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Research Paper

Assessment of health risk induced by heavy metal contents in drinking water

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ABSTRACT

Investigation of the quality of drinking water was carried out aiming to evaluate health risks and toxicity arising from the content of heavy metals. Samples were analysed for the content of Pb, Cd, Cr, Ni, Cu, Fe, Zn, Al, and Mn. Water quality and health risk assessment were evaluated by comparing the obtained data with current National, EU, and WHO regulations as well as by using the hazard quotient and cancer risk (*HQ* and *CR*). Results showed that Al (in one sample) and Ni (in five samples) exceeded the maximum allowed limits. Based on the metal pollution index, MPI, it was concluded that none of the samples exhibited 'very good quality' ($MPI > 0.3$), whereas the overall quality of Glina bottled water was classified as toxic to humans and Trebeshina as moderately toxic. Selected samples exhibited no evident health risk to humans ($HQ < 1$). Among the toxic metals analysed, Ni, Cd, and Cr exhibited higher values of cancer risk index ($CR > 10^{-4}$), whereas Pb exhibited the lowest value. Bottled water such as Qafeshtama, Lajthiza, Tepelena, Dukat, Spring, Living, and Aqua Pana as well as tap water collected in the area of Student's City in Tirana can be considered safe for human consumption.

Key words: cancer risk, drinking water, health risk assessment, heavy metals, toxicity

HIGHLIGHTS

- Heavy metals can cause toxicity.
- Severe health effects are closely related to long term use.
- Toxicity and Cancer Risk indexes were used to evaluate water safety.

1. INTRODUCTION

Throughout history, the quality of drinking water has been a factor in determining human welfare. Currently, waterborne toxic chemicals pose the greatest threat to the safety of water supplies in industrialized nations (U.S. Department of Health & Human Services 1999). There are many possible sources of chemical contaminants including wastes from industry, pesticide runoff from agricultural lands, general municipal wastes, etc. (Lippmann 1999). Inadequate management of chemical waste means that drinking water of hundreds of millions of people is dangerously contaminated or chemically polluted (WHO 2011). According to the World Health Organization (WHO), access to safe drinking water has been acknowledged as being essential to health, a basic human right, and a component of effective policy for health protection (WHO 2011).

Metals are considered heavy pollutants due to their toxicity, durability, and bioaccumulation in the environment. Among the heavy metals, As, Cd, Pb, Cr, Cu, Hg, and Ni are of major concern, mainly due to their presence at relatively high concentrations in drinking water and their effects on human health (USEPA 2012, 2014; Montuori *et al.* 2013).

Heavy metals include essential elements like iron and toxic metals like cadmium and mercury. Most of them have a tremendous affinity for sulphur and disrupt enzyme function by forming bonds with sulphur groups in enzymes. Protein carboxylic acid ($-CO_2H$) and amino ($-NH_2$) groups are also chemically bound by heavy metals. Cd, Cu, Pb, and Hg ions bind to cell membranes, hindering transport processes through the cell wall (Malachowski 1995).

According to the International Agency for Research on Cancer (IARC), inorganic As and Cd are classified as human carcinogens (IARC (International Agency for Research on Cancer) 2016). Arsenic is related to cancer risk and skin damage, whereas Cd is linked to kidney damage and cancer. Other effects such as heart diseases and blood cholesterol from Sb,

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anemia from Pb, kidney and liver damage from Hg, and gastrointestinal disorder from Cu are also reported (U.S. Department of Health & Human Services 1999; USEPA (U.S. Environmental Protection Agency 2014).

Sources of drinking water are mainly represented by fresh surface water (lakes, rivers, reservoirs) and groundwater aquifers (Manahan 2001; Cullaj *et al.* 2011). In the last decades, the use and demand of bottled water have increased, raising concerns regarding the quality of bottled water and the packaging material (mostly used polyethylene terephthalate (PET)) playing an important role as an adequate barrier against humidity, oxygen, and carbon dioxide (Chapa-Martínez *et al.* 2016).

Drinking water standards today are set by international organizations such as the WHO and US Environmental Protection Agency (USEPA), whereas each country sets national criteria for drinking water quality (USEPA 1977, 1992; WHO 2011). Thus, for example, Albania has a DCM (Decision of the Council of Ministers No. 379, dated 26.02.1998) 'On the approval of the hygienic-health regulation for the control of the quality of drinking water' that determines the recommended values for different parameters (including some metals) in drinking water (Decision of Council of Ministers 1998).

Commonly, human health risk evaluation is based on the comparison of the estimated concentrations with the recommended guidelines for a certain element, which in fact is not sufficient as it cannot provide adequate information on the hazard level as well as on the distinguishing of the most potential contaminant due to the long-term exposure (USEPA 1977, 1992, 1997). Human health risk of a certain hazardous substance, even if below the recommended value, is dependent on the type of element; the level of the element to which a person is exposed; the duration of exposure, and the quantity consumed (USEPA 1989, 1997, 2004, 2006, 2009). The most used guidelines on health risk assessments with regard to human exposure to different contaminants are based on the USEPA and WHO recommendations (USEPA 1989, 1997, 2004, 2006, 2009). Accordingly, risk assessment is defined as 'the process of estimating the probability of occurrence of an event and the probable magnitude of adverse health effects on human exposure to environmental hazards over a specified period of time'. The health risk assessment of each potentially toxic metal is usually based on the quantification of the risk level and is expressed in terms of a carcinogenic or a non-carcinogenic health risk (Adamu *et al.* 2014; Wongsasuluk *et al.* 2016). The two principal toxicity risk factors evaluated are the slope factor (SF) for carcinogen risk characterization and the reference dose (RfD) for non-carcinogen risk characterization. The estimations of the magnitude, frequency, and duration of human exposure to each potentially toxic metal are reported as an average daily dose ($ADDi$), considering the fact that the main route of exposure to harmful substances by consuming drinking water is by ingestion.

The carcinogenic risk, CR is the possibility of an individual to develop any type of cancer during lifetime exposure to carcinogenic threats. According to USEPA (1989), the SF directly transforms the ADD of pollutants exposed over a lifetime to the continual risk of a cancer patient. Risk value, $CR < 10^{-6}$ represents no carcinogenic risk to health, while a $CR > 1 \times 10^{-4}$ suggests a high risk of developing cancer. A risk value ranging from 1×10^{-6} to 1×10^{-4} signifies an acceptable risk to human health (USEPA 1989).

Albania's water resources amount to 41.7×10^9 m^3 or 13.3×10^3 m^3 per capita, of which about 65% are generated within Albania and the rest comes from neighboring countries. Consumption of drinking water is about 20–50 L per person per day (Cullaj *et al.* 2011). After 1990, due to population growth, the construction of the Bovilla Reservoir in 1998 was essential to address the demand for drinking water in the capital area (Cullaj *et al.* 2011). Bottled water is one of the few alternatives to drinking water that consumers can use. Nowadays, in Albania exist more than 14 springs which are used for bottled water production, among which eight are traded almost all over Albania, while the rest have mainly local use. The increasing use of industrialized water worldwide is associated with a loss of confidence in water supply.

In December 2021, the WHO updated chemical background documents for asbestos, Mn, Ni, and Ag. A number of chemical background documents were also published in December 2020. According to the DGWQ list of chemicals to be controlled, published by the WHO, heavy metals are of main importance (WHO 2022). The main purpose of this study was the evaluation of health risks associated with oral exposure to selected heavy metals being present in different types of drinking waters that are consumed preferably by Albanian inhabitants.

2. MATERIALS AND METHODS

2.1. Selection of water samples

Water samples were collected from different sources in Albania, including bottled, tap, and spring water (15, 2, and 3 samples, respectively). Bottled water was collected randomly in the markets of Albania, comprising of nationally produced and imported brands. Tap water was collected in two different areas of Tirana city, aiming to differentiate water quality being supplied by different sources (respectively, Student's city is supplied by Selita natural spring water while the city center is supplied by the Buvilla reservoir). Water from natural springs is consumed untreated by many inhabitants of the three villages, Llogoraja, Tragjasi, and Dukati.

Samples collection and treatment were carried out in accordance with the standard methods ISO 5667, Part -5 and APHA/ AWWA, 2017 (ISO 5667-5:2006 2006; APHA 2017). Samples were collected in polyethylene bottles, previously washed with nitric acid, HNO_3 1: 1, and rinsed with deionized water. Initially, the water was allowed to flow for a few minutes and then collected in PET bottles with a volume of 1 L. Once the water samples arrived at the laboratory, spring water samples were filtered while all samples were acidified with 1 ml of nitric acid, HNO_3 to pH <2. After acidification, the samples were stored in the refrigerator at 4 °C until the day of analysis.

2.2. Methodology of metals determination

Determination of the concentration of metals was performed by atomic absorption spectroscopy technique with graphite furnace atomization, AAS/GFAET. For this purpose, the Analytik Jena novAA400 instrument, equipped with a graphite furnace and autosampler type MP89 was used. For each element, instrumental conditions were first optimized, including HCL intensity, spectral bandwidth, wavelength, and graphite furnace program. The concentration of metals (Al, Zn, Cu, Fe, Cr, Mn, Pb, Cd, Ni) was calculated by the linear regression method.

2.3. Quality control of results

Quality control of results was performed through the analysis of replicates, blanks, and by analysis of a certified reference sample, CRM for the concentration of heavy metals in water, SPS-WW2 Batch 114. The experimental results for the CRM were within the limits of the confidence interval reported in the sample certificate. Statistical treatment of the results was carried out by using MINITAB19 and the Excel Analysis Tool Pack. Basic statistics such as mean and standard deviation were calculated by the descriptive statistics while the multivariate cluster analysis was used for the estimation of significant correlation between metals content in selected samples.

2.4. Metal pollution index

The pollution state of selected samples can be estimated by different indexes of pollution, of which the metal pollution index, *MPI* can be used as an indicator of the overall water quality related to heavy metals content and it is calculated by the following equation (Edet & Offiong 2002; Shehu *et al.* 2016):

$$MPI = \sum_{i=1}^{n} \frac{C_i}{MACi}.$$

where C_i is the measured concentration of each metal and $MACi$ is the maximum admissible concentration of the ith metal. *MPI* values greater than 1 represent a threshold warning (Edet & Offiong 2002). Table 1 presents the MPI classification for water used for drinking and domestic purposes (Edet & Offiong 2002).

Table 1 | Classification of water quality based on the MPI

MPI	Characteristics class
<0.3	Very pure I
0.3–1.0	Pure II
1.0–2.0	Slightly affected III
2.0–4.0	Moderately affected IV
4.0–6.0	Seriously affected V
>0.6	Seriously affected VI

2.5. Human health risk assessment

2.5.1. Average dose daily intake

There is a lack of information with regard to levels of toxic substances present in drinking waters in Albania, including heavy metals. The largest number of publications has been mainly focused on the evaluation of the environmental status of sources of water, while only few publications can be found with regard to human health risk assessment by both ingestion and/or dermal route (Shehu *et al.* 2021; Vallja *et al.* 2021). Bamuwuwamye *et al.* (2017) reported Pb to be a major contributor to non-cancer risks.

The two principal toxicity risk factors evaluated are the *SF* for carcinogen risk characterization and the reference dose (*RfD*) for non-carcinogen risk characterization (Li *et al.* 2013; Bamuwuwamye *et al.* 2017). The estimations of the magnitude, frequency, and duration of human exposure to each potentially toxic metal in the environment are reported as an *ADD* and it is calculated using the following equation:

$$ADDi = \frac{Ci \times IR \times EF \times ED}{BW \times AT}.$$

Here, $ADDi$ (mg/kg/day) is the average daily dose through ingestion of water, Ci is the concentration of the metal (mg/L), IR is the ingestion rate, EF represents exposure frequency, ED is exposure duration, BW indicates body weight, AT is the average time for non-carcinogens, ET represents exposure time, and CF is the conversion factor (Wongsasuluk *et al.* 2016). Values of all the above parameters are presented in Table 2.

2.5.2. Hazard quotient

The human health risk of metals in the water samples was assessed as a non-carcinogenic hazard quotient, using the calculation as follows:

$$\text{HQ (for non-carcinogenic effect)} = \frac{ADD}{RfD}$$

$$\text{Hazard index} = \text{HI}i = \Sigma HQi$$

An $\text{HI} < 1$ signifies an acceptable level of risk, whereas $\text{HI} > 1$ represents an unacceptable risk of non-carcinogenic effects (APHA 2017).

2.5.3. Carcinogenic risk

The *CR* is the possibility of an individual to develop any type of cancer during lifetime exposure to carcinogenic threats. According to USEPA (1989), the *SF* directly transforms the ADD of pollutants exposed over a lifetime to the continual risk of a cancer patient. Risk value, $CR < 10^{-6}$ represents no carcinogenic risk to health, whereas a value of $CR > 1 \times 10^{-4}$ suggests a high risk of developing cancer. A risk value ranging from 1×10^{-6} to 1×10^{-4} signifies an acceptable risk to

Table 2 | Standard values for calculating exposure assessment of trace metals in waters (USEPA 1989; Demir *et al.* 2015)

Index	Name	Value	Unit
Ci	Concentration of metal in water	–	mg/L
IR	Water ingestion rate	2	L/day
Ef	Exposure frequency	365	Days/year
Ed	Exposure duration	70	Years
Bwt	Average body weight	70	kg
At	Averaging time	25,550	Days
Cf	Unit conversion factor	1×10^{-3}	L/cm^3
RfDi	Cd = 0.0005; Cr = 1.5; Cu = 0.037; Ni = 0.020; Pb = 0.036; Zn = 0.3; Mn = 0.14; Fe = 0.7		

human health, (USEPA 1989). The CR was calculated according to the formula:

$$CR = ADD \times SF$$

3. RESULTS AND DISCUSSIONS

3.1. Variation of metals concentration

Variation of metal concentrations in water samples is presented in Figures 1 and 2. Descriptive statistics are presented in Table 3. Water quality assessment with regard to heavy metals was based on the recommended values of the Albanian legislation, respectively Decision no. 379, dated: 25.05.2016 as well as on the WHO guidelines (WHO 2022, Guidelines for Drinking Water Quality).

The mean concentration of heavy metals in selected water samples followed the order: Al (41.7 μg/L) > Ni (18.1 μg/L) > Cu (8.7 μg/L) > Fe (7.41 μg/L) > Zn (5.5 μg/L) > Pb (2.1 μg/L) > Cr (1.8 μg/L) > Mn (0.42 μg/L) > Cd (0.076 μg/L).

Among the analyzed metals, Al exceeded the maximum value (200 μg/L) recommended by DCM 379 of the Albanian legislation as well as the maximum value recommended by the European Directive in a tap water sample collected in the area of Tirana city center (Council Directive [98/83/EC] of 3 November 1998; Decision of Council of Ministers 1998). Also, the content of Al exceeded the limit value of 100 μg/L set by the WHO (WHO 2011, 2022). The reason stands in the fact that this area of the city is supplied with water by the Bovilla reservoir where aluminum salts are used in drinking water treatment processes to enhance the removal of particulate, colloidal, and dissolved substances via coagulation (Cullaj *et al.* 2011).

The concentration of Ni in bottled water samples 'Trebeshina', 'BI', 'Evian' and 'Frassasi' exceeded the maximum allowed value (20 μg/L) recommended by the Albanian legislation while in bottled sparkling water 'Glina' the concentration of Ni has resulted in higher than the maximum allowed value 70 μg/L, recommended by WHO (Decission of Council of Ministers 1998; WHO 2011, 2022).

With the exception of Glina water, where the Pb concentration resulted in close to the maximum permitted value, 10 μg/L recommended by the WHO, concentration of Pb was not exceeded in selected samples (WHO 2011, 2022). Concentrations of Fe, Mn, Cr, Zn, Cu, and Cd in selected samples were below the maximum allowed values, based on the

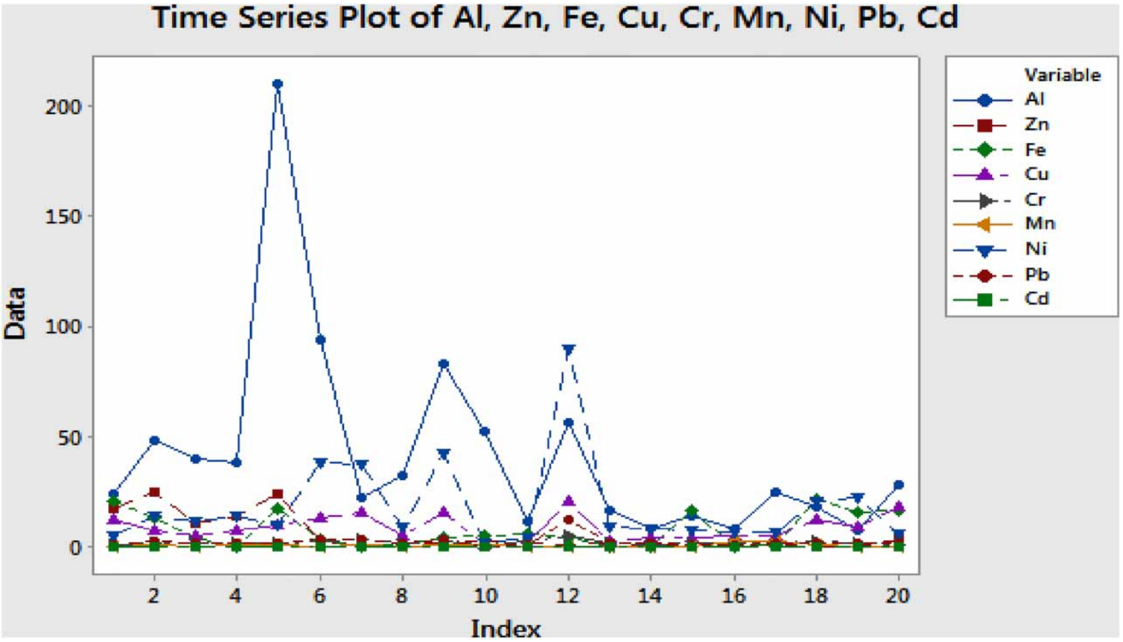
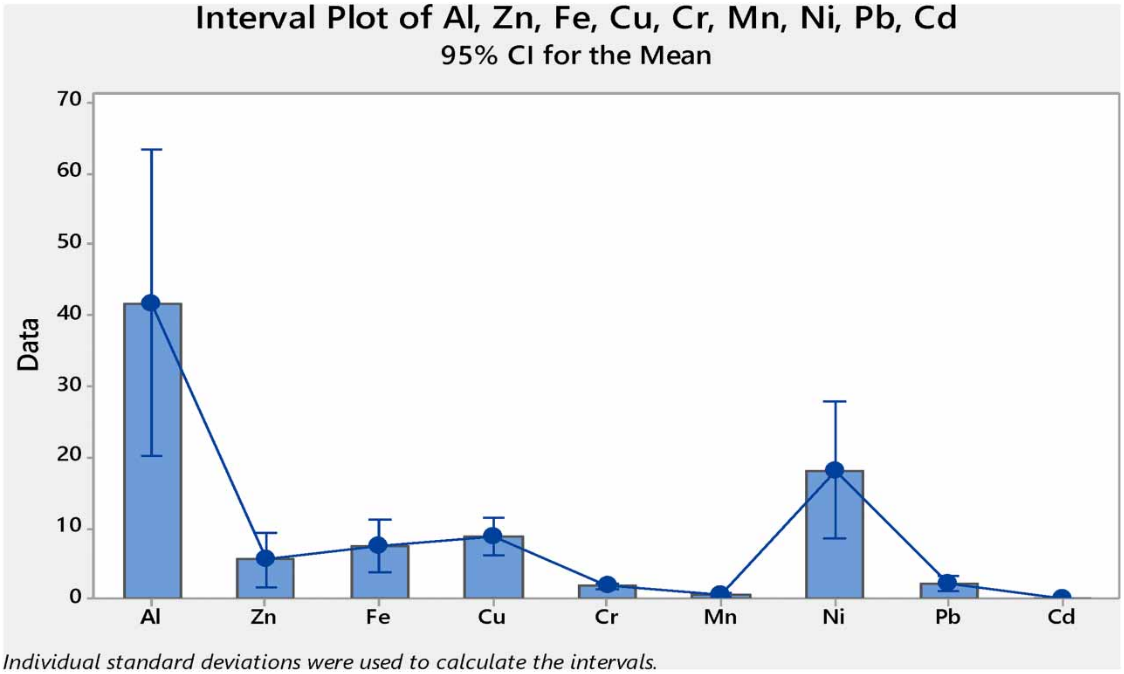


Figure 1 | Variation of metals in water samples.



Individual standard deviations were used to calculate the intervals.

Figure 2 | Confidence intervals of metals in selected samples.

Table 3 | Descriptive statistics of metal concentrations

Al	20	0	41.7	10.3	46.2	7.5	14.4	26.3	50.8	209.8
Zn	20	0	5.46	1.80	8.06	0.04	0.75	1.57	8.97	24.71
Fe	20	0	7.41	1.76	7.87	0.00	0.10	4.10	16.58	21.50
Cu	20	0	8.69	1.29	5.75	0.90	4.38	7.69	12.95	20.38
Cr	20	0	1.75	0.21	0.93	0.47	1.18	1.62	2.39	4.53
Mn	20	0	0.42	0.13	0.60	0.00	0.07	0.15	0.50	2.00
Ni	20	0	18.07	4.62	20.66	1.55	6.44	9.63	22.03	89.87
Pb	20	0	2.13	0.56	2.50	0.09	0.97	1.71	2.15	12.11
Cd	20	0	0.076	0.006	0.026	0.05	0.06	0.065	0.10	0.13

Albanian legislation as well as on the EU and WHO recommendations (Decision of Council of Ministers 1998; WHO 2011, 2022).

3.2. Pearson correlation and cluster analysis

Correlation coefficients and simple cluster analysis were used to evaluate existing similarities of elements within and between samples (Figure 3). It was concluded that samples exhibited a high percentage of similarity coefficients, more than 90% regarding metals concentration (Figure 4). Despite the above, samples being produced in Albania were classified in the same group, while imported water like Frassasi, Aqua Pana, and Evian correlated better with each other.

A high correlation was observed between Ni–Cu (0.71), Pb–Ni (0.94), Cr–Ni (0.88), Cd–Cu (0.75), Ni–Cu (0.71), Pb–Cr (0.88) (Table 4 and Figure 3). Accordingly, metals were classified into three main groups: first group – Cu, Pb, Ni, Cd, Cr; second group – Al, Zn, Fe; and third group – Mn. Considering the above classification it is evident that metals were grouped according to their origin, i.e. metals with natural origin (second group) and metals originating by anthropogenic activities (first and third groups) (Lippmann 1999).

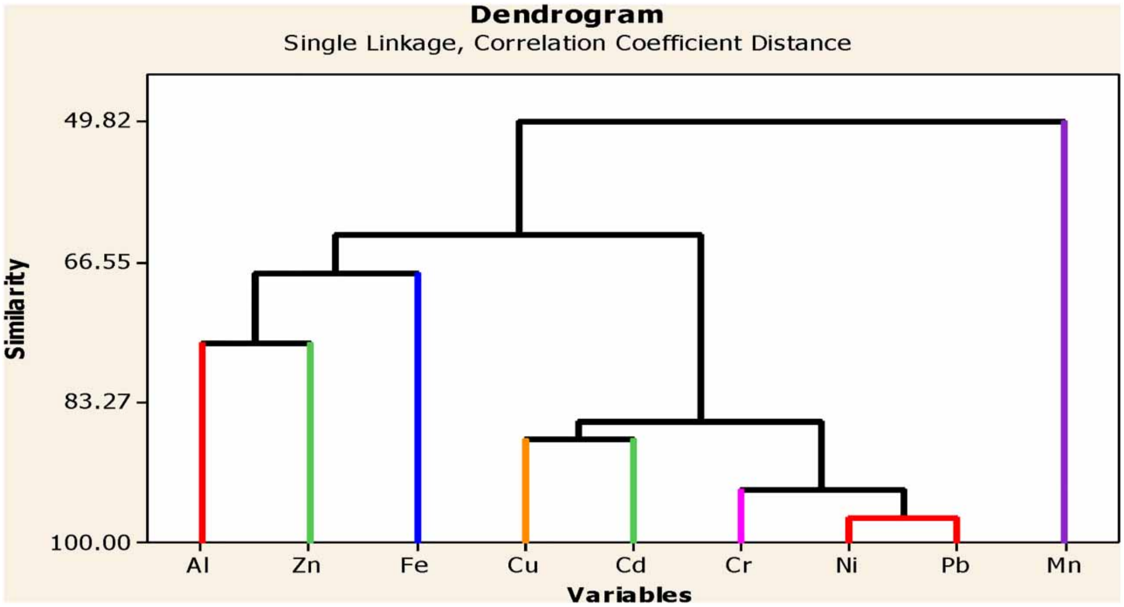


Figure 3 | Cluster analysis of metals.

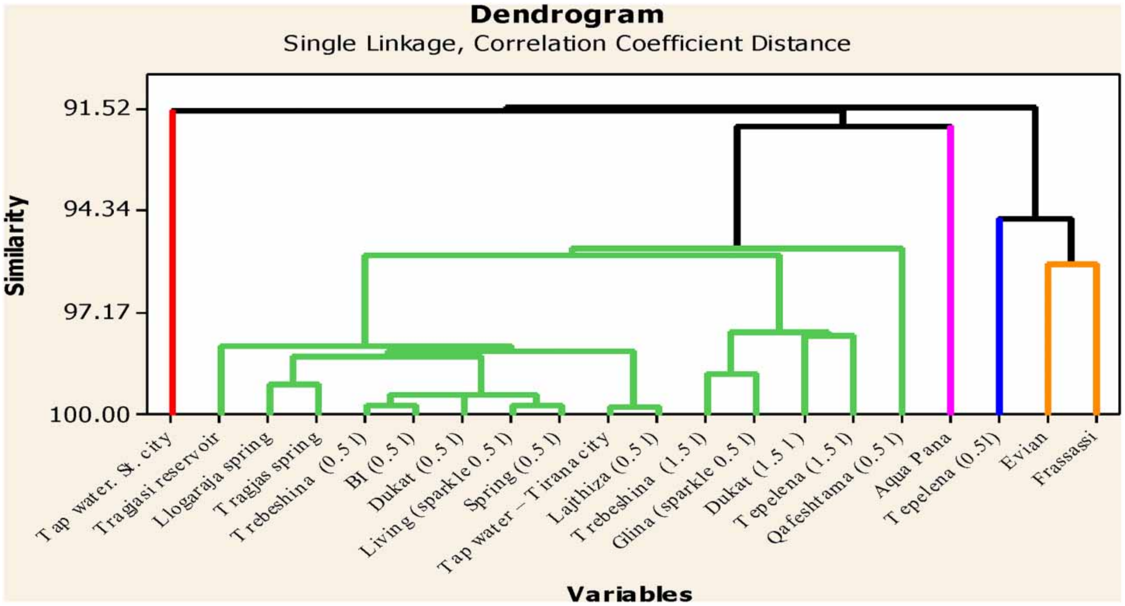


Figure 4 | Cluster analysis of samples.

3.3. Water quality assessment based on *MPI* values

MPI values revealed that none of the samples exhibited 'very good' quality, i.e. with a value of *MPI* <0.3 (Figure 5). Tap water collected at Student's City, bottled water 'Living', 'Qafështama', 'Lajthiza', 'Spring', 'Tepelena', 'Dukat' and 'Aqua Panna' exhibited 'good quality'. Frassasi and Evian bottled water; tap water taken in the area of Tirana city center; and stream water collected in the village of Tragjas were classified as 'slightly toxic', *MPI* 1–2. 'BI' Water and Trebeshina water were

Table 4 | Correlation matrix of elements

	Al	Zn	Fe	Cu	Cr	Mn	Ni	Pb
Zn	0.53							
Fe	0.16	0.36						
Cu	0.23	0.01	0.27					
Cr	0.17	−0.21	−0.17	0.58				
Mn	0.00	−0.01	−0.25	−0.22	−0.19			
Ni	0.18	−0.22	−0.16	**0.71**	**0.88**	−0.20		
Pb	0.16	−0.11	−0.15	**0.65**	**0.82**	−0.19	**0.94**	
Cd	0.17	−0.23	−0.10	**0.75**	0.55	−0.27	0.63	0.44

Values in bold present positive correlation that exist between metals, mainly related to their origin in water.

classified as moderately toxic, with values *MPI* 2–4. The only sample which was classified as ‘toxic’ water with regard to metals content was Glina bottled water, *MPI* 4–6.

3.4. Health risk assessment

3.4.1. *ADD* calculations and *HQ* assessment

The *HQ* was calculated as the ratio of ADD/RfD (Tables 5 and 6). The human health risk assessment showed *HQ* values that suggest an acceptable level of non-carcinogenic health risk. Values of *HQ* ranged between 1×10^{-6} and 1.3×10^{-1} and followed the order: Ni > Cd > Pb > Cu > Al > Fe > Zn > Mn. However, all calculated values have resulted to be lower than 1, which means that all samples in the study are characterized by a low level of health risk.

3.4.2. *CR* evaluation

The risk of cancer is considered the possibility of an individual to develop a type of this disease during their lifetime as a result of exposure to a certain contaminant. In the present study, *CR* was assessed only for elements which are considered toxic for humans, respectively, Cr, Pb, Cd, and Ni. Results are presented in Table 7.

Values of *CR* followed the order: Ni > Cr > Cd > Pb. *CR* values of Ni varied from 0.006 to 0.030 suggesting high cancer risk in all selected samples. *CR* values for Cr and Cd ranged between 0.003–0.026 and 0.003–0.009, respectively, also suggesting a high cancer risk, while with regard to Pb, only one sample has exhibited a low cancer risk; Lajthiza bottled water and three

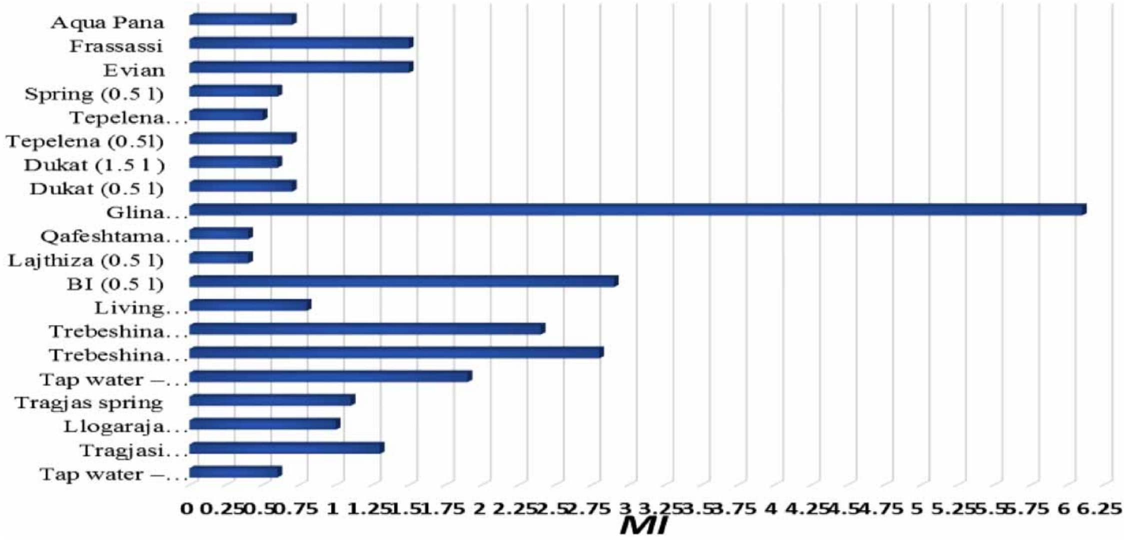


Figure 5 | The MPI of selected samples.

Table 5 | Calculation of $ADDi \times 10^{-6}$ (mg/kg/day)

Sample	Al	Zn	Fe	Cu	Cr	Mn	Ni	Pb	Cd
Tap water – Student's city	690	510	600	370	25	2.6	140	26	2.3
Tragjasi reservoir	1,400	720	370	220	49	22	390	66	1.7
Llogaraja spring	1,100	320	110	140	34	0	320	52	1.5
Tragjas spring	1,100	400	0	220	45	9.9	400	51	2.0
Tap water – Tirana city	6,100	700	500	280	49	16	290	48	1.7
Trebeshina (0.5 L)	2,700	57	87	380	72	2.9	1,100	91	3.8
Trebeshina (1.5 L)	650	19	0	460	84	11	1,100	100	3.8
Living (sparkle 0.5 L)	930	45	32	140	55	2.6	250	36	2.0
BI (0.5 L)	2,400	41	130	440	72	11	1,200	84	3.5
Lajthiza (0.5 L)	1,500	58	140	26	17	26	45	2.6	1.7
Qafeshtama (0.5 L)	340	33	160	46	74	0	1,100	14	1.7
Glina (sparkle 0.5 L)	1,600	21	100	590	130	3.2	26,000	350	2.9
Dukat (0.5 L)	470	52	0	68	39	0	270	39	2.0
Dukat (1.5 L)	240	24	0	120	21	2.0	230	51	1.5
Tepelena (0.5 L)	400	46	490	110	35	0	220	25	1.7
Tepelena (1.5 L)	240	16	0	140	34	0	190	19	1.7
Spring (0.5 L)	720	29	12	150	44	0	190	39	1.5
Evian	510	1.2	620	360	62	8.4	600	51	1.7
Frassassi	220	2.0	460	260	51	5.5	650	51	2.3
Aqua Pana	810	87	490	0	28	2.0	170	45	2.9

Table 6 | Hazard quotient, $HQ \times 10^{-3}$

Sample	Al	Zn	Fe	Cu	Cr	Mn	Ni	Pb	Cd
Tap water – Student's city	0.69	1.69	0.85	9.16	168	0.02	7.19	7.37	4.64
Tragjasi reservoir	1.39	2.39	0.53	5.61	325	0.16	19.7	18.8	3.48
Llogaraja spring	1.14	1.06	0.16	3.39	228	0	16.2	14.8	2.9
Tragjas spring	1.09	1.33	0	5.54	300	0.070	19.8	14.5	4.06
Tap water – Tirana city	6.06	2.32	0.71	6.87	325	0.11	14.4	13.8	3.48
Trebeshina (0.5 L)	2.72	0.19	0.12	9.46	0.05	0.02	55.1	25.9	7.54
Trebeshina (1.5 L)	0.65	0.06	0	11.6	0.06	0.08	53.7	28.8	7.54
Living (sparkle 0.5 L)	0.93	0.15	0.04	3.48	0.04	0.02	12.6	10.4	4.06
BI (0.5 L)	2.49	0.14	0.18	11.0	0.05	0.08	61.1	23.9	6.96
Lajthiza (0.5 L)	1.50	0.19	0.20	0.65	0.01	0.18	2.25	0.75	3.48
Qafeshtama (0.5 L)	0.34	0.11	0.22	1.14	0.05	0	5.37	3.89	3.48
Glina (sparkle 0.5 L)	1.63	0.07	0.15	14.8	0.09	0.02	130	111	5.8
Dukat (0.5 L)	0.47	0.17	0	1.70	0.03	0	13.5	11.1	4.06
Dukat (1.5 L)	0.23	0.08	0	3.1	0.01	0.01	11.7	14.6	2.9
Tepelena (0.5 L)	0.40	0.16	0.70	2.66	0.02	0	11.0	7.04	3.48
Tepelena (1.5 L)	0.24	0.05	0	3.41	0.02	0	9.45	5.38	3.48
Spring (0.5 L)	0.72	0.10	0.02	3.63	0.03	0	9.29	9.86	2.9
Evian	0.51	0.004	0.89	9.06	0.04	0.06	29.9	14.7	3.48
Frassassi	0.22	0.007	0.66	6.6	0.03	0.04	32.6	14.7	4.64
Aqua Pana	0.81	0.29	0.70	13.1	0.02	0.01	8.64	12.8	5.8

Table 7 | *CR* values

Sample	Cr	Pb	Cd	Ni
Tap water – Student's city	0.005	8.59×10^{-5}	0.006	0.007
Tragjasi reservoir	0.010	0.0002	0.004	0.020
Llogaraja spring	0.007	0.0002	0.003	0.016
Tragjas spring	0.009	0.0002	0.005	0.020
Tap water – Tirana city	0.010	0.0002	0.004	0.015
Trebeshina (0.5 L)	0.014	0.0003	0.009	0.006
Trebeshina (1.5 L)	0.017	0.0003	0.009	0.006
Living (sparkle 0.5 L)	0.011	0.0001	0.005	0.013
BI (0.5 L)	0.014	0.0003	0.008	0.006
Lajthiza (0.5 L)	0.003	$\mathbf{8.8 \times 10^{-6}}$	0.004	0.023
Qafeshtama (0.5 L)	0.015	$\mathbf{4.6 \times 10^{-5}}$	0.004	0.006
Glina (sparkle 0.5 L)	**0.026**	0.0012	0.007	0.013
Dukat (0.5 L)	0.008	0.0001	0.005	0.014
Dukat (1.5 L)	0.004	0.0002	0.003	0.012
Tepelena (0.5 L)	0.007	$\mathbf{8.3 \times 10^{-5}}$	0.004	0.011
Tepelena (1.5 L)	0.007	$\mathbf{6.3 \times 10^{-5}}$	0.004	0.010
Spring (0.5 L)	0.009	0.0001	0.003	0.010
Evian	0.012	0.0002	0.004	**0.030**
Frassassi	0.010	0.0002	0.006	**0.030**
Aqua Pana	0.005	0.0001	0.007	0.009

$CR = ADD \times SF$.

Bold values present no tendency to develop a cancer risk.

samples have exhibited moderate cancer risk (Tepelena and Qafeshtama bottled water as well as tap water sample collected at the area of Student's city which is known to be supplied by the Selita natural springs). Trebeshina water and BI water were characterized by higher values of this parameter due to Cd while Glina water was due to Cr content. Waters Evian and Frassasi were characterized by higher *CR* values due to Ni content.

4. CONCLUSIONS

In this study, the quality of drinking water and the evaluation of the human health risk from heavy metals were carried out. In total, 20 samples, including bottled, tap, and natural spring water were selected for this study.

Results revealed that the mean concentration of heavy metals followed the order: Al > Ni > Cu > Fe > Zn > Pb > Cr > Mn > Cd.

Among the analyzed metals, Al exceeded the maximum recommended value in the tap water sample collected in the area of Tirana city center. The concentration of Ni in bottled water samples 'Trebeshina', 'BI', 'Evian', and 'Frassasi' exceeded the maximum allowed value (20 μg/L) recommended by the Albanian legislation (Decission of Council of Ministers 1998) while in bottled sparkling water 'Glina' the concentration of Ni has resulted higher than the maximum allowed value 70 μg/L, recommended by WHO (WHO 2011, 2022).

With the exception of Glina water, where the Pb concentration resulted close to the maximum permitted value, 10 μg/L, concentration of Pb was not exceeded in selected samples. Concentrations of Fe, Mn, Cr, Zn, Cu, and Cd in selected samples were below the maximum allowed values, based on the Albanian legislation as well as on the EU and WHO recommendations. The presence of heavy metals (Ni, Cu, Zn, Cd, Sb, Pb) is due to the anomalies caused by the interactions between the water and the plumbing system, especially in the cases of Pb and Ni, which are particularly soluble in acid water (Dinelli *et al.* 2012).

With regard to *MPI*, it was concluded that none of the selected samples exhibited 'very good' quality. Tap water collected at Student's City area, bottled water such as 'Living', 'Qafështama', 'Lajthiza', 'Spring', 'Tepelena', 'Dukat' and 'Aqua Panna' exhibited 'good quality'. Frassasi and Evian bottled water; tap water taken in the area of Tirana city center; and stream water collected in the village of Tragjas were classified as 'slightly toxic'; 'BI' water and Trebeshina water were classified as moderately toxic; whereas Glina bottled water was classified 'toxic'.

Based on cluster analysis results, metals were classified into three main groups: first group – Cu, Pb, Ni, Cd, Cr; second group – Al, Zn, Fe; and third group – Mn. Considering the above classification it is evident that metals were grouped according to their origin, i.e. metals with natural origin (second group) and metals originating by anthropogenic activities (first and third groups) (Lippmann 1999).

The human health risk assessment of metal content in drinking water, based on the *HQ* values, suggests an acceptable level of non-carcinogenic health risk. Values of *HQ* ranged between 1×10^{-6} and 1.3×10^{-1} and followed the order: Ni > Cd > Pb > Cu > Al > Fe > Zn > Mn.

Different studies from Pakistan and Turkey indicated that studied drinking water sources are safe for consumption, but also could present risk at As and Cu, due to plumbing and pipe corrosion, with *HQ* values ranging from 1.0 to 8.7 (Muhammad *et al.* 2011; Demir *et al.* 2015).

With regard to *CR* calculated values, it was concluded that selected samples exhibited high values of *CR*, suggesting a high cancer risk index, *CR* of Ni, Cr, Cd, Pb $> 10^{-4}$. Only one sample has exhibited a low cancer risk (Lajthiza bottled water) and three samples have exhibited a moderate cancer risk (Tepelena and Qafeshtama bottled water as well as tap water sample collected at the area of Student's city) with regard to Pb.

The above conclusions have been achieved based on the findings of just one time investigation. It is important to emphasise the CR index values, *CR* depends on factors such as concentration of metal, a daily dose of water consumption and body weight. In this study, calculations were made by using the maximum daily dose (i.e. 2 L/day), while usually the dose is lower, leading to lower values of *CR*. According to the formula of *CR* calculation, we can suggest that water with a certain concentration of a toxic metal can affect more people having low body weight compared to those with high BW, in a lifetime term.

While this study was conducted on a relatively low number of samples, we advise that future studies should expand our approach to larger number of water samples. Further investigation on the sources of these contaminants should be carried out, including water pipes and containers. Even though water intended for human consumption are being analysed before starting the water extraction (usually monthly) during the exploitation of the water resource, we recommend the number of parameters should be extended by including analysis of heavy metals, while health risk assessment should be considered when national standard values are determined. The future tendencies will consist of the comparison between the bottled water and the drinking water in centralized systems.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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