them. The sampling depth ranged between two and fifteen meters. The wells water samples were collected between September and November of the 2014. Sampling and in-situ field measurements of groundwater were performed based on the EPA Guide for Ground-Water Sampling [8]. The measurements of water temperatures, pH, electrical conductivity (EC), TDS, and salinity were performed by using a multiparameter Consort 3030. Alkalinity was determined by titration methods in order to quantify the carbonate species in the groundwater [9]. Groundwater samples were filtered through 0.45um cellulose membranes and then transferred into pre-washed HDPE bottles. Samples used for the analysis of major cations, including Ca²⁺, Mg²⁺, Na⁺, K⁺, Cr_{total} , Fe_{total} , and Mn_{total} , were acidified to pH < 2 by adding a few drops of ultrapure nitric acid. 25 ± 1 mL sub-sample and an acid mixture (HNO₃ 67%, high purity, Merck and HCl 37%, Merck) were dispensed into a digestion vessel, and then were digested on a hot plate by using a TOPwave Microwave-assisted pressure digestion [10-12]. All chemical reagents were of analytical grade. Deionized water (resistivity of 18.2 M Ω cm) was obtained with a Milli-Q System. The cations concentration was determined using an iCAPTM Q ICP-MS. The relative standard deviation (RSD) for analyzed parameters was 0.01%-3.58% (table 1). Limit of quantification (LOQs) was performed by standard curve. Metals calibration curves showed good linearity over the concentration range (0.1 to 10.0 mg/L) with R^2 correlation coefficients in the range of 0.994 to 0.999.

Dissolved anions (i.e. SO_4^{2-} , NO_3^{-} and CI^{-}) were determined using Dionex ICS-3000 Ion Chromatography system. The ion chromatographic analysis of nitrate in water samples [13] collected from different wells is accomplished using direct UV detection of analyte at 210 nm. This method was chosen because is free from

the most ionic interferences due to the specificity of UV detection. In this analysis nitrate was determined in 10 minutes using an IonPac® AS9 analytical column with AG9 guard; the eluent was 1.8 mM Na₂CO₃/1.7 mM NaHCO₃; the flow rate was 2.0 mL/min and sample volume 25μ L.

Chloride and sulphate anions were determined in less 12 minutes using an IonPac® AS24 column with an electrolytically generated KOH eluent [13]. The sample was injected direct with detection limits in the single digit ppb concentration range. The linearity, limits of detection and quantification of chloride and sulphate determination were verified [13]. Calibration standards were prepared fresh daily and immediately analyze. The calibration curve was linear with an R² correlation coefficient greater than 0.9997 for nitrate in the range of 15 ppb to 75 ppm. The calibration curves were linear with an R² correlation coefficient higher than 0.9998 for chloride and 0.9996 for sulphate anions, with a range of injection from 0.1 to 10 mg/L for both injecting calibration standards. The LODs for nitrate was 3 μ g/L for nitrate, 4 μ g/L for chloride and 8 μ g/L for nitrate, 15 μ g/L for chloride and 28 μ g/L for sulphate. Quality control (QA) of chemical analyses was conducted by analyzing blanks and duplicate samples [13].

A statistical analysis of quantitative source apportionment for the chemical investigated elements was performed. The hydrochemical parameters were interpreted with Principal Component Analysis (PCA). Pearson correlation coefficient matrix using a Student's t distribution in MatLab is used to determine the linear dependence between the analysed parameters. Schoeller diagram achieved with the RockWare AqQA program and Durov diagrams are used for a better interpretation of relationships between hydrochemical parameters.

3. RESULTS AND DISCUSSION

Concerning this study, it is well to know that the groundwater hydrostructures of Targoviste Plain are well individualized due to geological, hydrogeological and geomorphological conditions. Topography, hydrology, hydrological and statistics data were processed and digitized using ArcGIS 10.2. Thematic maps have been made based on spatial database. The spatial distribution of the ions concentrations were achieved using geostatistical non-parametric and non-linear estimation/simulation variable spatial methods [14] as well as Kriging indicator [15-19] IDW, Kriging and cokriging interpolations [20]. Also, in this study for a better representation of spatial distribution of obtained ions concentrations (table 1), the interpolation function with barriers using Kernel function Polinomial Order 5 [21, 22] was used (figures 2 and 3). This method was chosen due to the role of "barrier" represented by the mainly arteries of Targoviste Plain (e.g. Ialomita River and Dambovita River).

Table 1 summarized the values for 15 hydrochemical parameters for 240 wells water samples collected from chosen wells, with the concentration range of each variable between a minimum and maximum, with an average for each parameter. The measured pH value was minimum 6.53 in one of the wells from Baleni site and maximum 7.39 in one of the wells from Bratesti site. The average

of pH for all collected samples was 6.87. For all analyzed samples the pH value is in the limits approved by Romanian and international legislation.

Parameter		Minimum	Maximum	Average	RSD [% }
pH		6.53	7.39	6.87	0.02-0.07
Conductivity	[µS/cm]	455	5020	1286.42	1.71-2.90
Salinity	[‰]	0.2	2.6	0.63	0.05-0.09
TDS	[mg/L]	217	2550	621.61	1.54-3.10
Ca ²⁺	mg/L	20.40	94.60	40.98	0.14-1.10
	meq/L	1.02	4.72	2.06	0.05-0.17
Mg ²⁺	mg/L	6.90	38.40	15.01	0.94-1.76
-	meq/L	0.57	3.16	1.24	0.04-0.08
Na ⁺	mg/L	0.99	4.69	2.03	0.02-0.05
	meq/L	0.99	4.69	2.03	0.02-0.05
K ⁺	mg/L	0.07	0.33	0.14	0.01-0.03
	meq/L	0.07	0.33	0.14	0.01-0.03
NO ₃ ⁻	mg/L	21.50	60.40	36.14	0.64-1.15
	meq/L	0.35	0.97	0.58	0.01-0.04
Cl	mg/L	37.75	98.75	61.35	0.54-2.10
	meq/L	1.06	2.79	1.74	0.01-0.14
HCO ₃ ⁻	mg/L	53.50	336.25	171.53	0.58-3.58
	meq/L	0.88	5.51	2.82	0.02-0.15
SO_4^{2}	mg/L	13.75	31.20	19.34	0.55-1.55
	meq/L	0.29	0.65	0.41	0.01-0.02
Cr _{total}	mg/L	0.01	0.09	0.03	0.01-0.03
	meq/L	0.00	0.04	0.02	0.00-0.01
Mn _{total}	mg/L	0.01	0.17	0.04	0.00-0.01
	meq/L	0.00	0.08	0.04	0.00-0.02
Fe _{total}	mg/L	0.11	1.22	0.31	0.01-0.03
	meq/L	0.01	0.13	0.12	0.00-0.01

 Table 1

 The hydrochemical parameters for sampled wells water

Total dissolved solid (TDS) concentrations ranged from 217 mg/L to 2550 mg/L, with a median value of 621.6 mg/L. The TDS showed a linear relationship with the measured electrical conductivity ($R^2 = 0.9698$) indicating that the dissolved constituents of the groundwater comprise the major ions. Ninety-five samples (39.58% of the total of 240 samples) showed high TDS values exceeding the admitted level for drinking water according with WHO regulations (e.g. TDS values must be at least 100 mg/L and optimal 200-400 mg/L [23, 24]). The concentrations of the major cations and anions from wells water samples are Ca²⁺ (20.40–94.60 mg/L) and HCO₃⁻ (53.50–336.25 mg/L) followed by Cl⁻ (37.75–98.75 mg/L), NO₃⁻ (21.50–60.40 mg/L), Mg²⁺ (6.90–38.40 mg/L), SO₄²⁻ (13.75–31.20 mg/L) and Na⁺ (0.99–4.69 mg/L). The maximum admitted concentrations (MAC), according with Romanian legislation [24], for several ions are: 250 mg/L for SO₄²⁻ and Cl⁻ as well, 200 mg/L for Na⁺ and 100 mg/L for Ca²⁺ and Mg²⁺, respectively. The obtained data for the SO₄²⁻, Cl⁻, Na⁺, Ca²⁺ and Mg²⁺ not exceed the admitted level. However the obtained low concentration of Mg²⁺ in analyzed samples represents a signal for human healthy, because the presence of Mg²⁺ in drinking water has an important role especially, in cardiac automatism. It well known that the magnesium deficiency (e.g. 10-40 mg/L [23]) increases the risk of morbidity of the newborns and hypertonic crisis. It is appreciated that magnesium

in drinking water can assure 20%-40% from the daily necessary. Potassium ions concentration, not normalized in the Romanian legislation concerning drinking water quality, varied between 0.07 mg/L and 0.33 mg/L. Besides the essential macro-elements, chlorides and bicarbonates registered values which reveal an intense mineralization of the analyzed water samples. Twenty-one samples (8.75% of the total samples) showed high nitrate concentrations, exceeding the allowable limit for drinking water in Romania of 50 mg/L as NO₃⁻ and thirty-two samples presented values close to the allowed limit, values ranged from 40.30 to 49.61 mg/L. The samples with nitrate concentration lower than 20 mg/L, can suggests that the wells water may be partially influenced by natural sources of nitrate, and/or by attenuation processes including denitrification.



Figure 2 - Spatial distribution of analyzed ions in selected wells.





Based on the measured data table, the Schoeller diagram (figure 4) was achieved using the RockWare AqQA program. Absolute concentrations in meq/L are used. The columns represent, from left to right the analyzed ions, including SO_4^{2-} , HCO_3^{-} Cl⁻, Mg^{2+} , Ca^{2+} , Na^+ , and K^+ . The inclination of the line joining the representative points of the two ions measures its relationship.

The major hydrochemical parameters are shown in a Durov diagram alongside TDS concentrations (figure 5) and in a Schoeller diagram (figure 4) as well. Most of the well water samples belong to the Ca–HCO₃ and Ca–NO₃–Cl water types, while five samples belongs to the Ca–SO₄ type, and are shown as an outliers. Wells water with higher values of TDS is usually associated with Ca–NO₃–Cl type waters, since nitrate pollution in groundwater is often accompanied by major solute enrichments, such as Cl-, from anthropogenic sources, while Ca²⁺ is the dominant cation (figures 4 and 5).

The increasing of Ca^{2+} concentration may be linked to nitrate pollution via microbial nitrification, a reaction that releases hydrogen ions (H⁺) and enhances the dissolution of natural and agricultural carbonates such as lime (CaO). The Ca–HCO₃ type waters with low TDS are thought to represent the typical hydrochemistry of natural recharging groundwater, as controlled by the dissolution of carbonates in the soil zone.

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Figure 4 – Schoeller diagram showing the hydrochemical parameters of sampled wells water $(n_{wells} = 80)$



Figure 5 - Durov diagram showing the hydrochemical parameters of sampled wells water $(n_{wells}$ = 80) with TDS concentrations

3.1 Statistical approaches

In figure 6 it is represented the Tukey boxplot of the analyzed parameters. The hydrochemical characteristics of wells water samples were represented on a logarithmic scale. The highest and lowest occurring value within this limit are drawn as bar of the *whiskers*, and the outliers as individual points. The lowest datum lies within 1.5 *inter quantile range* (IQR) of the lower quartile, and the highest datum lies within 1.5 IQR of the upper quartile. Any data not included between the whiskers is plotted as an outlier with a + sign. Outliers are observations that fall below Q1 - 1.5(IQR) or above Q3 + 1.5(IQR).



Figure 6 - Box and whisker plot of components represented on a logarithmic scale

Component correlations. It computed Pearson correlation coefficient matrix using a Student's t distribution in MatLab as can be observed in figure 7. The values were rounded to the second decimal. It was observed a very strong linear dependence between EC-TDS indicated by very close to one value of the coefficients. It was observed a close to one correlation coefficient between pH and HCO_3^- level and strong correlation between pH and Ca^{2+} , Na^+ , K^+ , Mg^{2+} concentration. There is a strong linear correlation (at pH values > 0.7) between the metals Fe_{total}, Mn_{total}, and Cr_{total} as well.

Principal Component Analysis (PCA). The total analyzed data of the n samples of the m variables is stored in an $n \times m$ data matrix X. Due to the fact that the variables are in different units and the difference in the variance of different columns is substantial it scaled the variable to have unit variance, by standardizing the data. Let Σ be the covariance matrix of the standardized data set X. Due to the fact that Σ is a symmetric matrix its eigendecomposition looks:

$\Sigma = V \Lambda V^t$,

where V is the orthogonal eigenvector matrix, and Λ is a diagonal matrix whose entries are the eigenvalues of Σ . The columns of V are the normalized eigenvectors of Σ and preserve important information regarding the multivariate variability

expressed by the eigenvalues. Once eigenvectors are found its order them by eigenvalue, highest to lowest. This gives the components in order of significance.

						Correlati	on Matrix						
5	0.03	0.03	0.07	0.34	0.30	0.96	-0.03	0.02	-0.04	0.82	0.74	0.82	0.82
5 0.03	1	1.00	0.39	0.42	0.14	0.07	0.87	0.92	0.84	0.11	0.14	011	0.11
0		1	minie.	-	diam	-100 1.	àn.	1000	parest.	-	-	-	-
0 0.03	1.00	1	0.38	0.42	0.14	0.07	0.87	0.91	0.83	0.11	0.13	0.11	0:10
0	-		Mart.	atting .	dia:	-100	àn.	1000	moto	and a	the as	all a	-
0.07	0.39	0.38		0.25	-0,14	0.08	0.48	0.35	0.35	0.10	0.28	0.10	0,10
6 0.34	0.42	0.42	0.25		0.03	0.37	0.31	0:35	0.31	0.38	0.29	0.38	0.32
	A	-	1.	IIII.	1	-		- Martin	-1111-	-	-	-	120
2 0.30	0.14	0.14	-0.14	0.03	.	0.37	0.16	0.11	-0.04	0.36	0.35	0.36	0.36
0.96 42	0.07	0.07	0.08	0.37	0.37		-0.02	0.06	-0.04	0.86	0.79	0.86	0.86
1 -0,03*	0.87	0.87	0.48	0.31	0.16	-0.02		0.83	0.74	0.05	0.13	0.05	0.04
5 0.02	0.92	0.91	0.35	0.35	0.11	0.06	0.83		0.85	0,11	0.11	0.11	0,11
5 -0.04	0.84	0.83	0.35	0.31	-0.04	-0.04	0.74	0.85	h	-0.02	-0.05	-0.02	-0.02
6 0.82	0.11	0,11	0.10	0.33	0.36	0.86	0.05	0.11	-p.02		0.92	1.00	1.00
2	Mar .	****	torn.	value .	ALL THE	with .	A	- Million	Illiin.	III	-	/	1
4 0.74	0.14	0.13	0.28	0.29	0.35	0.79	0.13	0.11	-p.05	0.92		0.92	0.92
0	A		and par.	LANDER	- Marin	14.	- Brown	-dill'eter	Hiller	-		-	124
4 0.82	0.11	0,11	0,10	0.33	0.36	0.86	0.05	9.11	-0.02	1.00	0.92	1	1.00
			Ten est	HBJHK"	Die op	Mar,	145° **	*1481ch. *	Mares.			IIII I	1
2 0.82	0.11	0,10	0,10	0.32	0.36	0.86	0.04	9.11	-p.02	1.00	0.92	1.00	

Figure 7 - Correlation matrix.



Figure 8 - Principal Component Analysis (PCA).

In figure 8 it was observed that the first 6 components explain 96.22% of the total variance. The first 2 eigenvectors defined as principal components PC's explain 75.69%. of the total variance in data. The first component extracted in the principal component analysis accounts for a 42.85% amount of total variance in the observed variables and will be correlated with some of the observed variables.

components i er une i ez						
LOADINGS						
	PC1	PC2				
pH	0,3260	-0,1945				
EC	0,1981	0,3945				
TDS	0,1962	0,3938				
NO ₃ ⁻	0,1277	0,1864				
SO4 ²⁻	0,2121	0,1103				
Cl	0,1667	-0,0538				
HCO ₃ -	0,3450	-0,1896				
Fe _{total}	0,1669	0,3825				
Mn _{total}	0,1868	0,3833				
Cr _{total}	0,1299	0,3908				
Ca ²⁺	0,3671	-0,1791				
Mg ²⁺	0,3535	-0,1506				
Na ⁺	0,3671	-0,1791				
K ⁺	0,3657	-0,1814				

Table 2 Loadings of the 13 variables – determined hydrochemical parameters for the first two principal components PC1 and PC2

The second extracted component has two important characteristics, first, this component accounts for a maximal amount of variance in the data set that was

not accounted for by the first component respectively 32.83% and secondly the second component is uncorrelated with the first component. The principal component loadings are presented in table 2 and figure 9.



Figure 9 - Results of the PCA analysis including the loadings for each variable and the principal component scores for each observation in a single plot.

The first principal component is correlated with five of the original variables 'pH', ' HCO_3 ', Ca, Mn, Na and K. This suggests that these five criteria vary together. If one increases, then the remaining components also increase. They are all positively related as they all have positive signs. The second principal component is correlated with EC, TDS, and metals Fe, Cr and Mn. They are all positively related with PC2.

CONCLUSIONS

Interpretation of hydrochemical parameters reveals that: chemistry of wells water from studied area displays $Ca^{2+}>Mg^{2+}>Na^+>K^+$ and $HCO_3^->Cl^->NO_3^->SO_4^{2-}$ trend; the major elements data plotted on Scholler diagram indicate that, most of the wells water belong to the Ca–HCO₃ and Ca–NO₃–Cl water types; the Durov diagram for wells water samples indicate that most of the samples are in the phase of mixing, dissolution with few in reverse ion exchanges. Comparisons with WHO data, standards for drinking water, indicate that the wells water in the studied area are suitable for drinking purposes except Baleni and Bucsani areas. 39.58% of the total of wells water samples showed high TDS values exceeding the admitted level for drinking water according with WHO regulations.

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