

# Multielement determination using inductively coupled plasma optical emission spectrometry for metal characterization of water from artesian wells in Semberija region: Multivariate analysis of data

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## Abstract

The concentrations of fifteen metals (Mg, Na, Ca, K, Se, Zn, Mn, Fe, Pb, Cr, Cu, Cd, Sb, Ni and Co) were determined in water taken from ten artesian wells (AW) in Semberija in order to obtain a general metal profile of water in this region. The principal components analysis (PCA) was used in this classification. Two factors controlling the metal variability were obtained by using principal component analysis, which accounted for nearly 71.5% of the total variance. Natural (lithogenic) factor is represented by PC1, while anthropogenic factor is represented by PC2. PC1 with high contribution of Mn, Mg, Na, K, Ca, Zn and Se accounting for 41.84% of the total variance, while PC2 exhibits high loading for Cd, Ni, Sb, Cr and Pb (29.66%). Three general areas (clusters) with different metal characteristics were detected. Water from artesian wells in first cluster (AW1–AW6) had much higher metal concentration compared with those in the second (AW7–AW9) and third cluster (AW10). That is as a result of anthropogenic inputs. Also, the analysis of water demonstrated slightly elevated values for Mn (concentrations up to 0.176 mg/L), while concentrations of the other investigated elements are below the values recommended by the World Health Organization (WHO) and the United States Environmental Protection Agency (US EPA).

**Keywords:** metals, artesian wells, ICP-OES, Semberija, principal component analysis.

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Several metal ions such as sodium, potassium, magnesium and calcium are essential to sustain biological life. At least six additional metals, chiefly transition metals, are also essential for optimal growth, development and reproduction, *i.e.*, manganese, iron, cobalt, copper, zinc and molybdenum. Heavy metals in the environment originate from two anthropogenic sources, one is connected with human activity and the other is in charge for the natural circulation of the metals throughout nature. The occurrence of heavy metal ions in water, soils and sediments can result in serious environmental and human health problems [1]. Heavy metals are dangerous because they tend to bioaccumulate. Several metal ions are very toxic even in low concentrations [2], while others are essential in low concentration, but hazardous in higher concentrations. Determination of metals in environment is important in the context of environmental pollution monitoring, intoxication, clinical diagnosis, etc.

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Well water is an important resource for the northern part of Bosnia and Herzegovina (B&H), the Semberija region. The whole region is abundant in ground water, stored in an alluvial aquifer. The aquifer has very good hydraulic characteristics, but is therefore quite sensitive with respect to water quality. There are several potential groundwater contaminants, both anthropogenic and natural. Some contamination sources include agriculture, livestock waste and faulty septic system. During the development of the sewerage system, the care was not taken to protect groundwater [3]. As a result, there are numerous sources of potential groundwater pollution. Mobile pollutants leaching to the groundwater are quickly transported by the considerable groundwater flow [4]. Domestic well water (100 to 300 m deep) supplies residents of this area, especially those who live in villages. But most of these privately owned domestic wells are not controlled by authorized institutions, which would confirm its chemical and microbiological quality. During decades before the war in B&H started (1992), systematic water quality testing and analysis were done. During the war, the monitoring system was destroyed and establishment of a new one needs appropriate human and financial resources. Therefore, the quality of potable water is still unsatisfactory in some parts of the country, especially in the

rural areas where much of the potable water is supplied from domestic wells [5].

The main approaches to ground water quality monitoring were identified as determination of physical, chemical and biological properties of ground water [6]. However, as far we know, there is no data on metal concentration in water from artesian wells. The study will attempt to identify any potential drinking water hazards. Well water quality is important because of possible health hazards that people may face when using well water for domestic purpose. Also, the second purpose of this work is to assess the pollution distribution in the study area, using pattern recognition technique of principal component analysis.

## EXPERIMENTAL

### Study area

Semberija is located between two rivers: Drina on the east and Sava on the north and Majevica mountain. Semberija lies on the part of the Pannonian basin. Many lakes and swamps were left after the regression

of the Pannonian Sea at the end of Miocene. Alluvial deposits of gravel and sand (60–160 m), layers of clay and sands with intercalations of gravel were found in Semberija [3]. It has variable thickness and even disappearing in some zones. Thus, there are some sensitive areas where the groundwater is not protected naturally. The general slope of the aquifer is from west to east and from south to the north. The principal direction of groundwater flow is from the south to the north, towards the Sava River and parallel with the Drina. The Semberija alluvium aquifer is mainly recharged by the Drina River.

Ten sampling stations were selected along the Sava River in the north Semberija, near the mouth of the Drina River. The working area and sampling points are shown in Figure 1.

### Water sampling and analysis

The series of investigation were conducted from February 2011 to January 2012. Artesian well waters were analyzed at depths from 100 to 200 m. Sampling periods occurred once a month, every 18<sup>th</sup> of the

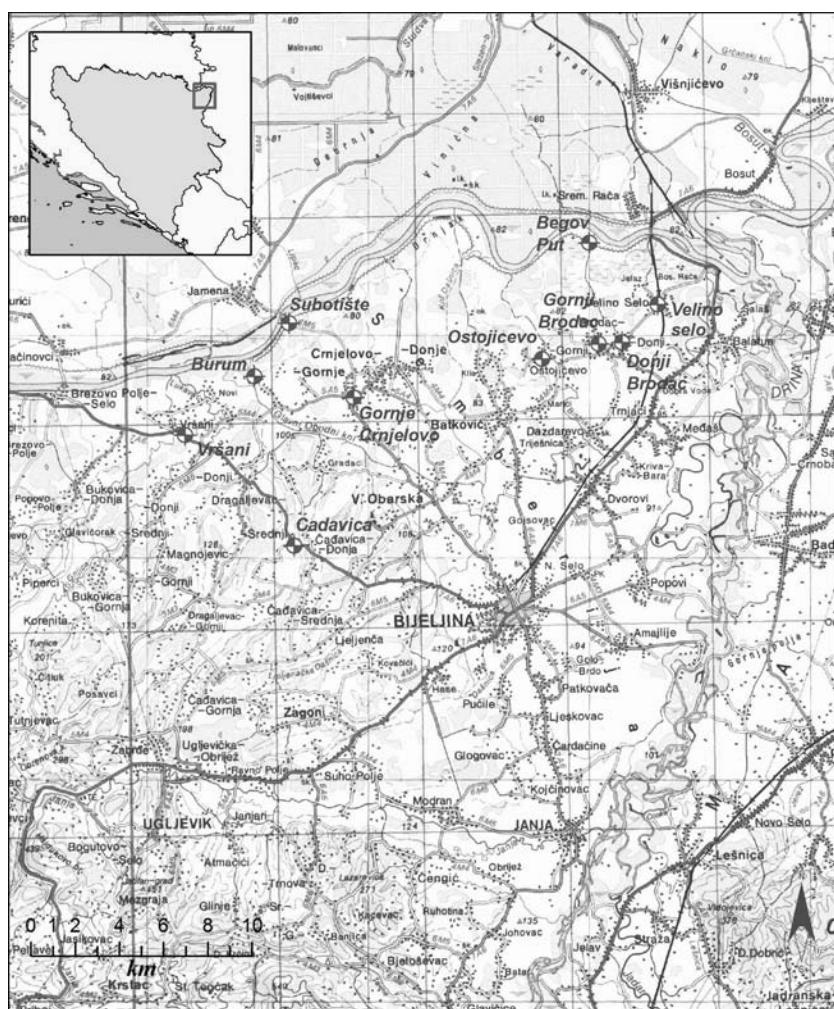


Figure 1. A map of study area and location of artesian wells.

month. Water samples ( $3 \times 2$  L) were collected in clean PVC sample bottles filtered in a Whatman 0.45  $\mu\text{m}$  membrane filter and acidified by the addition of 3 mL of conc.  $\text{HNO}_3$  per liter of water. All samples were stored at 4 °C until analysis. The metal concentration in artesian well water samples were analyzed by iCAP 6000 inductively coupled plasma optical emission spectrometer (ICP-OES) (Thermo Scientific, Cambridge, UK). For ICP-OES measurements emission line was chosen based upon tables of known interferences and baseline shifts. The analytical lines used for each element, as well as the instrumental conditions, are given in Table 1.

*Table 1. Operational parameters for ICP-OES measurements*

Parameter	Value
Flush pump rate	100 rpm
Analysis pump rate	50 rpm
Rf power	1150 W
Nebulizer gas flow	0.7 L/min
Coolant gas flow	12 L/min
Auxiliary gas flow	0.5 L/min
Plasma view	Axial/radial
Metal	Detection wavelength, nm
Ca	422.673
Cd	228.802
Co	238.892
Cr	283.563
Cu	324.754
Fe	259.94
K	766.49
Mg	285.213
Mn	257.61
Na	589.592
Ni	221.647
Pb	220.353
Sb	252.85
Se	196.09
Zn	213.856

### Reagent and standards

Ultra scientific (USA) ICP multi-element standard solution of about  $20.00 \pm 0.10$  mg/L was used. Sample bottles were treated with 5% nitric acid and washed with ultra-pure water 0.05  $\mu\text{S}/\text{cm}$  (MicroMed high purity water system, TKA Wasseraufbereitungs system GmbH).

### Statistical analysis

Data were reported as mean  $\pm$  standard deviation (SD) for triplicate determinations. Principal component analysis (PCA) was performed using a statistical package running on a computer (Statistica 8.0, StatSoft, Inc.,

Tulsa, OK, USA). A probability of  $p < 0.05$  was considered to be statistically significant [7].

### RESULTS AND DISCUSSION

Fifteen elements were analyzed in water from ten artesian wells during one year. The results, expressed in milligram per liter (mg/L) or microgram per liter ( $\mu\text{g}/\text{L}$ ) (Table 2), were obtained from triplicate measurements and rounded according to their standard deviation (SD).

According to World Health Organization [8], Ca, Na, K, Mg, Fe, Zn, Cu, Cr, Co and Se among tested elements are essential for human health. A second group of elements that have some beneficial health effects include Mn and Ni. The third group is composed of the potentially toxic elements Pb, Cd, Hg, As, Al, Li and Sn.

Based on mean values (Table 2), the metals follow the decreasing concentration order: Na > Ca > Mg > K > Fe > Mn > Zn > Cu > Cr > Co > Ni > Sb > Pb > Cd > Se. Na, Ca, Mg and K, those are the elements with major content in all samples with average concentration of 169; 17.29; 5.44; 2.059 (AW1), 162; 16.67; 4.746; 1.112 (AW2), 164; 20.44; 5.38; 1.607 (AW3), 133; 14.05; 4.44; 0.985 (AW4), 153; 19.25; 4.84; 1.160 (AW5), 82.3; 24.48; 15.81; 1.31 (AW6), 103.6; 14.23; 10.81; 1.209 (AW7), 107.5; 19.33; 14.23; 1.467 (AW8), 52.6; 45.6; 21; 1.462 (AW9) and 63.1 mg/L; 48.5; 20; 1.597 mg/L (AW10), respectively. Sodium is widely distributed in drinking water. It has been detected in almost all evaluated surface and groundwater systems. The taste threshold concentration of Na in water depends on the associated anion and the temperature of the solution. At room temperature, the average taste threshold for Na is about 200 mg/L [9]. World Health Organization (WHO) [9] does not provide health-based guideline for the Na content in drinking water and the limit that has been set by the United States Environmental Protection Agency (US EPA) [10] is 20 mg/L. Taking into account the guidelines, concentrations of Na in all tested samples are below the recommended value. K occurs widely in the environment and is an essential element in humans [8]. Although K may cause some health effects in susceptible individuals, K intake from drinking-water is well below the level at which adverse health effects may occur. The origin of Ca and Mg in the water is related to their high prevalence in nature. WHO [9] and US EPA [10] guideline do not make recommendations regarding minimum concentrations of essential elements, including Ca and Mg, because of the uncertainties surrounding mineral nutrition from drinking-water. The increased presence of soluble salts of these two elements in water (100–300 mg/L) [9] can influence on taste threshold.

**Table 2.** Range and mean $\pm$ SD of metal ions concentration in water from artesian wells

Sampling station	Code	Ca, mg/L	Cd, $\mu$ g/L	Co, $\mu$ g/L	Cr, $\mu$ g/L	Cu, $\mu$ g/L	Fe, mg/L	K, mg/L
Velino selo	AW1	15.73–19.21	0.026–0.768	0.47–3.59	0.513–0.568	0.23–3.36	0.021–0.094	1.637–2.555
		17.29 $\pm$ 0.05	0.089 $\pm$ 0.001	0.82 $\pm$ 0.04	0.709 $\pm$ 0.003	1.37 $\pm$ 0.04	0.041 $\pm$ 0.007	2.059 $\pm$ 0.006
Donji Brodac	AW2	15.18–18.07	0.025–0.068	0.46–4.65	0.512–1.972	0.22–1.27	0.018–0.067	0.873–1.714
		16.67 $\pm$ 0.07	0.082 $\pm$ 0.002	0.96 $\pm$ 0.03	0.684 $\pm$ 0.004	0.65 $\pm$ 0.03	0.029 $\pm$ 0.003	1.112 $\pm$ 0.004
Gornji Brodac	AW3	17.35–22.61	0.024–0.338	0.469–0.56	0.514–0.539	0.32–3.39	0.017–0.080	1.389–2.052
		20.44 $\pm$ 0.08	0.053 $\pm$ 0.001	0.57 $\pm$ 0.01	0.619 $\pm$ 0.002	1.91 $\pm$ 0.04	0.036 $\pm$ 0.002	1.607 $\pm$ 0.007
Begov put	AW4	11.07–15.87	0.023–0.028	0.459–0.492	0.509–0.544	0.29–4.07	0.021–0.125	0.651–1.320
		14.05 $\pm$ 0.04	0.043 $\pm$ 0.002	0.509 $\pm$ 0.008	0.527 $\pm$ 0.003	1.05 $\pm$ 0.04	0.047 $\pm$ 0.003	0.985 $\pm$ 0.002
Ostojićovo	AW5	17.34–23.18	0.022–0.198	0.459–1.122	0.512–0.542	0.29–2.47	0.01–0.001	1.828–1.643
		19.25 $\pm$ 0.05	0.114 $\pm$ 0.002	0.507 $\pm$ 0.004	0.528 $\pm$ 0.003	1.05 $\pm$ 0.04	0.026 $\pm$ 0.003	1.160 $\pm$ 0.003
Gornje Crnjelovo	AW6	20.53–28.07	0.022–0.159	0.462–0.831	0.522–6.831	0.18–3.17	0.014–0.029	1.196–1.654
		24.48 $\pm$ 0.08	0.037 $\pm$ 0.002	0.520 $\pm$ 0.008	1.056 $\pm$ 0.003	2.06 $\pm$ 0.03	0.024 $\pm$ 0.002	1.31 $\pm$ 0.01
Subotićte	AW7	10.95–17.62	0.019–0.028	0.459–2.171	0.514–1.966	0.18–2.69	0.022–0.042	0.807–1.592
		14.23 $\pm$ 0.04	0.025 $\pm$ 0.003	0.747 $\pm$ 0.008	0.724 $\pm$ 0.004	1.25 $\pm$ 0.07	0.028 $\pm$ 0.003	1.209 $\pm$ 0.007
Burum	AW8	15.74–26.13	0.021–0.028	0.466–0.711	0.516–1.600	0.18–4.06	0.023–0.099	0.117–1.883
		19.33 $\pm$ 0.07	0.025 $\pm$ 0.002	0.508 $\pm$ 0.006	0.664 $\pm$ 0.005	1.68 $\pm$ 0.09	0.047 $\pm$ 0.002	1.467 $\pm$ 0.003
Vršani	AW9	38.3–53.5	0.022–0.027	0.456–1.941	0.521–1.724	0.19–2.66	0.022–0.122	0.978–0.843
		45.6 $\pm$ 0.2	0.024 $\pm$ 0.003	0.508 $\pm$ 0.006	0.799 $\pm$ 0.006	1.03 $\pm$ 0.03	0.057 $\pm$ 0.004	1.462 $\pm$ 0.004
Čađavica	AW10	41.24–52.79	0.023–0.027	0.48–1.94	0.509–2.54	0.23–4.99	0.026–0.162	1.038–2.059
		48.5 $\pm$ 0.3	0.025 $\pm$ 0.003	0.71 $\pm$ 0.02	0.687 $\pm$ 0.006	1.62 $\pm$ 0.05	0.051 $\pm$ 0.002	1.597 $\pm$ 0.006

Sampling station	Code	Mg, mg/L	Mn, mg/L	Na, mg/L	Ni, $\mu$ g/L	Pb, $\mu$ g/L	Sb, $\mu$ g/L	Se, $\mu$ g/L	Zn, mg/L
Velino selo	AW1	5.15–5.71	0.007–0.009	144.9–200.5	0.07–7.35	0.025–0.113	0.18–0.39	0.041–0.064	0.007–0.021
		5.44 $\pm$ 0.03	0.008 $\pm$ 0.001	169 $\pm$ 1	1.76 $\pm$ 0.06	0.043 $\pm$ 0.002	0.29 $\pm$ 0.05	0.051 $\pm$ 0.002	0.013 $\pm$ 0.001
Donji Brodac	AW2	4.194–5.120	0.006–0.0098	129.8–181.6	0.05–0.801	0.018–0.052	0.09–0.25	0.023–0.033	0.019–0.03
		4.746 $\pm$ 0.002	0.008 $\pm$ 0.001	162 $\pm$ 1	0.178 $\pm$ 0.009	0.040 $\pm$ 0.001	0.18 $\pm$ 0.01	0.028 $\pm$ 0.001	0.023 $\pm$ 0.001
Gornji Brodac	AW3	4.86–5.98	0.007–0.023	142.3–179.4	0.07–0.97	0.015–0.037	0.23–0.48	0.035–0.053	0.016–0.04
		5.38 $\pm$ 0.02	0.014 $\pm$ 0.001	164 $\pm$ 1	0.24 $\pm$ 0.01	0.025 $\pm$ 0.001	0.37 $\pm$ 0.01	0.041 $\pm$ 0.002	0.031 $\pm$ 0.001
Begov put	AW4	4.21–4.73	0.0155–0.0246	103.8–179.4	0.08–3.38	0.032–0.128	0.21–0.36	0.016–0.033	0.008–0.022
		4.44 $\pm$ 0.03	0.0207 $\pm$ 0.0006	133 $\pm$ 1	0.81 $\pm$ 0.03	0.049 $\pm$ 0.001	0.031 $\pm$ 0.02	0.022 $\pm$ 0.001	0.013 $\pm$ 0.001
Ostojićovo	AW5	4.51–5.32	0.007–0.014	126.3–195.6	0.09–1.87	0.011–0.043	0.35–0.43	0.019–0.041	0.02–0.029
		4.84 $\pm$ 0.02	0.0098 $\pm$ 0.0001	153 $\pm$ 1	0.25 $\pm$ 0.01	0.022 $\pm$ 0.001	0.39 $\pm$ 0.04	0.029 $\pm$ 0.001	0.023 $\pm$ 0.001
Gornje Crnjelovo	AW6	14.92–17.21	0.064–0.102	68.3–115.4	0.06–1.7	0.039–0.259	0.31–0.52	0.028–0.045	0.006–0.012
		15.81 $\pm$ 0.03	0.073 $\pm$ 0.001	82.3 $\pm$ 0.6	0.49 $\pm$ 0.03	0.081 $\pm$ 0.006	0.043 $\pm$ 0.01	0.033 $\pm$ 0.002	0.008 $\pm$ 0.001
Subotićte	AW7	10.29–11.08	0.02–0.04	89.5–124.9	0.09–0.68	0.023–0.216	0.26–0.42	0.028–0.041	0.008–0.013
		10.81 $\pm$ 0.03	0.027 $\pm$ 0.001	103.6 $\pm$ 0.7	0.21 $\pm$ 0.02	0.053 $\pm$ 0.001	0.31 $\pm$ 0.01	0.031 $\pm$ 0.001	0.009 $\pm$ 0.001
Burum	AW8	12.93–19.92	0.067–0.111	72.7–182.2	0.08–1.29	0.035–0.101	0.15–0.47	0.028–0.044	0.042–0.056
		14.23 $\pm$ 0.07	0.083 $\pm$ 0.001	107.5 $\pm$ 0.9	0.39 $\pm$ 0.01	0.05 $\pm$ 0.01	0.36 $\pm$ 0.02	0.037 $\pm$ 0.001	0.048 $\pm$ 0.001
Vršani	AW9	18.8–23.8	0.093–0.164	36.5–81.2	0.06–0.55	0.044–0.231	0.11 $\pm$ 0.29	0.029–0.046	0.007–0.015
		21 $\pm$ 1	0.116 $\pm$ 0.002	52.6 $\pm$ 0.5	0.26 $\pm$ 0.01	0.062 $\pm$ 0.001	0.19 $\pm$ 0.02	0.036 $\pm$ 0.001	0.011 $\pm$ 0.001
Čađavica	AW10	18.5–20.9	0.129–0.221	43.6–99.8	0.08–4.33	0.041–1.737	0.38–0.45	0.026–0.051	0.211–0.535
		20 $\pm$ 1	0.176 $\pm$ 0.001	63.1 $\pm$ 0.5	0.72 $\pm$ 0.03	0.21 $\pm$ 0.03	0.41 $\pm$ 0.01	0.040 $\pm$ 0.002	0.276 $\pm$ 0.002

Trace elements, essential for human life, such as Fe, Mn Zn, Cu and Co in higher concentrations can have a negative impact on human health [11]. Based on the results given in Table 2, it can be concluded that these elements are present in the water samples at concentrations lower than the values recommended by the

WHO [9] and US EPA [10]: Cu 1.0 and 2.0 mg/L, Fe 0.3 mg/L [10], Zn 5.0 and <3.0 mg/L, respectively. Only concentrations of Mn in water from artesian wells: AW6 (0.073 mg/L), AW8 (0.083 mg/L), AW9 (0.116 mg/L) and AW10 (0.176 mg/L) are near or above of the recommended standard of 0.05 mg/L according to US

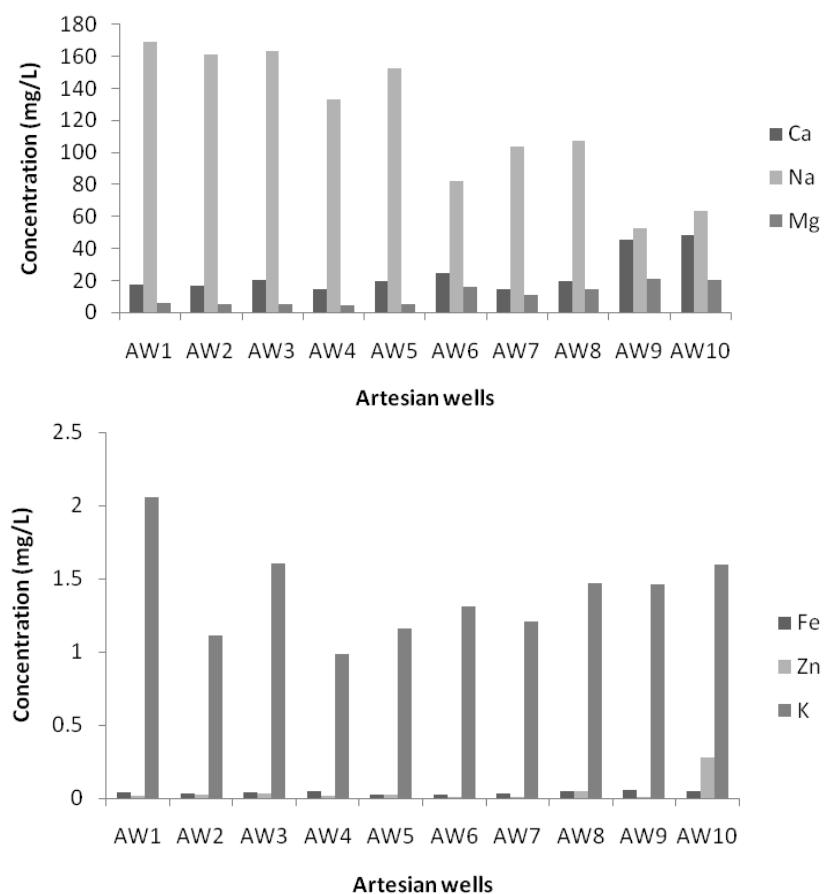
EPA [10] and <0.1 mg/L according to WHO [9]. Mn is naturally occurring in many surface water and groundwater sources. Also, several studies suggest a mainly non-anthropogenic source of Mn, which further supports the conclusion that it has mainly natural source [12,13]. There have been several epidemiological studies that report adverse neurological effects following extended exposure to very high levels in drinking-water [14–16]. Cobalt has both beneficial and harmful effects on human health. Cobalt is beneficial for humans because it is part of vitamin B12, which is essential to maintain human health. Small amounts of cobalt are naturally found in most rocks, soil, water, plants and animals, typically in small amounts. This element does not exist in its native form and is most often found in the form of arsenides and sulphides. Generally, cobalt compounds that dissolve easily in water are more harmful than those that are hard to dissolve in water [17]. Because of the low concentration of cobalt in water in relation to potential toxicity, there is no maximum permissible concentration in drinking-water given by WHO and US EPA.

Selenium is well known as an essential element for biological systems, both as a nutrient and as a potential toxicant, the difference between the necessary daily intake and the toxic value is small [18]. Also, selenium can be present as impurities in gravel, sands, and other

water contact materials. The data on exposure of the population to selenium in drinking water indicate that selenium in drinking water does not make a significant contribution to total selenium intake for most of the population [8]. WHO [9] and US EPA [10] have established recommended standard for drinking water for selenium of 0.04 and 0.05 mg/L, respectively. The water samples are found to have a lower level for Se than the recommended values.

Toxic metals like Pb, Cr, Sb, Ni and Cd have been associated with various forms of cancer, nephrotoxicity, central nervous system effects and cardiovascular disease in humans. Human activities have substantially altered the natural distribution of these metals in the environment, leading to potentially elevated concentrations of these metals in many environmental media [19]. WHO [9] and US EPA [10] guideline values are: for Pb 0.01 and 0.015 mg/L, for Cr 0.05 and 0.01 mg/L, for Sb 0.02 and 0.006 mg/L, for Ni 0.07 (WHO) and for Cd 0.003 and 0.005 mg/L, respectively. Obtained results (Table 2) showed that the concentrations of Pb, Cr, Ni, Sb and Cd in water samples are lower than those recommended by the WHO and US EPA.

Compared metal concentrations in water from different artesian wells, metal levels in water samples from AW1– AW6 are higher than those in water samples from AW7–AW10 (Figure 2).



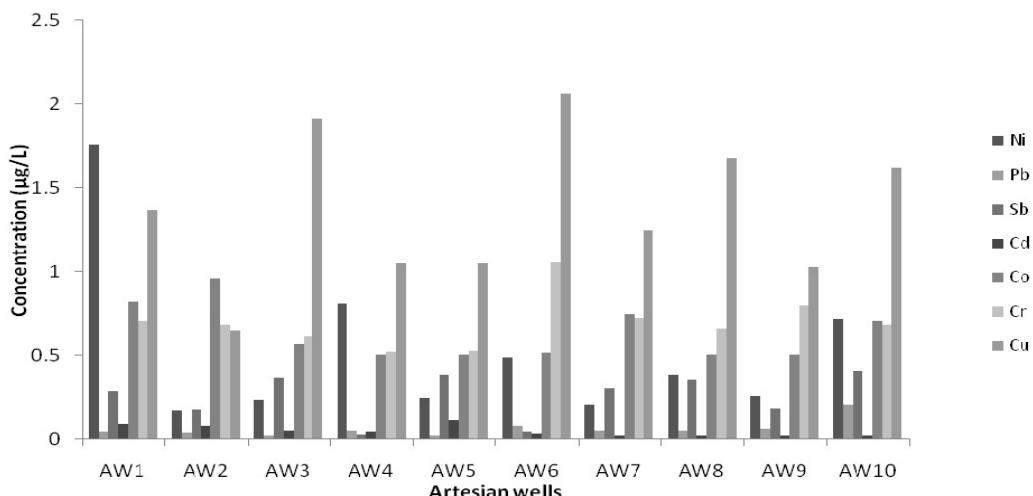


Figure 2. Comparison of metal levels in water from different artesian wells.

Principal component analysis (PCA) and cluster analysis (CA) are the most common multivariate statistical methods used in environmental studies [20,21]. PCA was applied to assist in the identification of source of pollutants. The PCA results are graphically displayed using loading plot (Figure 3).

It shows the correlations between variables (metals). Each point, whose coordinates are the loadings on the principal components, corresponds to a variable. High level of a variable affects most the principal component

on which this variable has a high loading. The variables that have small factor loadings in any principal component have little influence. Table 3 displays the factor loadings as well as eigenvalues.

Factor loadings  $>0.71$  are typically regarded as excellent and  $<0.32$  very poor [22]. In this study, all principal factors extracted from the variables were retained with eigenvalues  $>1.0$ , as suggested by the Kaiser criterion [23]. Two factors were obtained. The first factor accounts for 41.84% of the total variability

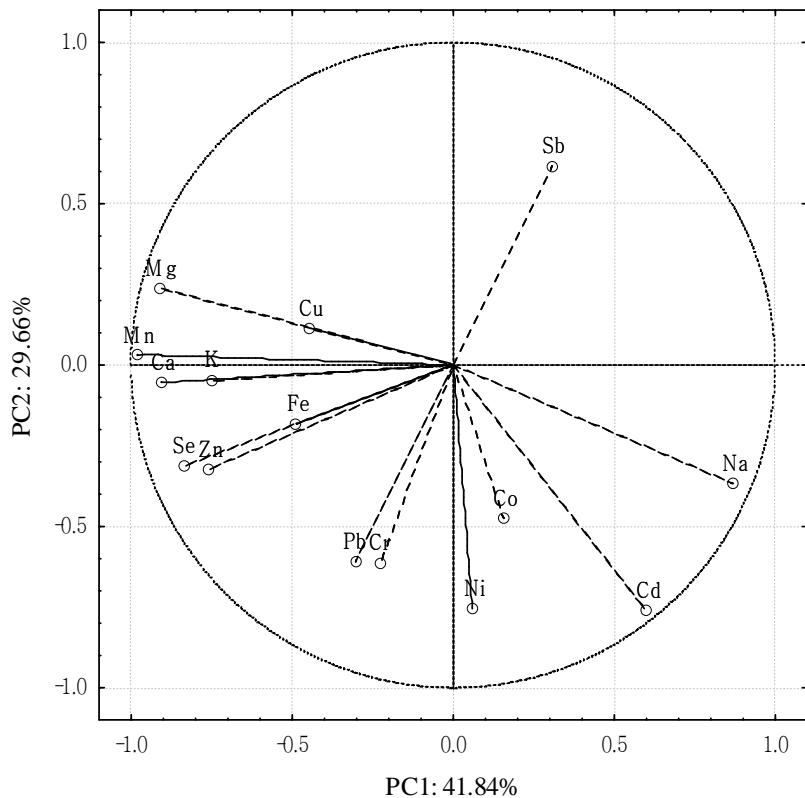


Figure 3. Principal component score plot (PC1 and PC2) of the studied metals' contents based on ICP-OES measurement.

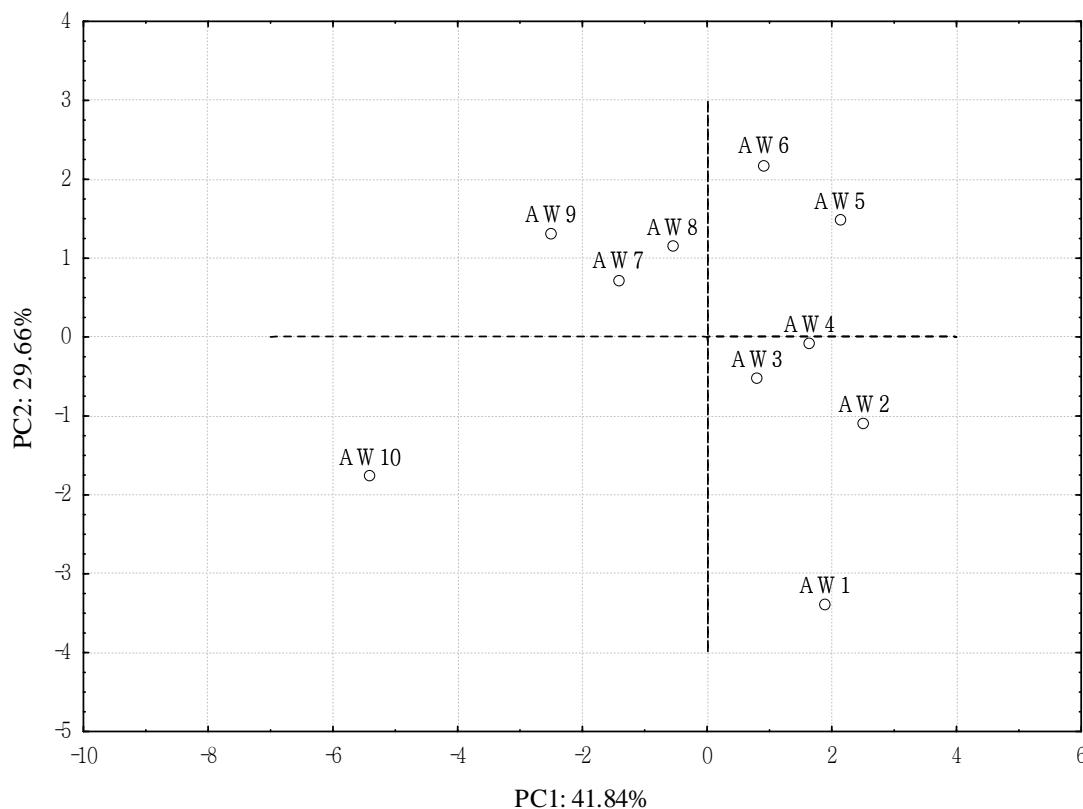
and the second one represents 29.66% of the total variance. PC1 and PC2 explain the largest possible variation in the data and therefore account for most of the information (71.5%). Factor 1 is dominated by Mn, Mg, Na, Ca, K, Zn, Se, Fe and Cu, while Na is negatively correlated with other elements. In this case, factor loadings of Cu (0.447) and Fe (0.448) are not as high as the loadings of the other elements of the group which may suggest a different origin from the other elements. According to International Sava River Basin Commission [13] occurrence of Fe and Mn in alluvium is natural. Moreover, Mn, Mg and Ca are correlated to each other because they have similar factor loadings, as well as Zn and Se. PC1 with high contribution of Mn, Mg, Na, Ca, K, Zn and Se could be considered to be dominated by the natural factor of the lithogenic process. Factor 2 is dominated by Cd, Ni, Sb, Cr, Pb and Co. Co (0.475) is with the smallest factor loading referring to the other elements suggesting another source. A strong correlation between Cd and Ni could be an indicator of the common source or sources of the two elements. Cr and Pb are also correlated, suggesting another common source or sources. PC2 loaded by Cd, Ni, Sb, Cr and Pb indicate the likely influence from anthropogenic factors.

When the location relates to the concentrations of metals found in water from artesian wells, three clearly defined groups can be observed (Figure 4).

*Table 3. Principal component analysis (PCA loadings > 0.4 are shown in bold)*

Element	Component	
	1	2
Mn	<b>0.982</b>	-0.03
Mg	<b>0.913</b>	-0.236
Ca	<b>0.908</b>	0.053
Na	<b>-0.869</b>	0.367
K	<b>0.836</b>	0.312
Zn	<b>0.758</b>	0.325
Se	<b>0.748</b>	0.046
Fe	<b>0.488</b>	0.181
Cu	<b>0.447</b>	-0.114
Cd	-0.601	<b>0.761</b>
Ni	-0.059	<b>0.755</b>
Sb	-0.306	<b>-0.617</b>
Cr	0.228	<b>0.612</b>
Pb	0.303	<b>0.611</b>
Co	-0.157	<b>0.475</b>
Percent of variance	41.843	29.656
Cumulative percent	41.843	71.499

The first group including artesian wells AW1, AW2, AW3, AW4, AW5 and AW6 are located in the positive quadrant. The mean values of the metals in water from



*Figure 4. Principal component score plot (PC1 and PC2) of the studied water samples from different artesian wells based on ICP-OES data for the metals contents.*

these artesian wells were greater than those in the second and third group. Artesian wells, AW7, AW8 and AW9, in the second group are located in the second quadrant with negative contribution to PC1 and positive contribution to PC2. Artesian well, AW10, from third group is located in the third quadrant with negative contribution to PC1 and PC2.

It is important to note that artesian wells AW1–AW6 are located in region with a high density of traffic and human activities. High mean values of Pb, Cd and Cr in water are related to heavy traffic on the border between Bosnia and Herzegovina and Serbia. Atmospheric deposition of heavy metals is considered to be a significant factor in soil and water pollution [24,25]. This region is also a part of Drina River Basin that there are certain environmental “hot spots” which are potential threat to the environment (chemical factory in Goražde, aluminium factory in Zvornik and Glinica, viscose factory in Loznica, etc.). The Drina River Basin is well known for its significant coal, bauxite and iron resources, the exploitation which has multiple negative impacts on soil and water quality (through contamination of groundwater and as a result of flooding). Other potential sources of pollution include agricultural activities and solid waste disposal [26].

On the other hand, artesian wells, AW7–AW9 are located in the region of the Sava River basin. The main causes of groundwater pollution in the Sava River Basin are intensive agriculture, insufficient wastewater collection and treatment on municipal level, inappropriate waste disposal sites, urban land use and mining activities [13]. Also, the chemical status of surface and underground water can be affected by sediment quality. The quality of sediments in the Sava River Basin has been estimated at the national and international level [27]. The findings of the study based on an analysis of sediments sampled at 20 locations along the Sava River indicated a moderate elevation of Hg levels in sediments (up to 0.6 mg/kg) and Cr and Ni (up to 400 and 210 mg/kg, respectively) in industrially impacted sites. Contamination of Sava sediments by Pb, Zn, Cu, Cd and As was not significant. Obtained data also indicate that the concentrations of elements in sediments of the Sava River gradually increase from the Sava River spring to its outflow to the Danube River. These results are in accordance with Cr, Ni, Pb and Cd concentrations in water from artesian wells located near the Sava River. The water from artesian wells, regarding Cr, Ni, Pb and Cd concentrations, follows the increasing order: AW8 < AW7 < AW4. Higher concentrations of Cr, Cd and Ni at these sampling sites indicate heavy industry and chemical industry activities along the Sava River. Higher concentrations of Pb in water are related to heavy border traffic [27].

In general, influences between air, soil and water pollution are mutual. Just as the atmosphere can transfer a large amount of heavy metals into soil and water [28,29], soil dust can also contribute to the concentrations of heavy metals in the water and air [30].

## CONCLUSION

The investigation of water from artesian wells in ten sample sites in Semberija region during one year showed that the concentrations of the investigated metals are lower than those recommended by the WHO and US EPA. Mn concentrations were exceeded WHO and US EPA quality guideline values. Higher Mn concentrations are attributed to a main origin in soil. Obtained results also indicate that metal levels in water samples from artesian wells: AW1–AW6 are higher than those in water samples from AW7–AW10. Furthermore, data indicate that, in general, the concentrations of Cr, Ni, Pb and Cd in water from artesian wells along the Sava River (AW8, AW7 and AW4) gradually increase from the Sava River spring to its outflow to the Danube River. This is in accordance with data obtained from the analysis of sediments sampled at 20 locations along the Sava River. PCA was used to identify the sources of metals and classified sampling sites according to metal concentrations. According to the results of PCA, the original variables could be reduced to two factors, which accounted for 71.5% of the total variance. Natural factor controls PC1 of water samples while anthropogenic factor is represented by PC2. Mn, Fe and Co are attributed to natural origin in soil. Cr, Ni, Pb and Cd originate mainly from industrial sources as well as from traffic sources. Beside metal concentrations all artesian wells were classified into three groups: the first group including artesian wells AW1–AW6, second including AW7–AW9 and the third group including AW10. Metal concentration is higher in the first group, followed by the second and the third group. These findings indicate that more attention should be paid to the application of systematic measures for improving the quality of groundwater in this area that is susceptible to pollution.

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## ИЗВОД

### МУЛТИЕЛЕМЕНТНО ОДРЕЂИВАЊЕ МЕТАЛА КОРИШЋЕЊЕМ ОПТИЧКЕ ЕМИСИОНЕ СПЕКТРОМЕТРИЈЕ СА ИНДУКОВАНО КУПЛОВАНОМ ПЛАЗМОМ У ЦИЉУ КАРАКТЕРИЗАЦИЈЕ ВОДЕ ИЗ АРТЕШКИХ БУНАРА СЕМБЕРИЈЕ: МУЛТИВАРИАНТНА АНАЛИЗА ПОДАТАКА

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(Научни рад)

У раду је одређен садржај петнаест метала (Mg, Na, Ca, K, Se, Zn, Mn, Fe, Pb, Cr, Cu, Cd, Sb, Ni и Co) у води из артешког бунара (AB) на територији Семберије у циљу праћења квалитета подземних вода. Метода главних компоненти (PCA) је коришћена циљу класификације испитиваних узорака у погледу садржаја метала. Методом главних компоненти екстражована су два фактора који заједно објашњавају 71,5% укупне дисперзије посматраних мерења. Природни (литогени) фактор представља PC1, док антропогени фактор представља PC2. Први фактор објашњавају Mn, Mg, Na, K, Ca, Zn и Se, што представља 41,84% дисперзије посматраних мерења, док други фактор карактерише висока засићеност за Cd, Ni, Sb, Cr и Pb (29,66%). Појава ових метала у води је резултат индустријског загађења и повећаног обима саобраћаја у близини испитиваних локалитета. На основу кластер анализе добијена су три јасно одвојена кластера. Први кластер чине артешки бунари (AB1–AB6) који се одликују већом концентрацијом метала у поређењу са онима у другом (AB7–AB9) и трећем кластеру (AB10). Повећане концентрације су резултат антропогеног фактора. Такође, анализа воде је показала благо повишене концентрације за Mn (концентрација до 0,176 mg/L), док су концентрације других испитиваних елемената испод вредности које препоручују Светска здравствена организација (WHO) и Агенција за заштиту околине Сједињених Америчких Држава (US EPA). Добијени резултати указују на то да треба више пажње посветити примени системских мера у циљу побољшања квалитета подземних вода у овој области која је подложна загађењу.

Кључне речи: Метали • ICP-OES • Артешки бунари • Семберија • Анализа главних компоненти