

Article

# Quality and Health Risk Assessment Associated with Water Consumption—A Case Study on Karstic Springs

Ana Moldovan <sup>1,2</sup>, Maria-Alexandra Hoaghia <sup>1,\*</sup>, Eniko Kovacs <sup>1,3</sup>, Ionuț Cornel Mirea <sup>4</sup> , Marius Kenesz <sup>5</sup>, Răzvan Adrian Arghir <sup>4</sup>, Alexandru Petculescu <sup>4</sup>, Erika Andrea Levei <sup>1</sup> , and Oana Teodora Moldovan <sup>5</sup> 

<sup>1</sup> INCDO-INOE 2000, Research Institute for Analytical Instrumentation, 67 Donath Street, 400293 Cluj-Napoca, Romania; ana.moldovan@icia.ro (A.M.); eniko.kovacs@icia.ro (E.K.); erika.levai@icia.ro (E.A.L.)

<sup>2</sup> Faculty of Materials and Environmental Engineering, Technical University, 103-105 Muncii Boulevard, 400641 Cluj-Napoca, Romania

<sup>3</sup> Faculty of Horticulture, University of Agricultural Sciences and Veterinary Medicine, 3-5 Manastur Street, 400372 Cluj-Napoca, Romania

<sup>4</sup> Department of Geospeleology and Paleontology, Emil Racovita Institute of Speleology, Calea 13 Septembrie 13, 050711 Bucharest, Romania; ionut.cornel.mirea@gmail.com (I.C.M.); razvanarghir@gmail.com (R.A.A.); alexpet@gmail.com (A.P.)

<sup>5</sup> Emil Racovita Institute of Speleology, Clinicilor 5, 400006 Cluj-Napoca, Romania; marius\_kenesz@yahoo.com (M.K.); oanamol35@gmail.com (O.T.M.)

\* Correspondence: alexandra.hoaghia@icia.ro

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**Abstract:** In rural areas without centralized water supply systems, inhabitants often use groundwater of unknown quality as drinking water, without understanding the possible negative consequences on their health. Karstic spring waters from Dobrogea region in Romania were assessed for their potential to be used as drinking water source, according to their quality and seasonal variation. The physico-chemical parameters of waters were compared with the guideline values for drinking water established by the World Health Organization and the Directive 98/83/EC. The nitrate and Cr concentrations exceeded the guideline value in the springs from Southern Dobrogea, but met the quality criteria in those from Northern Dobrogea, thus, to be used as drinking water, the karstic springs located in Southern Dobrogea require treatment for nitrates removal. Heavy metals pollution indices showed low to medium cumulative heavy metal pollution in all springs, while the human health risk assessment by oral exposure indicated possible noncarcinogenic risks of nitrates, both for adults and children in springs from South Dobrogea. A rigorous monitoring of the water quality before human consumption is recommended for all four studied water sources.

**Keywords:** karstic springs; drinking water quality; nitrate; health risk assessment; metal pollution indices; Dobrogea; Romania

## 1. Introduction

Groundwater represents a significant freshwater source and a critical natural resource, and, in many areas, it constitutes the primary source of drinking water. Groundwater or aquifer vulnerability depends on the properties of the layers situated above the saturated zone to attenuate the pollutants' effects, by retention or neutralization by chemical reactions [1]. The infiltration of the pollutants is predominantly diffuse in karst areas and their discharge is concentrated (e.g., natural springs or tube

wells), deteriorating the quality of drinking water [2]. The quality of groundwater is superior to surface water, but it is influenced by various drivers such as anthropogenic pollution (urbanization, industrial sources, sanitation, intensive agricultural practices) and natural processes (geological substrates, recharge water quality) [3,4].

Contamination with nutrients (especially phosphates and nitrates) in agricultural and urban areas, release of Ni, Cr, and Mn by bedrock weathering and seawater intrusion along coastal aquifers by overexploitation were the main factors and mechanisms controlling the distribution of major and trace elements in groundwaters used for irrigation and drinking purposes in Attica region, Greece [5]. The quality and quantity of karstic springs is also influenced by the aridity level and droughts [6]. The major factors influencing the evolution of groundwater chemistry in the Jinta Basin, China were found to be rock weathering, evaporative concentration of salt under water–rock interaction and precipitation, whereas the dissolution of carbonate had little influence [7]. The increase of as concentration following continuous exchange with the shallow aquifer and the high concentration of K and nitrates following substantial anthropogenic soil use were the main contamination mechanisms of the groundwater in Sant'eufemia Plain (Calabria, Italy) [8–10].

Among the wide variety of pollutants impacting groundwater, heavy and trace metal contamination raises serious concerns, the majority having toxic effects on the aquatic ecosystem and on human health when their concentrations exceed the maximum permissible limits or when it accumulates over long periods of time [11–13]. Cadmium (Cd), lead (Pb), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), and zinc (Zn) are the most prevalent heavy metals that humans are exposed to and are harmful even at low concentrations. For instance, Cd affects the kidney, skeleton, skin, muscles, and can cause cancer [14,15]. Pb is also highly toxic, causing high blood pressure, headache, abdominal pain, lung, and stomach cancers [16,17]. Toxic metals negatively influence the nervous, circulatory, and immune systems, causing cognitive disorders, behavioural issues, and liver disorders [18,19]. Nitrate represents another important groundwater pollutant, especially in rural areas, deriving mainly from agricultural practices, waste and manure disposal, and lack of sewage management. The exposure to high nitrate levels can generate lethal diseases such as methemoglobinemia in infants and cancer in adults [20].

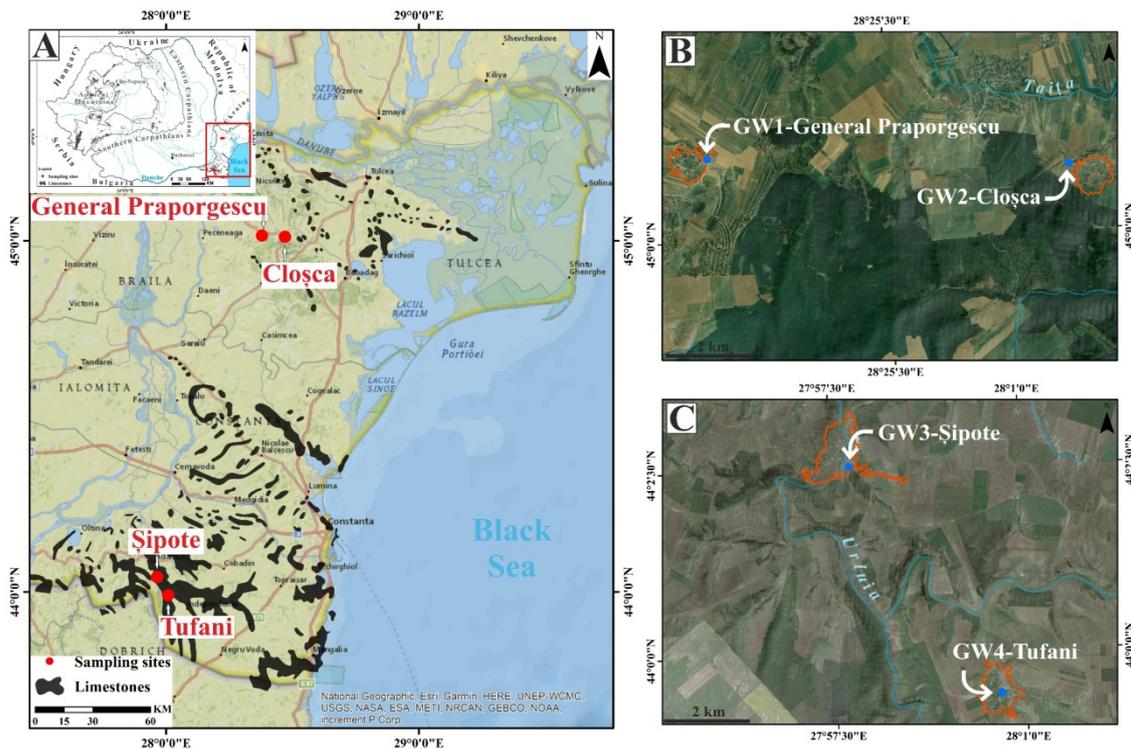
There are two main routes through which pollutants from water reach the human body: ingestion and dermal absorption. For the assessment of possible noncarcinogenic health risks, the Chronic Daily Intake (CDI), the Hazard Quotient (HQ), the Hazard Index (HI), and Total Hazard Index (THI) are most commonly applied [14,17,18]. In addition, several indices such as Heavy metal Pollution Index (HPI) and Heavy metal Evaluation Index (HEI) have been developed and used to assess the pollution of groundwater [20–24].

At European level around 90% of the population has access to public water supply and sanitation, but in Romania only 69.4% of the population has access to the public water supply system. While the water distribution network reaches 98.7% of the urban population, only 35.3% of the rural population is connected to the public network [25]. In rural areas without a water supply system, households are using untreated and often groundwater of unknown quality groundwater pumped from tube wells without understanding the possible consequences on their health. In Dobrogea area, characterized by aridity, drought, and porous environment, the karstic springs are considered the main drinking water sources, due to the mean annual precipitation (350–450 mm). In this context, assessing and monitoring groundwater quality is needed in order to ensure that rural populations have access to a good quality and safe drinking water, as specified by the EU Water Framework Directive (WFD 2000/60/EC), Groundwater Directive (GWD 2006/118/EC), and the values recommended by the World Health Organization (WHO) guideline for drinking purposes [26–28]. This study presents the seasonal variation of karstic spring waters quality from the Dobrogea region in Romania, used as drinking water sources by the local population. The water quality was assessed using the Water Quality Index (WQI), HEI, and HPI. The health risk through ingestion and dermal routes was assessed using CDI, HQ, HI, and THI.

## 2. Materials and Methods

### 2.1. Description of the Study Area

Four karstic springs (GW1—General Praporgescu (Praporgescu), GW2—Cloșca (Closca), GW3—Șipote (Sipote), and GW4—Tufani) located in four remote rural areas from south-eastern Romania were selected for this study (Figure 1, Table 1). The GW1 and GW2 springs are situated in Northern Dobrogea, while GW3 and GW4 are situated in Southern Dobrogea. Approximately 90% of the population in the studied localities uses GW1-GW4 water sources for drinking and other household needs. The long-term use of unknown quality groundwaters as drinking water could induce potential health risks.



**Figure 1.** (A) Dobrogea map with the location of the four karstic springs. (B) Representation of the village’s administrative boundaries and the sampling points GW1—Praporgescu and GW2—Cloșca; (C) Representation of the village’s administrative boundaries and the sampling points GW 3—Șipote and GW4—Tufani.

**Table 1.** Geology and geographic particularities of the tested springs area [29].

Spring	GW1	GW2	GW3	GW4
Area	Northern Dobrogea		Southern Dobrogea	
Altitude (m a.s.l.)	139	88	57	78
Geology	Sandstone, conglomerate limestones	Sandstone, limestone	Limestone, marl limestone, clays, dolomites	Lumashelic limestone, Nubeculoria limestone, clays, diatomites
Soil	Carbonate chernozems	Chernozems, alluvial soils	Rendzinas, rocks	Alluvial soils
Surface use	Arable land/forest/soft loam	Arable land/forest/soft loam	Arable land	Arable land/soft loam
No. of inhabitants	181	101	566	362
Water flow (L/min)	42–120	120–200	2.3–21	6.0–12.5
Temperature (°C)	12.9–15.8	14.2–15.5	4.7–20.4	10.5–15.5

Praporgescu spring (GW1, 45°0'52.99" N, 28°22'42.93" E) belongs to the Danube basin at the limit with Taita basin, the last also including the Closca spring (GW2, 45°0'40.04" N, 28°28'9.70" E). GW1 is situated in the eastern part of the General Praporgescu village, while GW2 in the western part of the Closca village. Sipote spring (GW3, 44°2'31.39" N, 27°57'45.76" E) is situated in the south-eastern part of Sipote village, while Tufani spring (GW4, 43°59'21.22" N, 28°0'28.93" E) is located at almost 8 km south-east from Sipote, both springs belong to the Urluia basin. The main anthropic activities in the surrounding areas of the springs are related to agricultural practices (pastoral, arable, and mixed farming). The local population uses water from these four karstic springs as the main source of drinking water for human and livestock consumption, albeit the water quality is not assessed and monitored by the local or national authorities.

Northern Dobrogea is characterized by faulted limestones and dolomitic limestones, but the karst landscape is isolated (e.g., small ridges) and disrupted by the loess cover, the most important karst features being represented by cliffs (e.g., Somova, Mahmudia, Murighiol). Southern Dobrogea is represented by a platform region composed of three main karst units (Jurassic, Cretaceous, and Eocene), characterized by a semiburied plateau, the main karst feature being represented by large closed depressions filled with loess and dry valleys [29]. From hydrogeological perspective, Northern Dobrogea belongs to the North Dobrogea Orogen Karst, where the carbonate rocks are represented mostly by Triassic dolomitic limestones (Figure 2), and is characterized by a low hydraulic gradient of the aquifer accumulations and a dry pluviometric regime (250–530 mm). These factors determine relatively reduced discharges of the karstic springs [30]. In Southern Dobrogea, the geological settings sustained the development of a karstic aquifer of platform type (Figure 2), represented mostly by almost horizontal limestone layers (which can impose a slow underground flow), thick layers of carbonate successions and vertical faults, low precipitations, and few temporary water courses (Valea Baciului, Urluia, Cerchez). This karstic aquifer is formed by two superposed aquifers represented by the upper aquifer (developed in the Sarmatian limestones) and the lower aquifer (represented by a unitary karstified limestone and dolomitic complex in the Jurassic and Barremian limestone formations) [31]. The main difference between Northern and Southern Dobrogea groundwaters is the main drainage direction. The northern region is characterized by East–South drainage direction, while the southern region, by two superposed aquifers (upper and lower). Both regions are affected by drought and low precipitation input, slow underground water flow, and scarce superficial flow.

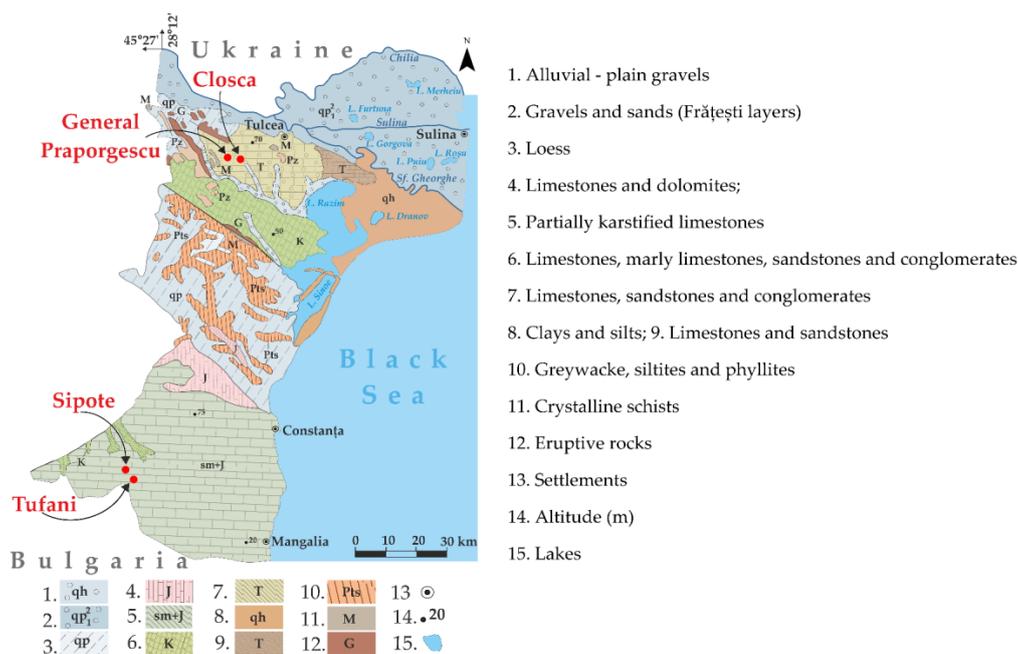
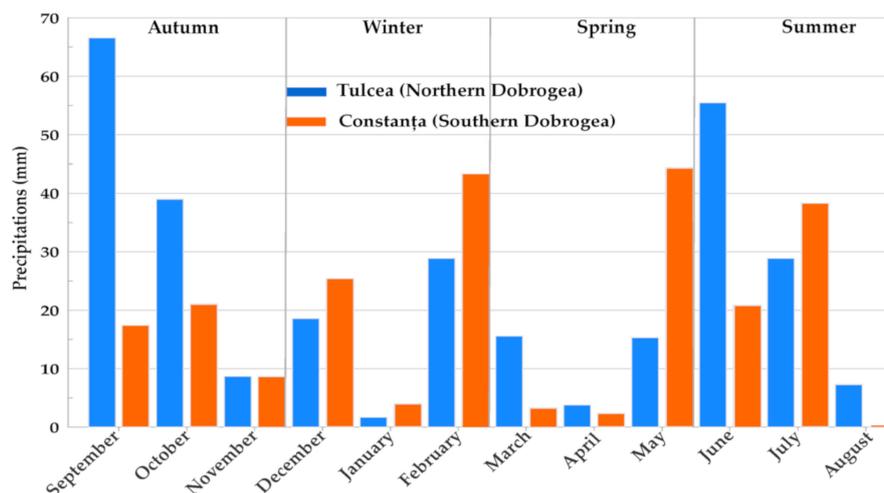


Figure 2. Hydrogeological map of Dobrogea (modified after Ghenea) [32].

The number of inhabitants that use GW3 and GW4 as drinking water sources are 3-fold higher, while the flow rates are one order of magnitude lower than of GW1 and GW3. The human induced alteration of the groundwater flow by intensive usage in the case of GW3 and GW4 might contribute to the increase of pollutants concentration and water quality decline of these springs by the mobilization of naturally occurring trace elements from the aquifer materials through which the water flows [33].

From a climatic perspective, Dobrogea represents one of the most arid regions of Romania, where drought can affect large areas, especially during summer. Records for the period 1961–2009 from nine meteorological stations located in Dobrogea showed a rainfall variation between 257 and 535 mm, while the annual average temperature ranged between 10.1 and 11.8 °C [34]. For the present study, data from the European Climate Assessment and Dataset [35] and data from two representative meteorological stations (Tulcea and Constanta) for Northern and Southern Dobrogea were used. The average rainfall for the sampling period (September 2019–August 2020) reached 299 mm for Northern Dobrogea and 229 mm for Northern and Southern Dobrogea were used. The average rainfall for September 2019–August 2020 period reached 298.9 mm for Northern Dobrogea and 229.2 mm for Southern Dobrogea (Figure 3). The annual mean temperature for Northern Dobrogea was 13.5 °C, with a minimum temperature of −3.2 °C and a maximum of 28.3 °C, and a mean annual temperature of 14.3 °C, with a minimum −2.6 °C and a maximum of 28.1 °C for Southern Dobrogea (Figure 4). At global scale, Dobrogea has a semiarid climate, according to the Köppen–Geiger climate classification [36]. Moreover, giving a different Köppen–Geiger climate classification at a regional scale [37], Northern Dobrogea is characterized by a warm continental climate, while Southern Dobrogea is situated in a warm oceanic climate.



**Figure 3.** Monthly average precipitation in Northern and Southern Dobrogea (Tulcea and Constanta meteorological stations) between September 2019 and August 2020.

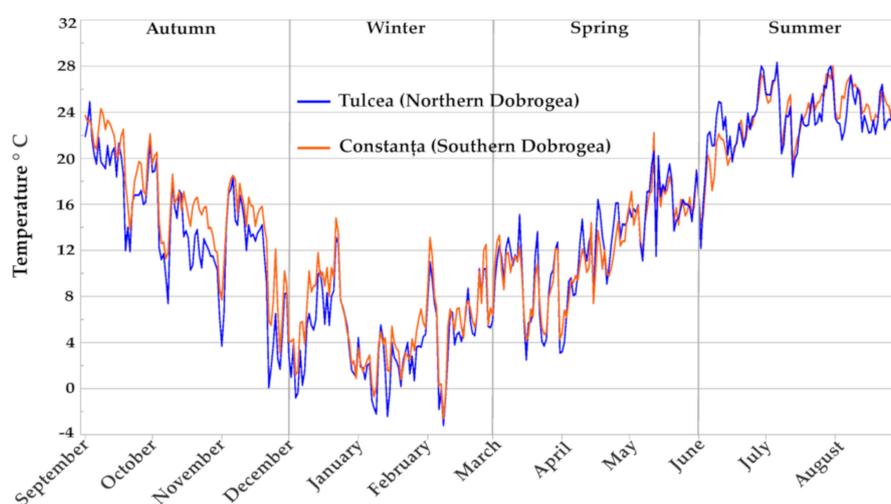
In Table 2, the mean temperatures and precipitation, according to the Tulcea and Constanta meteorological stations for the studied period are presented.

**Table 2.** Average temperatures and precipitation in Northern (Tulcea) and Southern Dobrogea (Constanta).

Parameters	Meteorological Station	Autumn	Winter	Spring	Summer
Temperatures (°C)	Northern Dobrogea	14.2	4.31	12.3	23.3
	Southern Dobrogea	16.3	5.52	11.9	23.5
Precipitations (mm)	Northern Dobrogea	114	49.2	34.7	91.7
	Southern Dobrogea	47.2	72.7	50.1	59.2

Land use of the territorial functional regions is presented in Figure 5. In Northern Dobrogea, the territorial administrative unit (TAU) Cerna (including General Praporgescu village) covers a surface

of  $\approx 200$  km<sup>2</sup>, the largest area being covered by nonirrigated arable land ( $\approx 122$  km<sup>2</sup>), broad-leaved forest ( $\approx 27$  km<sup>2</sup>), and natural grasslands ( $\approx 22$  km<sup>2</sup>), while, in the TAU of Horia (including Closca village), with a surface of  $\approx 40$  km<sup>2</sup>, the largest area is covered by nonirrigated arable land ( $\approx 26$  km<sup>2</sup>) and pastures ( $\approx 5$  km<sup>2</sup>) [38]. In Southern Dobrogea, the Deleni (including Sipote village) and Independența (including Tufani vilage) TAUs cover 170 km<sup>2</sup>, respectively, 190 km<sup>2</sup>. The main functional areas are represented by nonirrigated arable land (122 km<sup>2</sup>, respectively, 140 km<sup>2</sup>), pastures (27 km<sup>2</sup>, respectively, 20 km<sup>2</sup>), and broad-leaved forest (10 km<sup>2</sup>, respectively, 20 km<sup>2</sup>) [38]. In all the studied areas, the urban fabric had low occupancy surface: 6 km<sup>2</sup> in Cerna TAU, 7 km<sup>2</sup> in Horia TAU and 3 km<sup>2</sup> in Deleni and Independența TAUs [38]. Thus, the main anthropogenic activities in the area that could negatively impact the karstic waters are agriculture, animal husbandry and household activities by diffuse infiltration of the fertilizers and manure. Industrial or commercial units, mineral extractions sites, vineyards, mixed forest lands, inland marshes, and water bodies are functional areas category with a surface occupancy rate of less than 3%.



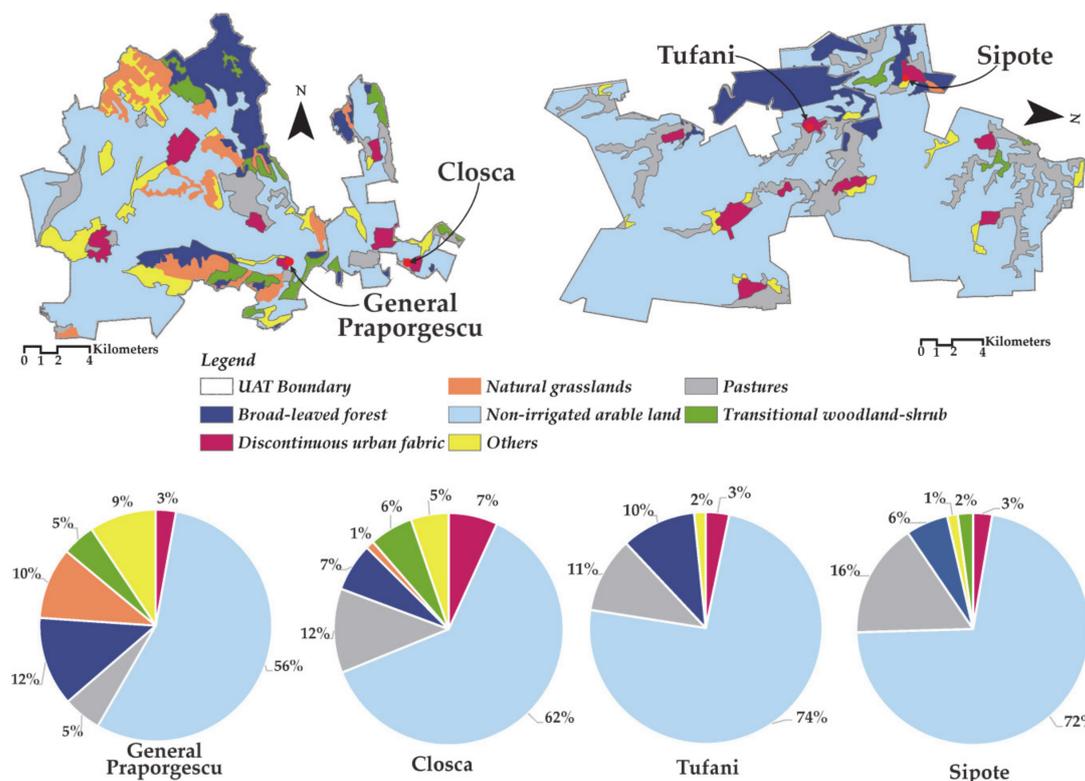
**Figure 4.** Daily mean temperature from Northern and Southern Dobrogea (Tulcea and Constanța meteorological stations) between September 2019 and August 2020.

## 2.2. Field Sampling and Analytical Procedures

The water samples were collected from karstic springs GW1-GW4 in four seasons (autumn 2019, winter 2019, spring 2020, and summer 2020). The samples were stored in precleaned polyethylene bottles and kept at 4 °C during transportation. The field-based water parameters such as temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO) were measured in situ using a Hanna HI 9829 Multiparameter (Hanna, Woonsocket, RI, USA). The instrument was calibrated on-site using HI 9828-25 (Hanna, Woonsocket, RI, USA) standard solution for pH and EC and HI 7040-L (Hanna, Woonsocket, RI, USA) standard solution for DO.

In the laboratory, total alkalinity and bicarbonates were determined by titration with 0.1 N HCl against bromocresol green. For the anions and metals determination, the water samples were filtrated through 0.45  $\mu$ m cellulose acetate membrane filters. Anions ( $F^-$ ,  $Cl^-$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ) were measured using a 761 IC compact ion chromatograph (Metrohm, Herisau, Switzerland), equipped with a Metrosep column 5–100/4 column and a Metrosep A Supp 4/5 mm guard column. A total of 20  $\mu$ L of sample were injected with flow rate of 0.7 mL/min. Dissolved organic carbon (DOC) was measured by catalytic combustion followed by nondispersive infrared detection using a Multi N/C 2100 S analyzer (Analytic Jena, Jena, Germany) after filtering the samples through 0.45  $\mu$ m polytetrafluoroethylene membrane filters. Turbidity (TU) was measured using a Turb 555 IR (WTW, Weilheim, Germany) turbidimeter. For the metal determination, 50 mL of filtered water were acidulated with 0.5 mL 63%  $HNO_3$ . The major elements (Fe, Na, Mg, K, and Ca) concentration was measured

by inductively coupled plasma atomic emission spectrometry (ICP-OES) using an Optima 5300 DV Spectrometer (Perkin Elmer, Waltham, MA, USA), while trace elements (Cu, Zn, Ni, Cr, Co, Cd, and Pb) concentration was determined by inductively coupled mass spectrometry (ICP-MS), using an ELAN DRC II Spectrometer (Perkin Elmer, Waltham, MA, USA). Based on the Ca and Mg concentrations, the total hardness (TH) as equivalent  $\text{CaCO}_3$  was calculated. All reagents were of analytical grade.



**Figure 5.** Land use categories in the vicinity of the karst springs from Northern and Southern Dobrogea.

The analytical data quality was ensured through the use of calibration standards, procedural blank measurements, and duplicate samples. The accuracy of anions determination was tested by analyzing the concentration of anions from IC 1 Multi-element standard (Certipur Merck, Darmstadt, Germany), while the accuracy for metals determination was tested using NIST 1643e freshwater certified reference material (National Institute of Standards and Technology (NIST), Canada). The mean recoveries were found to range from 89% to 100% for anions and 94% to 102% for metals. Ultrapure water from a Millipore system (Molsheim, France) was used for all the dilutions.

### 2.3. Data Treatment and Statistical Analysis

#### 2.3.1. Water Quality Index (WQI)

The WQI represents a mathematical tool used in assessing the composite influence of specific chemical indicators on the quality status of different types of water [39]. The WQI is computed in four steps, calculated using the following Equations (1)–(4) [39]:

$$\text{WQI} = \sum_{i=1}^n SI_i \quad (1)$$

$$SI_i = W_i \times q_i \quad (2)$$

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

$$q_i = \frac{C_i}{S_i} \times 100 \quad (4)$$

where  $SI_i$  represents the subindex of the  $i$ th indicator,  $W_i$  is the relative weight,  $q_i$  represents the quality rating for each chemical indicator,  $w_i$  is the weight of each element (pH 0.11, EC 0.0004,  $F^-$  0.666,  $Cl^-$  0.004,  $SO_4^{2-}$  0.004, and  $NO_3^-$  0.02),  $n$ ,  $C_i$ , and  $S_i$  represent the total number ( $n = 6$ ), the concentration, and the guideline value (according to drinking water quality guidelines established by the World Health Organization (WHO) and according to the Directive 98/83/EC [25,40]). In this study, a total of six chemical parameters were considered, with guideline values according to WHO and the Directive 98/83/EC for  $F^-$  ( $1.5 \text{ mg L}^{-1}$ ), pH (6.5–9.5), EC ( $2500 \text{ }\mu\text{S cm}^{-1}$ ),  $Cl^-$  ( $250 \text{ mg L}^{-1}$ ),  $NO_3^-$  ( $50 \text{ mg L}^{-1}$ ), and  $SO_4^{2-}$  ( $250 \text{ mg L}^{-1}$ ). The WQI classifies the water quality as excellent ( $WQI < 50$ ), good ( $WQI = 50\text{--}100$ ), poor ( $WQI = 100\text{--}200$ ); very poor ( $WQI = 200\text{--}300$ ) and unsuitable for drinking ( $WQI > 300$ ) [39].

### 2.3.2. Heavy Metal Pollution Index (HPI) and Heavy Metal Evaluation Index (HEI)

The HPI estimates the overall combined effect of individual heavy metals concentration of the quality of water sources [41]. The HPI was calculated using Equation (5) based on the concentration of Cd, Cr, Cu, Ni, Pb, Zn, and Fe and the values established by the WHO guideline and by the Directive 98/83/EC [28,40].

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

where,  $Q_i$  is a subindex calculated according to Equation (6) and  $W_i$  is the unit weightage (the ratio between  $k$  ( $k = 1$ ) and the guideline values) of the  $i$ th parameter and  $n$  is the total number of the considered chemical elements ( $n = 7$ ) [37].

$$Q_i = \sum_{i=1}^n \frac{|C_i - I_i|}{S_i - I_i} \times 100 \quad (6)$$

where,  $C_i$ ,  $I_i$ , and  $S_i$  are the concentration of the  $i$ th element, the ideal, and the standard values, according to the Directive 98/83/EC and WHO guidelines regarding the drinking water quality [28,40]. The used factors are indicated in Table 3. Waters with  $HPI < 100$  are characterized as unpolluted, while with  $HPI > 100$  are classified polluted with heavy metals, considered not suitable for drinking purposes [41].

**Table 3.** The values of coefficients ( $S_i$ ,  $I_i$ , guideline value, and  $W_i$ ) used in HPI computation.

Heavy Metal	$S_i$ * ( $\mu\text{g L}^{-1}$ )	$I_i$ * ( $\mu\text{g L}^{-1}$ )	$W_i$
Cr	50	-	0.02
Cd	3	-	0.333
Cu	1500	50	0.001
Fe	300	-	0.003
Ni	70	20	0.01
Pb	10	-	0.100
Zn	15,000	5000	0.00007

\*  $S_i$ —standard value or guideline values and  $I_i$ —ideal values according to WHO and Kumar et al. [40,42].

The HEI presents the overall groundwater quality with respect to heavy metals content, and is computed using Equation (7) [43]:

$$HEI = \sum_{i=1}^n \frac{H_c}{S_i} \quad (7)$$

where,  $H_c$  is the determined value of the  $i$ th parameter and  $S_i$  represents the guideline value, according to WHO and the Directive 98/83/EC [28,40] (Table 2). The HEI classifies the water as low ( $HEI < 1$ ), medium ( $1 < HEI < 2$ ), and highly polluted ( $HEI > 2$ ) [43].

### 2.3.3. Human Health Risk Assessment

Health risk assessment allows the noncarcinogenic health risk level determination following the consumption of inadequate water [14]. In this research, the populations were divided into two age groups: children (0–21 years) and adults (21–72 years). The human health risk was determined for oral and dermal exposure [18,44]. The chronic daily intake (CDI) of the elements was computed using Equations (8) and (9) [45–48]:

$$CDI_{oral} = \frac{CW \times IR \times EF \times ED}{BW \times AT} \quad (8)$$

where,  $CW$  is the metal or ion concentration ( $\mu\text{g L}^{-1}$ ) [45],  $IR$  is the ingestion rate ( $2.2 \text{ L day}^{-1}$  for adults/ $1 \text{ L day}^{-1}$  for children) [47,48],  $EF$  is the exposure frequency ( $365 \text{ days year}^{-1}$ ) [45],  $ED$  is the exposure duration (70 years for adults/10 years for children) [47,48],  $BW$  is the average body weight (70 kg for adults/25 kg for children) [47,48], and  $AT$  is the average time of the exposure (25,500 days for adults/3650 days for children) [45]:

$$CDI_{dermal} = \frac{CW \times SA \times K_p \times ET \times EF \times ED \times CF}{BW \times AT} \quad (9)$$

where,  $CW$  is the metal or ion concentration ( $\mu\text{g L}^{-1}$ ) [46],  $SA$  is the skin surface area ( $18,000 \text{ cm}^2$  for adults/ $6600 \text{ cm}^2$  for children) [46,48],  $K_p$  is the permeability coefficient ( $1 \times 10^{-3} \text{ cm h}^{-1}$  for  $\text{NO}_3^-$ , Cd, Cr, Cu, Ni, and Fe,  $6 \times 10^{-4} \text{ cm h}^{-1}$  for Zn,  $1 \times 10^{-4} \text{ cm h}^{-1}$  for Pb) [47,48],  $ET$  is the exposure time ( $0.58 \text{ h event}^{-1}$  for adult/ $1.00 \text{ h event}^{-1}$  for children [47,48],  $EF$  is the exposure frequency ( $350 \text{ days year}^{-1}$ ) [47,48],  $ED$  is the exposure duration (30 years for adults/6 years for children) [47,48],  $CF$  is the conversion factor ( $1/1000 \text{ L cm}^{-3}$ ),  $BW$  is the average body weight (70 kg for adults/25 kg for children) of the consumers [47,48], and  $AT$  is the average time of the exposure (10,950 days for adults/2190 days for children) [47,48].

In order to evaluate the noncarcinogenic health risks, the hazard quotient (HQ) was calculated, for both oral and dermal pathways, using Equation (10). According to the United States Environmental Protection Agency (U.S. EPA), HQ results higher than 1.0 indicate the presence of noncarcinogenic risk [45,48].

$$HQ = \frac{CDI}{R_fD} \quad (10)$$

where, the  $R_fD$  is the reference dose ( $\mu\text{g kg}^{-1} \text{ day}^{-1}$ ) equal to 300/45 for Fe, 40/12 for Cu, 1.4/0.42 for Pb, 300/60 for Zn, 20/5.4 for Ni, 3/0.015 for Cr, 0.5/0.005 for Cd [49], and 1600/1100 for  $\text{NO}_3^-$  (oral and dermal exposure) [50].

The overall potential for noncarcinogenic effects of more than one element is defined as the sum of the calculated HQ for each element and expressed as the hazard index (HI). If HI is lower than one ( $HI < 1.0$ ), no chronic risks are assumed to occur and if HI is higher than one ( $HI > 1.0$ ), possible chronic risk generated by water ingestion could appear [47].

Assuming that the risk is cumulative, the total noncarcinogenic risks following exposure to contaminated drinking water is evaluated using the total hazard index (THI) calculated according to Equation (11) [18]:

$$THI = HI_{oral} + HI_{dermal} \quad (11)$$

## 3. Results and Discussion

### 3.1. Physico-Chemical Parameters of the Spring's Water

The temporal variations of the water quality parameters were slightly influenced by the seasonality of rainfall and temperature (Table 4). The pH of GW1 and GW2 were circumneutral, with values in the range of 7.2–7.8, while GW3 and GW4 were slightly alkaline. Generally, higher pH was found in summer and spring than in autumn and winter, however the seasonal variations were low. In general,

the pH indicates the water capacity to react with the acidic or alkaline materials present in water [51]. The average EC was slightly higher in GW3 and GW4 than in the other two springs, with the highest values in autumn and spring in all springs. The mean values of the EC in all four karstic springs were within the values recommended by the WHO guideline for drinking purposes and by the Directive 98/83/EC [28,40]. Generally, DO increases with the decrease of temperature. In the case of karstic waters, the water temperature is more or less constant, and thus the DO values are less season-dependent [52,53]. During the whole year, the water temperature was relatively constant for GW1 (12.9–15.8 °C), GW2 (14.2–15.5 °C), and GW4 (12.5–15.5 °C) and slightly seasonal variations of DO were observed in these springs. In the case of GW3, the water temperature varied widely (4.7–20.4 °C), the highest DO (10.1 mg L<sup>-1</sup>) being measured in winter, when the water temperature was 4.7 °C, and the lowest in summer (7.8 mg L<sup>-1</sup>), when the water temperature was 20.4 °C. The average concentration of DOC was comparable in GW1, GW3, and GW4, and slightly lower in GW2. In all springs, the highest DOC was measured in summer and the lowest in winter, although the seasonal variation was low. TU is caused by suspended organic (decomposed organic matter or living organisms) and inorganic (silt, clay) particles and its increase may indicate a fast transport pathway connecting potentially contaminated surface water with the groundwater. The average TU of GW3 and GW4 were one order of magnitude higher than of GW1 and GW2. TU of GW1 and GW2 was very low and no seasonal variation was noticed, while the TU of GW3 and GW4 varied with the season, being the highest in summer and spring, respectively. The TU in all springs met the recommended drinking water standards, according to the Directive 98/83/EC [28]. The concentration of metals and anions higher than the guideline values alters the quality of water used as drinking water sources [54,55]. With some exceptions, the seasonal variations of the chemical parameters were low. The concentration of Cl<sup>-</sup> was comparable in the four studied springs. The Cl<sup>-</sup> concentration in GW1 and GW2 was the highest in summer and the lowest in spring, while in GW3 and GW4 was the highest in autumn and the lowest in spring (GW3) and summer (GW4), respectively.

The nitrate and fluoride concentrations were much higher in GW3 and GW4 than in GW1 and GW2, while the sulphates were higher in GW1 and GW2 than in the other two springs. The highest concentration of F<sup>-</sup> was measured in GW4, reaching the maximum in autumn, while the highest SO<sub>4</sub><sup>2-</sup> with very low seasonal variations was measured in GW1. The concentrations of nitrites were below the detection limit in all the samples and seasons. The maximum concentration of NO<sub>3</sub><sup>-</sup> was determined in GW3 in autumn (268 mg L<sup>-1</sup>) and the lowest in GW2 in summer (23.1 mg L<sup>-1</sup>). However, important seasonal variation for NO<sub>3</sub><sup>-</sup> was not observed in any of the studied springs.

The NO<sub>3</sub><sup>-</sup> in GW3 and GW4 exceeded the guideline value (50 mg L<sup>-1</sup>), while GW1 and GW2 were below the guideline value. High levels of NO<sub>3</sub><sup>-</sup> in the drinking water in the dry season as well as medium to high-risk levels for infants, children, and adults were reported in Ghana [56,57]. A positive correlation between Cr and NO<sub>3</sub><sup>-</sup> occurs due to bedrock geology and intensive agricultural practices [5]. The HCO<sub>3</sub><sup>-</sup> was the dominant anion with a mean concentration of 506 mg L<sup>-1</sup>, for GW1, 525 mg L<sup>-1</sup> for GW2, and 501 mg L<sup>-1</sup> for GW3. The highest value of HCO<sub>3</sub><sup>-</sup> was determined in autumn in GW4 (683 mg L<sup>-1</sup>), a value that exceeded the recommended value for drinking water purposes by the Directive 98/83/EC (500 mg L<sup>-1</sup>) [28]. The variations of temperature and precipitation regime influence the water quality of karstic springs. Karstic springs water is also influenced by the dissolution of minerals and weathering processes in the bedrock. Agricultural practices alter the quality of karstic springs as well, due to the use of fertilizers based on nitrogen compounds. Mainly, nitrates exceed the guideline values according to the WHO guidelines [36] and to the Directive 98/83/EC [28].

**Table 4.** Physico-chemical parameters of the four studied karstic springs (SUM = summer, AUT = autumn, WIN = winter, SPR = spring,  $DWS_i$  = drinking water standards according to the Directive 98/83/EC [28], and  $S_i$  = guideline values according to WHO [40]) from Dobrogea region, Romania.

Springs	Season	pH	EC	DO	HCO <sub>3</sub> <sup>2-</sup>	DOC	TU	TH	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>	Na	K	Ca	Mg	Fe	Cu	Zn	Ni	Cr	Co	Cd	Pb
			μS cm <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	NTU	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	μg L <sup>-1</sup>						
GW1	SUM	7.7	1036	9.72	510	4.8	0.07	245	59.5	90.5	24.7	0.54	63.9	2.23	98.2	32.2	0.03	1.63	2.86	5.57	5.35	<0.21	<0.32	<0.20
	AUT	7.5	1124	8.75	567	4.0	0.01	179	55.1	109	29.4	0.59	68.3	1.66	71.7	45.4	<0.01	<0.71	8.26	4.28	4.52	<0.21	<0.32	<0.20
	WIN	7.6	1052	7.15	363	3.0	0.07	165	52.5	103	27.5	0.55	58.6	1.69	66.0	36.6	0.09	2.15	3.35	5.08	6.09	1.67	0.79	<0.20
	SPR	7.8	1217	7.79	543	3.4	0.04	252	52.0	106	26.5	0.47	58.5	1.36	101	41.1	<0.01	<0.71	<1.00	2.31	3.08	0.263	<0.32	0.21
	Mean	7.7	1107	8.35	496	3.8	0.05	210	54.8	102	27.0	0.54	62.3	1.73	84.1	38.8	0.02	1.74	4.82	4.31	4.76	0.94	0.41	<0.20
GW2	SUM	7.5	967	7.20	490	3.0	0.01	295	53.5	77.8	23.1	0.25	46.6	2.25	118	36.9	0.02	1.68	3.17	6.42	3.37	<0.21	<0.32	<0.20
	AUT	7.2	1134	6.33	537	1.2	0.01	242	51.7	88.8	28.6	0.28	51.9	2.00	96.7	38.9	<0.01	<0.71	<1.00	5.31	2.27	<0.21	<0.32	<0.20
	WIN	7.2	1006	5.44	519	1.9	0.06	260	50.3	86.5	27.2	0.29	50.1	1.93	104	35.5	0.04	3.34	2.91	6.48	5.61	1.62	0.83	<0.20
	SPR	7.4	1099	4.59	531	2.6	0.02	295	50.0	83.0	26.7	0.22	45.2	1.54	118	37.5	<0.01	<0.71	<1.00	2.62	2.08	0.57	<0.32	0.24
	Mean	7.3	1051	5.89	519	2.2	0.02	273	51.4	84.0	26.4	0.26	48.5	1.93	109	37.2	0.02	2.15	3.04	5.21	3.33	1.08	0.41	<0.20
GW3	SUM	8.5	1204	7.80	500	4.5	1.70	126	65.1	30.0	192	0.54	76.3	5.29	50.4	68.3	0.14	1.54	1.64	3.30	26.7	<0.21	<0.32	<0.20
	AUT	8.4	1362	8.57	480	3.7	1.40	95	66.4	33.0	268	0.73	84.5	4.62	38.1	79.9	<0.01	<0.71	<1.00	2.00	35.4	<0.21	<0.32	<0.20
	WIN	8.4	1224	10.1	470	2.9	0.40	161	65.0	31.0	207	0.66	82.8	4.87	64.6	52.0	<0.01	1.87	1.26	3.79	18.8	1.51	0.70	<0.20
	SPR	8.3	1335	8.29	497	3.9	0.32	142	56.0	27.0	200	0.66	68.5	4.91	56.7	68.4	<0.01	<0.71	<1.00	1.37	21.0	0.52	<0.32	0.23
	Mean	8.4	1281	8.69	487	3.8	0.95	131	63.1	30.0	215	0.65	78.0	4.92	52.4	67.1	0.04	1.74	1.45	2.62	25.5	0.77	0.35	<0.20
GW4	SUM	8.1	1173	10.2	570	4.4	0.22	130	43.3	15.7	93.5	1.13	82.1	14.1	51.9	45.5	0.02	2.41	1.47	2.67	44.7	<0.21	<0.32	<0.20
	AUT	7.9	1311	8.70	683	3.3	0.30	69	47.7	35.4	85.4	1.34	147	3.15	27.6	58.7	<0.01	<0.71	<1.00	<0.48	50.1	<0.21	<0.32	<0.20
	WIN	8.0	1154	8.33	615	2.8	0.28	75	43.6	32.0	75.0	1.05	124	3.35	30.2	46.3	<0.01	1.96	<1.00	2.14	32.8	1.41	0.69	<0.20
	SPR	8.1	1298	8.72	677	3.4	1.17	68	43.5	32.5	78.0	1.00	131	2.70	27.1	59.6	<0.01	<0.71	<1.00	0.89	35.1	0.23	<0.32	0.29
	Mean	8.0	1234	8.99	636	3.5	0.44	85	44.5	28.9	82.2	1.13	121	5.80	34.2	52.5	<0.01	1.62	0.62	1.90	43.1	0.82	0.42	<0.20
$DWS_i$		6.5–9.5	2500	NA	500	NA	NA	NA	NA	250	50	1.5	200	NA	NA	NA	0.2	2000	NA	20	50	NA	5.0	10
$S_i$		6.5–8.5	2500	NA	NA	NA	5.0	NA	NA	250	50	1.5	50	NA	NA	NA	2.0	2000	NA	70	50	NA	3.0	10

The K, Ca, and Mg concentrations in the spring water of the study area did not differ substantially between the sampling seasons: the average values for K varied between 1.73 (GW1) and 5.80 mg L<sup>-1</sup> (GW4), for Ca between 34.2 (GW4) and 109 mg L<sup>-1</sup> (GW2), and for Mg, between 37.2 (GW2) and 67.1 mg L<sup>-1</sup> (GW3). These elements may originate from the dissolution of bedrock minerals such as dolomitic limestone and limestone [5]. The highest variation of Na was observed in GW4, where the concentration in autumn was almost twice the concentration in summer. Based on the TH values, the GW1 and GW2 are classified as very hard (TH < 180), GW3 as hard (121 < TH < 180), and GW4 as moderately hard (61 < TH < 120) waters [58]. Hard water may cause unpleasant taste, scale formations in pipes, and reduces the lather-forming ability of soap, and it may have a potential impact on human health [59]. Calcium and magnesium are essential minerals with important roles in numerous biologic and cellular functions in the human organism [60,61]. Both the high and low levels of these elements in water are associated with health problems. The low levels of Ca or Mg in drinking water may favor osteoporosis, higher incidence of fractures, and disturbed bone development in children, while very high levels of Ca and Mg may increase the risk of renal lithiasis and arthritis. Additionally, there is evidence that suggests a protective or beneficial effect of water Ca and Mg against various neurological, cardiovascular, and metabolic diseases [61–63].

The concentrations of Fe, Cu, Zn, Ni, Co, Cd, and Pb were lower than the guideline values set by the Directive 98/83/EC [28] in all springs and seasons. The highest concentration of Fe was obtained in GW3, of Cu and Ni in GW2 in winter, while of Zn in GW1 in autumn. Cr was the metal with the highest variation among all karstic springs in all seasons, the highest values being determined in GW4, where in autumn exceeded the guideline value (50 mg L<sup>-1</sup>). For GW1 and GW2, the highest concentration of Cr was determined in winter and the lowest in spring, while GW3 and GW4, in autumn, respectively, in winter. Opposite to Cr, the Co, Cd, and Pb had very low seasonal variations in all springs. Co and Cd concentrations had values higher than the detection limits only in winter and spring, and Pb in spring. Comparing springs, GW3 had the highest metal concentration, but regarding the temporal distribution of the metal concentration, GW1 and GW3 had the highest concentration of metals in winter, GW2, in summer and GW4, in autumn.

The Piper diagram allows the visualization of the spring's chemistry and the identification of the water's geochemical facies [64]. According to the Piper diagram, GW1, GW2, and GW3 are classified as Ca-Mg-HCO<sub>3</sub><sup>-</sup> type, while GW4 of Na-HCO<sub>3</sub><sup>-</sup> type which indicates the lateral movement of the water from the karstic dolomitic limestones (Figure 6). Studies in the Attica region, Greece indicated the presence of diverse processes between groundwater and seawater besides the dissolution of carbonate minerals [4]. In the Jinta Basin, China the groundwaters are of Mg-Na-SO<sub>4</sub><sup>2-</sup> and Na-Mg-SO<sub>4</sub><sup>2-</sup>-Cl<sup>-</sup> and Mg-SO<sub>4</sub><sup>2-</sup>-HCO<sub>3</sub><sup>-</sup> types due to the evaporative crystallization and rock weathering (evaporation of salt, dissolution of silicate rock, and sulphate minerals) [6]. In Italy (Calabria), four main water types were identified: Ca-HCO<sub>3</sub><sup>-</sup>, Na-Cl<sup>-</sup>, Ca-SO<sub>4</sub><sup>2-</sup>, and Ca-HCO<sub>3</sub><sup>-</sup>, due to the interactions between water and rocks [8].

The Total Ionic Salinity (TIS) plot (Figure 7) indicated that the studied samples have different TIS values ranging between 15 and 25 meq L<sup>-1</sup>. The lowest values were obtained for the Ca-Mg-HCO<sub>3</sub><sup>-</sup> type (sample GW3) in summer and the highest for GW2 in spring. The Na-HCO<sub>3</sub><sup>-</sup> type (GW4) in spring has the highest TIS value.

The groundwater dynamics depend on the tectonic, structural, and morphological settings in which the carbonate rocks are developed, while karst aquifers are directly influenced by the recharge, circulation, and discharge of underground waters [13]. Due to their enhanced permeability, karst aquifers are vulnerable to pollution as runoff can easily reach through conduits into the springs, especially during precipitation. Nutrients (nitrogen, phosphate) and metals are frequently present in surface runoff. Agricultural activities are the main sources of diffuse water pollution in the Dobrogea region. Our data showed that the Southern Dobrogean spring waters pollution with nitrates and Cr is of anthropogenic nature. The local sources of nitrates come from fertilizers used on arable lands, especially natural manure used by the residing population. Besides, due to the lack of centralized

sanitation, nitrates infiltrate the porous geological substrates. Cr is presumably also derived from anthropogenic activities, such as agriculture, sewage sludge. There are no mining deposits or industrial sites in the region.

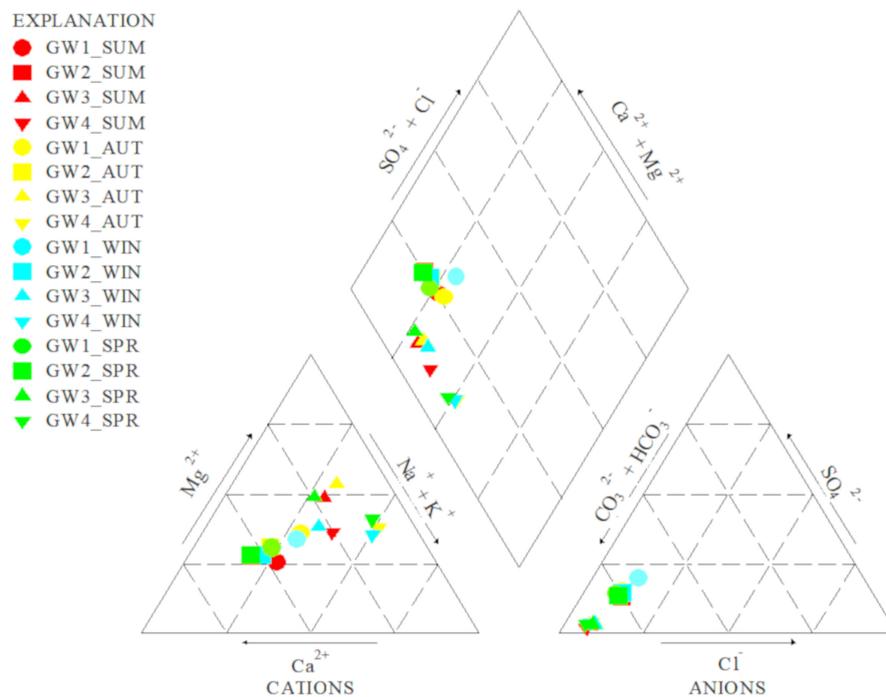


Figure 6. Piper diagram of the studied karstic spring waters.

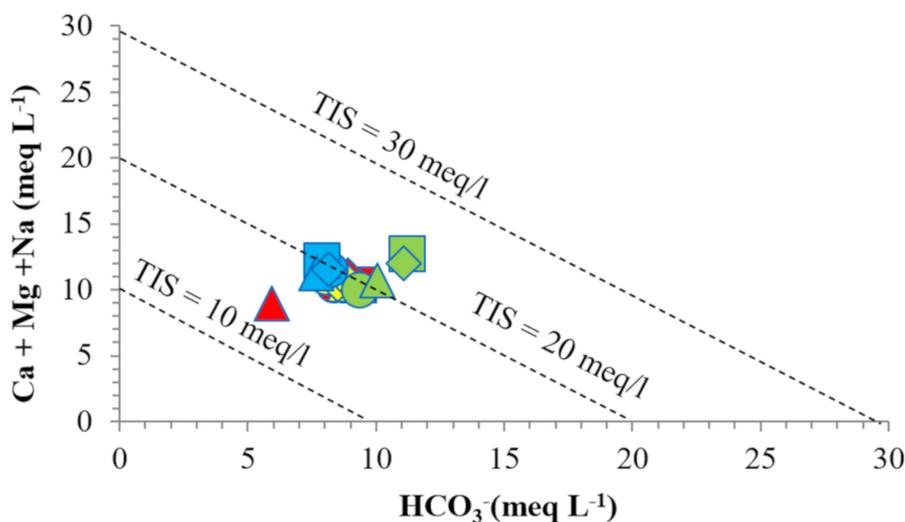


Figure 7. Correlation diagram of  $\text{HCO}_3^-$  and  $\text{Ca}+\text{Mg}+\text{Na}$ .

### 3.2. Water Quality Indices

The WQI (Table 5) ranged between 24.1 and 89.8 indicating good to excellent water quality. Generally, the WQI was comparable between seasons, GW1 and GW2 having excellent quality ( $\text{WQI} < 50$ ), while GW3 and GW4 good quality ( $50 < \text{WQI} < 100$ ) in all four seasons. The highest WQI was obtained in GW4 (89.8), followed by GW3 (65.8) in autumn.

In several studies conducted in Romania on groundwater sources, the WQI indicated various water quality ranging from poor to excellent. The water quality degradation was attributed to high  $\text{NO}_3^-$ , Cu, Ni, Pb, and Zn concentrations that resulted from anthropogenic activities (agriculture, house holding, and industry) [23,64].

**Table 5.** The WQI, HPI, and HEI results calculated for all four seasons.

Indices	Season	GW1	GW2	GW3	GW4
WQI	SUM	42.2	25.7	51.6	78.8
	AUT	45.0	27.3	65.8	89.8
	WIN	42.8	27.7	58.5	73.3
	SPR	38.6	24.1	58.4	70.7
HPI	SUM	94.8	89.2	142	179
	AUT	95.5	89.4	162	196
	WIN	123	119	151	179
	SPR	97.0	94.4	135	164
HEI	SUM	0.19	0.17	0.59	0.94
	AUT	0.16	0.13	0.74	1.01
	WIN	0.46	0.47	0.70	0.92
	SPR	0.12	0.10	0.47	0.73

Some studies on groundwater from Asia (Bokaro district, India) and Africa (Bonkoukou, Niger) indicated high values for the WQI (>150), showing inadequacy for drinking purposes or poor quality, due to the anthropogenic activities (agricultural waste, untreated domestic waters), but also due to natural processes (rock weathering, intrusion of sea water) [65–68]. In Europe, studies on karstic waters in the Megara basin, Greece indicated generally good water quality (WQI < 100) with few cases of poor water quality [5]. In Bodrum Peninsula, Turkey, karst waters were characterized by very poor quality with WQI values around 250, due to the high amount of total hardness, turbidity, and chemical oxygen demand [69]. The WQI of groundwaters used in groundwater resources from the Heihe drainage area (China) ranged between 45 and 729 indicating that the water quality ranges from excellent to very poor and unsuitable. Waters with low quality are characterized by high amounts of TDS, Ca, Mg, Na,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ , due to the weathering of rocks and evaporation processes [7].

The heavy metal pollution status is indicated by the cumulative concentrations of the studied metals (Cd, Cr, Cu, Ni, Pb, Zn, and Fe). The HPI ranged between 89.2 and 196 (Table 5) indicating no heavy metals pollution for samples GW1 and GW2 in summer, autumn, and spring and pollution in the winter season. Heavy metal pollution was found for GW3 and GW4 in all seasons. The highest value was obtained in autumn (HPI = 196) in GW4, due to the increased amount of Cr; GW4 being characterized with the highest HPI values, in all seasons. Different studies on groundwaters from the northern part of Romania indicated no pollution, with HPI values ranging between 6.0 and 98. The high HPI values that were attributed to Fe, Cu, and Pb resulted from mining activities [23]. Another study reported no heavy metal pollution of groundwaters in the central part of Romania, although the guideline value for Cd was slightly exceeded, due to the industrial activities developed in the nearby proximity of the groundwater sources [70]. In several other studies, HPI was also successfully used for the assessment of drinking water contamination with heavy metals [71–73].

The HEI values indicated medium pollution with Cd, Cr, Cu, Ni, Pb, Zn, Fe in sample GW4, in spring, the computed value of HEI being higher than the unity, due to the high Cr amount, while the rest of the samples were characterized with low pollution (HEI < 1.0). The highest value was obtained in GW4 in all seasons, followed by GW3 in autumn and winter. The lowest values were obtained in spring and autumn in samples GW1 and GW2. Studies conducted in Africa indicated medium and high degree of pollution (HEI = 14.3–64.2), due to anthropogenic activities (leachate percolation from landfill sites) and lithogenic factors [72]. In Seini town, northwestern Romania low degree of heavy metal pollution of groundwater due to mining activities was reported by Dippong et al. [23].

### 3.3. Exposures and Health Risk Assessments

The long-term consumption of contaminated groundwater could cause potential health risks. To assess the noncarcinogenic health risks following the long-term exposure to contaminated water use, the health risk assessment model recommended by the US EPA was used. The chronic noncarcinogenic

risk following oral and dermal exposure was determined based on the average nitrate and metal (Fe, Cu, Zn, Pb, Ni, Cr, Cd) concentrations present in each of the drinking water sources. As shown in Table 6, the chronic daily intake (CDI) is much higher for oral exposure than for dermal exposure for all the elements.

**Table 6.** Chronic daily intake (CDI,  $\mu\text{g kg}^{-1}\text{days}^{-1}$ ) for adults and children.

	GW1		GW2		GW3		GW4	
	Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal
<b>Adults</b>								
Fe	1.10	$3.00 \times 10^{-3}$	$3.94 \times 10^{-1}$	$1.07 \times 10^{-3}$	$6.30 \times 10^{-1}$	$1.72 \times 10^{-3}$	$3.94 \times 10^{-1}$	$1.07 \times 10^{-3}$
Cu	$4.09 \times 10^{-2}$	$1.86 \times 10^{-4}$	$5.07 \times 10^{-2}$	$2.30 \times 10^{-4}$	$3.80 \times 10^{-2}$	$1.73 \times 10^{-4}$	$4.56 \times 10^{-2}$	$2.07 \times 10^{-4}$
Pb	$6.38 \times 10^{-3}$	$2.90 \times 10^{-6}$	$6.61 \times 10^{-3}$	$3.00 \times 10^{-6}$	$6.53 \times 10^{-3}$	$2.97 \times 10^{-6}$	$7.01 \times 10^{-3}$	$3.18 \times 10^{-6}$
Zn	$1.22 \times 10^{-1}$	$5.53 \times 10^{-5}$	$6.63 \times 10^{-2}$	$2.89 \times 10^{-5}$	$3.86 \times 10^{-2}$	$1.75 \times 10^{-5}$	$3.52 \times 10^{-2}$	$1.60 \times 10^{-5}$
Ni	$1.36 \times 10^{-1}$	$6.16 \times 10^{-4}$	$1.64 \times 10^{-1}$	$7.45 \times 10^{-4}$	$8.23 \times 10^{-2}$	$3.74 \times 10^{-4}$	$4.87 \times 10^{-2}$	$2.21 \times 10^{-4}$
Cr	$1.50 \times 10^{-1}$	$6.81 \times 10^{-4}$	$1.05 \times 10^{-1}$	$4.77 \times 10^{-4}$	$8.02 \times 10^{-1}$	$3.64 \times 10^{-3}$	1.28	$5.82 \times 10^{-3}$
Cd	$1.38 \times 10^{-2}$	$6.26 \times 10^{-5}$	$1.41 \times 10^{-2}$	$6.40 \times 10^{-5}$	$1.31 \times 10^{-2}$	$5.94 \times 10^{-5}$	$1.30 \times 10^{-2}$	$5.90 \times 10^{-5}$
$\text{NO}_3^-$	$8.51 \times 10^2$	3.86	$8.31 \times 10^2$	3.78	$6.83 \times 10^3$	$3.10 \times 10^1$	$2.46 \times 10^3$	$1.12 \times 10^1$
<b>Children</b>								
Fe	1.40	$5.32 \times 10^{-3}$	$5.00 \times 10^{-1}$	$1.90 \times 10^{-3}$	$8.00 \times 10^{-1}$	$3.04 \times 10^3$	$5.00 \times 10^{-1}$	$1.90 \times 10^{-3}$
Cu	$5.20 \times 10^{-2}$	$3.29 \times 10^{-4}$	$6.44 \times 10^{-2}$	$4.08 \times 10^{-4}$	$4.83 \times 10^{-2}$	$3.06 \times 10^{-4}$	$5.79 \times 10^{-2}$	$2.07 \times 10^{-4}$
Pb	$8.10 \times 10^{-3}$	$5.13 \times 10^{-6}$	$3.00 \times 10^{-6}$	$5.32 \times 10^{-6}$	$9.00 \times 10^{-3}$	$8.30 \times 10^{-3}$	$8.90 \times 10^{-3}$	$5.63 \times 10^{-6}$
Zn	$1.55 \times 10^{-1}$	$9.79 \times 10^{-5}$	$8.08 \times 10^{-2}$	$5.11 \times 10^{-5}$	$4.90 \times 10^{-2}$	$3.10 \times 10^{-5}$	$4.47 \times 10^{-2}$	$2.83 \times 10^{-5}$
Ni	$1.72 \times 10^{-1}$	$1.09 \times 10^{-3}$	$2.08 \times 10^{-1}$	$1.32 \times 10^{-3}$	$1.05 \times 10^{-1}$	$6.62 \times 10^{-4}$	$6.18 \times 10^{-2}$	$3.91 \times 10^{-2}$
Cr	$1.90 \times 10^{-1}$	$1.20 \times 10^{-3}$	$1.33 \times 10^{-1}$	$8.44 \times 10^{-4}$	1.02	$6.45 \times 10^{-3}$	1.63	$1.03 \times 10^{-2}$
Cd	$1.72 \times 10^{-2}$	$1.11 \times 10^{-4}$	$1.79 \times 10^{-2}$	$1.13 \times 10^{-4}$	$1.66 \times 10^{-2}$	$1.05 \times 10^{-4}$	$1.65 \times 10^{-2}$	$1.04 \times 10^{-4}$
$\text{NO}_3^-$	$1.08 \times 10^3$	6.84	$1.06 \times 10^3$	6.68	$8.67 \times 10^3$	$5.49 \times 10^1$	$3.12 \times 10^3$	$1.97 \times 10^1$

The GW4 and GW3 had higher oral CDI than GW2 and GW1 for both, adults and children, while the dermal CDI were comparable for the studied water sources. The oral CDI for nitrates was the highest both for adults and children. The CDI for Cr, Zn, and Ni were higher than for Cd, Pb, and Cu, in all samples, indicating that both, adults and children, have significant exposure to these compounds.

The highest value of  $\text{HQ}_{\text{oral}}$  (Table 7) was obtained for nitrates, while the highest  $\text{HQ}_{\text{dermal}}$  for Cr. The  $\text{HQ}_{\text{oral}}$  for the  $\text{NO}_3^-$  was higher than the unity in the case of GW3 and GW4 for both, adults and children, with the maximum values recorded in autumn (GW3) and summer (GW4), suggesting a possible health risk. The  $\text{HQ}_{\text{dermal}}$  for  $\text{NO}_3^-$  was lower than the unity in each season in all water sources for adults and also for children. In GW1 and GW2 both the  $\text{HQ}_{\text{oral}}$  and  $\text{HQ}_{\text{dermal}}$  were below 1 ( $\text{HQ}_{\text{oral}} < 1.0$  and  $\text{HQ}_{\text{dermal}} < 1.0$ ) for every parameter, indicating no health risks [73].

The  $\text{HQ}_{\text{oral}}$  and  $\text{HQ}_{\text{dermal}}$  for Cr had the lowest value in GW1 in spring, and the highest, in GW4 in autumn for Cr and in winter for Cd, for both, adults and children. For the other metals,  $\text{HQ}_{\text{oral}}$  and  $\text{HQ}_{\text{dermal}}$  were much lower than the unity, indicating no health risk. Narsimha et al. (2018) [74] reported that a high content of  $\text{NO}_3^-$  could generate a significant noncancer risk caused by a lifetime consumption of groundwater sampled from Telangana State, south of India. Noncarcinogenic risk induced by Cr and Cd was reported for the groundwater from the Aosta Valey, Italy, where the value of HQ for the heavy metals was higher than unity [75].

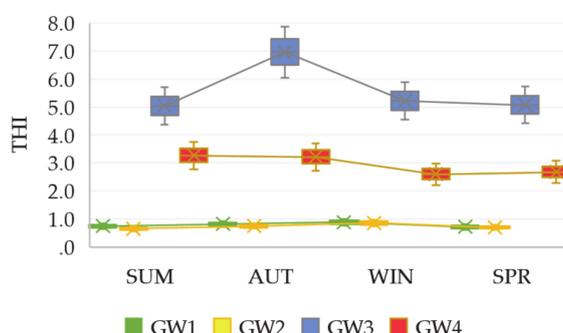
The obtained  $\text{HI}_{\text{oral}}$  values were higher than unity in the case of GW3 and GW4, in all seasons, and lower than unity for GW1 and GW2. The highest  $\text{HI}_{\text{oral}}$  was in the case of GW3 in autumn, being followed by the  $\text{HI}_{\text{oral}}$  for GW4 in summer. All  $\text{HI}_{\text{dermal}}$  values were lower than unity for all the water sources in all seasons.

The THI was the highest in GW3, followed by GW4. In both springs, the THI above 1 indicated possible noncarcinogenic risk, both for adults and children. In GW1 and GW2 the THI was below 1, suggesting the suitability of water for human consumption without any possible health risks. Although the average THI was below 1, in the case of GW1, in winter, the THI value was higher than the unity for children, suggesting that children may exhibit possible health risks by consumption of this water.

The THI had a low variation among seasons in the case of GW1 and GW2, and varied widely in the case of GW3 and GW4 (Figure 8).

**Table 7.** Average hazard quotient (HQ), hazard index (HI), and total hazard index (THI) for adults and children.

		GW1		GW2		GW3		GW4	
		Oral	Dermal	Oral	Dermal	Oral	Dermal	Oral	Dermal
<b>Adults</b>									
HQ	Fe	$3.67 \times 10^{-3}$	$6.67 \times 10^{-5}$	$1.31 \times 10^{-3}$	$2.38 \times 10^{-5}$	$2.10 \times 10^{-3}$	$3.81 \times 10^{-5}$	$1.31 \times 10^{-3}$	$2.38 \times 10^{-5}$
	Cu	$1.02 \times 10^{-3}$	$1.55 \times 10^{-5}$	$1.27 \times 10^{-3}$	$1.92 \times 10^{-5}$	$9.51 \times 10^{-4}$	$1.44 \times 10^{-5}$	$1.14 \times 10^{-3}$	$1.73 \times 10^{-5}$
	Pb	$2.13 \times 10^{-5}$	$4.83 \times 10^{-8}$	$2.20 \times 10^{-5}$	$5.01 \times 10^{-8}$	$2.18 \times 10^{-5}$	$4.95 \times 10^{-8}$	$2.34 \times 10^{-5}$	$5.30 \times 10^{-8}$
	Zn	$4.06 \times 10^{-4}$	$9.22 \times 10^{-7}$	$2.12 \times 10^{-4}$	$4.81 \times 10^{-7}$	$1.29 \times 10^{-4}$	$2.92 \times 10^{-7}$	$1.17 \times 10^{-4}$	$2.66 \times 10^{-7}$
	Ni	$6.79 \times 10^{-3}$	$1.14 \times 10^{-4}$	$8.20 \times 10^{-3}$	$1.38 \times 10^{-4}$	$4.12 \times 10^{-3}$	$6.93 \times 10^{-5}$	$2.43 \times 10^{-3}$	$4.09 \times 10^{-5}$
	Cr	$5.00 \times 10^{-2}$	$4.54 \times 10^{-2}$	$3.50 \times 10^{-2}$	$3.21 \times 10^{-2}$	$2.67 \times 10^{-1}$	$2.43 \times 10^{-1}$	$4.27 \times 10^{-1}$	$3.88 \times 10^{-1}$
	Cd	$2.76 \times 10^{-2}$	$1.25 \times 10^{-2}$	$2.82 \times 10^{-2}$	$1.28 \times 10^{-2}$	$2.61 \times 10^{-2}$	$1.19 \times 10^{-2}$	$2.60 \times 10^{-2}$	$1.18 \times 10^{-2}$
NO <sub>3</sub> <sup>-</sup>	$5.32 \times 10^{-1}$	$3.51 \times 10^{-3}$	$5.20 \times 10^{-1}$	$3.43 \times 10^{-3}$	4.27	$2.82 \times 10^{-2}$	1.63	$1.08 \times 10^{-2}$	
HI		$6.21 \times 10^{-1}$	$6.16 \times 10^{-2}$	$5.94 \times 10^{-1}$	$4.82 \times 10^{-2}$	4.57	$2.83 \times 10^{-1}$	2.09	$6.16 \times 10^{-2}$
THI		0.683		0.642		4.85		2.50	
<b>Children</b>									
HQ	Fe	$4.67 \times 10^{-3}$	$1.18 \times 10^{-4}$	$1.67 \times 10^{-3}$	$4.22 \times 10^{-5}$	$2.67 \times 10^{-3}$	$6.75 \times 10^{-5}$	$1.67 \times 10^{-3}$	$4.22 \times 10^{-5}$
	Cu	$1.30 \times 10^{-3}$	$2.74 \times 10^{-5}$	$1.61 \times 10^{-3}$	$3.40 \times 10^{-5}$	$1.21 \times 10^{-3}$	$2.55 \times 10^{-5}$	$1.45 \times 10^{-3}$	$3.05 \times 10^{-5}$
	Pb	$2.70 \times 10^{-5}$	$8.54 \times 10^{-8}$	$2.80 \times 10^{-5}$	$8.86 \times 10^{-8}$	$2.77 \times 10^{-5}$	$8.75 \times 10^{-8}$	$2.97 \times 10^{-5}$	$9.39 \times 10^{-8}$
	Zn	$5.16 \times 10^{-4}$	$1.63 \times 10^{-6}$	$2.69 \times 10^{-4}$	$8.52 \times 10^{-7}$	$1.63 \times 10^{-4}$	$5.17 \times 10^{-7}$	$1.49 \times 10^{-4}$	$4.71 \times 10^{-7}$
	Ni	$8.62 \times 10^{-3}$	$2.02 \times 10^{-4}$	$1.04 \times 10^{-2}$	$2.44 \times 10^{-4}$	$5.23 \times 10^{-3}$	$1.23 \times 10^{-4}$	$3.09 \times 10^{-3}$	$7.24 \times 10^{-5}$
	Cr	$6.35 \times 10^{-2}$	$8.03 \times 10^{-2}$	$4.44 \times 10^{-2}$	$5.62 \times 10^{-2}$	$3.40 \times 10^{-1}$	$4.30 \times 10^{-1}$	$5.42 \times 10^{-1}$	$6.86 \times 10^{-1}$
	Cd	$3.50 \times 10^{-2}$	$2.22 \times 10^{-2}$	$3.58 \times 10^{-2}$	$2.27 \times 10^{-2}$	$3.32 \times 10^{-2}$	$2.10 \times 10^{-2}$	$3.30 \times 10^{-2}$	$2.09 \times 10^{-2}$
NO <sub>3</sub> <sup>-</sup>	$6.76 \times 10^{-1}$	$6.22 \times 10^{-3}$	$6.60 \times 10^{-1}$	$6.08 \times 10^{-3}$	5.42	$4.99 \times 10^{-2}$	2.07	$1.91 \times 10^{-2}$	
HI		$7.89 \times 10^{-1}$	$1.09 \times 10^{-1}$	$7.54 \times 10^{-1}$	$8.53 \times 10^{-2}$	5.8	$5.01 \times 10^{-1}$	2.66	$7.27 \times 10^{-1}$
THI		0.898		0.840		6.30		3.38	

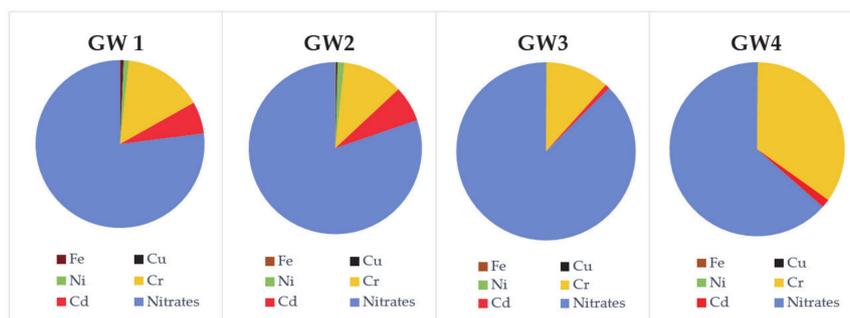


**Figure 8.** Seasonal variations of THI (SUM = summer, AUT = autumn, WIN = winter, SPR = spring).

The contribution of the metal and nitrate concentration to the noncarcinogenic health risk (Figure 9) decreased in the order NO<sub>3</sub><sup>-</sup> > Cr > Cd > Ni > Pb > Zn > Cu > Fe. Thus, the most important measure, especially in cases of GW3 and GW4, is the removal of nitrates before human use, together with creating a safety area around the source reception basin that could limit the nitrates infiltration from the surface.

Similarly to the South Dobrogea springs, the groundwater from the North-Western part of Romania was characterized by a high concentration of NO<sub>3</sub><sup>-</sup> and a low concentration of metals, but with a THI that indicates an intolerable noncarcinogenic risk (THI > 1.0) [23].

Many studies are focused on technologies for drinking water purification to reduce contamination. In this regard, various high-efficiency filters [76], absorbing materials [77], and permeable reactive barriers [78] have been introduced to effectively remove different metals and ions from groundwater and supply safe potable water for human consumption.



**Figure 9.** Contribution of Fe, Cu, Ni, Cr, Cd, and nitrates to the mean values of THI.

In the case of karstic waters, the remediation techniques are more challenging than in the case of other types of water resources, due to the high total ionic saturation, various flow pathways of the aquifer, the porosity of the bedrock, and the interaction between contaminants and the aquifer material [79,80]. In the case of sources with a high flow used by high number of population groups in-situ methods of remediation are feasible, but in the case of water sources with low sources used by small rural communities, like those from Dobrogea region, low cost methods would be more feasible. The most used methods for the nitrates and toxic metals removal are reverse osmosis (RO), electrodialysis (ED), ion exchange (IE), and biological remediation (BR) [79,81]. A possible treatment option could be a RO system with polyamide and cellulose triacetate membrane [79,81]. The ED technology based on the transfer of ions through a membrane by application of direct electric current has similar performance and operation costs with that of RO [81,82]. Compared to the RO and ED techniques, IE was found to be five times more economical and having similar removal efficiency ( $\approx 90\%$ ) [81]. Even so, one of the biggest disadvantages of IE is the exhaustion of the resins, a process influenced by the nature of the exchange resin and the contaminants [83,84]. The simultaneous removal of nitrates, Cr, and Cd could be achieved by bioremediation technics, using various microalgae, like *Chlorella vulgaris* and *Spirulina* spp., with high contaminants removal efficiency ( $>75\%$ ) [85].

#### 4. Conclusions

Karstic springs are the primary source for drinking water in Dobrogea region, given the low annual values of average precipitation (350–450 mm). However, the extremely porous environment does not protect the water source from the anthropogenic impact, allowing the infiltration of pollutants. Under those conditions, the protective cover (e.g., soil, loess) is a major factor in preventing the dispersion of the pollutants in the karst network. Moreover, the drought and aridity in this region can play an important role on the chemistry of waters in karst aquifers. Additionally, the different geological settings from north to south can imply changes in permissiveness of different pollutants (e.g., the karstic area of northern Dobrogea is more reduced than southern Dobrogea, since a large karst area can be more vulnerable to contaminants). With the exception of nitrates in Sipote and Tufani springs, the physico-chemical parameters met the quality guidelines for drinking waters set by WHO and by the Directive 98/83/EC. Samples are characterized as  $\text{Ca-HCO}_3^-$  type in all seasons and  $\text{Na-HCO}_3^-$  type in winter and spring. Additionally, the water quality index showed excellent water quality of Praporgescu and Closca and good quality of Sipote and Tufani springs. However, the presence of low to medium metal pollution (mainly with Cr) was indicated by the metal pollution indices, especially in Sipote and Tufani springs. The total hazard index indicated the presence of noncarcinogenic risks following consumption of water from Sipote and Tufani springs, both for adults and children, possible risks for children in the case of Praporgescu spring and no risks in the case of Closca spring. The highest share in the risk was given by nitrates, followed by Cr and Cd. With some exception, the seasonal variation of chemical parameters was low, the total hazard index had the highest value in autumn and summer. The results indicate the influence of natural (dissolution of rocks and weathering) and anthropogenic factors (agricultural practices) on the quality of karstic springs. The present study

would recommend a rigorous monitoring of water quality and the ban of using Sipote and Tufani springs as drinking water without proper treatment, especially for nitrates removal. Additionally, the presence of pathogenic bacteria should be assessed in these waters before consumption.

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