

Article

Evaluating Groundwater Metal and Arsenic Content in Piatra, North-West of Romania

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Abstract: The present study introduces a monitoring initiative focused on the quality of groundwater in the Piatra locality, situated in the North-West region of Romania. This paper employs an evaluation of 21 physico-chemical parameters, encompassing factors such as electrical conductivity, pH, chemical oxygen demand, turbidity, total hardness, NH_4^+ , NO_3^- , Cl^- , PO_4^{3-} , Li, Na, K, Ca, Mg, Ba, Sr, Al, Fe, Mn, Sn, and Ti. Additionally, it examines five heavy metals (Cr, Cu, Ni, Pb, and Zn) and arsenic in water sourced from six distinct private wells. Each well, with its characteristics, serves as a unique drinking water source. The assessment encompassed the evaluation of pollution levels, quality status, and risk factors for all drinking water sources, utilizing pollution, quality, and risk indices. The aim of this study was to establish the level of toxicity in water, assess its impact on human health, and disseminate information to the public about the appropriate utilization of individual water sources. The results indicated a general contamination with chloride, ammonium, manganese, chromium, and iron. Human health risk assessment indices revealed that the consumption of studied waters presented non-carcinogenic risks associated with Cr for adults and with Cr, As, Pb, and Cu for children for some of the groundwater sources. The water quality index (WQI) categorizes the samples as possessing excellent and good quality. This research represents one of the initial endeavors to assess the groundwater source quality in connection with the potential human health risks posed by the metals studied within the protected area of the Tisa River Basin.



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Keywords: groundwater; heavy metals; human health risk; drinking water sources

1. Introduction

Groundwater, found underground in soil, sand, and rock spaces known as aquifers, represents 97% of the world's drinking water [1]. Worldwide, approximately 2.5 billion people depend solely on groundwater to meet their daily drinking requirements [2]. According to the UNESCO Water Report 2023, over the last 40 years, a 1% water consumption increase per year has been estimated [3]. A projection by Burek et al. [4] states that this trend could eventually lead to a 20–30% increase by the year 2050.

In the case of Romania, according to the National Administration of Romanian Waters, there is around 9.6 billion m^3 of water beneath the surface, with almost half as part of the water table and the rest as part of deep-sea reserves [5]. Groundwater's advantage lies in its natural renewal through recharge, where precipitation infiltrates the soil to refill aquifers, ensuring a sustainable and dependable supply [6]. However, continental-scale projections for Europe suggest a probable 5–20% decrease in annual mean precipitation in southern Europe and the Mediterranean from 2071 to 2100, with precipitations for Romania already having decreased to 30 mm/decade [5]. In numerous rural regions of Romania, the primary concern is not merely the availability of water but rather the accessibility of potable water. The 2030 Agenda prioritizes developing water and sanitation infrastructure for an improved quality of life and health in Romania. Even with this

being a strategic priority, in 2016, only 65.2% of the population had water access, making Romania the least-developed EU country in this aspect, with significant rural disparities and limited national infrastructure and investment contributing to low wastewater collection (63.46%) and sewage treatment (56.71%) rates [7]. Despite the European Union's (EU) drinking water legislation, the quality of drinking water from both private and numerous public wells remains unregulated and frequently lacks protection against contaminants. The 98/83/EC Council Directive exempts drinking water systems catering to fewer than 50 individuals or producing less than 10 m³ per day [8]. In rural areas, individual well digging risks water quality and quantity due to expertise and design issues, especially during high-demand or drought periods [9]. The Piatra area, where the groundwater quality study was conducted, lies within the Upper Tisa region near the Ukrainian border and is intersected by the Tisa River and its tributary, Șugătag. This region, including the Upper Tisa River and Tisa meadow, is designated as a Natura 2000 protected area due to its rich biodiversity, housing various species such as amphibians, fish, and migratory birds like wild ducks, storks, and swans. The primary occupations of Piatra residents include agriculture, animal husbandry, and wood processing. The area offers picturesque landscapes and opportunities for recreational fishing. Geologically, it features Quaternary formations from the Pleistocene and Holocene periods, influenced by alluvium from flood periods. The protected area spans low terrace formations of the Tisa River, characterized by alluvial/proluvial materials like gravels, boulders, and sands [10]. Land use in Piatra includes forests, meadows, pastures, arable lands, and residential areas, with predominant alluvial, well-drained soils supporting diverse natural vegetation. The area experiences a temperate-continental climate, with increased humidity and cold temperatures influenced by the Baltic and Scandinavian regions [11].

According to soil taxonomic classifications, the area possesses diverse soil types: alluvisolts dominate the meadows along the Tisa River with well-drained properties and a pH range from moderately acidic to weakly alkaline, while Regosols are found along the Săpânța River on gravel/boulder deposits with slightly acidic pH levels; Gleysols occur in depressions between Teceu and Remeți and Săpânța and Câmpulung la Tisa, influenced by a prolonged water table presence and poor-quality humus; and Luvisols range from gelic luvisols to stagno-gleic luvisols, present in terraces and settlement areas, with varying pH levels from strongly acidic to moderately acidic [12–14]. Shallow dug wells pose contamination risks due to their wide diameter, shallow depth, and inadequate regulation, elevating their vulnerability to environmental shifts and fostering well deterioration. All the soils in the area exhibit unique behaviors from a pedological perspective [15]. Alluvisolts, though well-drained, pose risks if surface runoff or contamination seeps through soil layers, which can be mitigated by proper well construction. Regosols, which are slightly acidic, may lead to heavy metal leaching if not lined adequately. Gleysols, which are waterlogged, risk contamination from stagnant water and humus, necessitating well construction vigilance. Luvisols, with varying acidity, can affect water purity and surface contamination if not properly sealed or protected.

Thus, the assessment of groundwater quality considers biological, hydrological, and physico-chemical factors. Prolonged environmental interactions influence its chemical composition, with agricultural waste like fertilizers, insecticides, and pesticides threatening quality through infiltration [16]. Despite purification through evaporation and precipitation, water needs rely on limited rainwater and groundwater, facing persistent pollution driven by rapid resource degradation [17]. Contaminants impacting natural water sources comprise heavy metals (Cu, Ag, Zn, Cd, Hg, Cr, Mo, Mn, Co, and Ni), inorganic pollutants (PO₄²⁻, NO₃⁻, and NH₄⁺), metalloids (B, Si, and Te), organic pollutants (benzene, phenol, toluene, chloroaniline, and methylene blue), and microorganisms (*S. aureus*, *E. coli*) [18]. Certain heavy metals, such as Cr, Pb, Ni, and Cd, carry potential risks due to their toxic, genotoxic, and carcinogenic effects, while others like Se, Mo, Mn, Co, Cu, and Fe are essential micronutrients for various biological functions [18–27]. However, excessive intake of these metals can result in neurotoxic effects. Additionally, it has been

reported that approximately 20% of global cancer cases result from improper water consumption, and in 2022, 829,000 deaths worldwide were attributed to inadequate sanitation and various human activities near groundwater sources [28]. Evaluating the degree of heavy metal pollution through pollution indices—PI (pollution index) and HEI (heavy metal evaluation index)—is essential for safe water consumption. The overall quality of water can be assessed using chronic daily intake (CDI). The hazard quotient (HQ) and the hazard index (HI) are employed for the evaluation of non-carcinogenic health risks based on the consumption of water contaminated with metals [29]. Heavy metals, pesticides, and detergents, due to their accumulation in vital organs, are major pollutants, impacting key human body systems [30]. Human health risk assessment is vital for estimating the harmful effects and likelihood of health risks to ecosystems and human health [31]. In this process, spatial modeling of heavy metals in groundwater plays a crucial role, considering factors such as chronic daily intake, hazard quotient, and hazard index [32,33]. To prevent potential health risks, it is essential to implement risk factors for water sources characterized by high concentrations of contaminants [34]. Recent investigations in Nigeria, Algeria, Iran, Kenya, Thailand, Bulgaria, Slovakia, and Romania have shown high levels of non-carcinogenic outcomes for chemical elements including Ni, Hg, Cd, Pb, As, and nitrogen pollutants (NO_3^- , NO_2^- , and NH_4^+), which are prevalent in groundwater due to activities like household, agricultural, and industrial processes, carrying the potential to trigger cancer or methemoglobinemia [35].

The primary objectives of this investigation centered on assessing the quality and pollution levels of groundwater drawn from dug wells, specifically used for drinking purposes, aiming to ascertain its suitability for consumption and its potential impact on human health. Another objective is to identify the extent of the anthropogenic pressures and, implicitly, to elaborate measurements in order to reduce the negative anthropogenic influences. What sets this study apart is its comprehensive approach to evaluating groundwater quality in Piatra town, situated within the Plain of Tisa River. This method involves diverse methodologies, including statistical analysis of key physicochemical indicators, cluster analysis identifying wells influenced by similar pollution sources, human risk assessment, and the calculation and interpretation of water quality indices. By introducing innovative perspectives and methodologies, this study contributes to existing literature, aiming to enhance knowledge in the field. The findings are expected to provide insights into how groundwater responds to stress from human activities, offering valuable recommendations for population health risk prevention and sustainable practices.

2. Materials and Methods

2.1. Water Sampling

The samples of groundwater were gathered from six distinct locations within the town of Piatra, Romania, throughout all seasons in the year 2023. Figure 1 illustrates the locations of all six sampling points comprised exclusively of dug wells. The open dug wells, situated on residents' properties, are excavated to a depth of 4–10 m with an 80 cm diameter. They are constructed using cement/asbestos or rock tubes and equipped with a pulley system for water extraction. Sampling points were chosen randomly to ensure a comprehensive coverage of the town's entire area, encompassing potential sources of contaminated groundwater. Physicochemical parameter analysis was conducted within 48 h of sampling. Adhering to SR ISO 5667-3/2018 [36] guidelines, collected water samples were stored in clean polyethylene containers and refrigerated until analyzed in triplicate [37].



Figure 1. Sampling point (P1–P6) in the studied area.

2.2. Methods of Analysis

Field investigations and sample analysis were conducted over 2022 using portable devices. Electrical conductivity (EC) and pH were measured with a WTW INOLAB 740 conductometer (WTW, Weilheim in Oberbayern, Germany) and an HI 253 Hanna Instruments pH meter (Hanna Instruments, Woonsocket, RI, USA), respectively, following SR EN ISO 7888/1985 [38] and SR EN ISO 10523/2012 [39] standards [37]. Dissolved oxygen, chloride concentration, total hardness (ht), and aluminum were assessed using specified methods and instruments [37]. The measurement of Al^{3+} was conducted using a Specord 50 UV–VIS spectrophotometer (Analytik Jena, Jena, Germany) [37]. Ammonium, nitrates, phosphates, dissolved iron, and water turbidity were also measured following relevant standards and using appropriate devices, such as the WTW 355 IR portable turbidimeter (WTW, Weilheim in Oberbayern, Germany) [37]. The portable devices underwent calibration before each measurement [37]. The preservation of water samples involved the addition of nitric acid (HNO_3 , 65%, Merck, Darmstadt, Germany) in a 1:1 ratio until reaching an acidic pH range of 1–2. Following this, the samples underwent digestion with concentrated HNO_3 (70%, Merck, Germany) and H_2O_2 (30%, Merck, Germany), then were dissolved in concentrated HNO_3 , diluted with filtered ultrapure water, further diluted to a volume of 100 mL using an acid solution, and stored at 4 °C until the analysis [37]. All reagents utilized were analytical-grade (PA), with deionized water employed for their preparation.

In the case of samples investigated using the graphite furnace, preparation involved a filtration step followed by an acidification with concentrated HNO_3 , 0.5 mL for 100 mL of the water sample, excluding the mineralization stage [37]. Elements such as Mg, Ca, Mn, Fe, and Zn at parts per million (ppm) levels were examined through flame absorption atomic spectrometry (FAAS) using a Perkin Elmer NexION 300S spectrophotometer equipped with flame and graphite furnace atomizers (Perkin Elmer, Norwalk, CT, USA). An in-depth analysis was conducted on trace metals ($\mu g/L$), including Cu and Ni, through the utilization of graphite furnace atomic absorption spectrometry (GFAAS) employing a pyrolytic platform [37]. The spectrophotometer, featuring hollow cathode lamps tailored to individual metals and a continuous background correction system, employed an air-acetylene flame for samples at the ppm level and a graphite furnace for samples at the trace level [37]. Calibration, quality control of data, and assurance adhered to established

standard operating procedures, which included conducting triplicate analyses and measuring blanks in parallel. The findings were presented as the average values derived from three distinct replicates, employing analytical-grade reagents and certified 1000 ppm standard metal solutions for both calibration and standard preparation [37].

2.3. Statistical Analysis

Descriptive statistics of the registered data were accomplished by computing the mean, standard deviation, coefficients of variation, standardized skewness, and kurtosis for each water parameter with the help of Excel (Microsoft Office 2021, Microsoft Corporation, Washington, DC, USA). Cluster analysis, a classification method applied to environmental data, was employed to illustrate the similarity or dissimilarity of observation points or analyzed parameters using the Statgraphic program (version Centurion 19, 2023, The Plains, VA, USA).

2.4. Heavy Metal Evaluation Index (HEI)

The heavy metal evaluation index method was employed to investigate the overall quality of water based on the concentrations of heavy metals. The *HEI* values were calculated for the elements Zn, Pb, Ni, Cu, Cr, As, Mn, Fe, and Sr. Only the heavy metals with a maximum allowable limit were considered. As was also considered due to its high toxicity. *HEI* was calculated according to Equation (1) [40,41].

$$HEI = \sum_{i=1}^n \frac{C_{Mi}}{C_{(MAC)_i}} \quad (1)$$

where C_{Mi} is the measured concentration of the “*i*” considered a heavy metal and $C_{(MAC)_i}$ is the maximum admissible concentration in drinking water, according to Romanian legislation or another standard for drinking water quality. By using *HEI*, the water samples can be classified into the following pollution degrees: low pollution degree when $HEI < 40$, medium degree of pollution for $40 < HEI < 80$, and high degree of pollution when $HEI > 80$.

2.5. Water Quality Index (WQI)

The water quality index (*WQI*) is an approach to assessing the quality of diverse water samples, consolidating various indicators of water composition into a singular representative value that conveys comprehensive information about water quality [29,40,42–46]. The *WQI* method was used to assess the overall quality of groundwater samples based on a weighted arithmetic technique, considering 23 indicators of water quality: EC, pH, turbidity, NH_4^+ , NO_3^- , PO_4^{3-} , and the metals: Li, Na, K, Ca, Mg, Ba, Sr, Al, Fe, Mn, Cr, Cu, Ni, Pb, Zn, and As. For each water quality parameter, a weight (w_i) and a relative weight (W_i) were assigned based on Equations (2) and (3):

$$w_i = \frac{1}{S_i} \quad (2)$$

where S_i is the maximum allowable concentration in potable water (MAC), according to Law 311/2004 458/2002 Law M.O. No. 552/29 July 2002—law on the quality of drinking water, as shown in Table 1.

$$W_i = \frac{w_i}{\sum_{i=1}^n w_i} \quad (3)$$

where n is the number of the assessed water indicators; n was 23 in the present study.

Table 1. Physico-chemical composition of groundwater sources in Piatra locality, a Natura 2000 protected area, and standards (maximum allowable concentration—MAC) in accordance with Council Directive 98/83/EC [8].

Element Content in Water, µg/L	P1	P2	P3	P4	P5	P6	Mean	SD	CV, %	Stnd. Skewness	Stnd. Kurtosis	MAC
EC (µS/cm)	763	398	172	1205	192	252	497	410	82.49	1.29	0.34	2500
pH	7.08	7.12	7.55	7.18	6.98	7.61	7.25	0.26	3.61	0.72	−0.84	6.5–9.5
DO (mg/L)	6.79	5.65	9.06	5.33	9.77	9.55	7.69	2.01	26.13	−0.16	−1.34	
T (NTU)	1.31	3.92	8.75	1.14	2.56	5.48	3.86	2.90	75.20	1.01	0.22	5
NH ₄ ⁺ (mg/L)	0.88	0.48	0.28	1.09	0.04	0.77	0.59	0.39	66.82	−0.21	−0.64	0.5
NO ₃ [−] (mg/L)	4.21	2.38	1.28	2.23	0.15	5.32	2.60	1.89	72.95	0.33	−0.38	50
h _t (°g)	24.7	10.2	2.75	25.6	4.42	2.16	11.64	10.85	93.22	0.71	−0.99	min 5
Cl [−] (mg/L)	41.5	66.5	39.5	565.2	62.8	29.2	134.12	211.67	157.83	2.42	2.95	250
PO ₄ ^{3−} (mg/L)	0.86	0.13	0.15	0.19	0.17	0.14	0.27	0.29	105.44	2.42	2.94	0.4

Notes: The maximum allowable concentration (MAC) for drinking water, as stipulated by Law 311/2004 and Law M.O. No. 458/2002, in accordance with the law on the quality of drinking water (552/29 July 2002). SD represents the standard deviation; CV denotes the coefficient of variance; and Stnd signifies standardized. The values highlighted in bold surpassed the MAC.

WQI were computed following Equations (4) and (5) according to the literature [29,47–53]:

$$WQI = \frac{\sum_{i=1}^n Q_i \times W_i}{\sum_{i=1}^n W_i} \tag{4}$$

Q_i is the quality rating of each physico-chemical indicator determined following Equation (4):

$$Q_i = \left(\frac{C_i - V_i}{S_i - V_i} \right) \times 100 \tag{5}$$

In this context, C_i represents the measured value of each physico-chemical parameter or metal concentration, while V_i stands for the ideal value of the chemical indicator. The ideal value, V_i was zero for the considered indicators, with the exception of pH. The optimal value for pH was considered to be 7 [47,52,53].

2.6. Human Health Risk Assessment

Human health risk assessment by groundwater consumption was established according to the method described in the literature [46,54–56], by computing the chronic daily intake of water contaminants, CDI (mg/kg·day), hazard quotients (HQ) for each water contaminant, and the hazard index (HI). Nutrients such as NH₄⁺ and NO₃[−], metals (Al, Sr, Ba, Fe, Mn, Cr, Cu, Ni, Pb, and Zn), and As were considered to compute the hazard index, HI. The human health risk due to groundwater consumption was evaluated by calculating the chronic daily intake of water, CDI (mg/kg·day), hazard quotients (HQ), and the hazard index (HI), according to Equations (6) and (7) for adults (male and female) and children.

$$CDI = \frac{C \times IR \times EF \times ED}{BW \times AT} \tag{6}$$

where C is the measured pollutant concentration in the groundwater sample (mg/L); IR is the ingestion rate per unit time (1.5 L/day for a child and 2 L/day for an adult); EF: exposure frequency (350 days/year considering 15 days of holidays or visits); ED: exposure duration (6 years in the case of children; 30 years in the case of adults); BW: body weight; the average body weight for Romanian males is 85 kg, while for females, it is 72 kg [57], and an average body weight of 15 kg was considered for children [55].

The hazard quotients, HQ_i, for the considered pollutants in water were calculated according to Equation (7):

$$HQ_i = \frac{CDI_i}{RfD_i} \tag{7}$$

where RfD_i is the chronic oral reference dose, an estimate of the daily oral exposure level for the population, and the highest acceptable daily intake level for a specific element or pollutant that does not lead to adverse health effects [47,52,53].

The RfD values expressed in mg/kg/day are 0.97 NH_4^+ ; 1.60 NO_3^- ; 0.6 Sr; 0.7 Fe; 0.14 Mn; 0.0003 As; 0.0003 Cr; 0.0005 Cu; 0.0054 Ni; 0.0003 Pb; 0.3 Zn; 7 Al; and 0.2 Ba [58–61].

The hazard risk, HI , which aims to assess the human health risk through more toxic elements, was computed as the sum of all HQ , calculated for each particular pollutant according to Equation (8). HI values greater than one, $HI \geq 1$, are associated with considerable non-carcinogenic health hazards [47,53,62].

$$HI = \sum_{i=1}^n HQ \quad (8)$$

3. Results and Discussion

3.1. Physico-Chemical Characteristics of Groundwater Samples

The results for the physico-chemical content of the examined water samples (P1–P6) are presented in Table 1. As seen from Table 1, the electrical conductivity (EC) values for wells P1 to P6 exhibit a notable variation, suggesting diverse levels of ion concentration in the respective groundwater sources. Well P4 stands out with the highest conductivity at 1205 $\mu\text{S}/\text{cm}$, potentially indicating a higher concentration of dissolved ions or minerals. In contrast, wells P3 and P6 demonstrate the lowest conductivity values at 172 $\mu\text{S}/\text{cm}$ and 252 $\mu\text{S}/\text{cm}$, respectively, suggesting a lower presence of dissolved ions. Wells P2, P5, and P1 fall in between, showcasing moderate electrical conductivity values of 398 $\mu\text{S}/\text{cm}$, 192 $\mu\text{S}/\text{cm}$, and 736 $\mu\text{S}/\text{cm}$, respectively. These variations could be attributed to geological factors, such as differing soil compositions or proximity to potential contamination sources, influencing the conductivity of the groundwater in each well. A previous study [46] on another well within the region registered much higher values (1575–2480 $\mu\text{S}/\text{cm}$), attributed to the interaction with aquifer rocks. EC serves as evidence of salt content in water, and the ingestion of water with elevated EC levels may contribute to a range of health issues, including but not limited to cancer, diarrhea, hepatitis, and gastroenteritis, impacting vital organs such as the heart, kidneys, and stomach [48].

Dissolved oxygen (DO) indicates water stratification and the contamination degree [49]. In this study, DO varied between 5.33 and 9.77 mg/L. Wells P3, P5, and P6 have relatively high DO concentrations, measuring 9.06 mg/L, 9.77 mg/L, and 9.55 mg/L, respectively. These elevated levels suggest favorable conditions for aerobic organisms and may indicate well-oxygenated water. Conversely, wells P2 and P4 show lower DO values at 5.65 mg/L and 5.33 mg/L, possibly indicating reduced oxygen availability in these wells. Well P1 falls in between, with a dissolved oxygen level of 6.79 mg/L. Discrepancies in these values may be ascribed to a variety of factors, including groundwater flow patterns, biological activities, and environmental conditions. The low amounts of DO (P2 and P4) lead to a lack of freshness, a fad taste, and unfriendly conditions of microorganisms that make the water not potable [50]. High amounts of DO (P3, P5, and P6) increase the organic suspended matter rich in pathogens [49,50].

pH ranged between 6.98 and 7.61, within the thresholds established for drinking water, indicating a weak acidic to weak basic character, which can indicate a low pollution level with organic and inorganic compounds [51]. Due to rock interaction and rich amounts of carbonates, pH has a basic character and changes the taste of water, possibly leading to skin and eye rashes [52]. Turbidity ranged between 1.14 and 8.75 NTU. Such variations in the turbidity levels across the six wells indicate differences in water clarity. Well P3 exhibits the highest turbidity at 8.75 NTU, suggesting a higher concentration of suspended particles or sediments in the water. P6 follows closely with a turbidity of 5.48 NTU, indicating moderately cloudy water. Wells P2 and P5 demonstrate moderate turbidity levels at 3.92 NTU and 2.56 NTU, respectively. P1 and P4 exhibit lower turbidity levels at

1.31 NTU and 1.14 NTU, suggesting relatively clear water. These variations in turbidity may be influenced by factors such as land use, soil composition, and human activities in the vicinity of each well. High turbidity levels can indicate potential contamination or natural sedimentation processes. Higher values may be caused by the presence of bacteria, plankton, iron and aluminum hydroxide, sludge, and colloidal matter. Water characterized by elevated turbidity posed an epidemiological threat because it facilitated the suspension of particles, serving as a medium for pathogens [40]. The consumption of water with high turbidity levels may result in health issues, particularly intestinal diseases, and can also induce distortion in aquatic ecosystems [53].

With the exception of P1, P4, and P6, all other samples are highly rich in NH_4^+ , almost two times the MAC established for the drinking water. The high amount is related to anthropogenic activities, for example, the intense use of fertilizers or fecal deposits. If consumed, water with NH_4^+ in high amounts might cause convulsion, hepatic encephalopathy, coma, and death. Such water contaminated with NH_4^+ can be treated through energetic chlorination and filtration process [63]. The NO_3^- concentrations are below the MAC (50 mg/L), between 1.28 and 4.21 mg/L (Table 1). The sources of NO_3^- include intensive agricultural practices, sewage and septic tank leakage, manure and contaminated sludge deposits, as well as microbial decomposition. Groundwater contamination with NO_3^- is influenced by the geological and hydrogeological structure. Consuming water rich in NO_3^- is linked to the onset of illnesses like cancer and methemoglobinemia [62]. As for chlorides, all wells are within the allowable limit, except for well P4, which has more than double the maximum allowable limit of 250 mg/L. The anomalous presence of heightened chlorine levels in a singular well, as opposed to others within the same town, underscores the complexity of localized water quality dynamics. Chlorides (salts of metals with hydrochloric acid), indicative of water salinity, are essential for the body's electrolyte balance, but excessive salinity renders water unsuitable for drinking due to potential chemical aggressiveness [35]. PO_4^{3-} are lower than 0.4 mg/L, with potential sources represented by the intense use of fertilizers and detergents, but also with geogenic origin. An elevated phosphate concentration can change both the flavor and color of water [64]. Variations in the levels of ammonium, chlorides, nitrates, and phosphates among wells in the same close region or town can be attributed to diverse factors, including differences in geological formations, land use practices, and proximity to pollution sources. Additionally, variations in well construction, depth, and maintenance practices may influence the vulnerability of wells to contamination. These local factors influence the interaction of water with surrounding soils, rocks, and contaminants, contributing to the unique composition of each well and the resulting differences in water quality parameters. For example, one study [65] focuses on 10 wells from Remeti locality in very close proximity to Piatra town (the locale housing the six wells analyzed in the present paper). The ammonium levels reported in Remeti wells were up to more than four times higher than the MAC, presenting a maximum of 2.38 mg/L compared to the maximum in Piatra, which is P4 = 1.09 mg/L; also, in Remeti, phosphates were within admissible limits except for one well (0.78 mg/L) comparable to the ones in this study. Nitrate amounts were also excessively higher in wells from Remeti than in the P1–P6 samples in this study. This could be explained by more intense agricultural practices in the former compared to the latter, coupled also with the heavy practice in Romanian countryside involving the application of animal manure. Teceu locality is also in close proximity to Piatra town, and water analysis on a well in Teceu [46] revealed values for ammonium, chlorides, nitrates, and phosphates within the legal limits for potable water. However, it should be stated that [46] only analyzed one well in that specific town, which would be a limitation for stating the pollution levels for wells in the area.

3.2. Metal and as Content in Groundwater Samples

The concentrations of major metals (Ca, Mg, Na, and K), of metals found at lower concentrations (Li, Al, Ba, and Sr), of heavy metals (Fe, Mn, Sn, Ti, Cr, Cu, Ni, Pb, and Zn), and As are shown in Table 2.

Table 2. The metal and As content of groundwater sources in Piatra locality, a Natura 2000 protected area and standards (maximum allowable concentration—MAC) in accordance with Council Directive 98/83/EC [8].

Element Content in Water, µg/L	P1	P2	P3	P4	P5	P6	Mean	SD	CV, %	Std. Skewness	Std. Kurtosis	MAC
Li	2.3	3.1	2.5	6.1	2.4	4.7	3.52	1.55	44.07	1.17	−0.01	50
Na	18,345	16,889	25,455	59,745	24,332	11,045	25,969	17,361	66.85	1.95	2.12	200,000
K	2077	2045	2105	7245	2726	3044	3207	2020	62.99	2.23	2.57	10,000
Ca	1890	3558	1345	8921	2432	3779	3654	2746	75.15	1.83	1.86	100,000
Mg	10,124	20,144	8142	45,224	6885	12,784	17,217	14,505	84.25	1.93	1.90	50,000
Ba	17.2	20.1	15.5	80.2	31.6	27.3	31.93	24.41	76.31	2.12	2.35	700
Sr	88	126	75	446	132	204	178.5	138.6	77.64	1.92	1.92	200
Al	27.3	18.3	88.3	4.3	19.1	17.5	29.13	29.91	102.68	2.11	2.42	200
Fe	175	195	225	175	132	147	174.83	33.27	19.03	0.28	−0.13	200
Mn	2.8	3.2	8.5	1.4	1.7	3.1	3.45	2.58	74.89	1.99	2.20	50
Sn	22.1	94.5	18.3	68.9	57.4	11.3	45.42	33.31	73.34	0.49	−0.76	-
Ti	14.3	19.4	10.3	48.6	31.0	41.2	27.47	15.37	55.95	0.35	−0.89	-
As	5.4	8.5	0.22	9.8	6.2	0.55	5.11	3.99	77.99	−0.33	−0.88	10
Cr	7.6	12.6	55.8	3.4	2.6	1.7	13.95	20.90	149.81	2.25	2.60	50
Cu	2.5	4.1	3.3	2.5	5.1	6.4	3.98	1.55	38.84	0.70	−0.34	100
Ni	3.1	7.7	12.4	3.6	2.2	5.6	5.77	3.80	65.94	1.22	0.53	20
Pb	3.7	9.3	4.1	4.1	8.3	7.1	6.10	2.44	40.05	0.30	−1.21	10
Zn	4.2	5.3	21.3	15.3	1.2	1.8	8.18	8.20	100.23	1.04	−0.30	5000

Notes: The maximum allowable concentration (MAC) for drinking water, as stipulated by Law 311/2004 and Law M.O. No. 458/2002, in accordance with the law on the quality of drinking water (552/29 July 2002). SD represents standard deviation; CV denotes the coefficient of variance; and Stnd signifies standardized. The values highlighted in bold surpassed the MAC.

The average values for the metal concentrations in the groundwater samples were as follows: Na > Mg > Ca > K > Sr > Fe > Sn > Ba > Al > Ti > Cr > Zn > Pb > Ni > As > Cu > Li > Mn.

Calcium and magnesium are essential elements for the human body; thus, their presence in water is not typically a cause for concern, unless there are underlining medical conditions (i.e., kidneys). While their presence in high amounts leads to hard water, which is organoleptically changed, the World Health Organization (WHO) acknowledges that hard water has no known adverse health effects and may even contribute to the intake of essential minerals. However, the WHO does report that the taste sensitivity threshold for Ca²⁺ within the range of 100–300 mg/L, contingent on the accompanying anion, and it is likely that the taste threshold for magnesium is lower than that for calcium. In certain cases, consumers are known to tolerate water hardness exceeding 500 mg/L [66]. Here, the highest magnesium value is found in fountain P4, while the lowest value is found in well P3. All values fall within the maximum allowable limit of 50,000 µg/L. The presence of such ions, the presence of calcium- and magnesium-rich minerals in rocks and soils, and the characteristics of aquifers through which water flows. Also derived from geological source is potassium, with the highest level being observed in the water from fountain P4, while the lowest value is in the water from fountain P2. However, all values fall within the maximum allowable limit of 10,000 µg/L.

Aluminum (Al) stands out as the most prevalent metallic element found in the Earth's crust. While poorly absorbed in the gastrointestinal tract, its bioavailability increases in drinking water, potentially impacting human health. According to Law 311/2004, the legal limit for aluminum content is 200 µg/L. One potential origin of aluminum is the application of Al₂(SO₄)₃ during the water treatment procedure [29]. Recognized as a neurotoxin on a broad scale, exposure to aluminum has been associated with neurodegenerative conditions, including Parkinson's, Alzheimer's, and multiple sclerosis. Studies indicate cognitive decline at Al intake ≥0.1 mg/day from water, with elevated levels posing an increased risk

of cognitive impairment in the elderly, leading to heightened vulnerability to hip fractures and adverse health effects [67].

Manganese is also naturally abundant, and water rich in Mn is characterized by an unpleasant metallic taste and a muddy odor. The presence of manganese in the water distribution system forms deposits that can settle as a black precipitate [29]. According to Water Law 311/2004, the permitted limit for manganese content should not exceed 50 µg/L. The values obtained in the studied wells are low, ranging from 1.4 to 8.5 µg/L. Manganese originates from diverse sources, encompassing industrial practices like alkaline battery and cleaning product manufacturing, agricultural activities involving the application of fungicides, fertilizers, and pesticides, as well as mining operations.

Barium is a naturally occurring element that can be found in groundwater, including well water. While low levels of barium are generally considered to be naturally present and not harmful, elevated concentrations can pose health risks. Barium can enter groundwater through the weathering of certain rocks and minerals. Barium can deposit in muscles, lungs, and bones because it resembles calcium but is absorbed more quickly [41]. The highest barium value was observed in the water from fountain P4, while the lowest value was observed in the water from fountain P3. All values fell within the permissible limit, which is 7000 µg/L.

Arsenic is a toxic contaminant that is colorless, odorless, and tasteless and is commonly found in high concentrations in groundwater. Arsenic found in groundwater is susceptible to abrupt variations [29]. For this study, the measured values in groundwater vary between 0.22 and 9.8 µg/L. Wells P1, P3, and P6 exhibit arsenic concentrations well below the permissible limit at 5.4 µg/L, 0.22 µg/L, and 0.55 µg/L, respectively. Wells P2 and P5 approach the threshold with values of 8.5 µg/L and 6.3 µg/L, suggesting a moderate risk of arsenic exposure. P4 records the highest arsenic level at 9.8 µg/L, nearing the maximum limit and indicating a potential health concern. Communities relying on well water for drinking, particularly in rural areas, face heightened vulnerability to arsenic contamination. Geological conditions, often prevalent in rural regions, may lead to naturally occurring arsenic in aquifers. Limited resources for water monitoring and regulatory oversight contribute to the unknowing consumption of arsenic-contaminated water. Rural populations, dependent on wells and lacking alternative water sources, are at direct risk of health issues associated with arsenic exposure. Challenges in accessing clean water alternatives, agricultural practices, and a lack of awareness further compound the issue. Ingesting water containing a substantial amount of arsenic can result in significant immediate and/or prolonged health issues, including but not limited to vomiting, diabetes, heart diseases, cancer, spontaneous abortion, childhood cancer, and potential fatality [68]. Following ingestion, arsenic is swiftly absorbed by the gastrointestinal tract and undergoes metabolism. As for chromium, according to Water Law 311/2004, the legal limit is 50 µg/L. In this study, the obtained values varied between 1.7 and 55.8 µg/L. Sample P3 exceeds the legal limit of 50 µg/L, highlighting the need for immediate attention and remediation to ensure compliance with established water quality standards. The other samples, while below the legal limit, may still warrant monitoring and preventive measures to maintain water quality within acceptable levels. The variation in chromium levels, with higher concentrations in sample P3 compared to others in the same village, may stem from localized geological, anthropogenic, or hydrogeological factors. Chromium, a highly toxic heavy metal, is linked to health risks such as cancer, DNA damage, and oxidative stress. It is present in water in hexavalent (Cr(VI)) and trivalent (Cr(III)) forms, and Cr(VI) is especially toxic for individuals with respiratory issues [69].

In compliance with Water Law 311/2004, the permissible limit for nickel content stands at 20 µg/L. Recorded nickel values, ranging from 2.2 to 12.4 µg/L, are influenced by factors like pH, soil composition, and depth [29]. Acknowledged as a significant contributor to groundwater pollution by the U.S. Environmental Protection Agency, nickel's potential toxic and health risks necessitate a comprehensive understanding of public safety [70]. Despite being a crucial element for the good functioning of enzymes, blood,

the endocrine system, and gene synthesis, various studies highlight nickel's disruptive impact on glucose metabolism and insulin secretion through biological mechanisms [70]. The presence of nickel in drinking water from wells can exert various influences on the surrounding environment. Nickel concentrations, when used for irrigation, may result in soil contamination, impacting plant health and altering the overall ecosystem in the well area. Interactions with the aquifer and subsurface geology can lead to the leaching of nickel into the well water from surrounding rock formations or anthropogenic sources. The overall groundwater quality in the well area is affected, posing concerns for both human consumption and agricultural use. Persistent contact with heightened nickel concentrations in drinking water poses health concerns, while the potential for corrosion or deterioration of well infrastructure adds another layer of concern.

According to Water Law 311/2004, the legal limit for lead content is 10 µg/L. The obtained lead content values ranged between 3.7 and 9.3 µg/L. Lead is one of the 275 priority-controlled pollutants by the U.S. and Chinese Environmental Protection Agencies [68]. Lead and its compounds can enter groundwater through mining activities. Lead is challenging to eliminate after its accumulation in the human or animal body because it can cause a diverse array of physical and mental issues [71,72]. The accumulation of lead in the human body causes damage to all organs, including the central nervous system, affects the liver, thyroid, and bones, and causes brain injuries and infertility [29,72]. Due to the physiology of the body, children, being more vulnerable than adults to lead contamination, suffer from constant brain damage, with approximately 18 million affected by lead poisoning [72]. Controlling lead pollution in drinking water is of vital importance [71].

As for copper, according to Water Law 311/2004, the legal limit is 100 µg/L. The highest value was found in well P6 (6.4 µg/L). Increased copper levels can arise from natural processes, like the breakdown of rocks, and human activities, including mining, industry, and agriculture. Drinking water containing elevated copper levels may result in stomach and headache discomfort, along with irritation of the eyes and nose [73]. Hence, monitoring the copper content is essential.

According to Water Law 311/2004, the legal limit for zinc content is 5000 µg/L. The zinc content at the sampling points is low. Sampling point P3 recorded double the zinc content (21.3 µg/L) compared to other points, probably due to a higher interaction of groundwater with rocks. Zinc, a naturally occurring element, undergoes slow enrichment in groundwater through interactions with rocks, influenced by inorganic carbon content and pH, and it is recognized for its significant mobility within water systems. Zinc exhibits opalescence and an astringent taste [29]. The mobility of Zn in water is predominantly affected by pH, with other factors like clay content, phosphorus availability, concentration of organic matter, and redox conditions also contributing to its behavior [74].

The strontium content in well water samples falls within the admissible limits of 200 µg/L for four of the six samples, namely P1, P2, P3, and P5. Wells P4 and P6 notably surpass the permissible limit, with sample P4 reading almost twice the legal amount, raising concerns about potential health risks associated with elevated strontium levels. The variations in strontium concentrations among wells in the same village could be attributed to geological factors, such as the composition of the subsurface rocks, which may contain higher concentrations of strontium. As this element is essential for general human health, it may be neglected in the overall water assessment. However, Sr has the potential to substitute for calcium and magnesium in bone, potentially impacting bone growth and strength. One study [75] emphasizes the noteworthy inverse correlation between the incidence of rickets in children and the Ca/Sr ratio in the potable water available for public consumption in China. A lower Ca/Sr ratio is associated with a higher incidence of rickets, suggesting a potential link between the calcium-to-strontium ratio and bone health in children. This finding underscores the importance of considering the Ca/Sr ratio in assessing the overall effect of strontium in the water supply for public consumption, particularly in regions with high strontium concentrations, to ensure adequate management and supervision of water quality.

Iron is the most problematic element in water. The water samples from 5 of the 6 wells analyzed fall below the legal limit of 200 $\mu\text{g}/\text{L}$, with values ranging from 132 (P5) to 195 (P2) $\mu\text{g}/\text{L}$. Sample P3, however, registers iron values of 225 $\mu\text{g}/\text{L}$, thus surpassing the allowed amount. These values indicate a potential issue with iron contamination in the well water. Elevated iron levels in drinking water can lead to several problems, including unpleasant taste, discoloration, and staining of plumbing fixtures. Additionally, high iron concentrations may indicate the presence of other contaminants or geological conditions that contribute to the contamination. The presence of higher iron levels could likely be attributed to the historical mining activities in Maramures County (different metalliferous resources including iron, copper, and manganese [76]), home to Piatra town and the six analyzed wells.

3.3. Cluster Analysis of Water Samples

Figure 2 shows the cluster analysis in the Q mode for groundwater sampling points based on the metal and As concentrations. The pairs of wells P5–P6 and P1–P2 showed the highest similarity, while the highest dissimilarity was found for well P4, one of the deepest wells (740 cm). The water from the P4 well exhibited the highest concentrations of several elements, including Na, K, Ca, Mg, Ba, Sr, Ti, As, and Zn, while the level of Ni was found to be the lowest. P3 also showed high dissimilarity from the samples P1, P2, P5, and P6. P3 registered the highest concentrations of Cr, Al, and Zn compared to the average values of the other groundwater sources. In the case of the pair of wells P5 and P6, the lowest levels of Cu, Al, Pb, Ti, and Mn were measured. P1 and P2 are wells with low depths (210 and 200 cm) while the depths of P5 and P6 are medium (550 cm and 400 cm).

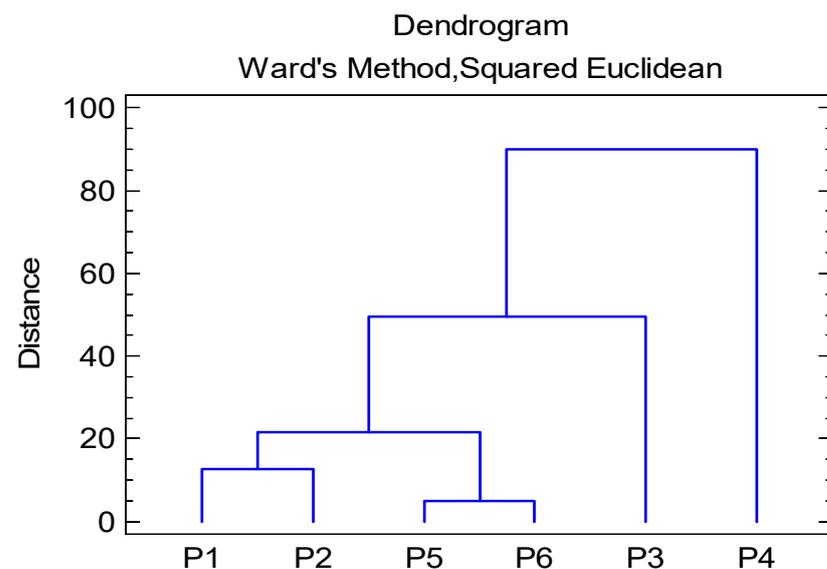


Figure 2. Cluster analysis in Q mode for groundwater sampling points based on the metal and As concentrations.

Cluster analysis was also performed in the R mode (Figure 3), showing the similarities or dissimilarities between the metals and As concentrations in groundwater samples.

The R mode cluster analysis reveals two primary clusters, namely C1 and C2. C1 contains the group of Al-Mn-Cr linked to Ni and also to the Fe-Zn pair of heavy metals. This element is derived from the aluminosilicates that include Al, Mn, Cr, Fe, and Zn. Cluster C2 comprises two subclusters: C2a and C2b. C2a includes the pair As-Sn and a group of eight alkaline and alkaline earth metals (K, Na, Li, Ba, Ca, Sr, and Mg), along with Ti, the element ranking as the Earth's ninth most prevalent [77,78]. Conversely, C2b encompasses the heavy metals Cu and Pb, nonferrous heavy metals naturally occurring in volcanic rocks.

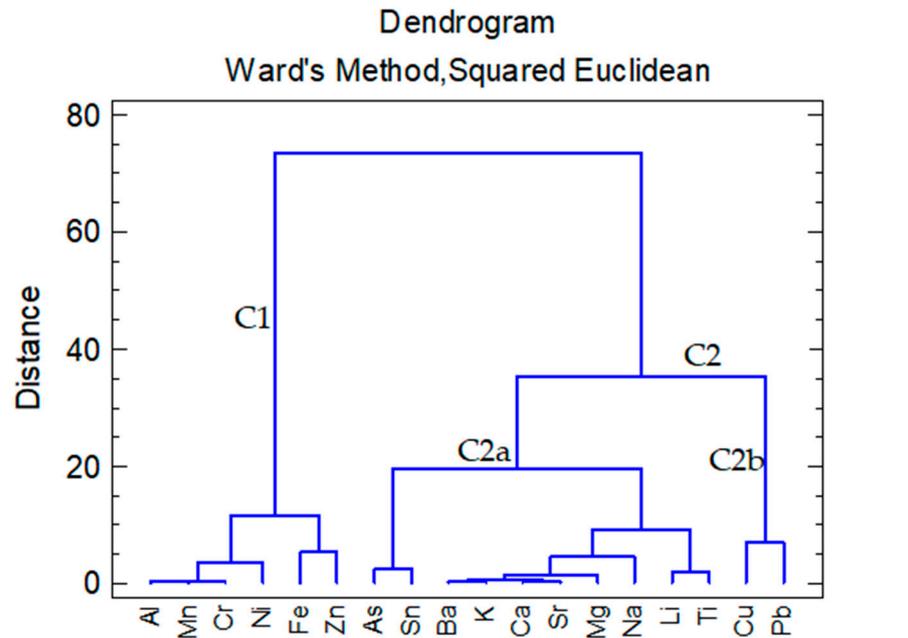


Figure 3. Cluster analysis in R mode for groundwater sampling points based on metal and As concentrations.

3.4. Heavy Metals Evaluation Index (HEI)

The HEI values depicted in Figure 4 varied in the range of 2.59 and 4.77 and can be classified as having a low pollution degree. The highest HEI value was calculated for P4 with 4.77, followed by P2 with 4.09, and the well with the lowest value of HEI was P1 (2.59). In the case of P4, Sr contributed the most to the HEI value (2.23), followed by As (0.98), Fe (0.88), and Pb (0.41).

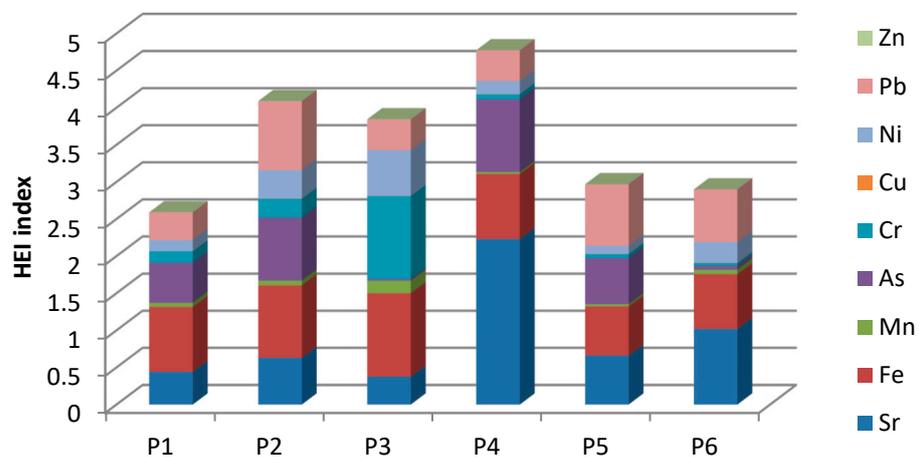


Figure 4. HEI values of the groundwater sources in Piatra locality based on As and metal concentrations (Sr, Fe, Mn, Cr, Cu, Ni, Pb, and Zn).

The highest values of elemental HEI values were due to Sr (P4, P6), As (P4, P2), Fe (P1–P4), Pb (P2, P5), and Cr (P3).

An investigation into the extent of heavy metal contamination of dug and drilled wells in Seini town, NW Romania, reported higher HEI values than in the present study, ranging values between 1.5 and 14, still below 40, showing a low degree of pollution due to anthropic influences [40].

In areas impacted by industrial operations, the health risk index (HEI) demonstrated significantly elevated values. For instance, in a plain located in western Iran, influenced by an industrial town, the HEI values varied from 21.4 to 133.3.

The computation of *HEI* provides a quick evaluation of the comprehensive quality of drinking water [79].

3.5. Water Quality Assessment by *WQI*

Table 3 displays the physico-chemical parameters employed in *WQI* computation, along with the corresponding parametric values, weights, relative weights, and the Q_i range.

Table 3. The physico-chemical parameters employed in *WQI* computation; the values and weights used; and the variation of Q_i .

Physico-Chemical Parameter, Measure Units	S_i * Value (p_{vi})	Weight, w_i	Relative Weight, W_i	Variation of Q
EC ($\mu\text{S}/\text{cm}$)	2500	4×10^{-4}	0.17×10^{-6}	6.88–48.2
pH (pH units)	9.5	0.11	0.000322	0.8–24.4
Turbidity, NTU	5	0.2	0.000585	22.8–175
NH_4^+ mg/L	0.5	2	0.00585	8–218
NO_3^- , mg/L	50	0.02	5.85×10^{-5}	0.3–10.64
Cl^- , mg/L	250	0.04	1.17×10^{-5}	11.68–226.08
PO_4^{3-} , mg/L	0.4	2.5	0.007319	32.5–215
Li, mg/L	0.05	20	0.058548	4.6–12.2
Na, mg/L	200	0.005	1.46×10^{-5}	5.52–29.87
K, mg/L	10	0.1	0.000293	20.45–72.45
Ca, mg/L	100	0.01	2.93×10^{-5}	1.35–8.92
Mg, mg/L	50	0.02	5.85×10^{-5}	13.77–90.45
Ba, mg/L	0.7	1.429	0.004182	2.21–11.46
Sr, mg/L	0.2	5	0.014637	37.5–223.0
Al, mg/L	0.2	5	0.014637	2.15–44.15
Fe, mg/L	0.2	5	0.014637	66.0–112.5
Mn, mg/L	0.05	20	0.058548	2.8–17.0
As, mg/L	0.01	100	0.292742	2.2–98
Cr, mg/L	0.05	20	0.058548	3.4–111.6
Cu, mg/L	0.1	10	0.029274	2.5–6.4
Ni, mg/L	0.02	50	0.146371	11–62
Pb, mg/L	0.01	100	0.292742	37–93
Zn, mg/L	5	0.2	0.000585	0.024–0.426

Notes: * according to Law 311/2004 458/2002; Council Directive. 98/83/EC; WHO, 2011 [8,66,80].

Figure 5 illustrates the assessment of groundwater quality for wells P1–P6 using the *WQI* method. *WQI* scores ranged from 31.75 to 63.43, with a mean value of 43.68 ± 12.50 . P1, P3, P5, and P6 were classified as having excellent water quality. P4, having a 50.97 score, was very close to being classified as excellent quality, and P2 water was in the good quality class.

The main contributors to the *WQI* scores were As with a score of WQI_{As} in the range of 0.64–24.88 with the highest value found for the P2 sample, Ni (1.6–9.08) with the highest value for P3, and Pb (10.83–27.23) with the highest value for P2. The high value of *WQI* for Cr was calculated for P3 (6.53) while P4 registered a high value for WQI_{Sr} (3.26). One study [46] stated that *WQI* indices, utilizing physico-chemical parameters of water, were employed to evaluate the water quality evolution of Teceu Lake. This lake is situated in the Upper Tisa protected area in the northwest of Romania, along with a groundwater source in close proximity. The assessment was conducted using *WQI* indices for the period spanning January to December 2022, presenting *WQI* in the range of 17.71–37.94 for groundwater source (excellent quality) while the *WQI* score of Teceu Lake water was between 22.95 and 146.31 and indicated excellent-quality, good-quality, and poor-quality water depending on the month in which the water samples were collected [46]. The *WQI* values showed an increasing trend during the month of the year, with maximum values in October and November, especially due to nutrient content, ammonium, and phosphates. In another

investigation [40], focusing on Seini town in the northwest of Romania, *WQI* indices were derived from sixteen chemical indicators, encompassing key physico-chemical parameters, Al, and heavy metals. The findings revealed that 65% of the groundwater samples exhibited excellent quality, while the remaining samples demonstrated poor and very poor quality. This was attributed to elevated concentrations of NH_4^+ , NO_3^- , Fe, Cu, and Pb surpassing the maximum allowable concentrations (MAC). Globally, *WQI* values ranging from 51.84 to 159.41 indicate that the water quality of four lakes situated in the Bangalore Urban district, the most densely populated district in the Indian state of Karnataka, falls within poor, very poor, and unsuitable categories. This assessment is based on the consideration of 10 parameters: pH, turbidity, total alkalinity, total acidity, total phosphorus, chemical oxygen demand (COD), biochemical oxygen demand (BOD), dissolved oxygen (DO), nitrates, and total nitrogen [81]. Moreover, in Cameroon, the *WQI* scores of groundwater in the Ngoua watershed, the primary water supply source for Douala city, located at the shore of the Atlantic Ocean, vary between 2.12 and 187.21. In the computation of the *WQI*, the main physico-chemical indicators of water were considered: pH, turbidity, EC, total dissolved solids, salinity, and the concentrations of major cations and anions. The main contaminants in groundwater in the area were sulfates and nitrates [82].

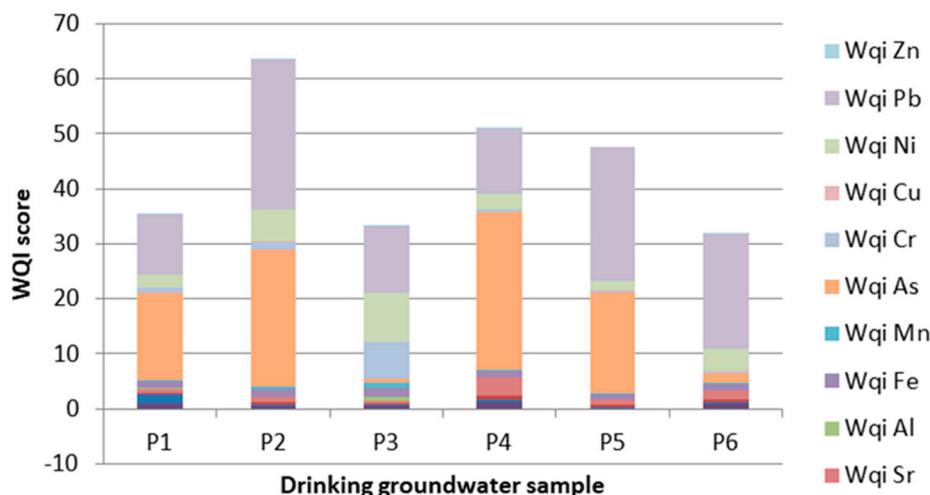


Figure 5. The water quality indices (*WQI*) of groundwater samples P1–P6 are shown as a stacked graphic, showing the main contribution to the *WQI* score.

3.6. Human Health Risk Assessment

The human health risk associated with P1–P6 groundwater consumption was assessed for adults (men and women) and children. The average *CDI* results of nitrogen compounds (NO_3^- and NH_4^+), metals, and As were obtained in the following order: $\text{NO}_3^- > \text{NH}_4^+ > \text{Sr} > \text{Fe} > \text{Cr} > \text{Pb} > \text{Ni} > \text{As} > \text{Cu}$. The highest values of *CDI* were found for NO_3^- in P6, with 0.12 mg/kg·day for adults (men and women) and 0.51 mg/kg·day for children. High *CDI* values were calculated for NH_4^+ in P4: 0.0245 mg/kg·day for men and women and in P1 (0.0198 mg/kg·day) in the case of men and women, while for children the *CDI* was 0.105 mg/kg·day. Between metals and As, the highest *CDI* was obtained for Sr in P4, with 0.01 mg/kg·day for adults and 0.042 mg/kg·day for children. *CDI* for Cr in P3 was 0.0013 mg/kg·day for men and women and 0.005 mg/kg·day for children. A high value of *CDI* was obtained for As in P4: 0.00022 and 0.00094 mg/kg·day for adults and children, and in P2: 0.00019 and 0.00081 mg/kg·day for adults and children. The hazard quotients and hazard index due to groundwater intake are shown in Table 4.

Table 4. Hazard quotients, *HQ*, and hazard index, *HI*.

Groundwater Sample/Pollutant	P1	P2	P3	P4	P5	P6
NH₄⁺						
Male	0.0204	0.01116	0.0065	0.0254	0.0009	0.0179
Female	0.0206	0.0112	0.0065	0.0255	0.0009	0.0180
Children	0.0870	0.0475	0.0277	0.1078	0.0040	0.0761
NO₃⁻						
Male	0.0594	0.0336	0.0180	0.0314	0.0021	0.0750
Female	0.0596	0.0337	0.0181	0.0316	0.0021	0.0754
Children	0.2523	0.1426	0.0767	0.1336	0.0090	0.3188
Sr						
Male	0.0033	0.0047	0.0028	0.0168	0.0050	0.0077
Female	0.0033	0.0048	0.0028	0.0168	0.0050	0.0077
Children	0.0055	0.0079	0.0047	0.0279	0.0083	0.0128
Fe						
Male	0.0056	0.0063	0.0073	0.0056	0.0043	0.0047
Female	0.0057	0.0063	0.0073	0.0057	0.0043	0.0048
Children	0.0240	0.0267	0.0308	0.0240	0.0181	0.0201
As						
Male	0.4061	0.6392	0.0165	0.7370	0.4662	0.0414
Female	0.4080	0.6421	0.0166	0.7404	0.4684	0.0416
Children	1.7260	2.7169	0.0703	3.1324	1.9817	0.1758
Cr						
Male	0.5715	0.9475	4.1962	0.2557	0.1955	0.1278
Female	0.5742	0.9519	4.2155	0.2569	0.1964	0.1284
Children	2.4292	4.0274	17.8355	1.0868	0.8310	0.5434
Cu						
Male	0.1128	0.1850	0.1489	0.1128	0.2301	0.2888
Female	0.1133	0.1858	0.1496	0.1133	0.2312	0.2901
Children	0.4795	0.7863	0.6329	0.4795	0.9781	1.2274
Ni						
Male	0.0130	0.0322	0.0518	0.0150	0.0092	0.0234
Female	0.0130	0.0323	0.0520	0.0151	0.0092	0.0235
Children	0.0550	0.1367	0.2202	0.0639	0.0391	0.0994
Pb						
Male	0.2782	0.6994	0.3083	0.3083	0.6242	0.5339
Female	0.2795	0.7026	0.3097	0.3097	0.6270	0.5364
Children	1.1826	2.9726	1.3105	1.3105	2.6530	2.2694
HI						
Male	1.38	2.50	4.72	1.43	1.53	1.02
Female	1.39	2.51	4.74	1.44	1.53	1.02
Children	6.24	10.86	20.21	6.37	6.52	4.74

The risk indices were applied for NH₄⁺, NO₃⁻, Sr, Fe, As, Cr, Cu, Ni, and Pb, for which the studied groundwater sources indicated high concentrations of these constituents around the MACs. Hazard quotient (*HQ*) values exceeded one for chromium in well P3 for both adults and children, as well as for children in groundwater sources P1–P4. High *HQ* Pb values for children showed that they are exposed to health risks due to water ingestion from all the groundwater sources investigated. The lowest *HI* values were assessed in the case of P6 (1.02 for adults and 4.74 for children), while the highest values were calculated

for P3 groundwater. In the case of children, *HQ* values higher than one were computed for Cr in P1–P4, for Pb in all the groundwater sources, and for As in P1, P2, P4, and P5, and for Cu in P6. Other research indicated significantly higher *HQ* values for children compared to those calculated for adults [56,83,84].

Conversely, the health risk assessment of the groundwater sample in Seini town, NW of Romania, indicated $HQ > 1$ for NO_3^- in some of the samples but low values of *HQ* for Cu, Pb, and Mn [40]. Napo et al., 2021 [56], assessed the health risk associated with oral exposure to groundwater in Togo's coastal sedimentary basin for males, women, and children, with a mean value of *HQ* of 0.963, 1.226, and 2.098, especially due to manganese, nitrate, arsenic, fluoride, and cadmium. The groundwater sources were affected by seawater intrusion, evaporite dissolution, and anthropogenic contamination. Moreover, groundwater in the Xinzhou Basin, situated in the semiarid region of central-eastern Shanxi Province in North China [83], was evaluated by computing the health risk posed by the contaminants NO_3^- , NO_2^- , and F^- , which exceeded the standard limits in some of the samples and found *HQ* oral values of 0.02 to 2.14 for men, 0.02 to 2.72 for women, and 0.04 to 4.66 for children. Health indices provide a precise evaluation of water quality risks for human consumption. Examining multiple parameters enhances the accuracy of identifying contaminants and health concerns. Utilizing these indices guides effective mitigation strategies, facilitates informed decision-making, and ultimately safeguards the well-being of communities relying on well water sources for multiple purposes.

4. Conclusions

This study delves into the assessment of water quality using pollution and quality indices, with a specific emphasis on evaluating potential human health risks linked to water consumption. The emphasis is on toxicological aspects that may impact human health, examining the correlation among chemical indicators that collectively influence well-being. The results indicate that groundwater specimens sourced from the safeguarded Tisa River Basin exhibit elevated levels of NH_4^+ , Fe, Cl^- , and Mn, surpassing maximum allowable concentrations (MACs). Additionally, Cr concentrations exceed the MACs. Notably, ammonium concentrations were highest in P1, P4, and P6, resulting from the melting of snow, seepage with organic content, and the breakdown of vegetation and phytoplankton. The *HEI* values showed low levels of pollution. The *WQI* method indicated P1, P2, P4, and P6 as excellent-quality water, while the groundwater in P4 and P2 was classified as good quality. However, health risk assessment indicated a risk associated with water consumption higher than one in the case of all the groundwater sources, but the highest *HQ* value was computed for Cr in the P3 groundwater source. *HI* values were greater than 1 for all groundwater samples whose ingestion poses a health risk to consumers. The highest health risk assessed was computed for children, who are more vulnerable to the water pollutant due to their low mass. The findings underscore the need for sustainable and protective policies to mitigate potential adverse effects on human health. This research serves as a valuable foundation for future studies, particularly in areas with industrial and agricultural activities. Furthermore, it provides crucial information for water treatment specialists to design centralized water supply systems, ensuring that residents are informed about water quality and the potential health implications associated with their consumption.

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