



Multivariate statistical analysis of water chemistry in wells from Sub-Carpathians of Curvature, Romania

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Abstract. The present study evaluates the physical-chemical parameters of drinking water from wells located in rural areas from Buzau County, in Sub-Carpathians of Curvature, Romania. Water samples were collected in September 2015 from 12 wells. The dissolved trace metals and metalloids, major cations (sodium, magnesium, calcium, potassium) and anions (fluorides, sulphates, nitrites, nitrates, phosphates and chlorides), alkalinity, pH, total dissolved solids and electrical conductivity were determined. The obtained data were assessed against the drinking water quality standards, Piper diagram, Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA). Concentrations of fluorides, nitrates, nitrites and phosphates were below the maximum allowable concentrations (MACs) for drinking water established by European legislation (Drinking Water Directive 98/83/CE) in all the analyzed samples. Concentration of chlorides exceeded MAC (250 mg L^{-1}) in 3 samples, concentrations of nitrates exceeded MAC (50 mg L^{-1}) in 2 samples, while concentration of sulphates exceeded MAC (250 mg L^{-1}) in 7 samples. Among the analyzed metals, Na concentrations exceeded MAC (200 mg L^{-1}) in 3 samples, while Cu, Pb, Zn, Fe, Cd, Cr, Cu, Ni and As concentrations did not exceed the corresponding MACs. Using the Piper diagram it was found that the majority of the samples are of Ca-Cl and Ca-Mg-Cl types. Multivariate statistical approaches revealed the relationships between physicochemical properties of waters.

Key Words: water quality, underground water, drinking water, multivariate statistics, Piper diagram.

Introduction. Groundwaters from aquifers together with surface waters (lakes, rivers) are the most common drinking water resources which, during the time, become vulnerable to anthropogenic contamination (Singh et al 2013). Inadequate water supply represents a major challenge in rural areas where domestic wells are used as drinking water sources without any treatment or assessment of the water quality. Drinking water quality has a direct effect on human health, thus the monitoring of its chemical composition and the assessment against the drinking water quality standards is essential (Diaz et al 2012; Celebi et al 2014).

In villages from Romania, approximately 50% of houses have fountains as source of potable water, and about 28% of them benefits of the connection to water supply systems (Both & Borza 2011). According to World Health Organization (WHO), there is a need of at least 20 liters of uncontaminated drinking water per person per day (Calin & Rosu 2011). Alteration of drinking water sources are directly influenced by contamination resulted from anthropogenic activities, such as tailings from mining activities, use of fertilizers and pesticides from agriculture, industrial effluents discharge, etc. (Sima et al 2011; Gilbert 2012; Stefanescu et al 2013; Botezan et al 2015; Chuah et al 2016). Most commonly, heavy metals and inorganic anions along with the microbiological load are the major water contaminants.

Whereas there are many studies on water quality in areas affected by anthropogenic contamination (Ozunu et al 2009; Hoaghia et al 2015a; Senila et al 2015), naturally-occurring processes in underground water are less studied and reported, even if

they play a significant part in the health and environmental risk assessment. Groundwater is assumed as the most trusted drinking water source due to the filtering effect of the aquifer; however the geochemistry of the area can influence the physical-chemical characteristics of groundwater, consequently in several areas around the world natural-occurring groundwater contaminations were reported (Rowland et al 2011; Polomcic et al 2014).

Usually, in the evaluation of water quality a complex data set is generated, containing numerous physicochemical parameters that are difficult to interpret and correlate. The simple investigation of the results and their comparing with the maximum admitted limits do not explain the complexity of the system. It is needed to extract significant information from these data sets by using multivariate statistical approaches to find hidden relationships between parameters and to accomplish grouping to differentiate groundwater in function of characteristics or sampling sites (Levei et al 2014; Zghibi et al 2014; Chow et al 2016).

The aim of this study was to assess the water quality in water from wells located in Buzau County, Curvature Sub-Carpathians, Romania, to establish the water type using Piper diagram and to find the relationships between different chemical parameters applying multivariate statistical approaches.

Material and Method. The study area is located in the Sub-Carpathians of Curvature in Buzau County (Patarlagele and Paltinis villages), Romania (Figure 1). Water samples were collected from 12 household and public wells, in September 2015. On site, 100 mL of water was filtered using 0.45 μm cellulose acetate filters and kept at 4°C during transport to the laboratory for the determination of anions and alkalinity. Another 100 mL of water sample was filtered using 0.45 μm cellulose acetate filters and acidified with a few drops of concentrated nitric acid (to obtain $\text{pH} < 2$), for the determination of dissolved metals/metalloids.

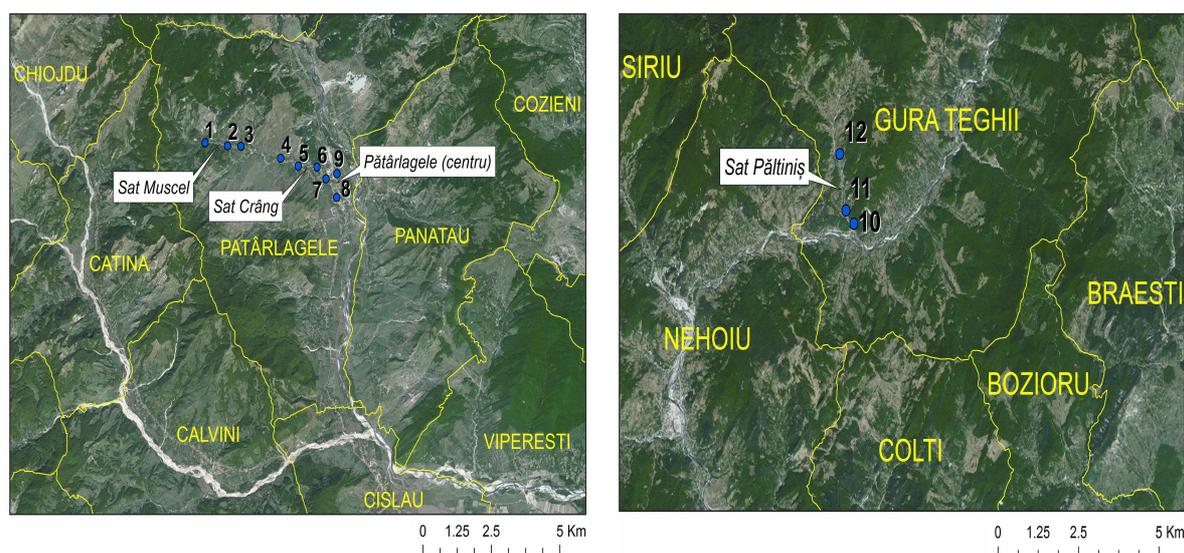


Figure 1. Sampling sites in Patarlagele and Paltinis localities in Sub-Carpathians of Curvature, Romania.

Ultrapure water obtained using a Millipore system was used for all dilutions. All used chemical reagents were of analytical grade. Ultrapure grade 65% (m/m) HNO_3 (Merck, Germany) was used for on-site acidulation and digestion of water samples before metals determination. Stock multi-element solutions of 1000 $\mu\text{g mL}^{-1}$ containing all the analyzed metals (Merck, Germany) were used to calibrate spectrometers for metals determination. Stock multicomponent solution containing Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , PO_4^{3-} of 1000 $\mu\text{g mL}^{-1}$ (Merck, Germany) were used to calibrate the ion chromatograph.

The major metals (Na, Ca, Mg, K, Fe) were determined by inductively coupled plasma atomic emission spectrometry using a ICP-AES Optima 5300 DV Spectrometer

(Perkin Elmer, Norwalk, USA) while trace elements by inductively coupled plasma mass spectrometry using a ICP-MS ELAN DRC II Spectrometer (Perkin-Elmer, Toronto, Canada). Anions were quantified directly in the filtered water by ion chromatography using the 761 Compact IC (Metrohm, Switzerland). The alkalinity was analyzed by volumetric method, pH and electrical conductivity were analyzed on site using a portable Multi 340i analyser (WTW, Germany), while TDS was calculated from EC using empirical formula $TDS=0.64*EC$. Three parallel samples were analyzed for the each parameter and the results are presented as the average of the 3 measurements.

The accuracy of metals determination was checked by analyzing NIST 1643e freshwater (NIST, Canada), while that of anions analyzing the BCR 616 artificial groundwater certified reference sample (IRMM, Belgium). Recovery degrees ranged between 95-110% for metals and 99-115% for anions, showing a good accuracy for the used analytical methods.

Results and Discussion. The concentration of main analyzed indicators in collected water samples and maximum allowable concentrations (MACs), according to Drinking Water Directive EC 98/83/EC (Official Journal of the European Communities, 1998), is presented in Table 1.

Table 1
Concentrations of selected parameters in wells water samples

| Sample | pH | EC | F ⁻ | Cl ⁻ | NO ₃ ⁻ | SO ₄ ²⁻ | Na | Mn | Cu | Zn | Pb |
|--------|---------|--------------------|----------------|-----------------|------------------------------|-------------------------------|------|------|--------------------|------|-----|
| | | μScm ⁻¹ | | | mg L ⁻¹ | | | | μg L ⁻¹ | | |
| 1 | 7.56 | 1340 | 0.15 | 16.4 | 0.87 | 643 | 181 | 1.1 | 4.5 | 8.3 | 0.9 |
| 2 | 8.09 | 636 | 0.19 | 2.09 | 0.47 | 28.4 | 11.3 | 0.2 | 2.5 | 3.6 | 1.2 |
| 3 | 7.48 | 2111 | 0.31 | 111 | 12.5 | 1246 | 105 | 7.7 | 7.5 | 1700 | 1.6 |
| 4 | 7.27 | 2510 | 0.43 | 748 | 16.4 | 691 | 212 | 5.1 | 4.2 | 11.8 | 2.2 |
| 5 | 7.72 | 863 | 0.26 | 74.0 | 33.0 | 122 | 67.5 | 0.2 | 4.9 | 7.3 | 0.6 |
| 6 | 8.44 | 2760 | 0.42 | 555 | 0.10 | 140 | 486 | 1.4 | 7.9 | 1.8 | 1.1 |
| 7 | 7.63 | 1638 | 0.35 | 90.5 | 99.0 | 241 | 69.6 | 1.3 | 5.2 | 9.7 | 1.7 |
| 8 | 7.02 | 2610 | 0.22 | 840 | 22.3 | 878 | 289 | 0.2 | 4.4 | 45.5 | 1.5 |
| 9 | 6.96 | 1827 | 0.29 | 255 | 34.1 | 155 | 139 | 32.7 | 9.8 | 920 | 1.3 |
| 10 | 7.46 | 1118 | 0.41 | 11.2 | 22.8 | 470 | 56.3 | 1.2 | 4 | 123 | 0.8 |
| 11 | 7.11 | 1005 | 0.15 | 31.1 | 56.5 | 288 | 18.5 | 0.2 | 2 | 12.9 | 0.9 |
| 12 | 7.17 | 1397 | 0.17 | 2.37 | 1.45 | 752 | 51.7 | 0.2 | 2.4 | 5.4 | 0.5 |
| MAC* | 6.5-8.5 | - | 1.20 | 250 | 50 | 250 | 200 | 50 | 100 | 5000 | 10 |

Results are presented as average values, n=3 parallel samples, *MAC - maximum allowable concentration.

As presented in Table 1, the pH values were found in the ranges of 6.96-8.44, being in the range of values considered as normal for drinking water. The EC values were in the range of 636–2760 μS cm⁻¹. Among the analyzed anions, sulphate was found in higher concentrations, with values between 28.4 and 1246 mg L⁻¹ exceeding the MAC in 7 of the analyzed samples. Chlorides concentrations were in the range of 2.09–840 mg L⁻¹, in 4 water samples exceeding the MAC (250 mg L⁻¹). Fluorides concentrations, ranging between 0.15–0.43 mg L⁻¹, were below the MAC in all the samples. The concentrations of nitrates were above the corresponding MAC in 2 samples.

The concentrations of Na were in the range of 11.3–486 mg L⁻¹, in 3 samples the values were above the MAC (200 mg L⁻¹). For the other major cations (Ca, Mg, K) there are not established maximum values for drinking water. The concentrations of Cu ranged between 2.0–9.8 μg L⁻¹, and were in all cases below MAC (100 μg L⁻¹). The concentrations of Zn were considerably below MAC (5000 μg L⁻¹), as well as the concentrations of Pb and Mn. The levels of Cr, Ni, Cd and As concentrations (data not displayed) did not exceeded MACs in any of the analyzed samples.

In order to identify the water facies in the studied area (Hoaghia et al 2015b), the Piper diagram was plotted using GW Chart (Version 1.29.0.0) free software for creating piper diagrams from the United States Geological Survey (Figure 2). Generally, the Piper diagram classified samples into Ca-HCO₃ type; Na-Cl type; Ca-Mg-Cl type; Ca-Na-HCO₃ type; Ca-Cl type and Na-CO₃ type (Sajil Kumar 2013). In our case, the water samples were found to be Ca-Cl type (samples 3, 4, 11, 12) and Ca-Mg-Cl (samples 5 and 9) type, Ca-HCO₃ (samples 2 and 10) and Na-Cl types (samples 1, 6, 7 and 8).

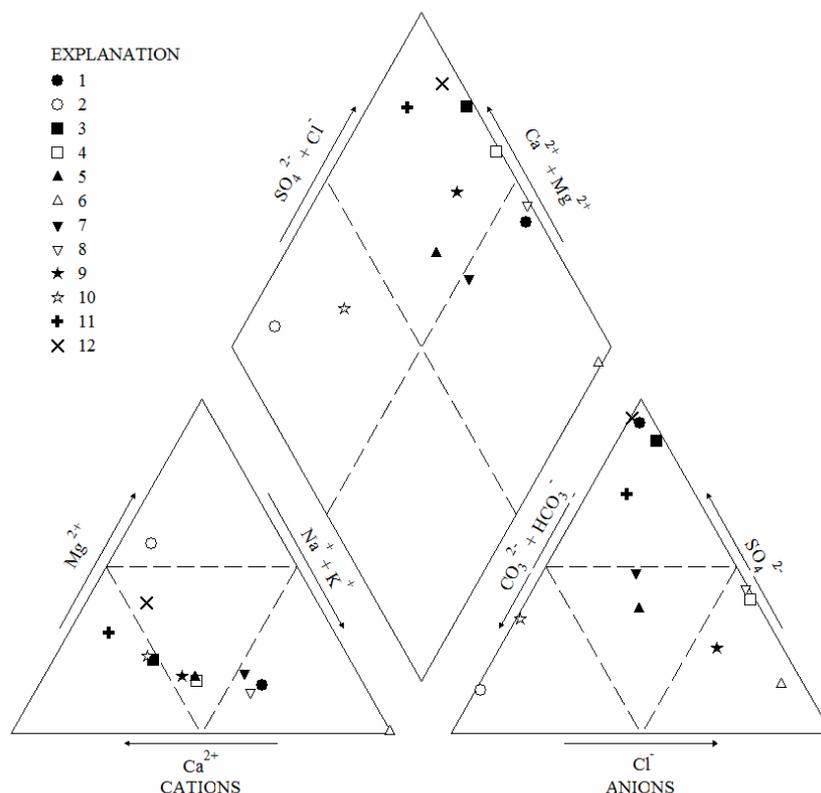


Figure 2. Piper diagram showing the well waters classification.

Principal component analysis (PCA) is used to extract the variables into significant principal components (PCs). PCs offer information on the most important parameters, which describe an entire data set by data reduction with minimum loss of original information. An eigenvalue provides a measure of the significance of the factor. Eigenvalues higher than 1 are typically used to define the number of principal components (PCs) (Senila et al 2012; Chow et al 2016).

The varimax rotated factor loadings of principal components (PCs) for the soil metals and physicochemical properties are presented in Table 2. The loadings in bold face correspond to variables with dominant influence on the selected latent factor. Five PC's with eigenvalues higher than 1, explains about 80% of the total variance of the system. The first component (PC1) exhibits 27% of the total variance with positive loadings on sulfates, Ca, Mg, Ni, and negative loadings on pH and Cr. This factor indicates the strong loading on sulfates with Ca and Mg in analyzed water samples and could be associated with the presence of sulphate minerals in the host rock and the pH influence in their presence in waters.

The second component (PC2) explains about 23% of the total variance and contains fluorides, chlorides, bicarbonates, Na, EC and Pb, showing mainly the association between Na, chlorides and bicarbonates and finally the influence on water electrical conductivity.

The third component (PC3) explains about 14% of the total variance and shows the correlations between nitrates, K and Li. The fourth component (PC4) explains about 11% of the variance and includes Mn, Cr, Cu, Zn and Cd. The latest principal component (PC5) contains only As indicating its different behavior in underground system.

Table 2

Varimax rotated factor loadings of experimental variables of significant PCs

| <i>Variable</i> | <i>PC1</i> | <i>PC2</i> | <i>PC3</i> | <i>PC4</i> | <i>PC5</i> |
|----------------------------------------|------------|------------|------------|------------|------------|
| Eigenvalue | 5.057 | 4.202 | 2.574 | 2.090 | 1.373 |
| Variability (%) | 27.584 | 22.920 | 14.042 | 11.402 | 7.491 |
| Cumulative % | 27.584 | 50.505 | 64.546 | 75.949 | 83.439 |
| Factor loadings after Varimax rotation | | | | | |
| F ⁻ | -0.141 | 0.541 | 0.485 | 0.159 | -0.322 |
| Cl ⁻ | 0.026 | 0.810 | -0.006 | -0.043 | -0.072 |
| NO ₃ ⁻ | 0.003 | -0.281 | 0.763 | -0.008 | -0.220 |
| SO ₄ ²⁻ | 0.766 | 0.394 | -0.106 | -0.050 | 0.211 |
| HCO ₃ ⁻ | -0.444 | -0.649 | 0.345 | 0.103 | 0.089 |
| Ca | 0.882 | 0.169 | 0.110 | 0.242 | -0.024 |
| Mg | 0.727 | -0.230 | -0.002 | -0.089 | 0.429 |
| Na | -0.375 | 0.840 | -0.163 | 0.104 | -0.008 |
| K | -0.024 | -0.071 | 0.878 | -0.026 | 0.226 |
| EC | 0.087 | 0.907 | 0.108 | 0.166 | 0.056 |
| pH | -0.748 | 0.176 | 0.048 | -0.083 | 0.092 |
| Li | 0.146 | 0.444 | 0.651 | 0.131 | 0.239 |
| Cr | -0.514 | 0.450 | -0.052 | 0.511 | 0.322 |
| Mn | 0.120 | -0.022 | 0.006 | 0.849 | -0.019 |
| Ni | 0.763 | 0.074 | 0.220 | 0.412 | 0.042 |
| Cu | -0.150 | 0.377 | 0.144 | 0.834 | -0.058 |
| Zn | 0.482 | 0.068 | 0.081 | 0.714 | 0.058 |
| Cd | -0.450 | 0.257 | 0.087 | -0.589 | -0.164 |
| Pb | 0.219 | 0.512 | 0.497 | 0.143 | 0.207 |
| As | -0.078 | 0.022 | -0.139 | -0.068 | -0.902 |

Hierarchical Cluster Analysis (HCA) is used to categorize the objects of the system into categories or clusters based on their similarity (Chow et al 2016). Hierarchical agglomerative clustering analysis was performed by using Ward's method, applying Euclidean Distance as the distance or similarity measure. The dendrogram considering the chemical parameters as objects is shown in Figure 3a, and contains 3 major clusters which confirms the results obtained by PCA, showing the correlations among different chemical parameters.

Cluster analysis considering the sampling points as variables is illustrated in Figure 3b. This approach reveals 4 clusters according to spatial distribution of parameters in the 2 localities. The first cluster shows the similarities between samples 3 and 9, the two samples having the highest concentrations of Zn. The cluster C2 shows the similarities between samples 2, 5, 6, 7 from Patarlagele, while a separate cluster C3 was formed between the samples 4 and 8, two samples with very high content of sodium, chlorides and sulphates. The fourth cluster, C4, is formed by the 3 samples located Paltinis (10, 11, 12) which showed similarities with the sample 1.

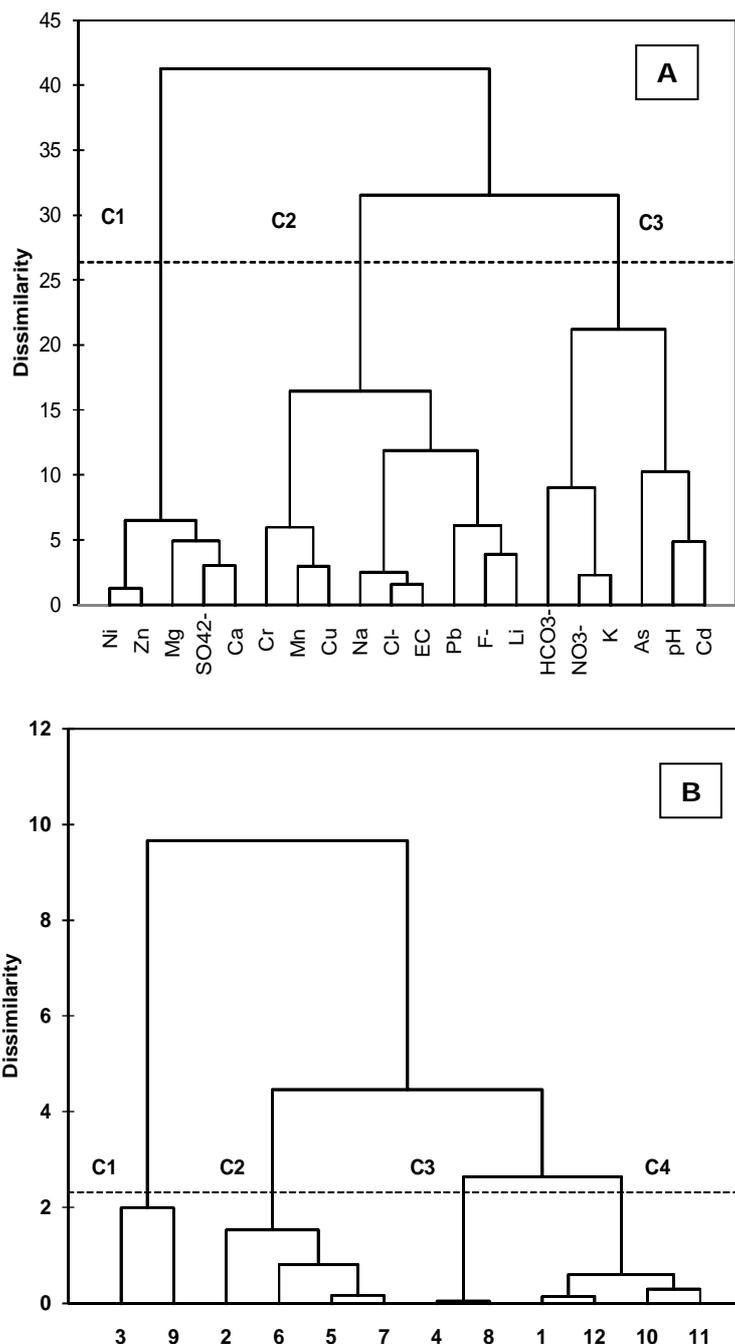


Figure 3. Dendrogram of chemical variables of the groundwater samples (a) and dendrogram of sampling locations (b).

Conclusions. Our results revealed a moderate pollution of groundwater in the studied area. The pH values of water samples were found in neutral range, while among the analyzed anions, sulphates were found in the higher concentrations, exceeding the corresponding MAC in 7 samples. Also, concentrations of chlorides were above the corresponding MAC in 4 samples. The concentrations of toxic metals were in all cases below the corresponding MACs. Multivariate statistical approaches were found to be very useful tools in order to reveal the hidden relationships between physicochemical properties of waters. PCA indicated five PC's with eigenvalues higher than 1, which explain about 80% of the total variance of the system. The dendrogram considering the chemical parameters as objects is showed 3 major clusters, while the dendrogram considering the sampling sites as objects grouped the sampling sites into 4 clusters.

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