

Groundwater quality assessment in urban environment

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Abstract The assessment of environmental effects generated by urban areas (with various activities as agriculture, industry, human activities) on groundwater quality became essential for the use and conservation of the water resources. The main objective was to apply a water quality index to the groundwater sources using the specific methodology, establishing the suitability for drinking for groundwater. Water resources were monitored in October 2011, the samples were collected from 22 points for groundwater, and more parameters were analyzed: pH, electrical conductivity, turbidity, oxygen regime, hardness, alkalinity, nutrients regime (nitrates, ammonium, phosphates) which were considered important and utilized for water quality index computation that reveal poor quality for groundwater. The oxidability should be included in computation formula and the final results used for water management, taking into consideration the limits of the current model. Multivariate statistical analysis was used to indicate the influence of urban area on the quality of groundwater resources. Results of the analysis highlight an influence of geology and a contamination of agricultural origin.

Keywords Water resources · Urban area · GWQI · Multivariate statistical analysis

Introduction

Water resources assessment represents one major concern of the present world due to the importance of water for human being and society and for implementing sustainable water-use strategies. One of the major challenge is represented by communicating the complex information about water quality into an appropriate manner to be usable and understandable by non-scientist as general public, managers and others categories.

An important source of water supply in different sectors of economies all over the world is represented by the groundwater, due to the facility of exploiting and to the better quality, in comparison with surface water. Nevertheless, the planners and the managers of water resources do not have to minimize the vulnerability of groundwater to the pollution and the population briefing about the quality status (Belkhiri et al. 2011; Manju et al. 2012; Romanelli et al. 2011; Zhang and Huang 2011). Moreover, a contaminated groundwater body could not be restored by eliminating the pollution sources, difficult to identify, especially the non-point sources, becoming necessary the regular monitoring of water quality (Ravikumar et al. 2011). An efficient groundwater quality monitoring could be realized using WQI for groundwater, the results being easy to understand by communicating the final index score that fit into one of five water status class. Nowadays, the methodology of computation water quality index was improved very much, existing various methodologies for computation. For the current study was chosen the first method that is represented by the Arithmetic Water Quality Index (WQI_A), because this is the originally index proposed by Horton (1965). Many researchers (Brown et al. 1972; Prati et al. 1971; Dinius 1987) have used this index in their research work, which is based on the weighted

Law No. 458/2002 regarding drinking water quality (in Romanian).

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arithmetic mean. More recently, the water quality indexes were computed for different regions indentifying sources of water quality pollution for surface water and groundwater (Prashant et al. 2011; Zare Garizi et al. 2011; Coletti et al. 2010; Ishaku et al. 2012; Sharma 2010; Saedi et al. 2010; Stigter et al. 2006).

Groundwater studies for Iasi City that were found were very old and contained only data regarding the degree of mineralization of water, without any characterization for the suitability for drinking (Pantazica 1974; Dragomir 1998) with sampling points located within the Iasi City build-up area.

In this study, the groundwater resources from the build-up area of Iasi City were assessed due to the numerous point and non-point sources of water pollution. A major concern related to the quality of water resources is about potential effects of urbanization on the availability and quantity of water resources, thus the percent of population recorded at water-sewerage system, which is lower than 85 % for water and 75 % for sewerage, so a certain percent of the population use local water resources for consumption without knowing the suitability for drinking or other use. The situation is similar for entire Romania's urban areas. Despite its signification, the lack of understanding water quality resources imposes to realize management

plans to improve water quality. So that GWQI was chosen to facilitate population's access to information concerning water quality.

The study represents a holistic assessment of the groundwater quality for various purposes, with three major objectives: (1) To establish water quality parameters for all the 22 sampling points, (2) to determine GWQI and (3) to highlight spatial variation of the groundwater and of the factors and sources that influence general water resources quality, the results being relevant not only for the studied area, could be integrated in national and international studies for water quality assessment and classify the resources into spatial types.

Water quality index was chosen with the purpose of showing the spatial variation of water quality in urban area of Iași city, Romania.

Study area

Iasi City is located in the northeastern part of country, being the largest city from Iasi County and its build-up area was chosen as area of study. The location of Iasi City is shown in Fig. 1. This area was selected due to the significant anthropic pressure on the environment exercised by the urbanization process during over 600 years. Water resources were very

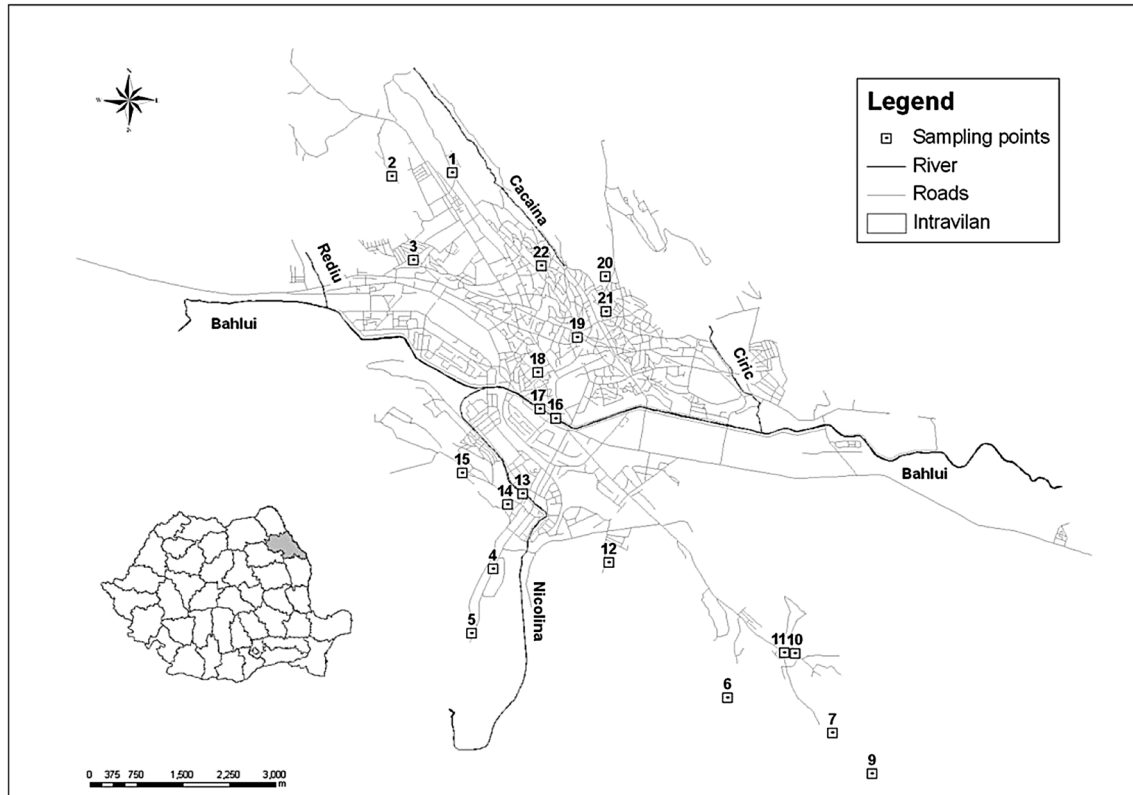
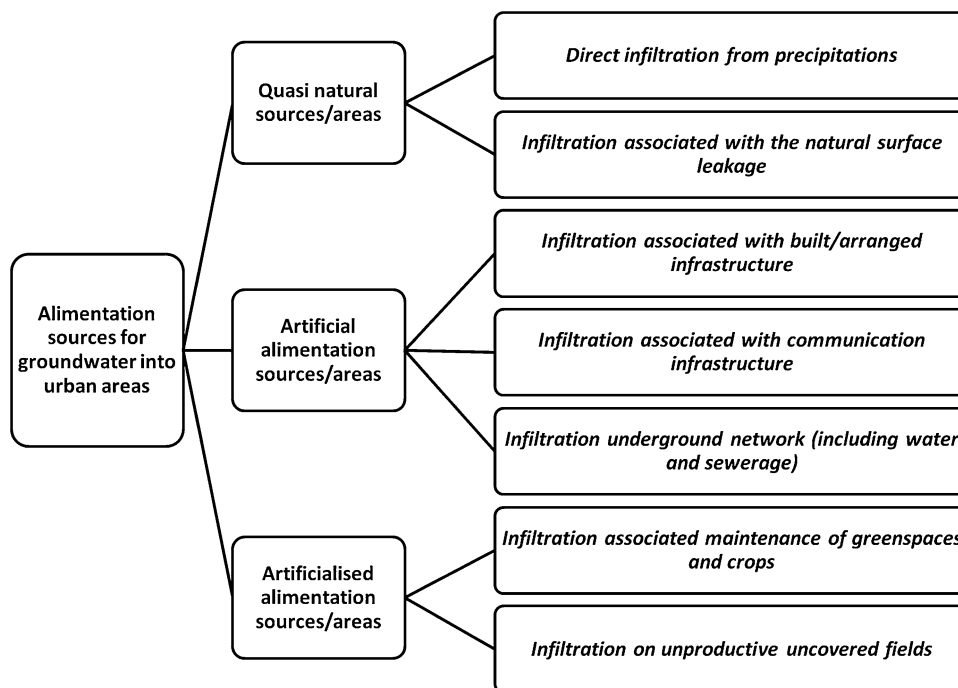


Fig. 1 Study area and sampling points location



Fig. 2 Alimentation sources in urban areas (after Ungureanu 2007)



important for urban development, but they were exploited without any preserving measures and not protected. Thus, there were selected 22 sampling points for establishing the urban Iasi City water resources’ quality. The study area has an altitude range from 32.4 to 381.2 m.

The underlying geology is composed of Quaternary sedimentary formations and clay, marl and oolitic limestone deposits from Neogene. The climate of the region is continental with four distinct seasons, with 9.72 °C the average multiannual temperature and the 575.57 mm/m² the average multiannual precipitations, that mostly falls in spring and summer. Land use in the city is predominantly in residential areas 23.7 %, orchards 17.39 % and green spaces and forests 13.67 %. All these natural and anthropic conditions can be synthesized over alimentation sources or areas for groundwater, as it can be observed in Fig. 2. The information synthesized by the scheme is useful to understand the interactions between natural and anthropogenic components of urban environment, not only for the studied area, and the effects on groundwater quality.

Materials and methods

Sampling points

The sampling was realized in October 2011, after studying the national literature and after discussions with Public Health Institute specialists, revealed that the fall season is

the most relevant season for groundwater sampling for the entire year, if samples are collected after 2 weeks without precipitations. Samples were collected from 22 points (Fig. 1) into sterilized polyethylene sample bottles and to prevent the unpredictable changes, as bacterial action and the formation of the oxides, the samples were acidified with a 30 % nitric acid (Yakubo et al. 2009). The samples were stored in ice-packed styrofoam boxes. The depth varied between 1 and 5 meters for 14 samples and over 5 meters for 8 sampling points. In the field were measured the pH, electrical conductivity and temperature, using Multi 350i/SET WTW multi-parameter instrument. The locations were established after field observations that were useful to identify the location of pumps and wells that exists in the city for groundwater. So that the distances between the sampling points are not equal, but GPS equipment that was used to georeference the sample collection points.

Parameters for monitored water quality and methods of analysis

The laboratory analysis of some physicochemical parameters: pH, calcium, magnesium, water hardness, chlorides were made by potentiometric methods using Multi 350i/SET WTW multi-parameter instrument, for oxidability and HCO₃ titrimetric method being used. For nitrates and phosphates, spectrophotometric method was utilized, with sodium salicylate for nitrates and molybdate salt for phosphates.

Table 1 Groundwater quality index computation input

Groundwater quality parameter	WHO 2004	Weight (w_i)	Relative weight (W_i)
pH	6.5–8.5	4	0.1379
Electrical conductivity	500	4	0.1379
Oxidability	No guideline (was used 5 from Romanian standard)	3	0.1034
Phosphates	10 mg/L	1	0.0345
Nitrates	45	5	0.1724
Water hardness	300	3	0.1034
Magnesium	50	1	0.0345
Bicarbonate	500	3	0.1034
Calcium	75 mg/L	2	0.0690
Chlorides	200 mg/L	3	0.1034
			$\Sigma Gw_i = 29$
			$\Sigma GW_r = 1.000$

Computation of GWQI

In groundwater quality index (GWQI), computation included ten parameters: pH, total solids, oxidability, phosphates, nitrates, water hardness, magnesium, bicarbonate, calcium and chlorides, being a method derived from water quality index.

After creating the database, GWQI was calculated according to the international formula of WQI computed in four steps, using a weighted arithmetic index method (Horton 1965; Brown et al. 1972):

$$W_i = \frac{w_i}{\sum_{i=1}^n w_i} \quad (1)$$

where w_i = the weight of each parameter (Table 1) were accorded due to relative importance of each parameter in overall quality of water for drinking purpose, except the oxidability that was included in the formula due to the implication in chemical reactions in groundwater from studied area, according 5 for nitrates and 1 for magnesium, take into consideration the impact on human health (Ishaku et al. 2012). First, the index was computed without oxidability, the results being easily different, three points fitting into good quality class, but after the inclusion of this parameter into the formula, the results changed, highlighting the relevance of oxidability into GWQI computation.

n = number of parameter.

$$SI = (w_i \times q_i) \quad (3)$$

where q_i = quality rating computed according to the formula:

Table 2 Groundwater quality index legend

Legend	Status
<50	Excellent water
50–100	Good
101–200	Poor
201–300	Very poor
>300	Unsuitable for drinking

$$q_i = \frac{C_i}{S_i} \times 100 \quad (2)$$

where C_i = Concentration of each chemical parameter, for each water sample and S_i = WHO standard

$$GWQI = \sum_{i=1}^n SI_i \quad (4)$$

where SI_i = the sub index for each parameter.

The final GWQI values are classified into five categories (Vasanthavigar et al. 2010) according to Table 2.

Methods of analysis

To assess water resources quality, there were used basic statistics for parameters commonly included in water quality indexes, such as mean, median, maximum, minimum, standard deviation and coefficient of variation. Multivariate statistical methods were applied using SPSS software, version 19.

Factor analysis (FA) is a method of multivariate statistical analysis for variables with many internal dependent relationships, useful for process large database grouping variables due to strong correlation or on basis of relationship between variables. The analysis and evaluation of the obtained results reveal that this method can provide the scientific basis for managing water resources. Factor analysis was used applying this technique in three phases: (1) preparation of the correlation matrix from the original data using Spearman correlation coefficient to reveal the dependency between variables; (2) extraction of the common factors using the procedure called factor analysis and (3) the rotation of axes related to the common factors using the Varimax procedure, aiming at a simple and easily interpreted solution. Factorial analysis used for water resources assessment was realized by Zare Garizi et al. (2011) and Coletti et al. (2010) that revealed important correlation between analyzed parameters and water quality index or by He et al. (2012).

Another multivariate statistical analysis was applied—hierarchical cluster analysis, being a simple approach to detect multivariate similarities in groundwater quality.



Dendrogram of the groups and their proximity were obtained as output. Cluster analysis reveals the groups statistically significant influenced by natural and anthropic conditions (Dudeja et al. 2011; Guggenmos et al. 2011; Yidana 2010).

The last statistical method used was discriminant analysis that targets the impact of the independent variables over the discrimination and identifies the most relevant parameters with influence on the water quality. Discriminant analysis represents a statistical method used to identify the possible factors responsible for the spatial variations in the groundwater quality (Zare Garizi et al. 2011; Boyacioglu and Boyacioglu 2010).

Results and discussion

Groundwater quality index results indicate differences in the suitability of the water conditioned by the values of the parameters used for index computation, revealing lower or stronger correlation.

The coefficient of variation (Table 3) reveals high values that confirm the influence of geology and soils on indicators of the degree of mineralization of water, but also

anthropic impact for nutrients regime, especially for nitrates and phosphates with the highest coefficient of variation 98.5 %. Mean values for nitrates—104.7 mg/L—were not fit into the limit 50 mg/L, maximum registered value is 292.6 mg/L, the water from this source being not suitable for drinking.

Spearman correlation matrix (Table 4) reveals high dependence among variables of the degree of mineralization due to the natural processes, with direct correlation between water hardness, calcium, magnesium, bicarbonate and electrical conductivity (Singh et al. 2006). Magnesium and calcium are highly interrelated with total hardness. This interrelationship indicates that the water hardness is permanent in nature, being influenced by the quaternary sediments. The relation between electrical conductivity and nitrates in ground water can be explained by the saline nature of the nitrates that establish an anthropic influence on groundwater resources (Hudak 2012). Correlation matrix does not reveal correlation between chloride level and other parameter, so that this parameter was excluded from factor analysis.

Factor analysis includes factorial loads matrix, Eigen values and total and cumulative variance values. The results are given in Table 5.

Table 3 Basic descriptive statistics (mean, median, standard deviation, coefficient of variation) for groundwater parameters

Variable	Units	Mean	Median	SD	Coefficient of variation (%)
pH	pH units	7.030	7.026	0.380	5.40
Electrical conductivity (EC)	µS/cm	1,478	1,361	768	52.00
Oxidability	mg O ₂ /L	4.53	3.86	1.80	39.74
Phosphates	mg/L	0.0147	0.0081	0.0145	98.50
Nitrates (NO ₃)	mg/L	104.72	93.05	80.01	76.41
Hardness	German degrees	6.4	5.6	2.9	44.44
Magnesium	mg/L	18.3	16.9	9.7	53.07
Bicarbonate	mg/L	542.8	512.4	222.8	41.05
Calcium	mg/L	27.8	25.4	12.8	46.05
Chlorides	mg/L	262.9	219.7	147.0	55.92

Table 4 Correlation matrix for 10 studied parameters

Variable	pH	EC	Oxidability	Phosphates	Nitrates	Hardness	Magnesium	Bicarbonate	Calcium
EC	0.477								
Oxidability	0.018	0.029							
Phosphates	0.003	0.698	0.014						
Nitrates	0.524	0.008	0.814	0.304					
Hardness	0.129	0.076	0.622	0.820	0.772				
Magnesium	0.186	0.020	0.198	0.498	0.603	0.000			
Bicarbonate	0.230	0.000	0.125	0.557	0.019	0.196	0.325		
Calcium	0.059	0.246	0.978	0.509	0.930	0.000	0.002	0.212	
Chlorides	0.915	0.622	0.308	0.323	0.568	0.759	0.793	0.356	0.553

Boldface values represent the SIG values that reject the null hypothesis, at significant level of 5 % (that the variable is independent)

Table 5 Rotated matrix for factor loadings, variance and the communality of groundwater quality parameters

Variable	Factor			Estimated communality
	F1	F2	F3	
pH	-0.153	0.812	0.316	0.783
EC	0.387	0.239	0.839	0.911
Oxidability	0.203	0.788	0.175	0.693
Phosphates	-0.083	0.868	-0.173	0.791
Nitrates	-0.136	-0.126	0.783	0.647
Hardness	0.987	-0.016	0.098	0.983
Magnesium	0.872	0.069	0.115	0.779
Bicarbonate	0.243	0.274	0.802	0.777
Calcium	0.917	-0.078	0.069	0.852
Eigen	3.413	2.341	1.461	
Variance (%)	37.923	26.016	16.233	
Cumulative variance	37.923	63.939	80.172	

After a few attempts, three relevant factors for the study case were chosen. The statistical method explains 80.1 % of the total variance of original variables, indicating a high degree of information conservation. The values for estimated communalities reveal that 98.3 % of water hardness indicators are explained by common factors (F1, F2 and F3), while 64.7 % of chlorides are explained by same factors.

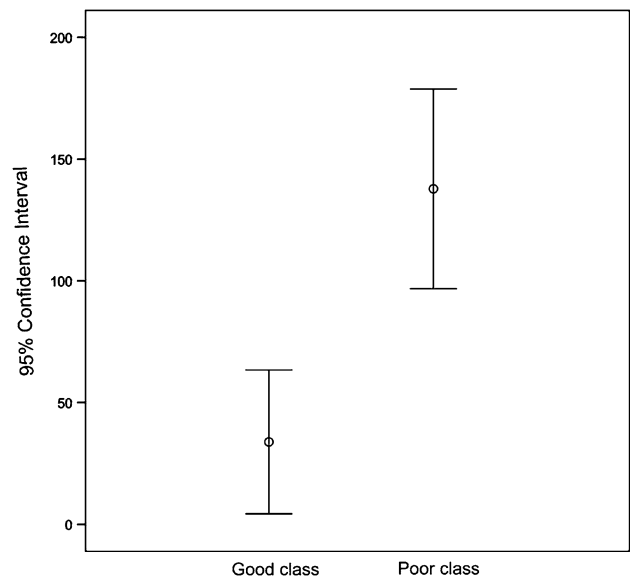
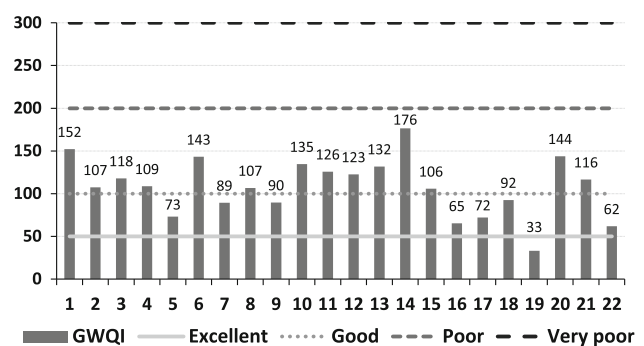
Factor loading can be divided into three major classes: strong (values over 0.75), moderate (0.5–0.75) and weak (0.3–0.5) according to Liu et al. (2003). To determine relevant factor for each factor, only values over 0.75 were taken into account.

Factor 1 accounts 37.9 % of variance and reflects high loading for calcium, magnesium and water hardness; this combination of variables highlights the natural degree of mineralization of water and could be related with the geology of the studied area, derived from the evaporation and dissolution processes.

Factor 2 explains 26 % of variance with strong absolute loadings on pH, oxidability and phosphates. The relationship between these variables could be identified as anthropic influence on groundwater due to the lower rate of decomposition of organic substances inside groundwater bodies.

Factor 3 accounts 16.2 % of variance and is represented by the electrical conductivity, nitrates and bicarbonate that explain the correlation between natural condition (dissolved solids and bicarbonate) and anthropic impact of domestic activities (nitrate level influenced by urban land use).

The factor analysis results are relevant not only for the current study, because the first factor highlights the relevance of geology into water natural characteristics, the second factor reveals the impact of urban area and the third

**Fig. 3** Error plot for nitrate**Fig. 4** Groundwater quality index

one reveals the correlation between natural and anthropogenic influences on water quality.

Another statistical method applied for the database was discriminant analysis that revealed that the most relevant of all parameters is the nitrate due to its influence on the final GWQI value and the suitability of the groundwater for different uses. Nitrates error plot (Fig. 3) shows significant differences between two quality classes. Nitrates' levels in groundwater reflect an old contamination with nitrogen, from different sources difficult to control. Nitrates represent a special parameter that is monitored, being included in provisions of Nitrates Directive 91/676/EEC, its implementation being problematic in many EU member states, especially into the countries adhered recently.

Statistical processing of variables included in the groundwater quality assessment (correlation matrix, cluster analysis, factor and discriminant analysis) reveals the good choice of the parameters for computation of the GWQI,

sustaining the obtained results and being useful in finding explanation for obtained value for computed index.

GWQI values (Fig. 4) show that a single point (number 19) fits into the excellent class, determined by the anthropic influence—water filters installed because the water from this point represents the only water source for an old monastery of the city. Other 7 sampling points (numbers 5, 7, 9, 16, 17, 18 and 22) fit into the good class due to the location into area where influence of the urbanization process was not very high (points numbers 5, 7, 9). On the other hand, natural conditions (higher depth on point 22) or anthropic interventions (as longitudinal dikes of Bahlui River that reduce the impact on groundwater resources (point numbers 16, 17) represent local factors favored a good preserving of groundwater resources. The rest of the sampling points was included in poor quality class due to higher content of nitrates. They are located into the old residential area of the city with constant influence on ground water quality because of fertilizer application in the gardens, subsistence agriculture, including animal growth and plant cultivation or to the lack of septic system of the buildings not connected to the central system of water and sewerage (Copou, Ticau districts from the North, or Galata district from the South area of the city—where was found point number 14 with highest value of GWQI—176) or newer residential districts such as Bucium.

The results are significant, not only for the current studied urban area, due to the location of the sampling points with higher values in peripheral districts, caused by the chaotic urban sprawl and the higher pressure exercised by the old residential districts on environment quality.

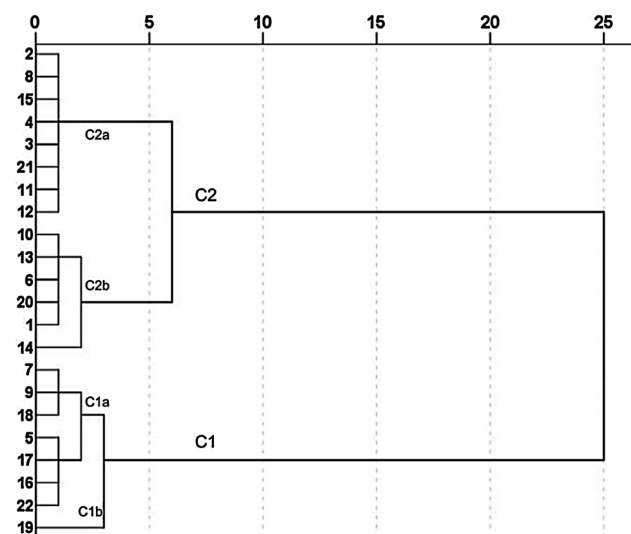


Fig. 5 Dendrogram of hierarchical cluster analysis for groundwater

Cluster analysis clearly grouped the sampling points into distinct clusters, significant in the geologic and hydrologic context, based on the similarity of object attributes. Cluster method was Ward’s method with dendrogram as output. Figure 5 shows two different clusters (C1 and C2) that in turn have two subdivisions. Each cluster presents similarities with GWQI classes excepting the representation of excellent class that was assimilated in good class (point number 19). Cluster 1 is characterized by lower nitrate concentrations (mean value 33.8 mg/L), electrical conductivity (1,063 mS/cm) and bicarbonate (407 mg/L), comparing with values for cluster 2 (nitrates 137.8 mg/L, electrical conductivity 1,671 mS/cm and bicarbonate 605 mg/L). These groups are separated geographically with good correspondence between spatial locations and HCA results.

The method represents an useful tool to establish the significant groups correlated with location, in accordance with the registered values, being more relevant than the other methods. Cluster analysis results correspond with the GWQI status class, verifying the accuracy of the index.

Conclusion

The GWQI was used to monitor the impact of urban environment on groundwater quality, taking into consideration the drinking water standards, highlighting the potability of each sampling point. The results are sustained by three different statistical method results that group the points into three different categories, also revealing the most significant chemical parameter that influence the final water quality and the utility of statistical method into the validation of the GWQI. The main concern is the fact that groundwater exploitable from the upper aquifers fits into poor quality class, being unsuitable for drinking purpose. The results are alarming due to the high percent of population not connected to the municipal water supply, using the water from local wells for domestic use, without knowing the quality of water they use. For that reason, the GWQI represents an useful communication tool to inform the local population, but also the Public Health Institute, Environment Agency about the water quality problems.

From the point of view of the groundwater quality index classes, the poor class represents the largest class, with only a point fitting into excellent class. Factor analysis revealed three major factor accounting over 80 % of variance grouping variables over natural condition influence and anthropic influence on ground water quality. Discriminant analysis shows that the most relevant parameter that ensures the differences between sampling points is nitrate presence, influencing water’s suitability for different uses. Cluster analysis of the obtained data puts into

evidence the establishment of two equilibrated main clusters correlated with spatial distribution, nitrate content and functional area of the city. The oxidability represents an important quality parameter that should be included into further groundwater studies, due to the high relevance.

More cities of the country should apply this methodology to improve the communication with inhabitants about the groundwater status. The communication problems concerning the groundwater quality can be overcome by using the GWQI results, facilitating a better water resources management and helping the interdisciplinary teams (scientists, water managers, policymakers) to take the best decisions. However, the loss of information caused by the standardization and aggregation of data into index computation should involve prudence in using it as final quantitative assessment of water potability.

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Nomenclature

GWQI Groundwater quality index
EC Electrical conductivity

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