ORIGINAL PAPER

ASSESSMENT OF DRINKING WATER QUALITY AND ASSOCIATED HEALTH RISK: A STATISTICAL APPROACH BASED ON PHYSICOCHEMICAL PARAMETERS AND HEAVY METALS CONTENT

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Abstract. *This study investigates the quality of ten different brands of bottled water purchased from various stores across Romania, using a comprehensive analysis of both physicochemical parameters and heavy metal content. The analyzed parameters include pH, total dissolved solids (TDS), dissolved oxygen, turbidity, free and total chlorine, and conductivity. Additionally, the concentration of various heavy metals was measured to assess compliance with current Romanian legislation and international water quality standards. Each water brand was subjected to eight repetitions of electroanalytical testing to ensure accuracy and consistency in the results. Furthermore, statistical analysis, including descriptive analysis, Pearson correlation, and Principal Component Analysis (PCA), was employed to identify key interdependencies both among the physicochemical parameters and between the identified heavy metals. This multifaceted approach offers a deeper understanding of the overall quality of bottled water available in Romania and highlights potential risks related to heavy metal contamination.*

Keywords: *bottled water; physicochemical indicators; heavy metals; statistical analysis.*

1. INTRODUCTION

In recent years, the increase in the use of bottled water has brought to public attention important aspects related to the quality of this product [1]. Bottled water can be classified as natural mineral water, spring water, or bottled drinking water depending on where it comes from. Bottled water is treated by various physicochemical processes; including deionization, reverse osmosis, ozone production, and UV radiation [2]. Drinking water must be pure and free of any microorganisms (germs, parasites, bacteria, etc.) that could be harmful to human health due to their quantity or concentration [3]. Heavy metals [4], nitrates, and chlorides are among the dangerous and persistent contaminants present in water [2] because the polarity of water allows these contaminants to be absorbed and adsorbed [1,5,6]. Through direct

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consumption of food, inhalation, or contact with the skin, these chemicals can accumulate in the body and have major negative consequences on human health, including potential disorders of the neurological, reproductive, and cardiovascular systems, as well as various types of cancer [1].

When evaluating drinking water based on physical, chemical, and bacteriological variables as well as customer satisfaction, water quality concerns are often the most significant aspect [7]. Drinking water should be completely free of pathogens that could be harmful to human health and meet standards for physicochemical contaminants. In addition, the long-term sustainability of drinking water sources depends on users' perception of water quality [8,9]. Even if a source of drinking water does not have a negative impact on human health, consumer perceptions and aesthetic qualities should still be considered. The quality of bottled water from different sources can be evaluated using physicochemical parameters [7].

Both natural and man-made activities are responsible for the accumulation of heavy metals in water [10,11]. The crust of the planet naturally contains a large number of heavy metals. Throughout human history, exposure to heavy metals has resulted from weathering and decomposition of metallic rocks and ores, which can transmit metals to groundwater [12-14]. Metal concentrations in soil differ significantly between geographic locations [15]. The abundance of heavy metals in the environment is significantly affected by anthropogenic activity [16]. Heavy metals can enter the human body through several pathways once released into drinking water, including direct consumption, skin contact, inhalation, or ingestion [17]. Due to their special qualities, which include toxicity, low biodegradability, and bioaccumulation, heavy metals in water have the potential to seriously harm the ecological environment and, in turn, human health [18,19,10]. Certain heavy metals, which are both structural and catalytic components of proteins and enzymes, are harmful to human metabolism and may have negative consequences if their levels exceed acceptable limits [20]. Depending on the element and its chemical form, long-term exposure to heavy metals can damage the brain, liver, and bones, which can pose a major health risk [21].

2. MATERIALS SI METHODS

2.1. MATERIALS

For this research, 10 different brands of bottled water were purchased from supermarkets in Romania, in the period January-February 2024, and eight measurements were made for each brand (Fig. 1). The first stage of the research consisted of the determination of eight physicochemical indicators using electroanalytical methods shortly after the acquisition, for which no prior preparation of the samples was necessary. The second stage of the research counted on the determination of the content of heavy metals, using inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Fisher Scientific Inc., Waltham, MA, USA).

To measure pH, dissolved oxygen, total dissolved substances (TDS), conductivity, and salinity, the multiparameter WTW™ inoLab™ Multi 9430 - IDS™ (WTW™1FD47K, Fisher Scientific, Leicestershire, UK) was used. Free and total chlorine was measured using the HACH Pocket Colorimeter™ II filter photometer (HACH, Loveland, CO, USA), and turbidity was measured using the Mi 415 Turbidimeter (Milwaukee Instruments, Rocky Mount, NC, USA).

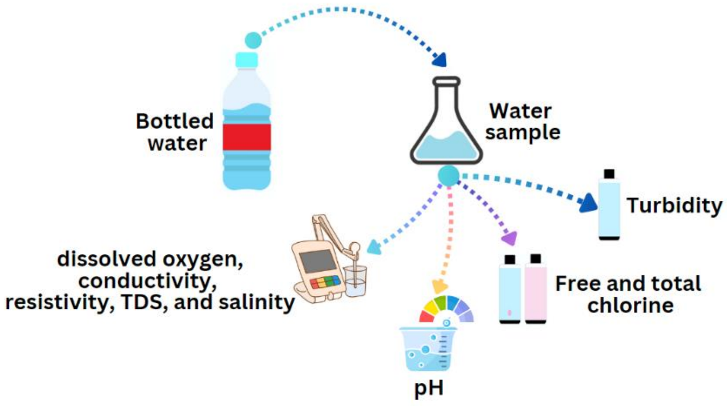

Figure 1. Schematic representation of the physicochemical parameters determined by electroanalytical methods.

2.2. PREPARATION OF SAMPLES FOR THE DETERMINATION OF HEAVY METAL CONTENT

The preparation of the samples consisted of the chemical digestion performed both at room temperature (30-40 min after the addition of the acids) and assisted by the TOP WAVE Digestor (Analytik Jena, Germany), according to the mineralization parameters presented in Table 1. The mineralization recipe consists of making a mixture of 15 mL sample, 7.5 mL hydrochloric acid, and 2.5 mL high-purity nitric acid (Merck, Germany). Mineralization was carried out in PM60 polytetrafluoroethylene (PTFE) tubes. After the assisted digestion was completed, the obtained samples were filtered into 25 mL volumetric flasks without being brought to the mark.

Table 1. The digestion parameters.

Steps	Temperature [°C]	Pressure [bar]	Power [%]	Ramp [min]	Time [min]
1	145	50	5	5	90
2	180	50	3	10	90
3	50	0	1	10	0
4	50	0	1	10	0
5	50	0	1	1	0

2.3. ANALYTICAL TECHNIQUES

Inductively coupled plasma mass spectrometry is a high-precision analytical technique that allows the identification of isotopes of chemical elements and the quantitative determination of the identified elements in the analyzed sample. Using an iCAP^{TM} Qc spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA), the concentrations of metals such as Cr, Mn, Fe, Ni, Co, Cu, Zn, Sr, and Pb were measured by inductively coupled plasma mass spectrometry (ICP-MS). Due to its high sensitivity, this method can detect metals at the ppb or ppt level (µg/kg or µg/L - ng/kg or ng/L) and can also analyze isotopes and perform multi-element analysis on a single sample. Applications range widely, from identifying water pollution to examining impurities in semiconductor materials or examining food, pharmaceuticals, etc. [22]. For performance evaluation, the standard material NIST SRM 1515 Apple leaves was used, and using blank solutions, the limit of detection (LOD) and quantification (LOQ) were calculated - the data obtained are presented in Table 2.

Table 2. Analytical performances of the ICP-MS method.

Elements	**SRM 1515 Apple Leaves (N=5) Average value ± SD [mg/kg]**		**LOD**	**LOQ**
	Certified values	**Measured values**	**[μg/L]**	
Cr	0.300 ± 0.000	0.311 ± 0.032	1.740	4.026
Mn	54.100 ± 1.100	56.700 ± 2.120	1.947	4.761
Fe	82.700±2.600	84.025±2.025	6.850	7.293
Ni	0.936 ± 0.094	0.906 ± 0.072	2.858	5.236
Co	0.09	0.084±0.009	4.160	7.078
Cu	5.690 ± 0.130	5.716 ± 0.237	2.089	3.918
Zn	12.450 ± 0.430	12.512 ± 0.685	9.959	12.609
Sr	25.100±1.1	24.966±1.229	3.526	5.166
Cd	0.013 ± 0.002	0.020 ± 0.009	0.770	1.587
Pb	0.470 ± 0.024	0.481 ± 0.085	7.132	8.373

2.4. DATA ANALYSIS

2.4.1. Statistical analysis

To investigate the relationship between the heavy metals identified in the analyzed water samples, but also to identify the existing correlations between the physicochemical parameters, specific statistical analyses were used, such as the principal component analysis method (PCA) and correlation methods through the Person indicator [23]. In addition, through cluster analysis and multiple regression, we will try to identify distinct groups of samples according to chemical characteristics and evaluate the relationship between heavy metal concentration and other chemical and physical variables (pH, water type, water source) [24]. Statistical processing and analysis were performed using the IBM SPSS Statistics for Windows, Version 26.0 statistical program. Armonk, NY: IBM Corp [25].

2.4.2. Health risk assessment

This chapter presents the equations and data that establish the estimated daily consumption of heavy metals following the consumption of bottled water, the daily intake of metals, and the health risk index [26]. To assess the health risk of heavy metals, the previously mentioned indices were calculated (equations (1), (2) and (3)):

- Estimated daily intake (EDI)

$$\mathrm{EDI} = \mathrm{C_{water}} \cdot \mathrm{I} \tag{1}$$

where C_{water} represents the metal content in water and I the average intake rate (2 L for adults, respectively 1.5 L for children under 12 years of age).

- Daily intake of metals (DIM)

$$\mathrm{DIM} = \frac{\mathrm{EDI}}{\mathrm{BM}} \tag{2}$$

where BM represents body mass (70 kg body mass for adults and 14 kg for children).

- Health risk index (HRI)

$$\mathrm{HRI} = \frac{\mathrm{DIM}}{\mathrm{RfD}} \tag{3}$$

where RfD represents the reference oral dose. The oral reference dose for each determined metal is: Cr(VI) – 3 µg/L/day; Mn – 140 µg/L/day; Ni – 20 µg/L/day; Cu – 40 µg/L/day; Zn – 300 µg/L/day; Cd – 1 µg/L/day; Pb – 35 µg/L/day [26]. Equation 4 shows the formula for calculating the risk index for each metal, based on equations (1)-(3).

$$\mathrm{HRI} = \frac{C_{water} \cdot I}{BM \cdot RfD} \tag{4}$$

3. RESULTS AND DISCUSSION

Drinking water should be free of taste, color, or odor and should be free of all chemicals and organisms that could be harmful to human health [27,28]. Due to the perception that bottled water is clean and safe, it is the fastest-growing food product in both developing and developed countries [29]. In this research, the physicochemical parameters of bottled water purchased from different supermarkets in Romania were examined, to identify any potential health risks related to the consumption of bottled water. Fig. 2 shows the extraction/collection and packaging areas of the ten bottled water samples.

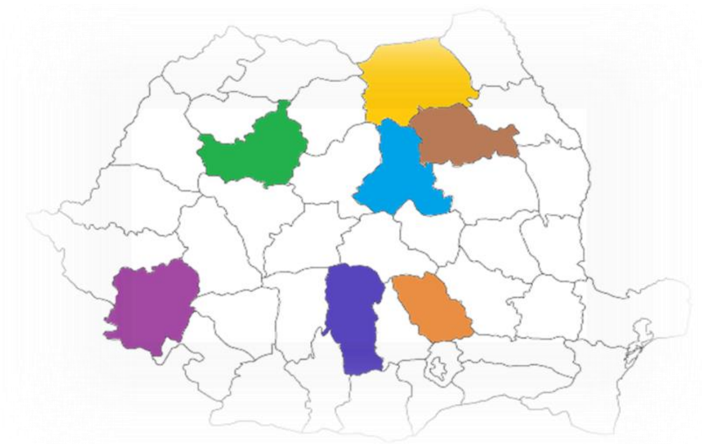

Figure 2. Highlighting the counties in Romania where water is extracted and bottled.

3.1. ANALYSIS OF THE PHYSICOCHEMICAL PARAMETERS IDENTIFIED IN BOTTLED WATER

From an organoleptic point of view, the taste and smell of bottled water must be pleasant, acceptable to consumers, and without abnormal changes - according to Law no. 458/2002, which, from a microbiological point of view, does not allow the presence of bacteria: *Escherichia coli*, *Enterococci* and *Pseudomonas aeruginosa* [30,31]. The objective of this study was to determine the quality of bottled water sold in Romania. Table 3 presents the minimum, maximum, and average values and variables for the 8 determined parameters.

Table 3. The maximum, minimum, average value, standard deviation, and variant of the physicochemical parameters.

Physicochemical parameters	Minimum	Maximum	Mean	Std. Deviation	Variance
pH	6.84	9.74	7.9961	0.55	0.31
TDS [mg/L]	170.00	694.00	431.40	161.16	25973.86
Conductivity [µS/cm]	170.00	695.00	430.02	160.58	25787.69
Dissolved oxygen [mg/L]	5.74	11.74	9.17	1.07	1.156
Salinity [‰]	0.00	0.50	0.08	0.08	0.07
Total chlorine [mg/L]	0.18	6.08	2.61	1.97	3.89
Free chlorine [mg/L]	0.08	7.75	2.54	2.35	5.54
Turbidity [FNU]	0.00	0.22	0.08	0.06	0.04

Anthropogenic activities, as well as environmental parameters (precipitation, UV radiation, temperature, etc.), affect pH levels, which can have a major impact on the capacity of ecosystems to support life [32]. Low flow, variety of organic matter, and decaying plants are other factors that contribute to changing pH values [33,34]. Table 4 shows the pH values measured in the ten bottled water samples and highlights the values that exceed the maximum limit allowed in Law 458/2002 (6.5–9.5) [30].

Table 4. pH measurements

Sample code	pH measurements							
	M1	**M2**	**M3**	**M4**	**M5**	**M6**	**M7**	**M8**
AI_1	8.27	8.22	8.27	8.27	8.24	8.22	8.15	8.07
AI_2	7.37	7.61	7.45	7.93	8.00	8.03	7.82	7.73
AI_3	7.52	7.66	7.56	7.75	7.68	7.82	7.60	7.55
AI_4	8.01	8.03	8.08	8.04	8.10	8.15	7.97	7.86
AI_5	8.13	7.99	7.55	8.04	7.79	8.03	7.80	7.97
AI_6	8.22	8.12	8.22	8.25	8.22	8.23	8.03	8.12
AI_7	7.35	7.62	7.55	7.75	7.73	7.79	7.45	6.84
AI_8	7.67	7.49	7.35	7.56	7.42	7.65	7.35	7.56
AI_9	7.87	7.82	7.97	7.80	8.22	8.01	8.12	7.79
AI_{10}	**9.67**	**9.67**	9.39	**9.72**	9.28	**9.74**	9.17	7.58

Dissociated, dissolved ionic compounds, and organic and inorganic salts are associated with high conductivity [34]. The conductivity determined at temperatures of 25°C recorded varied values (Table 5); sample AI_8 had the highest conductivity (695 µS/cm), while sample AI6 had the lowest values (170 µS/cm). However, none of the samples that were subjected to the determinations exceeded the drinking water quality limit of 2500 µS/cm established by Law no. 458/2002 [30].

Table 5. Conductivity measurements

Sample code	Conductivity measurements [µS/cm]							
	M1	**M2**	**M3**	**M4**	**M5**	**M6**	**M7**	**M8**
AI_1	348	335	325	304	335	348	335	318
AI_2	385	375	444	440	433	453	465	422
AI_3	600	598	590	593	594	596	597	593
AI_4	472	462	460	462	455	452	462	450
AI_5	349	349	292	346	324	345	348	283
AI_6	175	192	178	174	170	176	180	173
AI_7	647	651	672	648	675	650	650	670
AI_8	690	675	653	695	686	689	682	693
AI_9	341	340	328	337	348	335	339	318
AI_{10}	305	300	305	306	302	305	307	305

Total dissolved solids (TDS), also known as total dry residue, consists of dissolved organic matter and a range of inorganic salts such as sulfate, nitrate, bicarbonate (HCO^{3-}), sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^2)+ and potassium (K^+) as cations and dissolved organic matter as anions [35,36]. World Health Organization (WHO) regulations state that TDS levels in drinking water should not exceed 300-600 mg/L [37]. The ten bottled water samples have TDS values between 173 and 694 mg/L (Table 6).

Table 6. Total dissolved solids measurements

Sample code	TDS measurements [mg/L]							
	M1	**M2**	**M3**	**M4**	**M5**	**M6**	**M7**	**M8**
AI_1	347	335	325	304	318	346	335	321
AI_2	485	465	444	439	485	451	433	422
AI_3	598	597	590	592	595	596	594	597
AI_4	469	462	460	461	459	451	455	452
AI_5	350	348	292	345	305	344	324	282
AI_6	175	180	178	174	173	176	170	173
AI_7	647	650	672	647	643	684	675	653
AI_8	692	682	653	694	674	689	686	673
AI_9	339	339	328	336	340	335	348	319
AI_{10}	304	307	305	306	305	308	302	305

TDS in drinking water comes from natural sources, chemicals used in the water treatment process, as well as the nature of the pipes or hardware used to transport the water, i.e., plumbing can increase the amount of total dissolved solids [38,39]. In general, the total dissolved solids concentration is the sum of the cation (positively charged) and anion (negatively charged) ions in the water [40]. In this study, it was shown that there is a very strong correlation (R=0.705) between conductivity (Table 5) and total dissolved solids (Table 6). At the same time, an almost perfect correlation can be observed between conductivity and total dissolved solids (R=0.993) (Table 7).

Turbidity is produced by suspended, organic, and colloidal matter from sediments or soil, as well as by the presence of silt, plankton, $Fe(OH)_2$, $Al(OH)_3$, and bacteria [41,42]. The turbidity of the water samples (Table 8) varied between 0.00 FNU and 0.22 FNU and according to Law no. 458/2002 [30], the maximum allowed limit is ≤5 FNU, which means that all analyzed water samples are optimal for consumption.

Table 7. Pearson correlation

Physicochemical parameters	pH	TDS	Conductivity	Dissolved oxygen	Salinity	Total chlorine	Free chlorine	Turbidity
pH	1							
TDS	*-0.570*	1						
Conductivity	*-0.564*	**0.993**	1					
Dissolved oxygen	*-0.544*	0.240	0.221	1				
Salinity	-0.157	0.370	0.388	-0.043	1			
Total chlorine	**0.553**	-0.182	-0.175	-0.281	0.069	1		
Free chlorine	0.317	-0.061	-0.064	-0.140	-0.045	-0.096	1	
Turbidity	-0.171	-0.008	-0.015	0.253	0.077	0.086	-0.471	1

Table 8. Turbidity measurements

Sample code	Turbidity measurements [FNU]							
	M1	**M2**	**M3**	**M4**	**M5**	**M6**	**M7**	**M8**
AI_1	0.08	0.10	0.16	0.19	0.22	0.03	0.20	0.12
AI_2	0.10	0.10	0.20	0.10	0.20	0.10	0.20	0.10
AI_3	0.09	0.16	0.10	0.16	0.19	0.22	0.03	0.20
AI_4	0.10	0.10	0.10	0.00	0.10	0.00	0.10	0.00
AI_5	0.09	0.07	0.05	0.06	0.15	0.18	0.02	0.05
AI_6	0.09	0.05	0.02	0.18	0.15	0.06	0.07	0.04
AI_7	0.08	0.03	0.05	0.02	0.06	0.07	0.05	0.09
AI_8	0.08	0.04	0.01	0.06	0.09	0.02	0.01	0.00
AI_9	0.09	0.00	0.00	0.01	0.02	0.04	0.07	0.09
AI_{10}	0.09	0.03	0.01	0.02	0.00	0.00	0.01	0.05

In all analyzed samples, dissolved oxygen varied between 5.74 and 11.74 mg/L according to Table 9; Law no. 458/2002 (i.e. quality of drinking water) established the minimum allowed limit at 5 mg/L [30].

Table 9. Dissolved oxygen measurements

Sample code	O_2 measurements [mg/L]							
	M1	**M2**	**M3**	**M4**	**M5**	**M6**	**M7**	**M8**
AI_1	9.96	9.15	9.67	9.08	9.17	8.85	8.58	9.96
AI_2	11.74	10.39	11.17	10.33	8.80	9.55	10.83	11.69
AI_3	11.33	9.34	9.62	9.75	9.43	9.10	9.29	9.71
AI_4	9.90	9.27	9.16	9.04	9.12	9.05	9.75	9.82
AI_5	10.51	9.91	10.05	9.91	10.05	9.25	9.29	9.34
AI_6	7.41	7.32	8.24	8.42	8.14	8.06	7.48	7.95
AI_7	8.97	8.08	8.35	8.90	8.36	8.58	8.12	8.35
AI_8	10.10	9.23	9.13	9.43	9.37	9.15	9.32	9.28
AI_9	10.67	10.33	10.00	9.84	9.52	9.08	9.46	9.79
AI_{10}	5.74	7.81	6.75	8.33	6.86	7.71	8.03	8.50

As dissolved oxygen increases, the water is richer in organic matter and the possibility of pathogenic flora increases, indicating the biological and physical processes prevailing in the water. The value of dissolved oxygen is influenced by atmospheric pressure, air temperature, and the presence of microorganisms [43,44]. Both total chlorine and free chlorine can be found in the water, which indicates that the analyzed bottled water also has chlorine (Table 10) as a result of the treatment operations before bottling [45].

Table 10. Free and total chlorine measurements

Sample code	Free chlorine measurements [mg/L]							
	M1	**M2**	**M3**	**M4**	**M5**	**M6**	**M7**	**M8**
AI_1	0.54	0.34	0.62	0.75	0.43	0.10	0.29	0.71
AI_2	1.33	1.34	1.62	1.75	1.43	1.10	1.29	2.20
AI_3	0.61	0.67	0.60	0.61	0.59	0.51	0.55	0.52
AI_4	1.08	1.34	1.62	1.75	1.43	1.10	1.29	1.71
AI_5	0.47	0.50	0.08	0.09	0.43	0.46	0.75	0.37
AI_6	0.94	0.94	0.95	0.90	0.97	0.93	0.98	0.95
AI_7	0.28	0.28	0.23	0.27	0.25	0.28	0.26	0.28
AI_8	2.36	2.27	2.16	2.04	2.12	2.05	2.75	2.82
AI_9	0.32	0.28	0.37	0.48	0.35	0.39	0.18	0.32
AI_{10}	5.85	6.07	5.09	5.55	5.46	5.76	5.37	5.54
	Total chlorine measurements [mg/L]							
AI_1	5.77	5.34	5.62	5.75	5.43	5.10	5.29	5.71
AI_2	2.08	2.16	2.10	2.16	2.19	2.22	2.03	1.71
AI_3	3.41	3.32	3.24	3.42	3.14	3.06	3.48	3.95
AI_4	4.69	4.62	4.60	4.61	4.59	4.51	4.55	4.52
AI_5	0.91	0.85	0.72	0.47	0.55	0.84	0.76	0.53
AI_6	2.12	2.16	2.10	2.16	2.19	2.22	2.03	2.20
AI_7	2.16	2.10	2.16	2.19	2.22	2.03	2.20	2.12
AI_8	3.56	3.73	3.68	3.84	3.86	3.75	3.75	3.68
AI_9	7.40	7.34	7.62	7.75	7.43	7.10	7.29	7.71
AI_{10}	6.08	6.08	6.05	6.06	6.15	6.18	6.02	6.05

According to Law 458/2002 [30], free chlorine must have values ≥ 0.1 - ≤ 0.5 mg/L, and total chlorine has a value lower than 250 mg/L. In Table 10, the free chlorine values that fall within the limits allowed by the legislation in force are marked in green. Samples AI_5, AI_7 and AI_9 respect the maximum allowed values of free chlorine, for all measurements.

Table 11. Salinity measurements

Sample code	Salinity measurements [‰]							
	M1	**M2**	**M3**	**M4**	**M5**	**M6**	**M7**	**M8**
AI_1	0.10	0.10	0.00	0.10	0.10	0.10	0.00	0.10
AI_2	0.00	0.00	0.01	0.10	0.10	0.10	0.01	0.10
AI_3	0.20	0.20	0.01	0.20	0.10	0.20	0.01	0.20
AI_4	0.10	0.10	0.20	0.10	0.20	0.10	0.20	0.10
AI_5	0.10	0.10	0.00	0.10	0.00	0.10	0.00	0.00
AI_6	0.00	0.10	0.01	0.00	0.10	0.00	0.01	0.00
AI_7	0.20	0.20	0.01	0.20	0.10	0.20	0.01	0.50
AI_8	0.00	0.00	0.10	0.10	0.10	0.00	0.10	0.20
AI_9	0.10	0.10	0.02	0.10	0.00	0.10	0.02	0.10
AI_{10}	0.10	0.10	0.00	0.10	0.20	0.10	0.00	0.10

The salinity of the water samples varied between 0.00 and 0.50 ‰. According to Law no. 458/2002 [30], regarding the drinking water quality, the maximum allowed value is 2‰. Considering the salinity values, we can say that the analyzed water samples respect the allowed limits.

3.2. STATISTICAL ANALYSIS OF HEAVY METALS IN BOTTLED WATER

The statistics of the concentrations of heavy metals identified in the bottled waters from this analysis are presented in Table 13. Among the heavy metals (HMs) investigated, the highest average values detected were of Cr (535.7225 mg/L) followed by Pb (220.7193 mg/L), while the lowest mean concentration was observed for Cd (0.8044 mg/L). The coefficient of variation results showed that Sr showed the maximum variation followed by Pb, while the minimum variation was reported for Cd (Table 12).

Table 12. Statistics of the concentrations of various heavy metals

Heavy metals	Minimum	Maximum	Mean	Std. Deviation	Variance
Cr	492.2200	577.8638	535.722560	28.7505333	826.593
Mn	8.8666	128.6646	23.875440	37.0546017	1373.044
Fe	42.7267	178.8143	76.479520	38.7893286	1504.612
Co	18.2709	124.5196	84.390750	45.1921940	2042.334
Cu	3.6448	28.5432	9.398000	7.2679219	52.823
Zn	-.9779	147.9591	44.071170	68.3043859	4665.489
Sr	19.5554	443.5824	149.230380	163.5673230	26754.269
Cd	-0.0943	1.0022	0.080440	0.3262469	0.106
Pb	101.8440	281.9361	220.719370	82.1868295	6754.675

To identify groups of bottled water samples with similar characteristics, a cluster analysis was applied, using the K-means algorithm. This classification method allowed us to segment the samples into distinct groups based on chemical characteristics (heavy metal concentration). Thus, the analyzed samples can be grouped into two large main clusters, cluster I being formed by samples AI_7 and AI_2, and the second main cluster is divided into four secondary clusters depending on the concentration of heavy metals determined (Fig. 4).

Principal component analysis (PCA) orders variables according to the amount of variation they explain. Thus, two principal components with values greater than 1 were extracted by principal component analysis which explains 82.759% of the total variance of the 10 elements (Table 13).

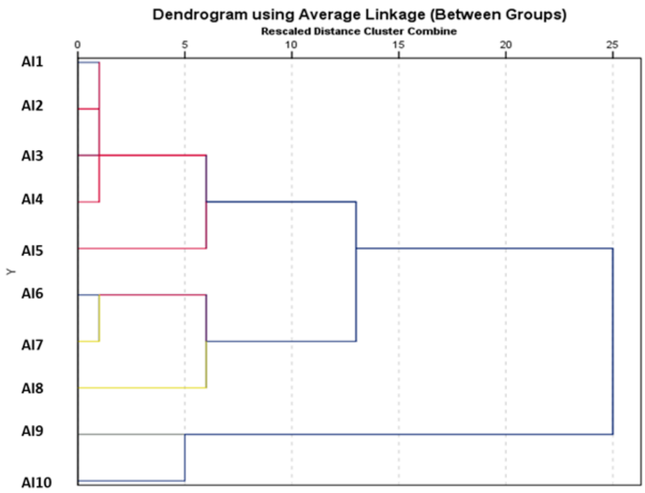

Figure 4. Cluster analysis of heavy metals from the identified samples

Table 13. Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	5.184	51.842	51.842	5.184	51.842	51.842	4.299	42.987	42.987
2	3.092	30.917	82.759	3.092	30.917	82.759	3.977	39.772	82.759
3	.835	8.348	91.107						
4	.560	5.596	96.704						
5	.222	2.224	98.928						
6	.074	.744	99.671						
7	.029	.286	99.957						
8	.004	.039	99.997						
9	.000	.003	100.000						
10	-1.028E-15	-1.028E-14	100.000						

Extraction Method: Principal Component Analysis.

The first PCA component with a variance value of 51.842% shows a strong loading for Fe (0.959), Mn (0.945), Cu (0.922), and Sr (0.734), while for the second PCA component, Fe (0.744), Co (0.984) and Pb (0.985) have strongly positive charges (Fig. 5).

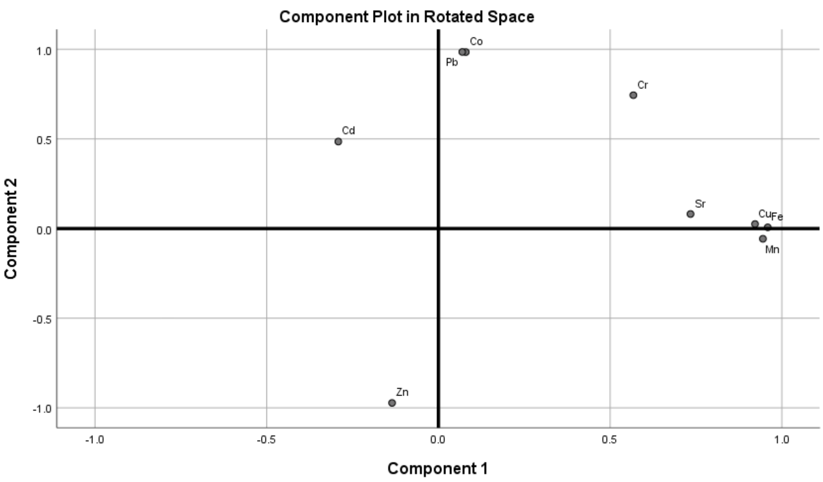

Figure 5. Component Plot in Rotated Space

The values of heavy metal concentrations in bottled water samples are influenced by a series of physicochemical quality indicators (e.g. pH, electrical conductivity, TDS, salinity, dissolved oxygen). The heavy metal content of the ten water samples is presented in Table 14. Chromium, manganese, copper, zinc, cadmium, and lead were determined. Zinc was not identified in samples AI_1, AI_5, and AI_6, while cadmium was determined in four samples (i.e., AI_1, AI_2, AI_4, and AI_5).

Table 14. The average concentration of metals in the analyzed bottled waters.

Sample code	Cr	Mn	Fe	Co	Cu	Zn	Sr	Cd	Pb
	[μg/L ± SD]								
AI_1	548.253 ±1.918	9.525 ±0.111	59.309 ±1.405	118.778 ±2.058	4.430 ±0.055	<LOD	32.265 ±0.368	1.002 ±0.020	281.936 ±0.566
AI_2	561.579 ±4.540	10.159 ±0.142	66.464 ±3.541	112.127 ±1.327	6.707 ±0.234	0.952 ±0.659	443.582 ±1.907	0.012 ±0.003	278.325 ±5.430
AI_3	534.911 ±2.662	8.867 ±0.129	86.081 ±2.364	113.143 ±0.857	6.851 ±0.121	2.594 ±0.452	221.499 ±1.553	<LOD	271.403 ±3.241
AI_4	563.406 ±2.375	9.091 ±0.084	59.697 ±5.238	124.519 ±0.922	12.909 ±0.612	0.839 ±0.266	40.559 ±1.256	0.024 ±0.002	281.341 ±1.783
AI_5	544.126 ±13.026	9.159 ±0.137	57.184 ±1.821	105.856 ±1.309	8.518 ±0.116	<LOD	25.122 ±0.186	0.042 ±0.002	267.067 ±5.152
AI_6	517.494 ±4.492	8.974 ±0.178	56.461 ±0.306	111.381 ±1.160	3.645 ±0.002	<LOD	19.555 ±0.226	<LOD	274.006 ±0.899
AI_7	577.864 ±5.115	128.665 ±0.308	178.814 ±1.004	99.202 ±1.793	28.543 ±0.810	8.965 ±0.398	396.934 ±4.418	<LOD	245.427 ±2.699
AI_8	521.211 ±2.770	18.437 ±0.110	92.718 ±0.679	20.780 ±0.127	8.399 ±0.197	147.959 ±0.449	230.076 ±28.709	<LOD	101.844 ±1.215
AI_9	496.163 ±5.093	17.876 ±0.333	65.340 ±0.319	19.850 ±0.079	4.575 ±0.119	138.909 ±1.987	46.160 ±1.006	<LOD	102.295 ±1.522
AI_{10}	492.220 ±1.719	18.004 ±0.162	42.727 ±0.976	18.271 ±0.126	9.403 ±0.171	141.896 ±0.613	36.550 ±0.186	<LOD	103.550 ±0.706

The minimum, mean, maximum, sum, and standard deviation values for the estimated daily intake (EDI) and daily metal consumption (DIM) following ingestion of heavy metals from the analyzed water samples for both children and adults are shown in Table 15.

Table 15. Values of estimated daily intake and daily consumption of heavy metals for children and adults

	Category	Descriptive Statistics	Heavy metal					
			Cr	Mn	Cu	Zn	Cd	Pb
EDI [μg/day]	Children	min	738.33	13.30	64.09	27.41	5.47	0.00
		max	866.80	193.00	268.22	186.78	42.81	221.94
		average	803.58	35.81	114.72	126.59	14.10	66.32
		median	809.28	14.76	93.78	162.93	11.44	2.66
		SD	43.13	55.58	58.18	67.79	10.90	102.30
	Adults	min	984.44	17.73	85.45	36.54	7.29	0.00
		max	1155.73	257.33	357.63	249.04	57.09	295.92
		average	1071.45	47.75	152.96	168.78	18.80	88.42
		median	1079.04	19.68	125.04	217.24	15.25	3.55
		SD	57.50	74.11	77.58	90.38	14.54	136.41
DIM [μg/(kg·day)]	Children	min	52.74	0.95	4.58	1.96	0.39	0.00
		max	61.91	13.79	19.16	13.34	3.06	15.85
		average	57.40	2.56	8.19	9.04	1.01	4.74
		median	57.81	1.05	6.70	11.64	0.82	0.19
		SD	3.08	3.97	4.16	4.84	0.78	7.31
	Adults	min	14.06	0.25	1.22	0.52	0.10	0.00
		max	16.51	3.68	5.11	3.56	0.82	4.23
		average	15.31	0.68	2.19	2.41	0.27	1.26
		median	15.41	0.28	1.79	3.10	0.22	0.05
		SD	0.82	1.06	1.11	1.29	0.21	1.95

Equation (1) established the estimated daily intake of heavy metals from the analyzed bottled water, and the minimum and maximum values determined for each metal are attributed to both children's and adults' consumption (Fig. 6). The daily intake of heavy metals is the ratio of the estimated daily intake to body weight, which for 10-year-old children is 14 kg and for 70-year-old adults is 70 kg.

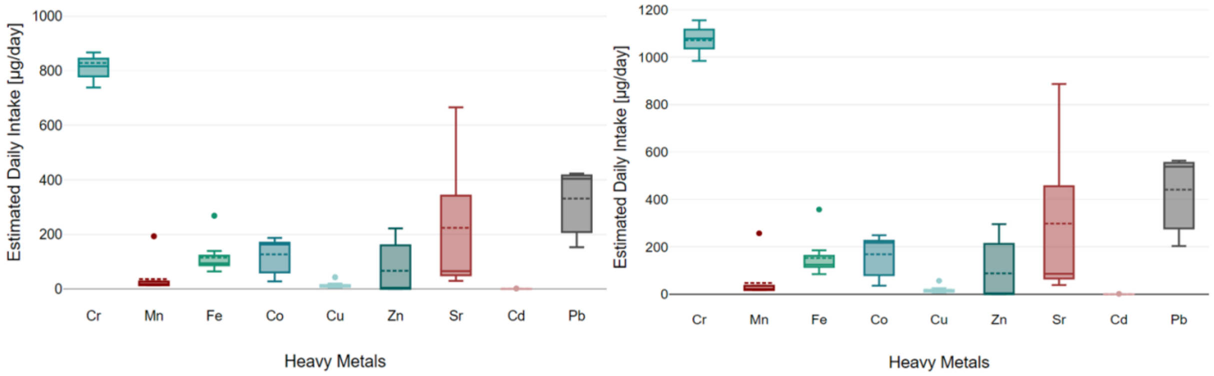

Figure 6. Box-plot representation of the estimated daily intake of six heavy metals from bottled water for children (left) and adults (right).

The minimum value of the amount of chromium that could be ingested by children with a water consumption of 1.5 L/day is 738.33 μg/day and the maximum value is 866.80 μg/day. In adults for a water consumption of 2 L/day, the minimum value of ingested chromium is 984.44 μg/day, and the maximum value is 1155.73 μg/day. For manganese, the estimated daily intake for children ranges from 13.30 to 193.00 μg/day, and for adults, it ranges from 17.73 to 257.33 μg/day. The minimum value of the amount of iron that can be ingested is 64.09 μg/day for children and 85.54 μg/day for adults, and the maximum value for children is 268.78 μg/day and 357.63 μg/day for adults. For cobalt, the estimated daily intake for children ranges from 27.41 to 186.78 μg/day, and for adults, it ranges from 36.54 to 249.04 μg/day. The estimated daily intake of copper for children is in the range of 5.47–42.81 μg/day, and for adults, it is in the range of 7.29–57.09 μg/day. For zinc, the estimated daily intake for children is in the range 0.00–221.94 μg/day, and for adults, it is in the range 0.00–295.92 μg/day. The minimum value of the amount of strontium that can be ingested is 29.33 μg/day for children and 39.11 μg/day for adults, and the maximum value for children is 665.37 μg/day and 887.16 μg/day for adults. The minimum and maximum intake of cadmium varied between 0.00-1.50 μg/day for children and 0.00-1.50 μg/day for adults. The estimated daily intake of lead for children is in the range of 152.77–422.90 μg/day, and for adults, it is in the range of 203.69–563.87 μg/day.

The daily intake of metals from bottled water was calculated for each metal and sample separately based on Equation (2). This index was established for both children and adults and is presented in Fig. 7. Daily metal intake was calculated for the six toxic metals identified in the bottled water samples. The minimum value of chromium for children is from 52.74 to 61.91 μg/(kg·day), and for adults the minimum value is 14.06 μg/(kg·day) and the maximum value is μg/(kg·day). For manganese, the daily intake for children varies between 0.95 and 13.79 μg/(kg·day), and for adults, it varies between 0.25 and 3,676 μg/(kg·day). The minimum and maximum iron intake varied between 4.58-19.16 μg/(kg·day) for children and 1.22-5.11 μg/(kg·day) for adults. The minimum value of cobalt for children is from 1.96 to 13.34 μg/(kg·day), and for adults the minimum value is 0.52 μg/(kg·day) and the maximum value is 3.56 μg/(kg·day). For children, the daily intake of copper varies between 0.39-3.06 μg/(kg·day), and for adults, the daily intake varies between 0.10 and 0.82 μg/(kg·day). For zinc, the estimated daily intake for children is in the range of 0.00–15.85 μg/(kg·day), and for adults, it is in the range of 0.00–4.23 μg/(kg·day).

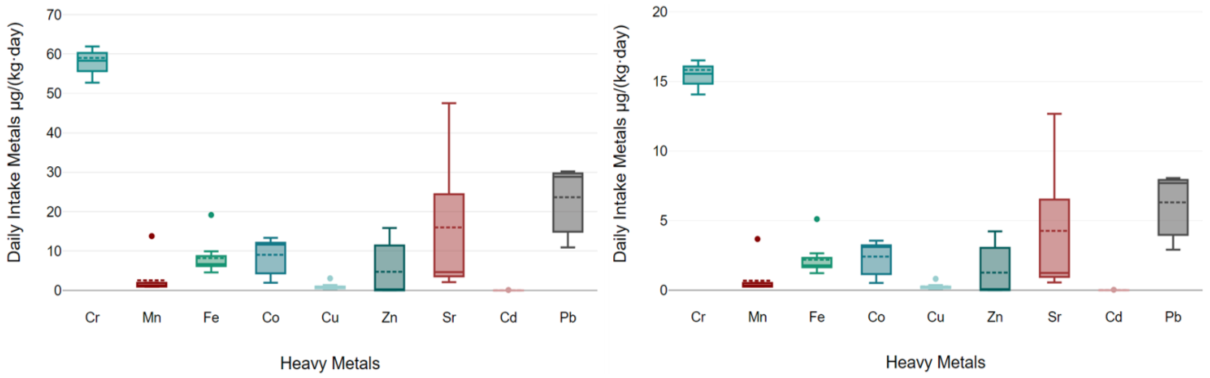

Figure 7. Box-plot representation of daily metal intake of six heavy metals from bottled water for children (left) and adults (right).

The estimated minimum value for strontium was 2.10 µg/(kg·day) for children and 0.56 µg/(kg·day) for adults, and the maximum value for children was 47.53 µg/(kg·day) for children, and 12.67 µg/(kg·day) for adults. The estimated daily intake of cadmium for children is in the range of 0.00–0.11 µg/(kg·day), and for adults, it is in the range of 0.00–0.03 µg/(kg·day). The minimum and maximum value of lead varied between 10.91-30.21 µg/(kg·day) for children and 2.91-8.06 µg/(kg·day) for adults.

Health Risk Index (HRI), in terms of the assessment of health risks induced by the consumption of contaminated food and/or drinking water, is presented in Fig. 8. It is used to estimate potential health effects that are a consequence of ingestion and to assess induced adverse effects.

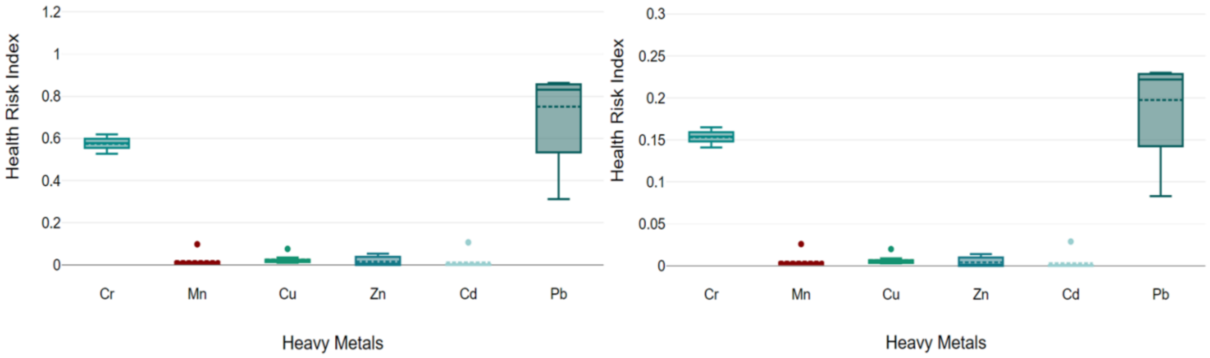

Figure 8. Box-plot representation of health risk index of six heavy metals from bottled water for children (left) and adults (right).

In this respect, when the HRI value is lower than 1 (Table 16), the ingested water does not have adverse effects on health. However, in this study, only the metals in bottled drinking water were considered, not the total content ingested daily; all samples exceed the maximum value for Cr if the RfD taken into account is the value for Cr(VI) (*i.e.*, 3 µg/L/day). If the RfD taken into account is 100 µg/L/day Cr(III) all the analyzed water samples are safe for consumption, both for adults and children.

Table 16. Health risk index values of six metals from bottled water samples.

Category	Sample code	Health risk index induced by HMs						
		Cr(VI)	**Cr(III)**	**Mn**	**Cu**	**Zn**	**Cd**	**Pb**
Children	AI_1	19.580	0.587	0.007	0.012	0.000	0.107	0.863
	AI_2	20.056	0.602	0.008	0.018	0.000	0.001	0.852
	AI_3	19.104	0.573	0.007	0.018	0.001	0.000	0.831
	AI_4	20.122	0.604	0.007	0.035	0.000	0.003	0.861
	AI_5	19.433	0.583	0.007	0.023	0.000	0.004	0.818
	AI_6	18.482	0.554	0.007	0.010	0.000	0.000	0.839
	AI_7	20.638	0.619	0.098	0.076	0.003	0.000	0.751
	AI_8	18.615	0.558	0.014	0.022	0.053	0.000	0.312
	AI_9	17.720	0.532	0.014	0.012	0.050	0.000	0.313
	AI_{10}	17.579	0.527	0.014	0.025	0.051	0.000	0.317
Adults	AI_1	5.221	0.157	0.002	0.003	0.000	0.029	0.230
	AI_2	5.348	0.160	0.002	0.005	0.000	0.000	0.227
	AI_3	5.094	0.153	0.002	0.005	0.000	0.000	0.222
	AI_4	5.366	0.161	0.002	0.009	0.000	0.001	0.230
	AI_5	5.182	0.155	0.002	0.006	0.000	0.001	0.218
	AI_6	4.929	0.148	0.002	0.003	0.000	0.000	0.224
	AI_7	5.503	0.165	0.026	0.020	0.001	0.000	0.200
	AI_8	4.964	0.149	0.004	0.006	0.014	0.000	0.083
	AI_9	4.725	0.142	0.004	0.003	0.013	0.000	0.084
	AI_{10}	4.688	0.141	0.004	0.007	0.014	0.000	0.085

4. CONCLUSIONS

The analysis of ten Romanian bottled drinking water of different brands provided valuable information on the overall quality and safety of these products. The comprehensive evaluation of the physicochemical parameters – including pH, total dissolved solids, turbidity, free chlorine, and total chlorine, but also conductivity – showed that most of the brands included in this study comply with the standards established by national and international regulations. At the same time, the methods used for repeated measurements ensured robust and consistent data, underscoring the reliability of the findings. On the other hand, statistical analysis, including Pearson correlations and principal component analysis, was essential in identifying significant relationships both between the physicochemical parameters and analyzed heavy metals. This helped to understand the dependencies between the physicochemical characteristics and the presence of heavy metals. While most bottled water brands have met safety standards, the detection of heavy metals in some samples raises concerns about potential health risks associated with long-term consumption. This emphasizes the importance of continuous monitoring and stricter enforcement of quality control measures to protect public health. In summary, this study highlights the critical role of comprehensive water testing methods in ensuring the safety and quality of bottled water. The results highlight the need for continuous monitoring, not only to ensure compliance with legal standards but also to protect consumers from potential contaminants such as heavy metals. Future research should focus on expanding the sample size and exploring the influence of external factors (such as storage conditions, packaging materials, and monitoring of extraction sources) on water quality.

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