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RESEARCH NOTE

Assessing the Water Quality Parameters of the Munzur Spring, Tunceli, Turkey

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Abstract
This study presents an analysis of the temporal variations in the upstream water quality parameters of the Munzur Spring. For this purpose, the spring water quality was monitored from 2007 to 2009 at different time periods. There were 5 water samples taken from 2008 to 2009 for hydrochemical and biological analyses, while 6 water samples were gathered between 2007 and 2009 for heavy metal analysis. The analysis results reveal that the water quality parameters were found to be in good agreement with the drinking water standards of Anonymous (1993) and Anonymous (2005). It was seen that the upstream source of the Munzur spring is periodically characterized by Ca^{+2} - Mg^{+2} - HCO_3^- and Ca^{+2} - Cl^- - HCO_3^- facies according to Anonymous (1978), and $CaCO_3$ and $CaCl_2$ facies according to Back (1960, 1966). The results of a tritium analysis indicated that the spring is recharged by daily precipitations. The spring water was also found suitable for irrigation purposes based on Wilcox and US salinity diagrams.
Keywords: Facies, heavy metals, hydrochemical parameters, Munzur Spring, water quality.

Türkiye'de Munzur Kaynağı Su Kalite Parametrelerinin Değerlendirilmesi
Özet
Bu çalışma, Munzur kaynak suyu kalite parametrelerinin zamansal değişimini göstermektedir. Bu amaçla 2007 ile 2009 yılları arasında beş farklı periyotta kaynak suyu kalite gözlemleri yapılmıştır. Hidrokimyasal ve biyolojik analizler için 2008 ile 2009 yılları arasında 5 numune, ağır metal analizleri için ise 2007 ile 2009 yılları arasında 6 numune alınmıştır. Analiz sonuçlarına göre su kalite parametreleri Anonim (1993), Anonim (2003) ve Anonim (2005) içme suyu standartlarına uygun bulunmuştur. Munzur kaynak suyunun Anonim (1978) kriterlerine göre Ca^{+2} - Mg^{+2} - HCO_3^- and Ca^{+2} - Cl^- - HCO_3^-, Back (1960, 1966)'e göre ise $CaCO_3$ ve $CaCl_2$ fasiyes özelliği gösterdiği görülmüştür. Tirityum analizi kaynağın günlük yağışlarla beslendiğini göstermiştir. Kaynak suyunun sulama suyu olarak da kullanılabileceği Wilcox ve US tuzluluk diyagramları ile anlaşılmıştır.
Anahtar Kelimeler: Ağır metaller, fasiyes, hidrokimyasal parametreler, Munzur kaynak suyu, su kalitesi.

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INTRODUCTION

Anthropogenic effects (urban, industrial, and agricultural activities, increase the consumption of water resources) as well as natural processes (changes in precipitation inputs, erosion, and weathering of crustal materials) degrade surface waters and impair their use for drinking, industrial, agricultural, recreation, and other purposes (Carpenter et al. 1998, Jarvie et al. 1998, Simeonov et al. 2003). Water pollutants that exceed certain concentrations are a threat to public health. Therefore, monitoring of surface water quality is an important issue for evaluating spatial and temporal variations of the surface water resources (Armagan et al. 2008).

A number of studies on the parameters important in terms of surface water pollution are presented in literature. Recently, Saygi and Atasagun (2012) investigated temporal changes in water quality and the trophic status in Lake Yenicaga, Bolu, Turkey. They utilized water quality parameters including K^+, Na^+, Mg^{+2}, Ca^{+2}, Cl^-, SO_4^{-2}, HCO_3^-, CO_3^{-2}, NO_3^-, NO_2^-, NH_4^+, PO_4^{-3}, and chlorophyll-a. Cicek and Ertan (2012) determined the water quality parameters of the Köprüçay River in Antalya, Turkey according to physicochemical parameters between February 2008 and January 2009. Gultekin et al. (2012) studied the water quality parameters of the surface waters during the wet season in Trabzon, Turkey. Pliuraite (2011) evaluated the status of three Lithuanian medium-sized streams receiving diffused pollution

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from agricultural lands in the spring, summer, and autumn of 2008 using selected physicochemical variables and a macroinvertebrate analysis. Ustun (2011) assessed the heavy metal contaminants including As (total), Cd, Cr (total), Cu, Mn, Ni, Pb, and Zn in the waters of the Nilufer Stream in Bursa, Turkey, from 2002 through 2007. Yeşilırmak (2010) studied the seasonal and spatial variations of water quality for irrigation in the Büyük Menderes River, Turkey, with emphasis on the water quality parameters including EC, SAR, Na^+, Cl^-, B, NO_3^--N, HCO_3^-, and pH gathered at 9 sites along the river from 1995 to 2006. Sangulin et al. (2010) presented the results of the impacts from fish farms in the coastal area of Zadar County in the middle of the Adriatic Sea, on the physical, chemical, and biological properties of the water column and sediment using water samples gathered twice a year from 2007 to 2009. Gedik et al. (2010) determined the water quality of the Fırtına Stream, Rize, Turkey, in terms of the physicochemical structure between May 2006 and April 2008. Armagan et al. (2008) investigated the seasonal variations in the surface water quality of the Balikligol Lakes, Sanliurfa, Turkey, with the use of water samples collected from 7 different points during a one-year period and analyzed the water quality parameters including water temperature, pH, EC, COD, DO, Fe, Na, Cr, Cu, Ni, and Pb. Bakan and Cüce (2007) presented a study on the water/sediment quality and SOD of the Kızılırmak River on the Black Sea Coast, of Turkey. Yesilnacar and Uyanik (2005) evaluated the quality of the water supplied from the Atatürk Dam Lake to the Şanlıurfa Tunnels in Turkey, the world's largest irrigation tunnel system, analyzing monthly water samples for water quality parameters including water temperature, pH, Cl^-, SO_4^{-2}, NH_4^+-N, NO_2-N, NO_3-N, TDS, color, and Na+ from 2000 to 2003. Lahr et al. (2003) determined the toxicity of the sediment and suspended solids by means of chemical analyses on the Dutch Lakes. Guzzella et al. (2002) applied advanced oxidation and adsorption technologies for the removal of organic micropollutants from lake water used as a drinking-water supply.

This paper evaluates the temporal variations in the upstream water quality parameters of the Munzur Spring for drinking and irrigation purposes. The spring is the main source of the Munzur Creek which merges with the Upper Euphrates. In this study, 5 water samples taken from 2008 to 2009 were used for hydrochemical and biological analyses, and 6 water samples gathered between 2007 and 2009 were utilized for heavy metal analysis. The study results were compared with the drinking water standards of Anonymous (1993), Anonymous (2003), and Anonymous (2005).

MATERIALS AND METHODS

Study Site

The Munzur spring originates in the Munzur Basin which is about 1702 km^2 and is generally comprised of varying topography with steep canyons (Fig. 1). The spring is characterized by karstic geology and recharged by the highly variable seasonal precipitations in the area. It is the main source of the Munzur Creek which is a tributary to the Upper Euphrates with flow rates ranging between 4.5 and 27 m^3/s.

Experimental Studies

In order to evaluate the water quality parameters of the Munzur Spring the hydrochemical, biological, and heavy metal analyses of the water samples were performed at the State Hydraulics Works Laboratories in Elazığ and Ankara. In this study, 5 samples obtained between 2008 and 2009 were used for the hydrochemical and biological analyses (Table 1) and 6 samples gathered between 2007 and 2009 were utilized for the heavy metal analysis (Table 2). The laboratory analyses were carried out using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

As shown in Table 3, the hydrogeochemical facies types of the Munzur spring were classified according to Anonymous (1978) and Back (1960, 1966).

The temporal variation of major anions and cations including Ca^{+2}, Cl^-, Mg^{+2}, Na^+, K^+, HCO_2^-, and SO_4^{-2} was assessed with the method proposed by Piper (1953). Fig. 2 illustrates the Piper diagram constructed for the study period. The classification of the water samples according to this method are given in Table 4.

To determine the periodical effect of waters from different sources on the Munzur spring the method proposed by Schoeller (1962) was utilized as shown in Fig. 3. In this method, a semi logarithmic paper was used to obtain temporal variations of ions. Here, the broken lines represent the parallel waters from the same formations (Canik 1998). Table 5 shows

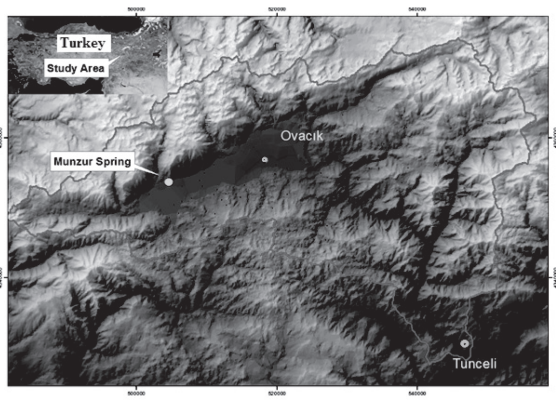

Fig. 1. Location map of the study area.

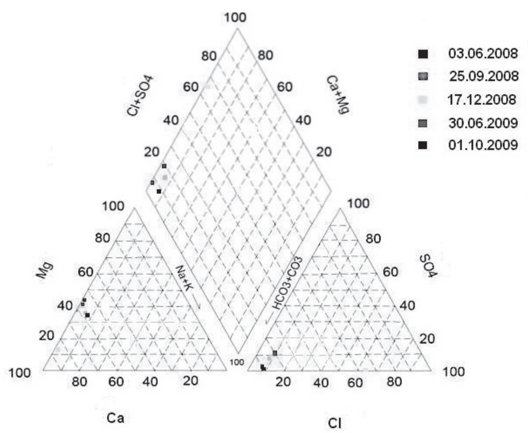

Fig. 2. Hydrogeochemical variations of the Munzur spring.

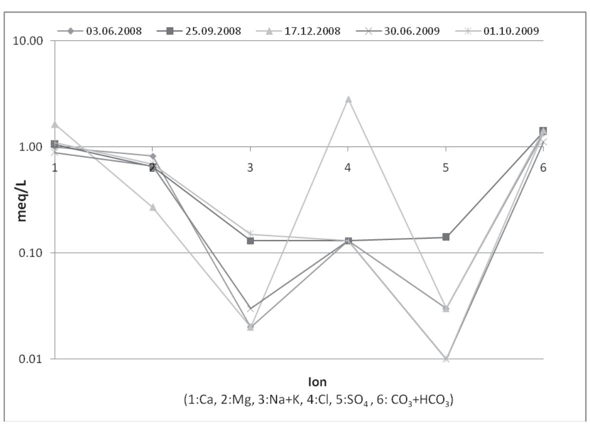

Fig. 3. Distribution of the water samples according to the Schoeller diagram.

the cation and anion arrangement of the water samples according to the Schoeller Diagram.

The suitability of the Munzur Spring water for irrigation was evaluated based on the Wilcox and USA Salinity diagrams for the study period (Figs. 4 and 5). The water quality parameters and their

Table 1. Hydrochemical and biological composition of the Munzur Spring.

Date	03.06.2008	25.09.2008	17.12.2008	30.06.2009	01.10.2009
Turbidity NTU	2	0	0	0	0
Color Pt-Co	5	5	5	5	5
Temperature (°C)	11.1	20.5	10.3	13.4	25
pH	8.09	8.2	8.28	8.1	8.2
EC (µS/cm)	152	151	158	138	159
Ca^{+2} (mg/L)	20.2	21.2	32.7	17.8	22
Mg^{+2} (mg/L)	10.6	8	3.4	8.1	8.5
Na^{+} (mg/L)	0.4	3.2	0.37	0.7	3.59
K^{+} (mg/L)	0.76	0.23	0.67	0.26	0.23
Cl^{-} (mg/L)	4.96	4.9	1	4.68	4.7
SO_4^{-2} (mg/L)	1.61	6.9	1.49	0.11	0.9
HCO_3 mg/L $CaCO_3$	82.5	86	87.5	68.5	84
NO_2 - N (mg/L)	0	0.02	0	0	0
NO_3 - N (mg/L)	0.85	9.44	2.07	5.227	3.544
NH_4^{+} - N (mg/L)	0	0	0	0	0
TDS (mg/L)	99	97	103	87	96
Fe^{+2} (mg/L)	0.02	0	0.04	0	0.12
Total Hardness (mg/L $CaCO_3$)	94	86	95.5	78	90
Total Nitrogen (mg/L)	1.72	3.174	2.97	1.59	1.35
Dissolved Oxygen (DO, mg/L)	7.9	6.9	6.95	*	7.9
Total Phosphorus (mg/L)	0.005	0.01	0.01	0	0
Biochemical Oxygen Demand (BOD, mg/L)	1	1	1	*	0
Chemical Oxygen Demand (COD, mg/L)	11	9	10	4	4
Total Coliform (EMS/100 mL)	8	4	4	4	34
Escherichia Coli (EMS/100 mL)	0	0	0	0	0
Fecal Streptoccoci (EMS/100 mL)	0	0	0	0	0

(*) Not analyzed

Table 2. Heavy metal composition of the Munzur Spring.

Date	06.11.2007	25.09.2008	17.12.2008	30.06.2009	30.09.2009	16.12.2009
Lead (µ g/L)	0	0	1.38	0	*	*
Zinc (µ g/L)	9.9	0	0.9	0	*	*
Chrome (µ g/L)	0	0	0.29	1.75	*	*
Manganese (µ g/L)	0.1	1.86	15.5	0.21	1.1	1.24
Iron (µ g/L)	49.5	0	0	0	111.5	*
Copper (µ g/L)	1.7	0	0	0	*	*
Cadmium (µ g/L)	1.7	0.03	0.03	0	0.08	*
Mercury (µ g/L)	0	0	0	0	*	*
Arsenic (µ g/L)	0	0.001	0.02	0,23	0.83	0.32

(*) Not analyzed

Table 3. Hydrogeochemical facies types of the Munzur spring.

Date	IAH [20]	Back [21, 22]
03.06.2008	Ca^{+2} - Mg^{+2} - HCO_3^-	$CaCO_3$
25.09.2008	Ca^{+2} - Mg^{+2} - HCO_3^-	$CaCO_3$
17.12.2008	Ca^{+2} - Cl^- - HCO_3^-	$CaCl_2$
30.06.2009	Ca^{+2} - Mg^{+2} - HCO_3^-	$CaCO_3$
01.10.2009	Ca^{+2} - Mg^{+2} - HCO_3^-	$CaCO_3$

Wilcox category (Wilcox 1955) and US laboratory classification are presented in Table 6. The residual sodium carbonate (RSC) concentrations are also given in the same table.

RESULTS AND DISCUSSION

The Quality of Drinking Water

As shown in Table 1, the water samples had pH

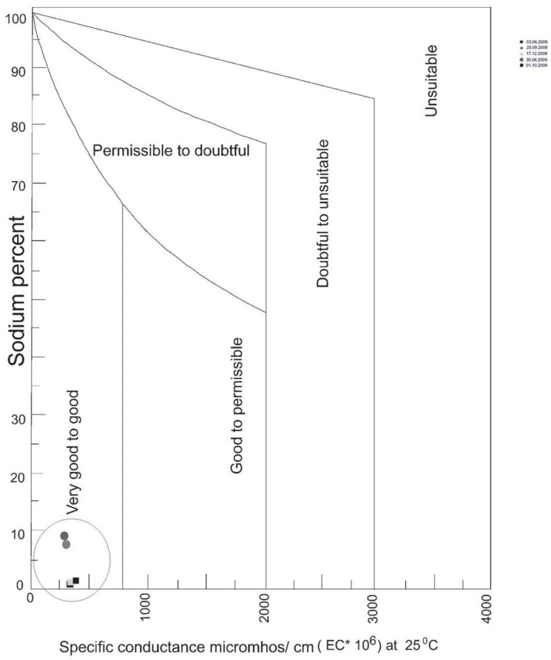

Fig. 4. Wilcox diagram of the water samples.

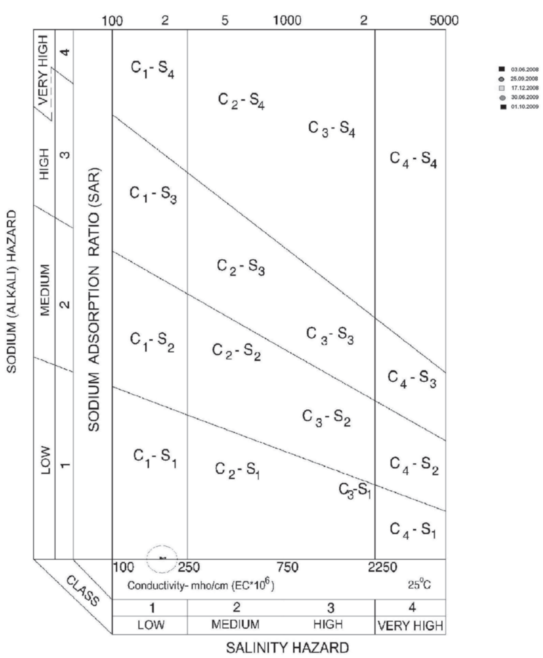

Fig. 5. USA salinity diagram of the water samples.

values between 8.09 and 8.28. Although they seem to be slightly alkaline, their pH values were found to be in good agreement with the drinking water standards of Anonymous (1993), Anonymous (2003), and Anonymous (2005). The samples were of clear water with zero or negligible turbidity. The total dissolved solids (TDS) were found to vary between 87 and 103 mg/L which are indicative of

Table 4. Classification of the water samples according to the Piper diagram.

Date	Dominant Cation	Dominant Anion	Water Feature
03.06.2008	Ca^{+2}	$CO_3^{-2} + HCO_3^-$	$Ca^{+2} + Mg^{+2} > Na^+ + K^+$
25.09.2008	Ca^{+2}	$CO_3^{-2} + HCO_3^-$	$Ca^{+2} + Mg^{+2} > Na^+ + K^+$
17.12.2008	Ca^{+2}	Cl^-	$SO_4^{-2} + Cl^- > CO_3^{-2} + HCO_3^-$
30.06.2009	Ca^{+2}	$CO_3^{-2} + HCO_3^-$	$Ca^{+2} + Mg^{+2} > Na^+ + K^+$
01.10.2009	Ca^{+2}	$CO_3^{-2} + HCO_3^-$	$Ca^{+2} + Mg^{+2} > Na^+ + K^+$

Table 5. Classification of the water samples according to the Piper diagram.

Date	Dominant Cation	Dominant Anion	Water Feature
03.06.2008	Ca^{+2}	$CO_3^{-2} + HCO_3^-$	$Ca^{+2} + Mg^{+2} > Na^+ + K^+$
25.09.2008	Ca^{+2}	$CO_3^{-2} + HCO_3^-$	$Ca^{+2} + Mg^{+2} > Na^+ + K^+$
17.12.2008	Ca^{+2}	Cl^-	$SO_4^{-2} + Cl^- > CO_3^{-2} + HCO_3^-$
30.06.2009	Ca^{+2}	$CO_3^{-2} + HCO_3^-$	$Ca^{+2} + Mg^{+2} > Na^+ + K^+$
01.10.2009	Ca^{+2}	$CO_3^{-2} + HCO_3^-$	$Ca^{+2} + Mg^{+2} > Na^+ + K^+$

Table 6. Irrigation water quality parameters of the Munzur spring water samples and their classifications.

Date	Na%	SAR	Wilcox Category	US Laboratory Classification	RSC
03.06.2008	0.54	0.01	Very good to good	C1-S1	-0.47
25.09.2008	7.00	0.14	Very good to good	C1-S1	-0.30
17.12.2008	0.52	0.01	Very good to good	C1-S1	-0.47
30.06.2009	8.87	0.17	Very good to good	C1-S1	0.42
01.10.2009	1.65	0.03	Very good to good	C1-S1	0.41

freshwater quality. The electrical conductivity (EC) of the samples ranged from 138 to 159μS/cm. The total hardness was found to vary from 78 to 95.5 mg/L $CaCO_3$ that means the samples were moderately hard waters according to Anonymous (2009). Both the sulphate and chlorine concentrations were found well below the upper limit (i.e., 250 mg/L) as defined by Anonymous (1993), Anonymous (2003), and Anonymous (2004). They varied from 0.11 to 6.9 mg/L and from 1 to 4.96 mg/L, respectively. The alkalinity of the samples ranged from 68.5 to 87.5 mg/L. As main sources of water hardness, Ca^{+2} and Mg^{+2} cations were found below Anonymous (1993), Anonymous (2003), and Anonymous (2005) permissible limits. The values changed between 17.8 and 32.7 mg/L for the former and between 3.4 and 10.6 mg/L for the latter. The sodium and potassium concentrations respectively were 0.4-3.59 mg/L, and 0.23-0.76 mg/L meeting Anonymous (1993), Anonymous (2003), and Anonymous (2005) standards. The water samples were found to have nitrate-nitrogen concentrations between 0.85 and 5.227 mg/L which are actually below Anonymous (1993), Anonymous (2003), and Anonymous (2005) permissible limits designated for drinking waters. Biological analysis revealed that the water samples had no or an insignificant number of fecal coliform during the study period.

The results of the heavy metal analysis are presented in Table 2. During the whole study period, the concentrations of lead, zinc, chrome, manganese, iron, copper, cadmium, mercury, and arsenic were all found under the limit values as defined by Anonymous (1993), Anonymous (2003), and Anonymous (2005).

Hydrogeochemical facies that are actually used to define underground water bodies with different chemical compositions in the aquifers were determined using the methods proposed by Anonymous (1978) and Back (1960, 1966). The first method revealed that the Munzur spring is periodically characterized by Ca^{+2} – Mg^{+2} - HCO_3^- and Ca^{+2} - Cl^- - HCO_3^- facies, while the second method indicated that it is also dominated by $CaCO_3$ and $CaCl_2$ facies (see Table 3). As pointed out by Afşin and Baş (1996), Ca^{+2} – Mg^{+2} - HCO_3^- facies may be an indication of fast flowing shallow aquifer waters with low anion concentrations. The general characteristics of hydrogeochemical facies are found consistent with the tritium analysis results where the tritium value was found as 6.4.

The water samples were classified using the Piper diagram as shown in Fig. 2. The diagram shows that the dominant cation was Ca+ during the entire study time and the dominant anion was CO_3^{-2}+HCO_3^- for four periods, and Cl- for only one period. As shown in Table 4 the spring water was evaluated as Ca^{+2}+ Mg^{+2} > Na^+ + K^+ with a carbonate hardness of more than 50% and as SO_4^{-2} + Cl^- > CO_3^{-2} + HCO_3^- with a carbonate hardness of less than 50%.

The periodical effect of waters from different sources on the Munzur spring was determined by the use of the Schoeller diagram which displays temporal variations of ions (see Fig. 3). As discussed by Canik (1998) the broken lines represent the parallel waters from the same formations. As shown in Table 5 the cation arrangement was found as Ca^{+2} > Mg^{+2} > Na^+ + K^+ for all water samples. The anion arrangement for the first two water samples was CO_3^{-2} + HCO_3^- > Cl^- > SO_4^{-2} and CO_3^{-2} + HCO_3^- > SO_4^{-2} > Cl^-, respectively. The last two samples both had the same anion arrangement, CO_3^{-2} + HCO_3^{-2} > Cl^- > SO_4^{-2}. The third sample's anion arrangement was Cl^- > CO_3^{-2} + HCO_3^- > SO_4^{-2} which actually indicates the possibility of a recharge of the spring by a different water body.

The quality of irrigation water

The Wilcox and USA salinity diagrams (Figs. 4 and 5) were utilized to assess the quality of the Munzur spring water for irrigation purposes. According to the Wilcox diagram, the sodium percentage values (less than 10% in all samples) reflected that the Munzur spring water was under the category 'very good to good'. The US Salinity diagram indicated that the Munzur spring water falls in the zone of a low-salinity hazard (C1) and a low sodium hazard (S1) type. The sodium adsorption ratio (SAR) ranged between 0.01 and 0.17 in the water samples. As shown in Table 6 the residual sodium carbonate (RSC) concentration was less than 1.25 m.eq/L (varying from -0.47 to 0.42 m.eq/L) and hence, suitable for irrigation.

CONCLUSIONS

The water quality parameters of the Munzur Spring were evaluated for drinking and irrigation purposes. Hydrochemical, biological, and heavy metal analyses were performed using water samples gathered from the spring source during different periods between March 2008 and January 2009. The hydrochemical analysis results revealed that all water samples were of clear water with zero or negligible turbidity. Their pH values were found in good agreement with Anonymous (1993), Anonymous (2003), and Anonymous (2005) standards. As an indicator of freshwater quality the total dissolved solids were found well below the standard limit of 500 mg/L. The spring aquifer was found to have a relatively high electrical conductivity.

The water samples were of moderately hard waters according to Anonymous (2009) standards. The analysis results showed that Ca^{+2} and Mg^{+2} cations, the main sources of water hardness, were found below Anonymous (1993), Anonymous (2003), and Anonymous (2005) permissible limits.

The nitrate-nitrogen concentrations of the water samples were found below Anonymous (1993), Anonymous (2003), and Anonymous (2005) permissible limits designated for drinking waters.

As indicated by the biological analysis the water samples had no or an insignificant number of fecal coliform during the study period. According to the heavy metal analysis results the concentrations of lead, zinc, chrome, manganese, iron, copper, cadmium, mercury, and arsenic were under Anonymous (1993), Anonymous (2003), and Anonymous (2005) limit values in all water samples.

The Munzur spring was found to be periodically characterized by different facies including Ca^{+2} - Mg^{+2} - HCO_3^- , Ca^{+2} – Cl^- - HCO_3^-, $CaCO_3$, and $CaCl_2$. Their general characteristics were found as being consistent with the tritium analysis results. The presence of the first facies may indicate that the spring is of fast flowing shallow aquifer waters with low anion concentrations.

The classification of water samples by Piper (1953) displayed that the dominant cation was Ca^{+2} and the dominant anions were $CO_3^{-2} + HCO_3^-$. The spring water was evaluated as $Mg^{+2} > Na^+ + K^+$ with a carbonate hardness of more than 50% and as $SO_4^{-2} + Cl^- > CO_3^{-2} + HCO_3^-$ with a carbonate hardness of less than 50%.

From the Schoeller diagram the water samples were evaluated as parallel waters from the same formations. All of them had the same cation arrangement as $Ca^{+2} > Mg^{+2} > Na^+ + K^+$ during the study period. However, the anion arrangements were all different for the first three water samples ($CO_3^{-2} + HCO_3^- > Cl^- > SO_4^{-2}$, CO_3^{-2} + HCO3- > $SO_4^{-2} > Cl^-$, and $Cl^- > CO_3^{-2} + HCO_3^- > SO_4^{-2}$, respectively). The last two had the same type of anion arrangement (i.e., $CO_3^{-2} + HCO_3^- > Cl^- > SO_4^{-2}$). Here, the third sample's anion arrangement actually indicates the possibility of a recharge of the spring by a different water body.

The Munzur spring water was assessed for irrigation purposes using the Wilcox and USA salinity diagrams. From the Wilcox diagram the spring water was found under the category of 'very good to good' for irrigation with sodium percentage values less than 10%. According to the US Salinity diagram the spring water falls in the zone of a low-salinity hazard (C1) and a low sodium hazard (S1) type. The residual sodium carbonate (RSC) concentration in the spring water was less than 1.25 m.eq/L and hence, suitable for irrigation.

Consequently, the water quality assessment of the Munzur spring revealed that the spring water meets Anonymous (1993), Anonymous (2003), and Anonymous (2005) drinking water standards and, therefore, it can be used for drinking and domestic uses. The Wilcox and US Salinity diagrams indicated that the spring water can be utilized for irrigation in and around the Munzur Basin area.

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