



“Gheorghe Asachi” Technical University of Iasi, Romania



GROUNDWATER CHARACTERIZATION IN SOUTHWESTERN ROMANIA USING FUZZY HIERARCHICAL CROSS CLUSTERING

Marin Senila¹, Costel Sarbu^{2,3}, Oana Cadar¹, Calin Baciu⁴, Michaela Ponta^{2,3},
Tiberiu Frentiu^{2,3*}

¹National Institute for Research and Development of Optoelectronics INOE 2000 INCD, Research Institute for Analytical Instrumentation, 67 Donath, 400293 Cluj-Napoca, Romania

²Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos, 400028 Cluj-Napoca, Romania

³Babes-Bolyai University, Research Center for Advanced Chemical Analytical Instrumentation and Chemometrics-Analytica, 11 Arany Janos, 400028 Cluj-Napoca, Romania

⁴Babes-Bolyai University, Faculty of Environmental Science and Engineering, 30 Fantanele, 400294 Cluj-Napoca, Romania

Abstract

A simultaneous hierarchical classification of groundwater in the Banat Plain-southwestern Romania and associated characteristics such as As(III), As(V), total As, trace metals (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn), pH and redox potential using Fuzzy Hierarchical Cross Clustering Algorithm was carried out. In samples containing more than 10 µg/L total As (13.9 – 77.3 µg/L), the As(V) species represented 57±20% and 73±18% in the others. Arsenic speciation pattern was in agreement with basic pH (8.31 – 8.49) and oxidizing conditions (369.0 – 409.1 mV) in aquifer. The contents of metals were below the threshold values excepting Mn. The Fuzzy Hierarchical Cross Clustering Algorithm emphasized pH and redox potential as main parameters responsible for water samples grouping. Part of water samples containing > 10 µg/L As have as associated parameters the content of Pb, Cr, Zn and Fe, and pH plays a key role in natural occurrence of these elements by desorption from Fe minerals/oxyhydroxides. The other water samples with > 10 µg/L As were grouped based on redox potential, As (III), As (V), total As, Cd, Ni, Cu, Al and Mn concentrations. The source of these elements was attributed to desorption processes from Al minerals/oxyhydroxides and Mn oxyhydroxides governed by the redox potential. The Fuzzy Hierarchical Cross Clustering emphasized the importance of trace metals quantification for classification of groundwater with naturally enriched As content.

Key words: arsenic speciation, Banat Plain, Fuzzy Hierarchical Cross Clustering, groundwater exploration, trace metal

Received: November, 2018; *Revised final:* February, 2019; *Accepted:* February, 2019; *Published in final edited form:* September, 2019

1. Introduction

Unlike surface resources, groundwater is less exposed to anthropogenic contamination and its quality is mainly dependent on the aquifer mineralogy and water-rock interactions. One of contaminants naturally occurring in groundwater is arsenic, which is the subject of several studies regarding processes governing its release as well as the associated health effects (Anawar et al., 2003; Biswas et al., 2014; Chakraborti et al., 2016; Chakraborti et al., 2017; Jang et al., 2017; Kuroda et al., 2017; Panagiotaras et al.,

2012; Park et al., 2016; Rahman et al., 2016; Su et al., 2016; Verma et al., 2016). Besides arsenic, quantification of trace metals is useful for the evaluation of water-rock interaction, identification of processes governing the natural or anthropogenic enrichment and discriminating between them (Cuoco et al., 2015; Ghrefat et al., 2016; Kim et al., 2014; Nshimiyimana et al., 2016; Rahman et al., 2015; Sappa et al., 2014; Tirkey et al., 2016). In Europe, the Pannonian Basin including eastern Hungary, western Romania, northern Serbia, northeastern Croatia and southern Slovakia, is characterized by an elevated As

* Author to whom all correspondence should be addressed: e-mail: fitebi@chem.ubbcluj.ro; Phone: +264593833; Fax: +264590818

content, which poses health risks to more than 1000000 inhabitants via drinking water (Dimkic et al., 2010; Gurzau E.S. and Gurzau A.E., 2001; Romanian National Institute of Statistics, 2012; Rowland et al., 2011). European Union member states have established threshold values (TVs) for groundwater bodies depending on hydrogeological conditions and natural background levels (NBLs) for contaminants referred to as risk factors from natural or anthropogenic sources (As, Cd, Pb, Hg, NH_4^+ , Cl⁻, SO_4^{2-} , NO_3^-) and synthetic substances (trichloroethylene, tetrachloroethylene) (EC Directive, 2006; Radu et al., 2010). In Romania, there were established TVs for all groundwater bodies according to NBLs (Order, 2014). Also, several studies were carried out in Romania concerning the quality of groundwater resources, which revealed the vulnerability to heavy metals, As, anions, pesticides, etc., due to anthropogenic activities such as mining, ore processing, non-compliant landfills, poor management of manure, climate change and natural conditions such as precipitation (Badila, 2017; Frentiu et al., 2007, 2008; Minea and Croitoru, 2017; Modoi et al., 2014; Muntean and Mihaiescu, 2016; Nistor et al., 2015; Rusu et al., 2017; Vasilache et al., 2012). Some technologies were proposed to decrease concentration of As species in groundwater below 10 $\mu\text{g/L}$ (Janos et al., 2016; Kobya et al., 2018; Pop et al., 2017).

Several epidemiological studies on human risk of exposure by water consumption with As concentration below or above the maximum allowable value (10 $\mu\text{g/L}$) reported major diseases such as anemia, vascular and heart diseases, neurological disorders and cancer. In the case of pregnant women the risk of spontaneous abortion can occur (Bloom et al., 2010, 2014; Chakraborti et. al, 2016; Neamtiu et al. 2015; Rahman et al., 2015; Sarkar and Paul, 2016; Surdu et al., 2015). Therefore speciation and monitoring of arsenic in drinking and groundwater water is necessary but represents a challenging analytical task (Rajakovic-Ognianovic et al., 2014).

A comparison of the experimental data with guideline values is too simplistic to clarify characteristics and behavior of contaminants in groundwater. Thus unsupervised chemometric methods such as Cluster Analysis (CA) and Principal Component Analysis (PCA) were widely used for the characterization of groundwater (Cuoco et al., 2015; Kelepertzis, 2014; Kim et al., 2014; Sappa et al., 2014; Spanos et al., 2015). However, CA and PCA approaches have limited capability and do not provide a simultaneous classification of sites and related physico-chemical characteristics.

The aim of this study was to provide a rapid characterization of groundwater based on As speciation and trace metal content using Fuzzy Hierarchical Cross Clustering (FHCC). The FHCC algorithm was applied in the classification in terms of As(III), As(V) and total As content, trace metals (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn), pH and redox potential (E_h) of samples collected from the shallow

groundwater body (GW-ROBA03) and depth groundwater body (GW-ROBA18) located in the Banat Plain-southwestern Romania. Characteristics of the groundwater were discussed in relation with natural feature of local aquifer, which made possible recognition of processes responsible for the occurrence of inorganic arsenic species and trace metals following water-rock interaction. Determinations for total arsenic and speciation analysis were carried out by hydride generation capacitively coupled plasma microtorch optical emission spectrometry (HG- $\mu\text{CCP-OES}$), while metals were quantified by graphite furnace atomic absorption spectrometry (GFAAS). Compared to previous examination, this approach is a significant step forward to describe natural enrichment of inorganic arsenic and co-occurring species in groundwater (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , HCO_3^- , Cl⁻, F⁻, SO_4^{2-} , PO_4^{3-} , NO_3^-) (Butaciu et al., 2017).

2. Material and methods

2.1. Reagents, standard solutions and CRMs

Ultrapure 30% HCl, NaBH_4 pro analysis, NaOH suprapur, L-cysteine for biochemistry, stock solution of As(V) 1000 $\mu\text{g/mL}$ and ICP multielement standard solution IV 1000 $\mu\text{g/mL}$, Merck (Darmstadt, Germany) were used in this study. A solution containing 3% -cysteine in HCl 0.01 mol/L (pH = 2.00 ± 0.01) was used for prereduction of As(V) to As(III), while the 0.6% NaBH_4 stabilized in 0.5% NaOH as derivatization agent. A solution containing 0.01 mol/L HCl (pH = 2.00 ± 0.01) was used as carrier and a solution of 0.3% L-cysteine in 0.01 mol/L HCl as blank. Calibration for As determination by HG- $\mu\text{CCP-OES}$ was carried out using standards in the range 0 – 100 ng/mL in 0.01 mol/L HCl. Calibration in GFAAS was performed using standards prepared from multielement standard solution IV by serial dilution with 2% (v/v) HNO_3 .

The reference materials ERM CA011b Hard Drinking Water UK - Metals, ERM-CA615 Groundwater (Institute for Reference Materials and Measurements – IRMM, Geel, Belgium), SRM 1643e Trace Elements in Water (National Institute for Standards and Technology, Gaithersburg, USA), LGC 6010 Hard Drinking Water and LGC 6019 River Water-River Thames (LGC Promochem, Wesel, Germany) were used in Quality Control of laboratory procedures for As determination by HG- $\mu\text{CCP-OES}$ and metals by GFAAS.

2.2. Site description

The groundwater bodies GW-ROBA03 and GW-ROBA18 are developed until 15-30 m and of higher depth of 30-350 m in the Banat Plain, Bega and Timis Rivers Basin, southwestern Romania. The Banat Plain was formed during Quaternary from detrital sediment transported by the rivers generating deposits of tens to hundreds meters thickness. The

deposits are generally coarse-grained and exhibit discontinuous finer intercalations (Enciu et al., 2014; Mutihac, 1990). The overlaying strata consist of clays, sandy clays, silty clays, silts, argillaceous silts and sandy silts. The main lithological units were described earlier (Butaciu et al., 2017; Radu E. and Radu C., 2011). The main flow direction is from north-east to south-west with 0.1-2.0‰ hydraulic gradient and 6-68 m/d hydraulic conductivity. The effective porosity is 5-25%.

Due to the elevated permeability of sediments, GW-ROBA03 is recharged through precipitations and hydraulic connection with the rivers. The deep aquifer GWROBA18 (Upper Pleistocene-Lower Quaternary) is also porous-permeable consisting of sands, rarely gravels and alternate layers of clay, sandy clay and marls (Pascu, 1983). The aquifer represents the main source of drinking water in the zone and has been considered as a risk factor for population because of exposure to arsenic of geogenic source, a common problem all over in the Pannonian Depression (Bloom et al., 2014; Neamtii et al., 2015; Romanian National Institute of Statistics, 2012; Rowland et al., 2011; Surdu et al., 2015). GW-ROBA03 was previously chosen as Pilot Study Groundwater to establish the Threshold Values for 10 contaminants for

Groundwater in Romania (EC Directive, 2006; Order, 2014; Radu et al., 2010).

The zone has temperate climate with average annual temperature of 10-11 °C and average annual precipitation amount around 600 mm. The main land use relates to maize and wheat production.

2.3. Sample collection, preparation and analytical methods

Water samples were collected from 18 locations (Fig. 1), namely 4 samples from GW-ROBA03 (sites 1; 2; 5 and 17) and 14 samples from GW-ROBA18. A volume of 1 L water was collected from each site, filtered ($< 0.45 \mu\text{m}$) and the pH and E_h were measured on-site. Samples were transferred in polyethylene flasks, flash-frozen on field and transported to laboratory. Speciation as As(III) and As(V) was carried by HG- $\mu\text{CCP-OES}$ in the original samples. Metal content was determined by GFAAS after acidification of water samples to 2% (v/v) HNO_3 . A number of 10 clay and 20 sand samples were collected and analyzed by X-ray diffraction (XRD) and X-Ray Fluorescence Spectrometry (XRF) to achieve the mineralogical composition and trace metal determination.

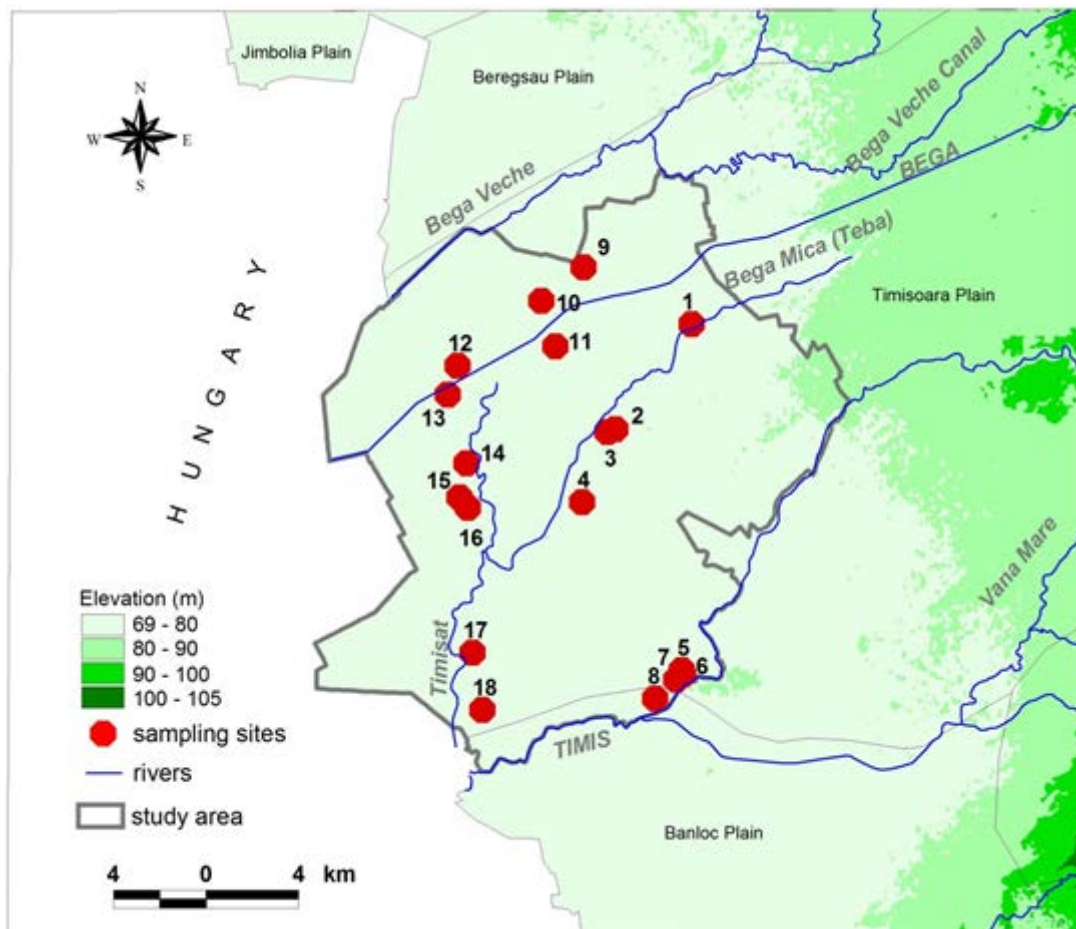


Fig. 1. Location of groundwater sampling points in the Banat Plain-southwestern Romania

Table 1. Operating conditions for As determination by HG- μ CCP-OES

<i>Parameter</i>	<i>Setting</i>
Hydride generator HGX-200	
Final concentration of L-CYSTEINE in sample	0.3%
HCl concentration /pH in the final sample	0.01 mol/L/pH=2.00 \pm 0.01 adjusted before derivatization
HCl concentration /pH in carrier	0.01 mol/L HCl/pH=2.00 \pm 0.01
Derivatization reagent (arsine generation)	0.6% NaBH ₄ stabilized in 0.5% NaOH
Sample flow rate	7 mL/min
Carrier flow rate	1 mL/min
Derivatization reagent flow rate	1 mL/min
μ CCP-OES prototype equipment	
Data acquisition and As emission signal processing	Spectra suite software, As 228.812 nm, peak height measurement, background correction using 0.3% L-CYSTEINE in 0.01 mol/L HCl (pH=2.00 \pm 0.01) as blank, 5 s integration time
Power plasma	10 W
Argon flow rate	150 mL/min
Plasma viewing	Radial, signal collection through 10 mm focal length lens
Calibration range	0-100 ng/mL As

2.4. Chemical and mineralogical analysis

Details about the hydride generation procedure for speciation and determination of As by HG- μ CCP-OES using a prototype equipment (Babes-Bolyai University, Cluj-Napoca, Romania) were already presented (Frentiu et al., 2014). The speciation method involves the selective derivatization of As(III) species in HCl medium and determination of total As after prereduction with 3% L-cysteine in 0.01 mol/L HCl (pH 2.00 \pm 0.01) (Cordos et al., 2006, Frentiu et al., 2007). The concentration of the As(V) species is determined by difference. The pH measurements in the water samples, blanks and 0.01 mol/L HCl was performed with 540 GLP pH-meter WTW GmbH (Weilheim, Germany).

Arsenic(III) determination. The pH value in water samples was adjusted to 2.00 \pm 0.01 with HCl and arsine was generated immediately after the addition of 0.3% L-cysteine.

Total arsenic determination. Prereduction of As(V) to As(III) with 0.3% L-cysteine in 0.01 mol/L HCl was achieved on water bath at 90 \pm 5 °C for 10 min. Derivatization was performed after pH adjustment to 2.00 \pm 0.01.

The derivatization reagent for quantification of total As and As (III) was 0.6% NaBH₄ stabilized in 0.5% NaOH. The low power and low Ar consumption plasma microtorch of the HG- μ CCP-OES analytical system was interfaced with CETAC HGX-200 hydride generator. The emission signal of arsenic was measured at 228.812 nm using the QE65 Pro microspectrometer of low resolution, Ocean Optics (Dunedin, USA). Memory effect was overcome by washing the sample channel of the HGX-200 generator between samples run with blank solution for 40 s. The operating conditions in HG- μ CCP-OES are presented in Table 1. The concentrations of Al, Cd, Cr, Cu, Fe, Mn, Pb, Ni and Zn were determined by GFAAS using the Perkin Elmer model PinAAcle 900T spectrometer (Norwalk, USA) under the experimental conditions recommended by the producer.

The E_h was measured according to the protocol described by Eaton et al. (2005). Analysis of sand and clay samples by XRD using the Bruker D8 Advance Diffractometer Bruker and XRF using the Tracer 5i handheld instrument (Massachusetts, USA) were carried out on powder (< 100 μ m). Major (>20%), minor (5-20%) and trace minerals (<5%) were considered.

2.5. Quality assurance/Quality control of laboratory procedures

The HG- μ CCP-OES method was validated for As determination with recovery of 100 \pm 9% for 95% confidence level, and precision in the range 1.2 – 7.1% for As(III), 3.1 – 9.5% for As(V) and 2.9 – 8.5% for total As (n=3 parallel measurements). Recovery of the arsenic species using the selective derivatization procedure was already assessed with values ranging within 98 – 105% for As(III) and As(V), and 98 – 104% for total As (Cordos et al., 2006). The detection limit in the HG- μ CCP-OES method was 0.2 μ g/L As (Frentiu et al., 2014). The detection limits in GFAAS were (μ g/L): 0.76 Al, 0.05 Cd, 0.40 Cr, 0.36 Cu, 0.65 Fe, 0.34 Mn, 0.33 Ni, 0.70 Pb and 0.35 Zn. The GFAAS method was validated for the determination of Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn with recovery of 92 – 106% and precision of 3.0 – 9.2%. The results obtained for the determination of As by HG- μ CCP-OES and metals by GFAAS in CRMs and the mean recovery are presented in Table 2.

The redox potential of water samples and ZoBell's solution (1.4080 g K₄Fe(CN)₆·3H₂O, 1.0975 g K₃Fe(CN)₆ and 7.4555 g KCl to 1000 mL solution) were measured. The redox potential of water sample was corrected for the difference between the potential of the calomel reference electrode and the standard hydrogen electrode (+183 mV). The E_h of water sample was calculated with (Eq. 1):

$$E_h = E_{observed} + E_{hZoBell / refence} - E_{hZoBell / observed} \quad (1)$$

Table 2. Results ($\mu\text{g/L}$) for the determination of As by HG- $\mu\text{CCP-OES}$ and metals by GFAAS in water CRMs

Element	ERM-CA011b		SRM 1643e		LGC 6019		LGC 6010		ERM-CA615		Recovery (%) ^c
	Certified ^d	Found ^e	Certified ^d	Found ^e	Certified ^d	Found ^e	Certified ^d	Found ^e	Certified ^d	Found ^e	
As ^a	10.15 \pm 0.34	10.30 \pm 1.78	60.45 \pm 0.72	59.85 \pm 0.87	-	-	55 \pm 5	56 \pm 3	9.9 \pm 0.7	9.8 \pm 0.3	100 \pm 9
Al ^b	209 \pm 11	218 \pm 16	141.8 \pm 8.6	146.3 \pm 8.0	73 \pm 13	77 \pm 10	208 \pm 19	202 \pm 20	-	-	103 \pm 9
Cd ^b	4.88 \pm 0.19	4.74 \pm 0.29	6.568 \pm 0.073	6.743 \pm 0.290	0.11 \pm 0.02	0.12 \pm 0.01	-	-	0.106 \pm 0.011	0.11 \pm 0.02	103 \pm 11
Cr ^b	48.2 \pm 1.6	50.1 \pm 2.0	20.40 \pm 0.24	20.10 \pm 1.97	0.78 \pm 0.20	0.82 \pm 0.14	48 \pm 3	46 \pm 4	-	-	101 \pm 11
Cu ^b	1936 \pm 75	1935 \pm 17	22.76 \pm 0.31	23.10 \pm 0.50	15.4 \pm 1.5	16.0 \pm 0.8	-	-	-	-	102 \pm 3
Fe ^b	186 \pm 11	180 \pm 12	98.1 \pm 1.4	97.7 \pm 5.2	287 \pm 7	283 \pm 24	236 \pm 6	240 \pm 8	5.11 \pm 0.26	5.13 \pm 0.27	99 \pm 6
Mn ^b	48.3 \pm 1.6	47.3 \pm 1.0	38.97 \pm 0.45	38.37 \pm 1.23	-	-	48 \pm 2	50 \pm 3	107 \pm 5	110 \pm 6	101 \pm 5
Ni ^b	19.27 \pm 0.68	18.73 \pm 0.61	62.41 \pm 0.69	61.18 \pm 1.64	2.6 \pm 0.6	2.5 \pm 0.2	48 \pm 4	50 \pm 5	25.3 \pm 1.1	25.6 \pm 1.6	99 \pm 7
Pb ^b	24.51 \pm 0.52	24.03 \pm 0.76	19.63 \pm 0.21	19.43 \pm 0.87	5.2 \pm 0.3	5.1 \pm 0.3	95 \pm 3	93 \pm 4	7.1 \pm 0.6	7.3 \pm 0.7	99 \pm 6
Zn ^b	597 \pm 19	605 \pm 10	78.5 \pm 2.2	76.6 \pm 1.2	59.7 \pm 2.5	57.5 \pm 4.8	542 \pm 16	550 \pm 20	-	-	99 \pm 5

Note: ^a HG- $\mu\text{CCP-OES}$ method; ^b GFAAS method; ^c Pooled recovery for 95% confidence level; ^d mean \pm U for 95% confidence level; ^e mean \pm CI (confidence interval) for n = 3 parallel measurements and 95% confidence level

The observed potential of ZoBell's solution was +189 mV, which meant a departure of +6 mV from the theoretical E_h , lower than the permissible error of the method (± 10 mV). The relative error for n=3 successive measurements of E_h was in the range 0.1 – 1.1%.

2.6. Statistics

In this study, an advanced chemometric method, namely FHCC (Sârbu et al., 1996, 2001), which offers an excellent possibility to associate each fuzzy partition of samples to a fuzzy set of characteristics (specific markers) was successfully applied for characterization and classification of groundwater based on trace metal content and arsenic species. FHCC, an unsupervised multidimensional algorithm more advanced than PCA and CA, was developed for the first time by Pop and Sârbu (1997). The algorithm was further used for modeling of contaminants around an abandoned uranium mine (Pourjabbar et al., 2014) and within a study on the fate of Hg and other contaminants in soil around a former chlor-alkali plant (Frentiu et al., 2015).

In classical cluster analysis each object must be assigned to exactly one cluster. This is a source of ambiguity and error in cases of outliers or overlapping clusters and affords a loss of information. This kind of vagueness and uncertainty can, however, be taken into account by using the theory of fuzzy sets introduced by Zadeh (1965). A central concept of fuzzy set theory is that it is permissible for an element to belong partly to a partition (class). Most fuzzy clustering algorithms are objective function based: they determine an optimal classification by minimizing an objective function. In objective function based clustering usually each cluster is represented by a cluster prototype. This prototype consists of a cluster centre

whose name already indicates its meaning, and gives some additional information about the size and the shape of the cluster. The degrees of membership to which a given data point belongs to the different clusters are computed from the distances of the data point to the cluster centers. The closer a data point lies to the centre of a cluster, the higher is its degree of membership to this cluster. Hence the problem to divide a dataset into (c) clusters can be stated as the task to minimize the distances of the data points to the cluster centres, since, it is desirable to maximize the degrees of membership (Pop et al., 1996; Ross, 2004).

3. Results and discussion

3.1. Groundwater characteristics and mineralogical composition

Table 3 presents the concentrations of As species and metals in groundwater samples and the corresponding Threshold Values for total arsenic, Cd, Cr, Cu, Ni, Pb, Zn in GW-ROBA03 and GW-ROBA18 according to Order, (2014). In the case of Al, Fe, Mn and pH for which TVs are not yet available, the values were compared to maximum admitted concentration (MAC) in drinking water in Romania set in Law, (2002). The TV value for total As (Order, 2014) was established only for GW-ROBA03 considered much more vulnerable to anthropogenic contamination via agricultural practices. The results of the analysis provided in Table 3 suggest that the two groundwater bodies are under the oxidative influence of aquifer (E_h between 369.0 – 409.1 mV, mean 384.0 mV) and alkaline pH (8.31 – 8.49, mean 8.40). These conditions explain the low concentrations of metals in groundwater compared to TVs or MAC. MAC for Mn, which could be present as oxyanion species, with high water mobility, was exceeded in 5 out of 18 water

samples. Total As was in the range 3.6 – 77.3 µg/L (mean 29.8 µg/L) and TV/MAC (10 µg/L) was exceeded in 15 out of 18 cases. Related to speciation analysis, the concentrations of As(III) and As(V) were within 0.5-18.8 µg/L and 2.5-63.2 µg/L, and TV/MAC was exceeded in 12 and 9 samples respectively. Obviously As(V) was the dominant species representing 57±20% of total in samples with more than 10 µg/L As and 73±18% in those with concentration below TV/MAC.

Consequently, this could represent a risk exposure for population when using groundwater as drinking water supply. The dominance of As(V) is in agreement with oxidative conditions in aquifer and it is presumed that pH and E_h influence processes responsible for the occurrence of As species and trace metals. The low metal concentrations in groundwater were in agreement with the relatively low values found in sand and clay samples (Table 4).

Table 3. Hydrogeochemical characteristics (µg/L), electrochemical parameters and summary statistics for the groundwater samples (n = 3 parallel measurements)

Sample	As(III)	As(V)	As	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	E _h (mV)	pH
GW-ROBA03														
1	9.8	8.2	18.0	38	0.41	0.83	11.6	57	5.3	9.48	0.57	38.0	402.2	8.39
2	16.5	4.4	20.9	12	0.22	0.28	1.25	41	2.1	4.09	0.22	15.2	409.1	8.45
5	13.7	38.3	52.0	56	0.22	0.21	1.19	23	2.7	5.36	0.30	15.4	395.1	8.45
17	0.5	3.4	3.9	6.8	0.18	0.16	0.91	18	1.8	3.66	0.23	31.8	374.2	8.42
GW-ROBA18														
3	13.5	37.1	50.6	6.1	0.30	0.91	3.54	48	22	9.75	0.12	40.1	374.5	8.35
4	12.9	11.6	24.5	1.7	0.21	0.11	0.78	22	2.1	4.61	0.21	11.3	380.1	8.41
6	14.1	32.6	46.7	3.1	0.23	0.14	1.51	19	370	5.14	0.33	11.8	388.8	8.44
7	13.8	30.4	44.2	7.9	0.36	0.11	0.71	20	274	7.7	0.11	6.51	385.4	8.49
8	14.7	51.6	66.3	1.2	0.43	1.61	7.09	19	23	6.74	0.19	37.9	382.1	8.38
9	11.4	6.1	17.5	5.8	0.23	0.10	0.65	33	2.5	4.02	0.24	47.9	378.9	8.46
10	11.4	28.6	40.0	5.5	0.21	0.11	0.91	25	69	2.03	0.12	46.1	379.6	8.41
11	18.8	20.4	39.2	74	0.25	8.97	1.65	132	5.8	8.03	0.11	20.2	406.6	8.33
12	9.0	4.9	13.9	12	0.17	0.24	1.26	16	2.1	2.26	0.17	11.5	380.4	8.31
13	14.1	63.2	77.3	1.4	0.23	0.12	1.08	21	700	3.5	0.54	39.7	381.1	8.48
14	1.2	7.5	8.7	1.2	0.20	0.12	0.76	18	32	2.57	0.38	37.8	369.0	8.37
15	3.7	2.5	6.2	1.6	0.21	9.84	0.47	24	5.1	6.18	0.23	9.95	378.9	8.46
16	0.6	3.0	3.6	1.4	0.24	0.18	1.04	18	1.1	3.07	0.35	20.2	372.1	8.40
18	0.7	2.9	3.6	11	0.19	1.09	1.12	79	35	5.94	0.29	28.7	374.3	8.43
Min	0.5	2.5	3.6	1.2	0.17	0.1	0.47	16	1.1	2.03	0.11	6.51	369.0	8.31
Max	18.8	63.2	77.3	74	0.43	9.84	11.6	132	700	9.75	0.57	47.9	409.1	8.49
Mean	10.0	19.8	29.8	13.7	0.2	1.4	2.1	35.2	86.4	5.2	0.3	26.1	384.0	8.40
Median	12.2	9.9	22.7	6.0	0.2	0.2	1.1	22.5	5.6	4.9	0.2	24.5	380.3	8.40
Std	6.1	19.9	23.8	23.0	0.1	3.2	3.3	34.1	213	2.5	0.1	14.1	12.4	0.10
TV Order 621/2014 ^a			10 ^b		5	50	100			20	10	5000		
MAC Law 458/2002 ^c			10	200				200	50					6.5-8.5

^a Threshold values for groundwater in Banat area, Romania; ^b Value refers only to GW-ROBA03; for GW-ROBA18 no TV has been set so that MAC for drinking water was taken into account; ^c Maximum admitted concentration in drinking water in Romania

Table 4. Content of arsenic and metals obtained by XRF in sand and clay samples

	M.U.	Sand (n=20)				Clay (n=10)			
		Min	Max	Mean	sd	Min	Max	Mean	sd
As	mg/kg	3.50	40.0	11.1	10.5	5.30	86.0	21.8	25.7
Cd	mg/kg	0.09	0.50	0.28	0.22	0.08	0.31	0.20	0.13
Cr	mg/kg	20.0	91.0	47.1	22.1	32.5	50.2	40.9	6.2
Co	mg/kg	18.0	133.0	80.2	30.2	34.0	86.0	56.7	16.5
Cu	mg/kg	32.0	181	96.7	53.6	33.0	151	53.2	35.6
Ni	mg/kg	11.0	56.0	27.8	14.8	1.20	1.70	1.43	0.22
Mn	mg/kg	149	1254	668	356	341	791	560	148
Pb	mg/kg	18.0	126	65.0	28.2	18.2	97.0	32.3	23.6
Zn	mg/kg	70.0	503	254	120	48.0	188	80.5	41.4
Fe ₂ O ₃	%	3.10	4.93	4.25	0.59	1.45	7.37	5.49	1.19
Al ₂ O ₃	%	0.95	4.52	2.49	1.33	0.62	4.63	2.85	0.60

The mineralogical analysis indicated the presence of quartz (SiO₂), Zeolite Beta, Sodium Aluminium Silicate - Na₂O-Al₂O₃-SiO₂, Muscovite chromian - K(Al,Cr)₂(Si₃,Al)O₁₀(OH,F)₂ as major minerals, Chlorite-serpentine - (Mg,Al)₆(Si,Al)₄O₁₀(OH)₈, Muscovite calcian - (K,Ca,Na)(Al,Mg,Fe)₂(Si,Al)₄O₁₀(OH)₂, Montmorillonite - Ca,Na)_{0.3}Al₂(Si,Al)₄O₁₀(OH)₂ × H₂O, Nontronite - (Na,Ca)_{0.3}Fe₂(Si,Al)₄O₁₀(OH)₂ × H₂O, Kaolinite - Al₂Si₂O₅(OH)₄ as minor minerals, Albite - NaAlSi₃O₈, Muscovite - (KF)₂(Al₂O₃)₃(SiO₂)₆(H₂O), feldspar - KAlSi₃O₈, Chlorite-clinocllore - (Mg,Fe)₅(Al,Si)₅O₁₀(OH)₈, Anorthite - CaAl₂ Si₂O₈, illite - (K,H₃₀)Al₂(Si₃,Al)O₁₀(OH)₂ × H₂O as traces.

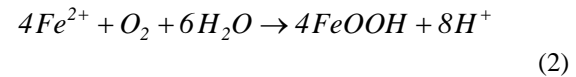
3.2. Groundwater classification and characterization using FHCC

Table 5 provides the hierarchical classification of groundwater samples and the characteristic parameters associated to each level.

The membership degree values and hierarchical classification reveal pH and redox potential as decisive factors for grouping samples and related characteristics. Thus the first hierarchical level A₁ encompasses samples with features sensitive to pH, namely Pb, Cr, Zn and Fe content. The second level A₂ contains samples with characteristics sensitive to redox potential, namely Cd, As(III), Ni, As(V), total As, Cu, Al and Mn content. Both groups contain samples with high As concentration. Thus 6 out of 9

samples belonging to the first group A₁ exhibited (µg/L) 9.8 – 16.5 (mean 13.6) As(III), 4.4 – 51.6 (mean 26.3) As(V) and 18.0 – 66.3 (mean 39.9) total As. Grouping of samples in A₁ is due to trace metals rather than As concentration. Desorption of Pb, Cr, Zn and As species from the surface of Fe minerals/oxides is governed by groundwater pH.

The concentration of Fe is controlled through the oxidative precipitation occurring in aquifer (E_h > + 2 mV) (Sappa et al., 2014) according to (Eq. 2):



Reaction 2 occurs when the electron activity (pe) calculated according to the (Eq. 3) (Sappa et al., 2014) fall in the range 5-7:

$$pe = 96.490 \times E_h / 2.303 \times RT \tag{3}$$

where: E_h is the redox potential (mV) and T is the water temperature (K).

In the case of our groundwater samples the pe values were in the range 6.33–6.91 satisfying the conditions for (Eq. 2). The phenomenon was also reported by (Sappa et al., 2014) who found similar values for pH and E_h in the groundwater system in Central Italy. The next levels of hierarchy (2 and 3) group groundwater samples with the highest concentration of As species. In some of them the feature relates to Cr, Zn and Fe concentration, in others to Pb.

Table 5. The hard fuzzy partition of groundwater samples and their characteristics ranked in descending order of their membership degree

Partition level	Fuzzy divisive partition	Samples		Associated characteristics	
		Location	Membership degree range	Characteristics	Membership degree range
0	A	1, ..., 18		Cu, Zn, Ni, Cd, Cr, Pb, Mn, Fe, Al, As(III), As(V), A _{Stotal} , E _h , pH	
1	A ₁	3, 6, 15, 17, 5, 1, 8, 4, 2	0.974 – 0.512	Pb, Cr, pH, Zn, Fe	0.999 – 0.849
	A ₂	18, 11, 10, 12, 16, 7, 14, 13, 9	0.907 – 0.811	Cd, As(III), E _h , Ni, As(V), A _{Stotal} , Cu	0.996 – 0.586
2	A ₁₁	17, 15, 6	0.872 – 0.715	Cr, Zn, Fe	0.999 – 0.831
	A ₁₂	3, 5, 4, 8, 1, 2	0.954 – 0.458	pH, Pb	0.975 – 0.972
3	A ₁₁₁	15	0.814	Cr, Fe	0.996 – 0.825
	A ₁₁₂	17, 6	0.871 – 0.712	Zn	0.932
4	A ₁₂₁	3, 5, 4, 2	0.942 – 0.447	pH	0.975
	A ₁₂₂	8, 1	0.658 – 0.456	Pb	0.971
5	A ₂₁	7, 13, 16, 9	0.897 – 0.806	Cd, Ni, As(V), E _h , Cu, Al, A _{Stotal} , Mn	0.985 – 0.544
	A ₂₂	18, 11, 10, 12, 14	0.955 – 0.575	As(III)	0.983
6	A ₂₁₁	13	0.856	Ni	0.978
	A ₂₁₂	7, 16, 9	0.892 – 0.764	As(V), Cd, Cu, Al, E _h , A _{Stotal} , Mn	0.864 – 0.528
7	A ₂₁₂₁	7, 9	0.865 – 0.724	Cd, Cu, Al, E _h , Mn	0.759 – 0.494
	A ₂₁₂₂	16	0.842	As(V), A _{Stotal}	0.851 – 0.331
8	A ₂₁₂₁₁	9	0.724	E _h , Mn	0.583 – 0.397
	A ₂₁₂₁₂	7	0.865	Cd, Cu, Al	0.748 – 0.536

The second class A₂ (9 samples) contains 6 samples with total As above the limit of 10 µg/L. In these samples concentrations (µg/L) of As species were 9.0 – 18.8 (mean 12.5) As(III), 4.9 – 63.2 (mean 22.4) As(V) and 13.9 – 77.3 (mean 35.2) total As. Associated characteristics for these samples were found to be As species as well as Cd, Ni and Cu content. The natural origin of arsenic and trace metals relates to desorption from Al minerals and Mn hydroxides, which is controlled E_h . The A₂ group is further divided over the partition levels (5-8). It is noteworthy the segregation of a subgroup of samples (A₂₂) based only on As(III) concentration and of a hierarchically lower group (A₂₁₂) recognized through As(V) and total As, as well as Cd, Ni, Cu, Al, Mn and E_h .

4. Conclusions

It was highlighted the helpfulness of the FHCC approach for a fast modeling of arsenic chemistry and trace metals of natural origin in groundwater in the Banat Plain-southwestern Romania.

The methodology made possible the recognition of natural occurring sources of arsenic species in groundwater as well as trace metals associated to a particular group. In the same time, single sample with distinct characteristics could be segregated.

The redox potential and pH value in aquifer were found to be responsible for the natural release of inorganic arsenic species and trace metals by desorption from Fe and Al minerals and Mn oxyhydroxides. Although the contents of trace metals do not exceed TVs or MAC, the FHCC approach highlighted them as distinguished characteristics associated to variability and grouping of groundwater samples.

Acknowledgements

This work was supported by a grant of Ministry of Research and Innovation, Romania, project number 33PFE/2018, within PNCDI III.

This work was also supported by a grant of Ministry of Research and Innovation, Romania, project PROINSTITUTIO - Contract no.19PFE/17.10.2018

References

- Anawar H.M., Akai J., Komaki K., Terao H., Yoshioka T., Ishizuka T., Safiullah S., Kato K., (2003), Geochemical occurrence of arsenic in groundwater of Bangladesh: sources and mobilization processes, *Journal of Geochemical Exploration*, **77**, 109-131.
- Badila A.S., (2017), Impacts of production and storing of organic manure over the quality of groundwater in the Basin of Geru River from Galati County, *Environmental Engineering and Management Journal*, **16**, 653-668.
- Biswas A., Neidhardt H., Kundu A.K., Halder D., Chatterjee D., Berner Z., Jacks G., Bhattacharya P., (2014), Spatial, vertical and temporal variation of arsenic in shallow aquifers of the Bengal basin: controlling, geochemical processes, *Chemical Geology*, **387**, 157-169.
- Bloom M.S., Fitzgerald E.F., Kim K., Neamtii I., Gurzau E.S., (2010), Spontaneous pregnancy loss in humans and exposure to arsenic in drinking water, *International Journal of Hygiene Environmental Health*, **213**, 401-413.
- Bloom M.S., Surdu S., Neamtii I., Gurzau E.S., (2014), Maternal arsenic exposure and birth outcomes: a comprehensive review of the epidemiologic literature focused on drinking water, *International Journal of Hygiene Environmental Health*, **217**, 709-719.
- Butaciu S., Senila M., Sarbu C., Ponta M., Tanaselia C., Cadar O., Roman M., Radu E., Sima M., Frentiu T., (2017), Chemical modeling of groundwater in the Banat Plain, southwestern Romania, with elevated As content and co-occurring species by combining diagrams and unsupervised multivariate statistical approaches, *Chemosphere*, **172**, 127-137.
- Chakraborti D., Rahman M.M., Ahamed S., Dutta R.N., Pati S., Mukherjee S.C., (2016), Arsenic groundwater contamination and its health effects in Patna district (capital of Bihar) in the middle Ganga plain, India, *Chemosphere*, **152**, 520-529.
- Chakraborti D., Rahman M.M., Das B., Chatterjee A., Das D., Nayar B., Pal A., Chowdhury U.K., Ahmed S., Biswas B.K., Sengupta M.K., Hossain M.A., Samanta G., Roy M.M., Dutta R.N., Saha K.C., Mukherjee S.C., Pati S., Kar P.B., Mukherjee A., Kumar M., (2017), Groundwater arsenic contamination and its health effects in India, *Hydrogeology Journal*, **25**, 1165-1181.
- Cordos E.A., Frentiu T., Ponta M., Abraham B., Marginean I., (2006), Optimization of analytical parameters in inorganic arsenic (III and V) speciation by hydride generation using L-CYSTEINE as prereducing agent in diluted HCl medium, *Chemical Speciation and Bioavailability*, **18**, 1-9.
- Cuoco E., Darrah T.H., Buono G., Verrengia G., De Francesco S., Eymold W.K., Tedesco D., (2015), Inorganic contaminants from diffuse pollution in shallow groundwater of the Campanian Plain (Southern Italy). Implications for geochemical survey, *Environmental Monitoring Assessment*, **187**, 1-17.
- Dimkic M., Djuric D., Josipovic J., Jevtic G., (2010), *Solutions for groundwater management in areas affected by high arsenic content: Vojvodina case study*, Intern. Conf. Transboundary Aquifers: Challenges and New Directions (ISARM), Paris, 65.
- Eaton A.D., Clesceri L.S., Greenberg A.E., (2005), *Standard Methods for the Examination of Water and Wastewater, Method 2580B Oxidation-Reduction Potential Measurement in Clean Water*, 19th Edition, American Public Health Association, Washington DC, 2-74-2-76.
- EC Directive, (2006), Directive 2006/118/EC of the European Parliament and of the Council of 12 December on the protection of groundwater against pollution and deterioration, *Official Journal of European Communities*, **L372/19**, 12.12.2006, Brussels.
- Enciu P., Balteanu D., Dumitrica C., (2014), Contributions to the knowledge of quaternary formations in the southwest Romanian Plain, *Quaternary International*, **357**, 1-12.
- Frentiu T., Butaciu S., Ponta M., Darvasi E., Senila M., Petreus D., Frentiu M., (2014), Simultaneous determination of As and Sb in soil using hydride generation capacitively coupled plasma microtorch optical emission spectrometry – comparison with

- inductively coupled plasma optical emission spectrometry, *Journal of Analytical Atomic Spectrometry*, **29**, 1880-1888.
- Frentiu T., Ponta M., Levei E., Gheorghiu E., Benea M., Cordos E., (2008), Preliminary study on heavy metals contamination of soil using solid phase speciation and the influence on groundwater in Bozanta – Baia Mare Area, Romania, *Chemical Speciation and Bioavailability*, **20**, 111-121.
- Frentiu T., Ponta M., Sarbu C., (2015), Prediction of the fate of Hg and other contaminants in soil around a former chlor-alkali plant using Fuzzy Hierarchical Cross-Clustering, *Chemosphere*, **138**, 96-103.
- Frentiu T., Vlad S.N., Ponta M., Baciu C., Kasler I., Cordos E., (2007), Profile distribution of As(III) and As(V) species in soil and groundwater in Bozanta Area, *Chemical Papers*, **61**, 186-193.
- Ghrefat H., El Waheidi M., Batayneh A., Nazzal Y., Zumlot T., (2016), Pollution assessment of arsenic and other selected elements in the groundwater and soil of the Gulf of Aqaba, Saudi Arabia, *Environmental Earth Sciences*, **75**, article number 229.
- Gurzau E.S., Gurzau A.E., (2001), *Arsenic in Drinking Water from Groundwater in Transylvania, Romania: An Overview*, In: *Arsenic Exposure and Health Effects IV*, Chappell W.R., Abernathy C.O., Calderon R.L., (Eds.), Elsevier, Amsterdam, 181-184.
- Jang Y.C., Shin Y., Kim H., Lee J.H., (2017), Human health risk assessment of arsenic in air, soil and water in an industrial complex in Korea, *Environmental Engineering and Management Journal*, **16**, 293-301.
- Janos P., Eletskaia A., Pilarova V., (2016), Comparison of some non-conventional sorbents for the removal of arsenic from waters, *Environmental Engineering and Management Journal*, **15**, 1721-1728.
- Kelepertzis E., (2014), Investigating the sources and potential health risks of environmental contaminants in the soil and drinking waters from the rural clusters in Thiva area (Greece), *Ecotoxicology and Environmental Safety*, **100**, 258-265.
- Kim K.H., Yun S.T., Park S.S., Joo Y., Kim T.S., (2014), Model-based clustering of hydrochemical data to demarcate natural versus human impacts on bedrock groundwater quality in rural areas, South Korea, *Journal of Hydrology*, **519**, 626-636.
- Kobyas M., Sik E., Demirbas E., Goren A.Y., Oncel M.S., (2018), Optimization of some cations for removal of arsenic from groundwater by electrocoagulation process, *Environmental Engineering and Management Journal*, **17**, 1079-1093.
- Kuroda K., Hayashi T., Funabiki A., Do A.T., Canh V.D., Nga T.T.V., Takizawa S., (2017), Holocene estuarine sediments as a source of arsenic in Pleistocene groundwater in suburbs of Hanoi, Vietnam, *Hydrogeology Journal*, **25**, 1137-1152.
- Law, (2002), Law no. 458/2002 of the Romanian Parliament on drinking water quality, published in Romanian Official Monitor, part. I, no. 552, from 29th of July, 2002, republished in *Romanian Official Monitor*, Part. I, no. 875, from 12th of December, 2011.
- Minea I., Croitoru A.E., (2017), Groundwater response to changes in precipitations in north-eastern Romania, *Environmental Engineering and Management Journal*, **16**, 643-651.
- Modoi O.C., Roba C., Torok Z., Ozunu A., (2014), Environmental risks to heavy metal pollution of water resulted from mining wastes in NW Romania, *Environmental Engineering and Management Journal*, **13**, 2325-2336.
- Muntean E., Mihaiescu T., (2016), Groundwater quality studies in two Transylvanian rural communities using parallel ion chromatography, *Environmental Engineering and Management Journal*, **15**, 2703-2708.
- Mutihac V., (1990), *Geological Structure of Romania* (in Romanian), Technical Press, Bucharest, Romania.
- Neamtii I., Bloom M.S., Gati G., Goessler W., Surdu S., Pop C., Braeuer S., Fitzgerald E.F., Baciu C., Lupsa I.R., Anastasiu D., Gurzau E.S., (2015), Pregnant women in Timis County, Romania are exposed primarily to low-level (<10µg/L) arsenic through residential drinking water consumption, *International Journal of Hygiene and Environmental Health*, **218**, 371-379.
- Nistor M.M., Dezsi S., Cheval S., (2015), Vulnerability of groundwater climate change and land cover: a new spatial assessment method applied on Belis District (Western Carpathians, Romania), *Environmental Engineering and Management Journal*, **14**, 2959-2971.
- Nshimiyimana F.X., Faciu M.E., El Blidi S., El Abidi A., Soulaymani A., Fekhaoui M., Lazar G., (2016), Seasonal influence and risk assessment of heavy metals contamination in groundwater, Arjaat village, Morocco, *Environmental Engineering and Management Journal*, **15**, 579-587.
- Order, (2014), Order of the Minister of the Environment no. 621/2014 on the approval of threshold values for groundwater in Romania, published in *Romanian Official Monitor*, Part. I, no. 535, from 18th of July, 2014.
- Panagiotaras D., Panagopoulos G., Popoulis D., Avramidis P., (2012), *Arsenic Geochemistry in Groundwater System*, In: *Geochemistry - Earth's System Processes*, Panagiotaras D., (Ed.), InTech Europe, University Campus STeP Ri, Rijeka, Croatia, 27-38.
- Park J.D., Choi S.J., Choi B.S., Lee C.R., Kim H., Kim Y.D., Park K.S., Lee Y.J., Kang S., Lim K.M., (2016), Arsenic levels in the groundwater of Korea and the urinary excretion among contaminated area, *Journal of Exposure and Science Environmental Epidemiology*, **26**, 458 - 463.
- Pascu M.R., (1983), *Groundwaters from Romania* (in Romanian), Technical Press, Bucharest, Romania.
- Pop A., Baciu A., Wanko G., Bodor K., Vlaicu I., Manea F., (2017), Assessment of electrocoagulation process. Application in arsenic removal from drinking water, *Environmental Engineering and Management Journal*, **16**, 821-828.
- Pop H., Sârbu C., (1997), The fuzzy hierarchical cross-classification algorithm, improvements and comparative study, *Journal of Chemical Information and Computer Sciences*, **37**, 510-516.
- Pop H., Sârbu C., Horovitz O., Dumitrescu D., (1996), A fuzzy classification of the chemical elements, *Journal of Chemical Information and Computer Sciences*, **36**, 465-482.
- Pourjabbar A., Sârbu C., Kostarelos K., Einax J.W., Buchel C., (2014), Fuzzy hierarchical cross-clustering of data from abandoned mine site contaminated with heavy metals, *Computers and Geosciences*, **72**, 122-133.
- Radu E., Balaet R., Vliegienthart E., Schipper P., (2010), Derivation of threshold values for groundwater in Romania, in order to distinguish point & diffuse pollution from natural background levels, *Environmental Engineering Research*, **15**, 085-091.
- Radu E., Radu C., (2011), *Lithological and Hydrogeological Considerations on the Phreatic Aquifer From Bega – Timis Interfluvium, Banat Plain, Romania, with Special*

- Regard to the Unsaturated Zone (CC Waters Project)*, Proc. of IWA Specialist Groundwater Conference, Belgrade, Serbia.
- Rahman M.M., Dong Z.M., Naidu R., (2015), Concentrations of arsenic and other elements in groundwater of Bangladesh and West Bengal, India: potential cancer risk, *Chemosphere*, **139**, 54-64.
- Rahman M.T.U., Siddiqi U.R., Kure S., Mano A., Udo K., Ishibashi Y., (2016), Mobilization of high arsenic in the shallow groundwater of Kalaroa, South-Western Bangladesh, *Exposure and Health*, **8**, 159-75.
- Rajakovic-Ognjanovic V.N., Jovanovic B.M., Zivojinovic D.Z., Rajakovic L.V., (2014), Challenging analytical task: analysis and monitoring of arsenic species in water, *Environmental Engineering and Management Journal*, **13**, 2275-2282.
- Romanian National Institute of Statistics, Statistical Yearbook, (2012), On line at: <http://www.insse.ro/cms/en/content/statistical-yearbook-2012>
- Ross T.J., (2004), *Fuzzy Logic with Engineering Applications*, Second Edition, John Wiley & Sons, Ltd., Chichester.
- Rowland H.A.L., Omoregie E.O., Millot R., Jimenez C., Mertens J., Baciuc C., Hug S.J., Berg M., (2011), Geochemistry and arsenic behavior in groundwater resources of the Pannonian Basin (Hungary and Romania), *Applied Geochemistry*, **26**, 1-17.
- Rusu L., Suceveanu M., Suteu D., Favier L., Harja M., (2017), Assessment of groundwater and surface water contamination by landfill leachate: a case study in Neamt County, Romania, *Environmental Engineering and Management Journal*, **16**, 633-641.
- Sappa G., Ergul S., Ferranti F., (2014), Geochemical modeling and multivariate statistical evaluation of trace elements in arsenic contaminated groundwater systems of Viterbo area, (Central Italy), *SpringerPlus*, **3**, 237, On line at: <http://www.springerplus.com/content/3/1/237>.
- Sârbu C., Horovitz O., Pop H., (1996), A fuzzy cross-classification of chemical elements, based on their physical, chemical and structural features, *Journal of Chemical Information and Computer Sciences*, **36**, 1098-1108.
- Sârbu C., Zwanziger W.H., (2001), Fuzzy classification and comparison of some Romanian and German mineral waters, *Analytical Letters*, **34**, 1541-1553.
- Sarkar A., Paul B., (2016), The global menace of arsenic and its conventional remediation - A critical review, *Chemosphere*, **158**, 37-49.
- Spanos T., Ene A., Simeonova P., (2015), Chemometric expertise of the quality of groundwater sources for domestic use, *Journal of Environmental Science and Health, Part A*, **50**, 1099-1107.
- Su C.L., Zhu Y.P., Abbas Z., Huq M.E., (2016), Sources and controls for elevated arsenic concentrations in groundwater of Datong Basin, Northern China, *Environmental Earth Sciences*, **75**, article number 570.
- Surdu S., Bloom M.S., Neamtiu I.A., Pop C., Anastasiu D., Fitzgerald E.F., Gurzau E.S., (2015), Consumption of arsenic-contaminated drinking water and anemia among pregnant and non-pregnant women in northwestern Romania, *Environmental Research*, **140**, 657-660.
- Tirkey P., Bhattacharya T., Chakraborty S., (2016), Arsenic and other metals in the groundwater samples of Ranchi city, Jharkhand, India, *Current Science*, **110**, 76-80.
- Vasilache V., Filote C., Cretu M.A., Sandu I., Coisin V., Vasilache T., Maxim C., (2012), Monitoring of groundwater quality in some vulnerable areas in Botosani County for nitrates and nitrites based pollution, *Environmental Engineering and Management Journal*, **11**, 471-479.
- Verma S., Mukherjee A., Mahanta C., Choudhury R., Mitra K., (2016), Influence of geology on groundwater-sediment interactions in arsenic enriched tectonomorphic aquifers of the Himalayan Brahmaputra river basin, *Journal of Hydrology*, **540**, 176-195.
- Zadeh L.A., (1965), Fuzzy sets, *Information and Control*, **8**, 338-353.