ORIGINAL PAPER

ASSESSMENT OF SPRING AND WELL WATERS QUALITY INTENDED FOR HUMAN CONSUMPTION AND ASSOCIATED HEALTH RISKS

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Abstract. *The contamination of water sources intended for human consumption with heavy metals is a global concern due to their toxicity and potential carcinogenicity. In recent decades, research into heavy metal concentrations in major sources of drinking water, such as groundwater, spring water, and surface water, has increased in Romania, although most studies have been sporadic and limited in scope. In this study, 294 water samples were collected from 14 springs and wells in two regions of Romania. The quality of these waters, their level of contamination, and the associated health risks were then analysed. This research aims to evaluate the carcinogenic health risks primarily associated with chromium (Cr), nickel (Ni), cadmium (Cd), lead (Pb), cobalt (Co), manganese (Mn) and copper (Cu) in adults and children, depending on the ingestion pathway of these heavy metals in spring and well waters, or through dermal exposure when they are used for sanitation and hygiene purposes. The assessment of the risk to human health associated with consuming water contaminated with heavy metals indicated that, among the 14 sampling points from which water intended for human consumption was collected, some showed heavy metal concentrations exceeding the limits set by national legislation. Therefore, long-term consumption of this water may pose an increased risk to human health. This research found that exposure to chromium, nickel, and cadmium through ingesting water posed a carcinogenic health risk to both children and adults. Children were found to be more susceptible than adults. Regarding the potential carcinogenic risk associated with the aforementioned metals, the risk was highest in spring water, followed by well water.*

Keywords: *spring water; well water; heavy metal; health risk; ICP-MS; statistical analysis.*

1. INTRODUCTION

Romania stands out globally for its pure mountain spring water, naturally filtered and mineral-rich. While access to clean drinking water is a growing global concern, Romania remains a rare place where over 3,000 natural, mineral, and thermal springs still flow freely

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through pristine forests and mountains, many of which are known for their therapeutic properties [1]. Spring water usually comes from a clean area and is naturally filtered for drinking safety. It is sensitive to climate change and surface pollution. Rain or drought can change the mineral and microbial content of lowland or hillside spring waters, making the water less safe to drink [2]. On the other hand, spring water contains fewer minerals and offers no clear health benefits. Regulations for spring water under the European Drinking Water Directive are less strict regarding its source and physical and chemical consistency [3]. Still, springs must be safely tapped and monitored for years to ensure that any changes do not pose a risk to human health.

Groundwater is the reserve that supplies wells, which provide the local water source for rural communities and are vital for irrigation. Pollution of groundwater, and consequently well water contamination, presents a risk with slow but lasting effects: pollutants that infiltrate aquifers and remain there for years or decades, making them difficult to eliminate and expensive to treat. In Romania, vulnerability is greater in rural areas with shallow wells and incomplete sewage systems, as well as in old industrial zones or near landfills [4]. Last but not least, well water pollution is often linked to agricultural practices where fertilisation does not balance nutrient levels (i.e., diffuse pollution). Studies of water samples collected from rural wells in the Targoviste Plain in the Muntenia region of Romania confirm elevated levels of heavy metals and nitrates, as well as microbiological contamination [4-6]. These are correlated with proximity to agricultural sources and the absence of well protection zones. Contaminants can alter the biogeochemical balance of soil and affect hydraulically connected watercourses (e.g., springs and groundwater-fed sections of rivers). Once established, groundwater contamination spreads slowly, and remediation becomes a long-term process. Therefore, the effective approach is to prevent contamination at the source, en route, and at the destination.

Sources of water pollution can naturally contain ores rich in heavy metals, some of which are toxic and can dissolve into groundwater, leading to contamination [7,8]. Although these dissolved elements are natural components of water and are not typically considered pollutants, their presence at elevated concentrations can indicate contamination. Understanding their behavior and patterns can help interpret how pollutants form and spread. The main sources of ions in groundwater and spring water are the weathering and dissolution of rocks and the dissolution of rainwater. Some minerals, such as carbonates (e.g., chalk, limestone, and dolomite) and evaporite minerals (e.g., rock salt, halite, and gypsum), are soluble in water, while others, like silicates (e.g., quartz, feldspar, and clay minerals), are less soluble. Therefore, the water's composition reflects the drainage basin's geological environment and the duration of water-rock interaction [8,9]. Conversely, human activities are a source of pollution that can contaminate drinking water sources and alter ecosystems, biodiversity, and natural resources [10-12]. Altering the environment to meet societal needs can have serious consequences, including global warming, ecological degradation, and loss of biodiversity. It’s important to remember that the health impacts of water pollution, including contamination of wells and natural springs, remain a major cause of illness and death in developing countries [11,13]. Recent studies have examined this issue by analyzing the impact of water pollution on human health and considering disease variability [10-16]. The growing negative impact of water pollution on food safety increases the risk of cancer, especially in regions that are primarily food-producing [14-16].

In line with these findings, the first goal of this research was to examine the physicochemical properties and heavy metal contamination levels in several well and spring water samples collected from a well-known region of the Subcarpathian Mountains in central Romania (specifically, the counties of Dâmbovița and Prahova). Since the rural populations in these counties routinely use water from wells and natural springs for personal consumption,

the second goal was to assess the associated risks, with a focus on potentially carcinogenic heavy metals such as nickel (Ni), chromium (Cr), cadmium (Cd), and lead (Pb). It's worth noting that the locations where samples were taken are public, meaning tourists also use these sources for drinking or cooling off, which broadens the exposure range across different age groups—from children to adults and the elderly. Additionally, two main pathways of exposure are worth highlighting: ingestion and dermal contact. Thus, the third aim was to evaluate the risk of heavy metal exposure in the analyzed waters by considering factors such as age groups, metal concentrations, exposure pathways, whether the metals are carcinogenic, and whether exposure is regular or occasional. As with any comprehensive study, statistical analysis will accompany this work to validate the findings.

2. MATERIALS AND METHODS

2.1. SAMPLING AND SAMPLE PREPARATION

The present study was performed on waters intended for consumption collected daily for 3 weeks in June 2025, from 14 springs and wells (i.e., 9 spring and 5 wells) in the Subcarpathian Mountains region in central Romania (specifically, the Dâmbovița and Prahova counties, Fig. 1). Immediately after sampling, physicochemical indicators (i.e., pH, conductivity, salinity, turbidity, and dissolved oxygen) were determined using electroanalytical methods; for this research step, sample pretreatment was not required.

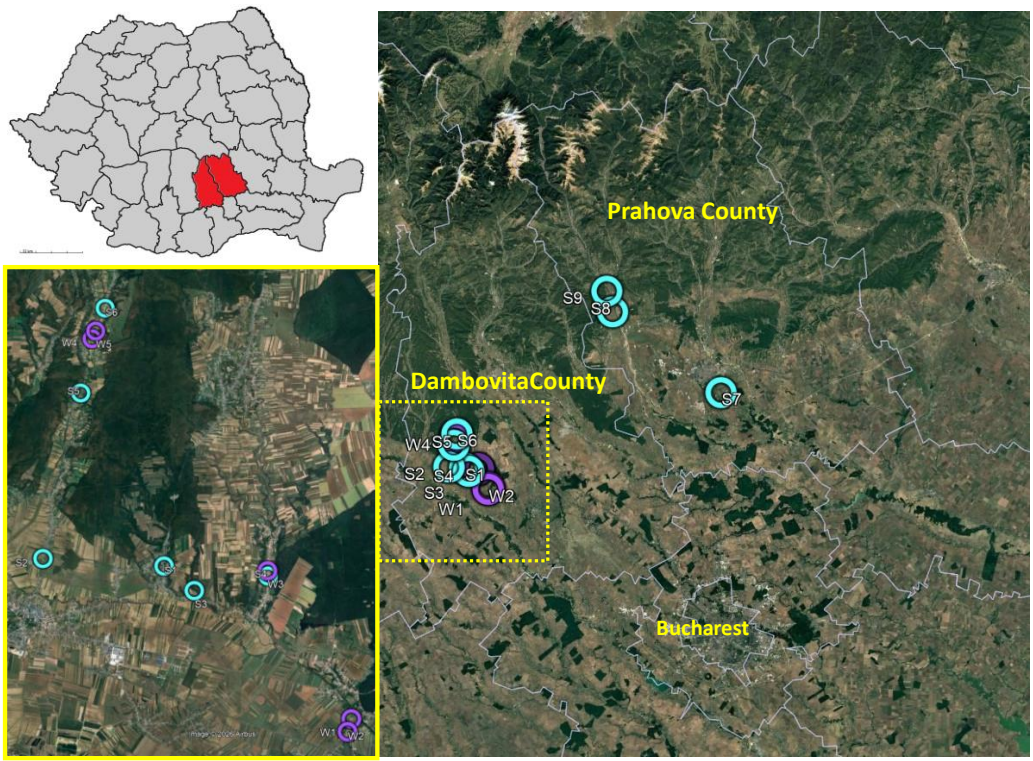

Figure 1. Sampling area: Dambovita and Prahova Counties (Romania). Blue circles represent the spring waters (coded from S1 to S9); purple circles represent the well waters (coded from W1 to W5).

The water samples were collected in accordance with the US EPA Guide (2016) [17]. The well/spring water samples were drawn using plastic bottles (1000 mL), which were first

washed with double-distilled water and then with the well/spring water. The bottle was then filled with a water sample, tightly sealed, and stored in an ice box at a temperature below 5°C. After that, the samples were acidified with nitric acid (pH < 2). The collection, preservation, and physicochemical analyses of the samples were conducted in accordance with the standard method for the examination of water and wastewater [18]. The physicochemical parameters studied, including pH, conductivity (EC), dissolved oxygen (DO), salinity, and turbidity, were determined as described by Eaton and Franson [18]. Samples were chemically digested in the TOPwave microwave digestion system (Analytik Jena, Jena, Germany) using the recipe and parameters shown in Table 1.

Table 1. Digestion recipe and method for water samples.

Mixture pre-digestion			Digestion parameters					Notes
Sample [mL]	HCl [mL]	HNO_3 [mL]	Temperature [°C]	Pressure [bar]	Ramp [min]	Time [min]	Power [%]	
15.0	7.5	2.5	145	50	5	5	90	25 mL flask; with filtration; without dilution
			80	50	3	10	90	
			50	0	1	10	0	
			50	0	1	10	0	
			50	0	1	1	0	

Similarly, 5 blank samples were prepared to determine the method's fundamental performance characteristics, namely the limits of detection (LOD) and quantification (LOQ) (Table 2).

Table 2. Limits of detection (LOD) and quantification (LOQ).

	Cr	Mn	Fe	Ni	Co	Cu	Zn	Cd	Pb
LOD	0.95± 0.05	2.07± 0.02	5.26± 0.13	2.72± 0.07	2.27± 0.09	2.48± 0.02	3.76± 0.05	0.45± 0.01	1.91± 0.02
LOQ	1.27± 0.10	2.73± 0.01	7.01± 0.16	3.48± 0.12	3.36± 0.11	3.13± 0.05	4.87± 0.08	0.63± 0.01	2.56± 0.05

2.2. ANALYTICAL METHODS

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

Inductively coupled plasma mass spectrometry (ICP-MS) was chosen to analyse the heavy metal concentrations, for which the iCAP™ Qc spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) was used. Calibration curves were obtained using a standard stock solution of ICP multi-element standard solution IV (Merck KGaA, Darmstadt, Germany), which was characterised by good linearity over the concentration range (i.e., 0.05 to 10.0 mg/L), with correlation coefficients (R^2) of 0.992–0.999. All chemical reagents used in this study were of high purity, HPLC grade. Milli-Q® Millipore ultrapure water (Merck KGaA, Darmstadt, Germany), with a resistivity of 18.2 MΩ · cm at 25°C, was used for dilution to avoid spectral interference.

3. DATA ANALYSIS

3.1. STATISTICAL ANALYSIS

Numerous methods and tools have been developed for statistical data analysis. In this respect, data analysis and identification/inference are vital components of statistical analysis and investigation [19,20]. IBM SPSS Statistics v. 26 was the statistical tool used in this research.

3.2. HEALTH RISK ASSESSMENT

3.2.1. Assessment of pollution level

In this study, four quality evaluation indices were calculated, including contamination factor CF_i (Equation 1), contamination degree *CD* (Equation 2), pollution load index *PLI* (Equation 3), and heavy metal evaluation index *HEI* (Equation 4) [21,22].

$$CF_i = \frac{C_i}{MAL_i} - 1 \tag{1}$$

$$CD = \sum_{i=1}^{n} CF_i \tag{2}$$

$$PLI = \sqrt[n]{\frac{C_1}{MAL_1} \times \frac{C_2}{MAL_2} \times \ldots \frac{C_n}{MAL_n}} \tag{3}$$

$$HEI = \sum_{i=1}^{n} \frac{C_i}{MAL_i} \tag{4}$$

where: CF_i - contamination factor of the metal "*i*"; C_i - concentration of the metal "*i*" (expressed as $mg \cdot L^{-1}$); MAL_i - maximum allowed limit of the metal "i" (expressed as $mg \cdot L^{-1}$) [23]; *CD* - contamination degree; *PLI* = pollution load index; *HEI* - heavy metal evaluation index.

The contamination level can be assessed following the ranges described in Table 3.

Table 3. Classification of drinking water according to the value of calculated indicators.

Classification	Reference Value / Range			
	CF_i	**CD**	**PLI**	**HEI**
Low level of pollution	$CF_i < 0$	$CD < 1$	$PLI < 2$	$HEI < 40$
Moderate level of pollution	$0 \leq CF_i < 2$	$1 \leq CD < 3$	$2 \leq PLI < 4$	$40 \leq HEI < 80$
High level of pollution	$2 \leq CF_i$	$3 \leq CD$	$4 \leq PLI$	$80 \leq HEI$

In 1996, Mohan et al. [24] proposed an index entitled heavy metal pollution index (HPI) calculated according to Equation (5):

$$HPI = \frac{\sum_{i=1}^{n} W_i \cdot Q_i}{\sum_{i=1}^{n} W_i} \quad (5)$$

where: W_i - the unit weight of the "*i*" analyzed metal, which is the inverse value of the maximum allowed limit established by national/international regulation; in this study, the MAL was taken from Romanian Law no. 458/2002 (Table 4). In this regard, the W_i has the following values: 0.020 for Cr and Mn, 0.005 for Fe, 0.050 for Ni, 0.010 for Cu, 0.0002 for Zn, 0.200 for Cd, and 0.100 for Pb, as well as $\sum_{i=1}^{n} W_i$ =0.405; Q_i - sub-index of the "*i*" analyzed metal; it is calculated as: $Q_i = \frac{C_i}{MAL_i} \times 100$, while in the equation proposed by Mohan et al., the term I_i – the desirable value, was involved, and we considered this term to be zero, because in the Romanian Law no. 458/2002, no ideal/desirable values are established [21]. The permissible or critical value of HPI for drinking water is 100 [24]. Also, Mohamed et al. [25] proposed the following standard rating of water quality: HPI < 50 signifies excellent quality; 50 ≤ HPI < 100 is good; 100 ≤ HPI < 200 is poor; 200 ≤ HPI < 300 is very poor quality, while HPI ≥ 300 means the sample is unfit for drinking water.

3.2.2. Assessment of human health risk

To establish the human health risk (for adults and children), a few indicators were calculated: estimated daily intake EDI_i (Equation 6), DIM_i (Equation 7), hazard quotient for non-cancer risks HI_i /HI_{nCR} (Equation 8), and potential cancer risks CR_i /CR (Equation 9):

$$EDI_i = C_i \times IR \quad (6)$$

$$DIM_i = \frac{C_i \cdot IR \cdot ED \cdot EF}{BW \cdot AT} \quad (7)$$

$$HI_i = \frac{DIM_i}{RfD_i}$$

$$HI_{nCR} = \sum_{i=1}^{n} HI_i \quad (8)$$

$$CR_i = DIM_i \cdot CSF_i$$

$$CR = \sum_{i=1}^{n} CR_i \quad (9)$$

where: EDI_i - estimated daily intake (expressed as mg·day^{-1}); C_i - concentration of the metal (expressed as mg·L^{-1}); *IR* - ingestion rate: for adults 2 L·day^{-1}, for children 1.5 L·day^{-1}; DIM_i - the chronic daily dose (expressed as mg·kg^{-1}·day^{-1}); *ED* - exposure duration: for adults 20 years; for children 6 years; *EF* - exposure frequency: for adults and children 365 days·year^{-1}; *BW* - body weight: for adults, 70 kg; for children, 14 kg; *AT* - average time: for adults 7300 days, for children 2190 days; HI_i - hazard quotient for non-cancer risks induced by each analyzed metal; HI_{nCR} - hazard quotient for non-cancer risks induced by water consumption; RfD_i - oral reference dose: Cr 0.003 mg·kg^{-1}·day^{-1}; Mn 0.014 mg·kg^{-1}·day^{-1}; Fe 0.7 mg·kg^{-1}·day^{-1}; Ni 0.02 mg·kg^{-1}·day^{-1}; Co 3 mg·kg^{-1}·day^{-1}; Cu 0.04 mg·kg^{-1}·day^{-1}; Zn 0.3 mg·kg^{-1}·day^{-1}; Cd 0.001 mg·kg^{-1}·day^{-1}; Pb 0.0014 mg·kg^{-1}·day^{-1}; CR_i - potential cancer risks

induced by each analyzed metal; CSF_i - cancer slope factor: Cr 0.5 mg^{-1}·kg·day; Ni 0.91 mg^{-1}·kg·day; Cd 6.3 mg^{-1}·kg·day; Pb 0.0085 mg^{-1}·kg·day; *CR* - potential cancer risks induced by water consumption.

4. RESULTS AND DISCUSSION

The physicochemical properties of the water samples are shown in Figs 2 and 3. The pH of well water ranged from 6.99 (W1) to 7.19 (W4), indicating a neutral to weakly alkaline medium (Fig. 2). In comparison, the pH of spring water ranged from 7.61 (S2) to 8.03 (S5), indicating moderate alkalinity. Dissolved oxygen levels in well water ranged from 5.91–7.22 $mg·L^{-1}$ (W4–W5), while spring water ranged from 5.20–9.70 $mg·L^{-1}$ (S3–S9) (Fig. 2).

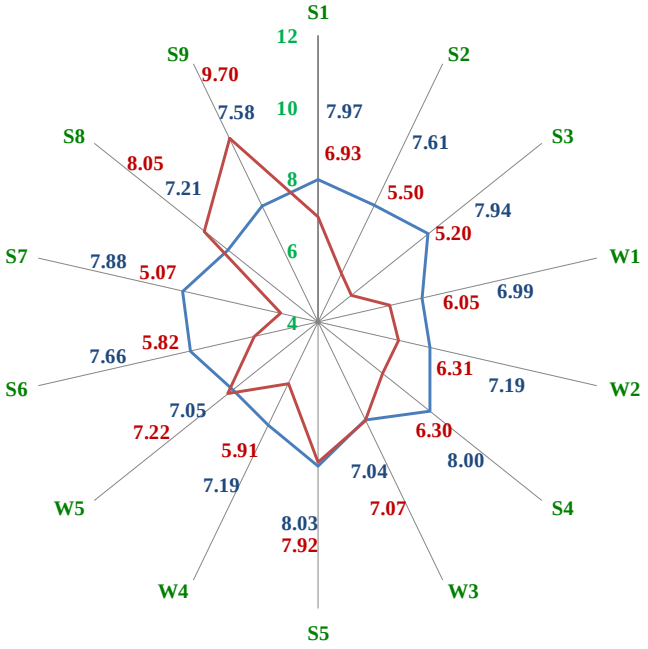

Figure 2. The obtained data for pH (blue line and values) and dissolved oxygen [mg/L] (red line and values) on the analyzed water samples.

Electrical conductivity (EC) is the ability of water to conduct an electric current and depends on the concentration of total dissolved solids (TDS). In this study, the EC ranged from 1334.45 µS·cm^{-1} (S4) to 2364.70 µS·cm^{-1} (S8). As is well known, salinity is considered a measure of all dissolved salts in water. If salty water is used for irrigation, salt may move from plant roots back into the soil, leading to plant dehydration. According to the data, high salinity of 0.5 ‰ was detected in well water samples (i.e., W11, W2, and W4, W5, except W3), followed by spring water S3, S7, and S9 (0.2‰**)** and S1, S3, S4, S5, and S6 (0.1‰**)**. These findings on EC and salinity provide important context for understanding the physicochemical properties of the water samples.

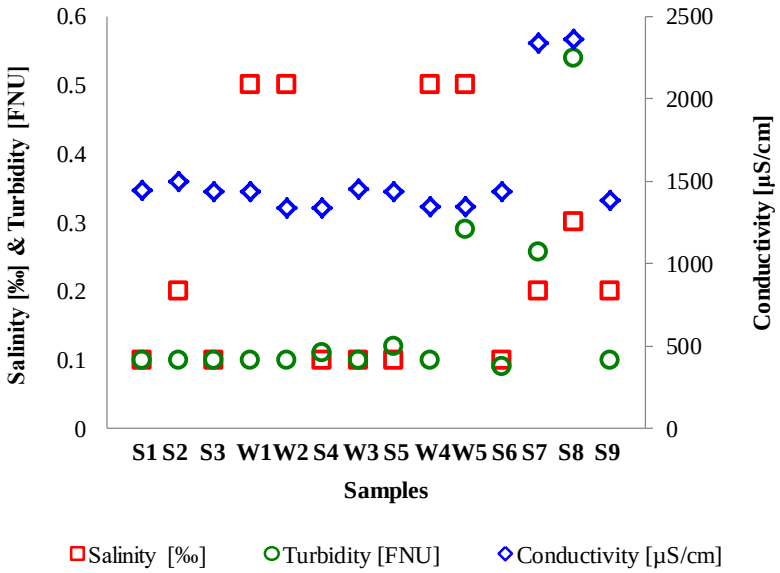

Figure 3. Salinity [‰] (red squares); turbidity [FNU] (green circles); conductivity [µS·cm^{-1}] (blue rhombuses). Note: The turbidity values for S7 and S8 were divided by 10 due to the high values (i.e., 2.57 FNU and 5.40 FNU, respectively).

Table 4 shows the average concentrations and standard deviations (SD) of heavy metals in the well and spring water samples. All findings on heavy metal concentrations in the study area are compared with the maximum allowable limits (MAL) established by Romanian Law no. 458/2002 [23].

Table 4 shows that samples exceeding the allowable limit are more frequently found in spring water intended for drinking. This is because the standards for drinking water are stricter than those for other uses, such as sanitation, hygiene, and other domestic purposes. In this regard, several exceedances were noted for manganese (S3, S4, and S7), cadmium (S1, S3, and S6), lead (S1), and nickel (S8 and S8). Regarding nickel, it is well to highlight that it is a metal found in the human body at low levels (1.2–4.6 µg·L^{-1} in the bloodstream), making its presence easy to overlook. When blood levels exceed 4.6 µg·L^{-1}, nickel poisoning can occur, which may cause health issues such as heart attacks, lung tissue problems, the development of malignant tumours, and disorders of the kidneys, nasal cavity, and throat. While nickel occurs naturally in groundwater at levels up to 0.02 mg·L^{-1}, higher concentrations in water may result from outdated infrastructure, potentially increasing the risk of poisoning [10,26-28]. Changes in nickel levels can have immediate effects, as both deficiency and excess are harmful. When combined with cobalt, nickel can help prevent bloating and improve digestion. Nickel also helps lower blood pressure, reduce nervousness, and improve iron absorption. Ni deficiency is associated with iron deficiency and anaemia. Furthermore, nickel supports tissue integrity by stabilising the DNA helix [29]. The highest Ni concentration in the water samples exceeded the Romanian legislation limit (20 µg·L^{-1}, Table 4), with values of 31.911 ± 2.460 µg·L^{-1} and 36.021 ± 2.113 µg·L^{-1} for S8 and S9, respectively. All the other springs and well water showed nickel concentrations within the limits permitted by Romanian legislation (Table 4). On the other hand, manganese shares a common origin with iron and is often found together in groundwater, with Mn concentrations up to 2 mg·L^{-1}. In stagnant water, manganese oxidises, but after ingestion, it is reduced again in the intestine. As an essential trace element, manganese functions as a coenzyme in several biological processes, including macronutrient metabolism, bone health maintenance, defence against free radicals, ammonia clearance, and neurotransmitter synthesis. It also has hypoglycaemic effects and acts as a lipotropic factor. Although prolonged exposure to high

manganese levels can cause neurological damage, deficiency is extremely rare [30]. Compared with the limit established by Romanian law [23], Mn exceeded the maximum in only one well-water sample (W4). This information significantly contributes to the analysis of water quality when the sampling area is taken into consideration.

Table 4. Average values (±standard deviation) of analyzed metals, expressed as μg·L^{-1}, compared to the maximum allowed limits (MAL) established by Romanian Law no. 458/2002 [23].

	Metals [μg·L^{-1}]								
	Cr	**Mn**	**Fe**	**Ni**	**Co**	**Cu**	**Zn**	**Cd**	**Pb**
S1	35.483± 1.775	34.367± 0.666	208.072± 3.248	10.412± 0.800	12.477± 0.415	11.263± 0.126	17.525± 0.541	6.649± 0.169	10.476± 0.996
S2	36.215± 1.441	25.592± 0.659	81.698± 1.607	6.376± 0.066	11.015± 1.528	31.364± 0.244	20.398± 0.882	2.046± 0.028	9.141± 0.603
S3	38.700± 2.542	76.342± 2.337	132.502± 1.025	3.733± 0.099	11.668± 1.125	14.272± 0.242	23.192± 1.011	7.688± 0.104	9.496± 0.640
W1	39.251± 2.295	8.955± 0.223	112.118± 1.357	4.985± 0.770	12.066± 1.525	14.376± 0.260	192.774± 4.960	4.936± 0.052	9.300± 0.883
W2	38.588± 2.581	37.779± 0.329	96.758± 7.069	1.539± 0.252	10.813± 1.657	17.468± 0.306	19.376± 0.699	2.794± 0.023	9.262± 0.726
S4	38.662± 2.508	68.305± 1.356	95.267± 2.029	8.042± 0.711	11.015± 0.567	21.701± 0.415	15.896± 0.380	5.556± 0.117	9.226± 0.928
W3	37.960± 3.037	6.509± 0.147	97.168± 1.077	8.265± 0.433	11.814± 1.595	9.017± 0.154	6.945± 0.487	3.838± 0.064	9.890± 0.927
S5	37.667± 2.012	24.595± 0.287	110.332± 3.763	9.385± 0.754	11.387± 0.837	8.221± 0.132	6.273± 0.491	3.065± 0.044	9.510± 0.928
W4	39.485± 2.536	32.407± 0.177	113.696± 2.883	7.534± 0.508	13.296± 1.113	16.795± 0.056	2.204± 0.208	3.016± 0.104	9.301± 0.842
W5	37.930± 3.324	197.717± 2.752	284.171± 2.826	9.095± 0.244	11.570± 0.213	26.746± 0.227	18.804± 0.196	4.854± 0.078	9.443± 0.648
S6	38.229± 2.383	5.289± 0.155	88.798± 0.979	9.090± 0.427	12.040± 0.678	11.285± 0.174	39.887± 0.922	13.925± 1.281	9.945± 0.433
S7	38.500± 2.720	130.460± 1.300	437.459± 7.462	9.198± 0.301	11.775± 0.305	12.496± 0.269	37.919± 0.996	3.827± 0.112	9.302± 0.238
S8	34.109± 2.536	18.890± 0.369	366.184± 5.049	31.911± 2.460	2.892± 0.151	24.320± 0.300	280.356± 4.004	2.468± 0.038	3.722± 0.038
S9	34.831± 2.171	8.868± 0.336	93.751± 1.472	36.021± 2.113	2.293± 0.154	12.479± 0.148	118.309± 1.316	1.960± 0.045	3.599± 0.045
MAL	50	50	200	20	NA	100	5000	5	10

NA – not available data; MAL - maximum allowed limits established by Romanian Law No. 458/2002 [23].

Chromium (Cr), a transition metal, exists in the environment as Cr(III) or Cr(VI). In water, chromium mainly originates from rock weathering, precipitation, and, most abundantly, industrial sources [31]. The two forms differ significantly in distribution, mobility, and toxicity. Cr(III) is essential for insulin regulation and carbohydrate metabolism. It helps maintain normal glucose metabolism, but can be toxic and carcinogenic in high quantities. Cr(VI) is mainly of anthropogenic origin. It is toxic and carcinogenic by inhalation and has no nutritional value. The adequate intake of chromium is 35 μg·day^{-1} for young men and 25 μg·day^{-1} for young women. According to the World Health Organisation's Guidelines

for Drinking Water Quality (2017), the permissible level of chromium in drinking water is 0.05 mg/L [32]. This same limit is also set by European and Romanian regulations [23]. Even though the level of chromium does not exceed the allowed limits of Romanian regulation (Table 3), the values around 37-39 $\mu g \cdot L^{-1}$ in all well water samples are close to the recommended dietary intake and may contribute significantly to total chromium exposure, raising concerns about potential long-term health effects.

Table 5. The obtained results for the quality evaluation indices: contamination factor CF_i, contamination degree CD, pollution load index PLI, and heavy metal evaluation index HEI.

Sample code	CF_i								CD	PLI	HEI
	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb			
S1	-0.290	-0.313	0.040	-0.479	-0.887	-0.996	0.330	0.048	-2.548	0.331	5.452
S2	-0.276	-0.488	-0.592	-0.681	-0.686	-0.996	-0.591	-0.086	-4.395	0.263	3.605
S3	-0.226	0.527	-0.337	-0.813	-0.857	-0.995	0.538	-0.050	-2.216	0.330	5.784
W1	-0.215	-0.821	-0.439	-0.751	-0.856	-0.961	-0.013	-0.070	-4.127	0.316	3.873
W2	-0.228	-0.244	-0.516	-0.923	-0.825	-0.996	-0.441	-0.074	-4.248	0.229	3.752
S4	-0.227	0.366	-0.524	-0.598	-0.783	-0.997	0.111	-0.077	-2.728	0.331	5.272
W3	-0.241	-0.870	-0.514	-0.587	-0.910	-0.999	-0.232	-0.011	-4.363	0.193	3.637
S5	-0.247	-0.508	-0.448	-0.531	-0.918	-0.999	-0.387	-0.049	-4.086	0.221	3.914
W4	-0.210	-0.352	-0.432	-0.623	-0.832	-1.000	-0.397	-0.070	-3.915	0.215	4.085
W5	-0.241	2.954	0.421	-0.545	-0.733	-0.996	-0.029	-0.056	+0.775	0.453	8.775
S6	-0.235	-0.894	-0.556	-0.545	-0.887	-0.992	1.785	-0.006	-2.331	0.283	5.669
S7	-0.230	1.609	1.187	-0.540	-0.875	-0.992	-0.235	-0.070	-0.145	0.438	7.855
S8	-0.318	-0.622	0.831	0.596	-0.757	-0.944	-0.506	-0.628	-2.349	0.457	5.651
S9	-0.303	-0.823	-0.531	0.801	-0.875	-0.976	-0.608	-0.640	-3.956	0.285	4.044

Based on data presented in Table 3, the obtained results shown in Table 5 allow us to classify the analyzed water samples as moderate (i.e., S1, S3, S4, S6, S7, S8, and S9) or low-polluted (other than samples mentioned before: S2 and W1-W5), according to CF_i values. It should be noted that the moderate contamination of spring waters can be explained by the water's ability to self-purify through stagnation, as is the case with well waters. Depending on CD, PLI, and HEI values, all groundwater samples are classified as low-polluted waters (CD < 1, PLI < 2, and HEI < 40, according to Table 3). These data confirm the links between the parameters used for pollution assessment and the contribution of each identified metal to the assessment of the quality of water for human consumption.

Table 6. The heavy metal pollution index (HPI) for the analyzed drinking waters and the deviation from the mean value.

Sample code	$Q_i \times W_i$								HPI	+/- deviation from mean HPI [%]
	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb		
S1	1.419	1.375	0.520	0.260	0.056	0.002	0.665	0.524	11.904	-5.91
S2	1.449	1.024	0.204	0.159	0.157	0.002	0.205	0.457	9.028	-28.64
S3	1.548	3.054	0.331	0.093	0.071	0.002	0.769	0.475	15.663	+23.80
W1	1.570	0.358	0.280	0.125	0.072	0.019	0.494	0.465	8.353	-33.98
W2	1.544	1.511	0.242	0.038	0.087	0.002	0.279	0.463	10.289	-18.68
S4	1.546	2.732	0.238	0.201	0.109	0.002	0.556	0.461	14.432	+14.07
W3	1.518	0.260	0.243	0.207	0.045	0.001	0.384	0.495	7.784	-38.48
S5	1.507	0.984	0.276	0.235	0.041	0.001	0.307	0.475	9.444	-25.36
W4	1.579	1.296	0.284	0.188	0.084	0.000	0.302	0.465	10.368	-18.05
W5	1.517	7.909	0.710	0.227	0.134	0.002	0.485	0.472	28.288	+123.60
S6	1.529	0.212	0.222	0.227	0.056	0.004	1.393	0.497	10.223	-19.20
S7	1.540	5.218	1.094	0.230	0.062	0.004	0.383	0.465	22.213	+75.57
S8	1.364	0.756	0.915	0.798	0.122	0.028	0.247	0.186	10.903	-13.82
S9	1.393	0.355	0.234	0.901	0.062	0.012	0.196	0.180	8.230	-34.95
mean HPI									**12.651**	

The order of groundwater samples in terms of CD and HEI values was S2 < W3 < W2 < W1 < S5 < S9 < W4 < S4 < S1 < S8 < S6 < S3 < S7 < W5 in the ranges of –4.395–+0.775 and 3.605–8.775, respectively. Similarly, for the obtained PLI values, the order is W3 < W4 < S5 < W2 < S2 < S6 < S9 < W1 < S3 < S4 < S1 < S7 < W5 < S8, with an average of 0.310 and a range of 0.193–0.457.

According to the HPI value, five levels of water quality were established: excellent (0÷25), good (26÷50), low (51÷75), poor (76÷100), and improper /not recommended (>100) [33]. Thus, the obtained results (Table 6) can classify all analyzed samples as excellent water, except W5, which is of good quality.

Regarding the assessment of the impact on human health, indicators such as EDI and DIM were calculated, necessary items to establish the main indicators, hazard quotient for non-cancer risks (abbreviated HI, data shown in Fig. 4), and potential cancer risks (abbreviated as CR, results are presented in Fig. 5), respectively.

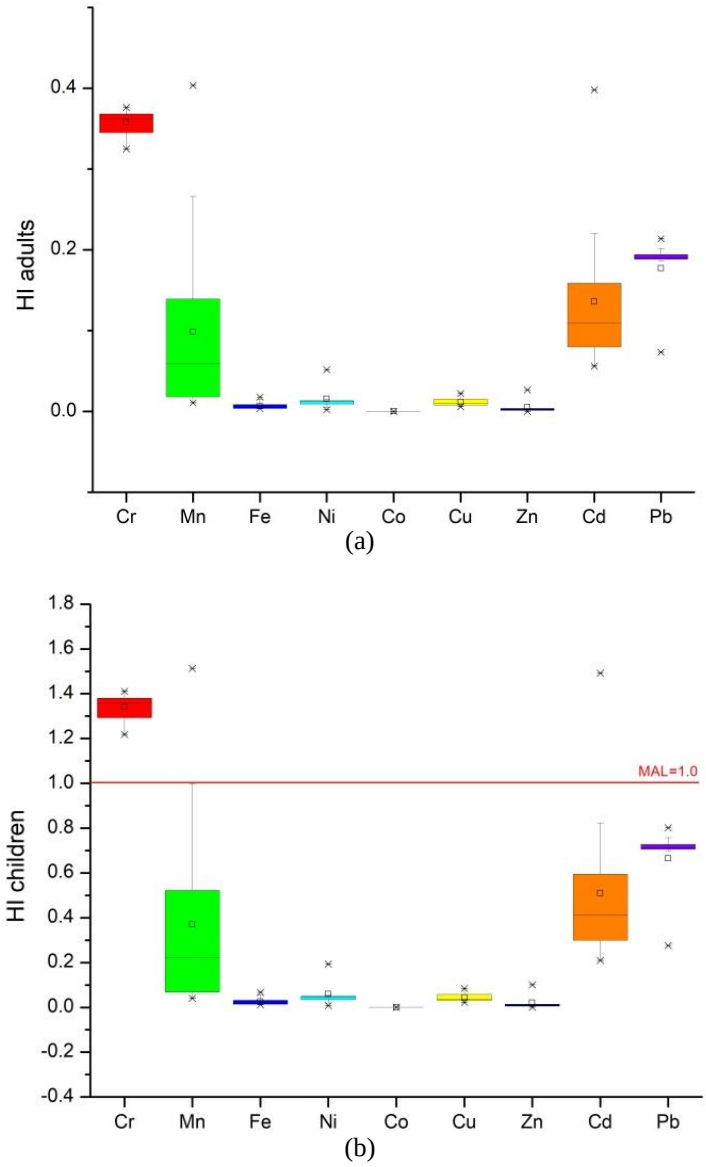

Figure 4. The hazard quotient for non-cancer risks induced by each analyzed metal for adults (a) and children (b). The maximum allowed level of HI_i is 1.0 – marked with a red line (b).

Fig. 4 shows the hazard quotient for non-cancer risk from metal content in adults and children. It should be noted that the values for adults are lower than those for children, with a

fixed value of 3.750, representing the ratio of exposure duration to body weight for each category. What is worrying in Fig. 4b is that all studied samples recorded HI values for Cr above the threshold established by regulatory organizations (i.e., value 1.0, marked with a red line).

The potential cancer risk can be interpreted as the probability of a human developing cancer; this indicator has a recommended value ($\leq 1.0 \cdot 10^{-6}$) and an acceptable range of $1.0 \cdot 10^{-6} \leq CR < 1.0 \cdot 10^{-4}$ (it is marked with red line in Fig. 5). Those values can be translated as the probability of one person in a million and one person in ten thousand to develop cancer in a lifetime. The obtained CR data for adults and children are shown in Fig. 5.

For all analyzed samples, the results are concerning because they exceed the acceptable range for the potential carcinogenic risk associated with the levels of Cr, Ni, and Cd in both age categories (i.e., adults and children). Even in the case of CR induced by Pb content, the values are close to the recommended value of $1.0 \cdot 10^{-6}$, with ranges of $8.740 \cdot 10^{-7}$–$2.544 \cdot 10^{-6}$ for adults and $3.278 \cdot 10^{-6}$–$9.541 \cdot 10^{-6}$ for children, respectively.

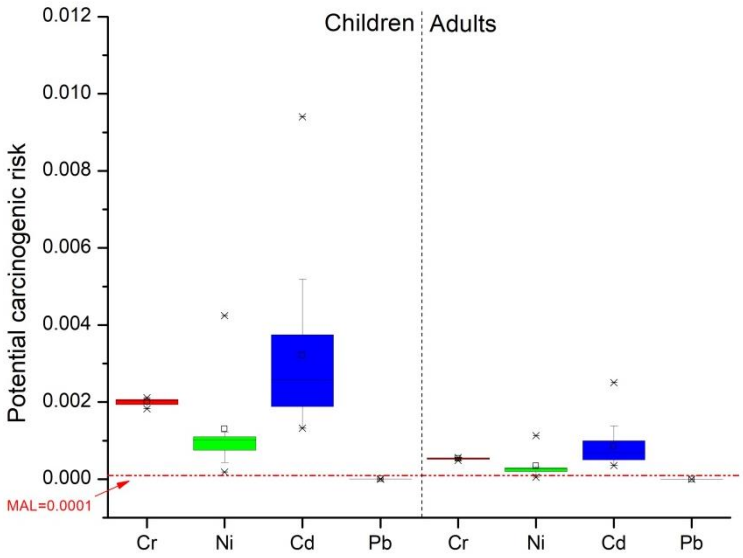

Figure 5. Potential cancer risks induced by each analyzed metal for children and adults; the maximum allowed level of CR_i is 1×10^{-4} – marked with a red line.

The final part of the study was dedicated to the statistical analysis of the main data (physicochemical indicators and metals). The principal component analysis (Fig. 6) shows the similarities between parameters, as follows: Fe-turbidity-conductivity (p=0.783-0.842), Cr-Pb (p=0.700), Ni-dissolved oxygen (p=0.793). This analysis used the correlation matrix to generate Fig. 7 via conditional formatting. This technique provides a scientific way to simplify data into green or red, indicating positive or negative correlations between the analyzed parameters. In this regard, strong positive correlations (p > 0.5, green boxes) were observed: conductivity-turbidity (p=0.783), conductivity-Fe (p=0.842), conductivity-Zn (p=0.534), turbidity-Fe (p=0.805), turbidity-Ni (p=0.511), turbidity-Zn (p=0.0.635), dissolved oxygen-Ni (p=0.793), Cr-Pb (p=0.700), Mn-Fe (p=0.571), Ni-Zn (p=0.634), as well as, strong negative correlations (p < –0.5, red boxes): salinity-pH (p=–0.754), turbidity-Pb (p=–0.544), dissolved oxygen-Cr (p=–0.660), dissolved oxygen-Cr (p=–0.694), Cr-Ni (p=–0.798), Ni-Pb (p=–-0.934), Zn-Pb (p=–0.727). The intermediary values (i.e., yellow and orange boxes)

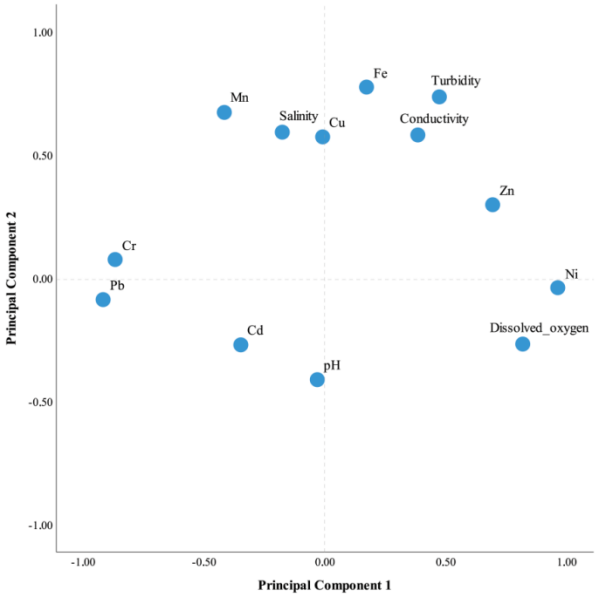

Figure 6. Principal component analysis based on physicochemical indicators and analyzed metals.

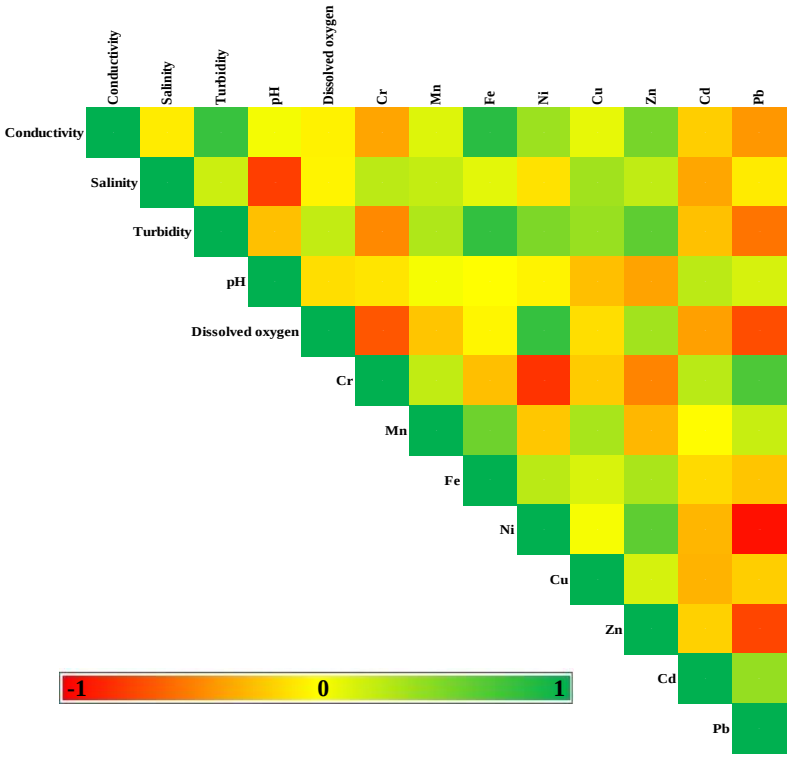

Figure 7. Correlation matrix of determined indicators and metals generated by IBM SPSS Statistics - Principal Component Analysis and modified by Microsoft Excel - Conditional Formatting.

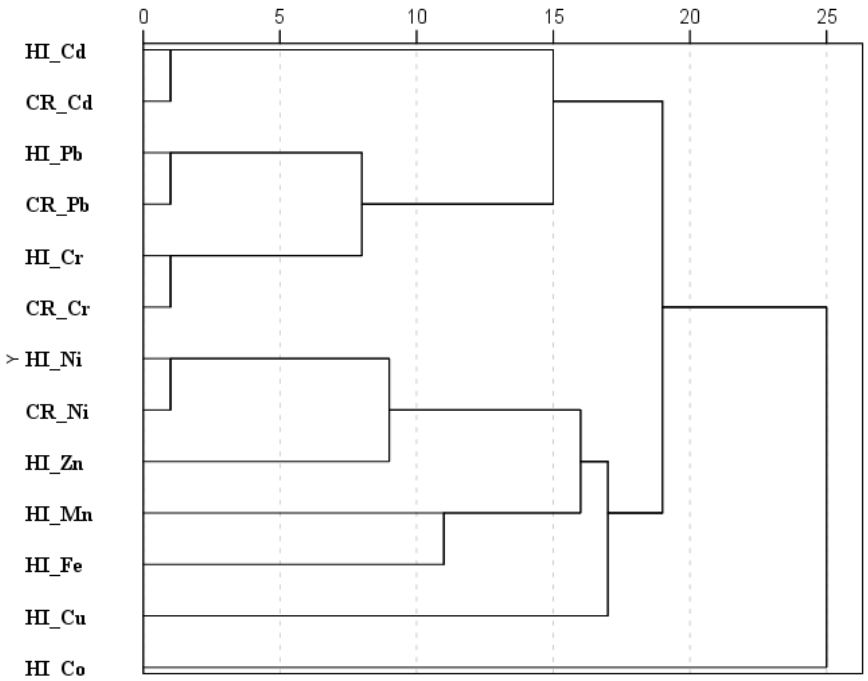

Figure 8. Hierarchical classification by dendrogram of health risk indicators based on average linkage between groups, for both age categories (i.e., adults and children).

Using the data sets of hazard quotients for non-cancer and potential cancer risks (for both age categories: adults and children), the resulting dendrograms are identical. This is the reason for just one dendrogram shown in Fig. 8. Regarding the values obtained in the proximity matrices, the values obtained for adults and children are similar, with small variations ranging from -0.026 to +0.014, but in 37 situations, identical values were obtained.

CONCLUSIONS

This research can raise awareness of the environmental impact of toxic heavy metals in water and assess their toxicological effects on human health. An environmental impact assessment is a tool used in environmental policy to address the effects of anthropogenic pollution on natural systems as part of sustainable development.

From the above explanation, the following heavy metals are suspected to originate from natural sources: Co, Fe, Mn, Cu, and Zn. In contrast, Pb, Cd, Ni, Cr, and Co are believed to originate from human activities. Cobalt is suspected to originate from both natural and anthropogenic sources. The levels of Cr and Cu in the water samples do not exceed safe limits, suggesting that industrial activities related to these two heavy metals are not a significant source of contamination. However, Ni and Cd exceeded the allowable limits in several spring water samples (S8 and S9 for Ni, and S1, S3, and S6 for Cd. Risk indices and statistical analysis revealed that a potential carcinogenic risk was associated with levels of Cr, Ni, and Cd in both age groups (i.e., adults and children). Even in the case of CR induced by Pb content, the values are close to the recommended value of $1.0 \cdot 10^{-6}$, with ranges of $8.740 \cdot 10^{-7}$–$2.544 \cdot 10^{-6}$ for adults and $3.278 \cdot 10^{-6}$–9.541·10-6 for children, respectively.

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