

Hydrochemistry and Quality Assessment of Water in Tannur Dam, Southern Jordan

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Abstract

The study was undertaken to assess the physicochemical and chemical quality of the Tannur dam water in southern Jordan. The water samples were collected in two intervals the first during May 2015 and the second during September 2015. All samples were analyzed for temperature, conductivity, dissolved oxygen, pH, major cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+), and major anions (Cl^- , NO_3^- , HCO_3^- and SO_4^{2-}). The hydrogeochemical analyses of thirty-six water samples were used to determine the properties and type of water in the Tannur dam. The ion concentration in the water samples was from dissolution of carbonate rocks and ion exchange processes in clay. The general chemistry of water samples was typical alkaline earth waters with prevailing bicarbonate chloride. The PHREEQC Hydrogeochemical modeling was used to obtain the saturation indices of specific mineral phases, which might be related to interaction with water and aquifer, and to identify the chemical species of the dissolved ions. Calcite and dolomite solubility were assessed in terms of saturation index where they show positive values indication oversaturated $\text{SI} > 0$. The hydrogeochemistry behavior is rather complicated and is affected by anthropogenic and natural sources. The positive correlation values between various parameters indicate that most of ions result from same lithological sources. The abundance of the major ions in water samples is in the following order: $\text{HCO}_3^- > \text{Ca}^{2+} > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$. Water samples of the Tannur dam are generally very hard, high to very high saline and medium alkaline in nature. High total hardness (TH) and total dissolved solids (TDS) in some samples identify the permissible for domestic and irrigation purposes. According to the residual sodium carbonate, SAR and conductivity values, the studied water is suitable for agricultural purposes.

Keywords

Hydrochemistry, Tannur Dam, Jordan, Saturation Indices, Water Quality

1. Introduction

1.1. Overview and Main Characteristics

Jordan is considered among the poorest countries in the world in terms of water resources. The scarcity of water resources in Jordan imposes strategic difficulties for economic development especially for agriculture [1]. The demand on water resources is increasing with time for domestic and agricultural purposes. Jordan is characterized by semiarid climate, which suffers from water shortage and limited water supply. In recent years, water demand increased rapidly through the high rate of population growth and population influxes together with the higher needs for the industry in the Jordan [2]. Several studies were reported to date addressing the quality of water in Jordan. Salameh and Bannayan [3] studied the water quality in southern part of Jordan as a part of a comprehensive report about the water resources in Jordan. Salameh [4] studied the water quality degradation in several sites in Jordan. El Naqa and Al Kuisi [2] studied the hydro-geochemical modeling of the water seepages through Tannur dam in southern Jordan. Al-Khashman *et al.* [5] studied the environmental assessment of spring water in Tafila district, southern Jordan. Al-Tabbal and Al-Zboon [6] studied the suitability assessment of groundwater for irrigation and drinking purpose in the northern region of Jordan. Al-Khashman and Jaradat [7] studied the assessment of ground water quality and its suitability for drinking and agricultural uses in arid environment. Al-Khashman *et al.* [8] investigated the monitoring and assessment of spring water quality in southwestern basin of Jordan.

In order to meet such water needs, the Ministry of Water and Irrigation have selected number of sites in the southern area, that are suitable for construction of storage dams to be used primarily for domestic, recharge of groundwater and irrigation purposes. The Tannur dam (**Figure 1**) is one of these sites and the first roller compacted concrete (RCC) dam. The dam provides irrigation water to the southern Ghors irrigation scheme and industrial water for local area. Construction of the Tannur dam commenced in January 1998 and completion is expected on time in May 2001 (**Figure 1**). The dam is 60 m high, 250 m long and impounds 18 million m³ of runoff from Wadi Hasa, one of the major wadis discharging to the southern Dead Sea area. The elevation at the dam is approximately 400 m (**Table 1**). It forms of water supply and irrigation project serving 1200 ha of farmland and industrial demand in southern Jordan [2].

The Tannur dam location is in a steep valley of Wadi El-Hasa at Tannur mountain, approximately 5 km downstream from the bridge of King's highway, about 40 km south of Karak (**Figure 2**). The dam is located in a narrow V-shaped valley with abutment sides rising at about 30° for up to 100 m above wadi. The rock foundation for half of dam height comprises interbedded limestone and marl, highly fractured in parts, and with the presence of gypsum seams and clay (weathered mudstone) layers.

The general characteristics of the dam are given in **Table 1**. Tannur dam is located in the southern Jordanian desert where the climate is arid, with rainfall



Figure 1. General view of the Tannur dam location.

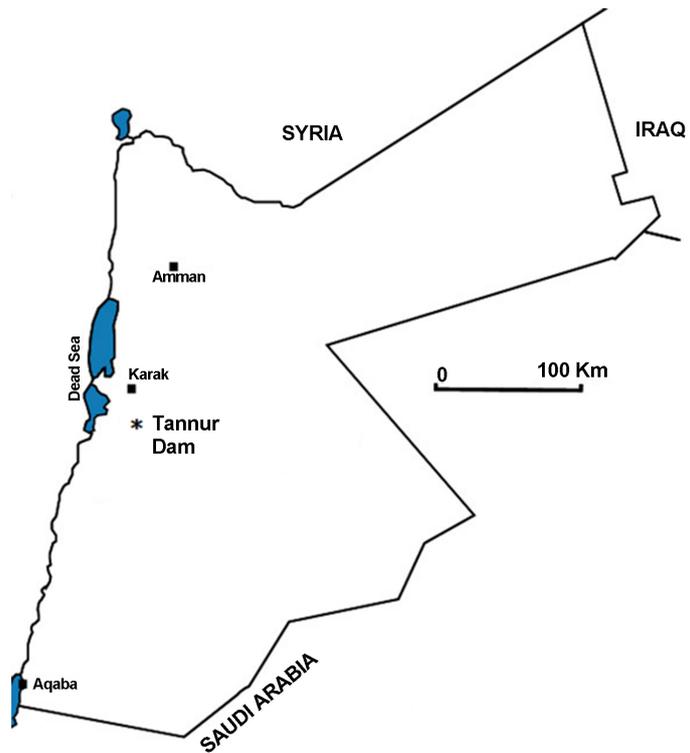


Figure 2. The Tannur dam location map.

Table 1. Characteristics of the Tannur dam.

Location	Wadi El-Hasa, Southern Jordan
Height	60 m
Length	250 m
Width at crest	12 m
Reservoir capacity	17 MCM
Annual yield	8 MCM
Roller Compacted Concrete (CRR) volume	220,000 m ³
Purpose	Irrigation, water supply-flood control
Construction (starting and completion) year	1999-2001

and runoff only occurring in the winter seasons (October to April). Annual rainfall is low, generally varied between 63 - 113 mm/year. The average temperature is 22.3°C, with minimum values of 3.4°C in January and maximum of 35°C in July [9]. The maximum sunshine duration occurs in June with absolute values of 12.2 hours/day, but in winter (December and January) the average minimum sunshine is only about 4.2 hours/day. The average relative humidity varies from 40.9% to 26.2% in the winter months and from 22.7% to 36.4% in the summer season. The prevailing wind direction is from westerly to southwesterly. This paper examines the hydrochemical properties and quality of water in Tannur dam related to its suitability for agriculture and domestic use. Furthermore, a geochemical model was carried out using the computer software PHREEQC to explain the thermodynamic condition of water during water-rock interaction.

1.2. Geology of the Study Area

The geology of the study area is shown in **Figure 3**. The outcropping rocks at the dam location and reservoir area belong to the Ajlun group of Late Cretaceous [2] [10]. Fuheis-Hummar-Shueib (FHS) formations represent the oldest rocks found in the dam site area, representing the dam foundation rocks. These formations

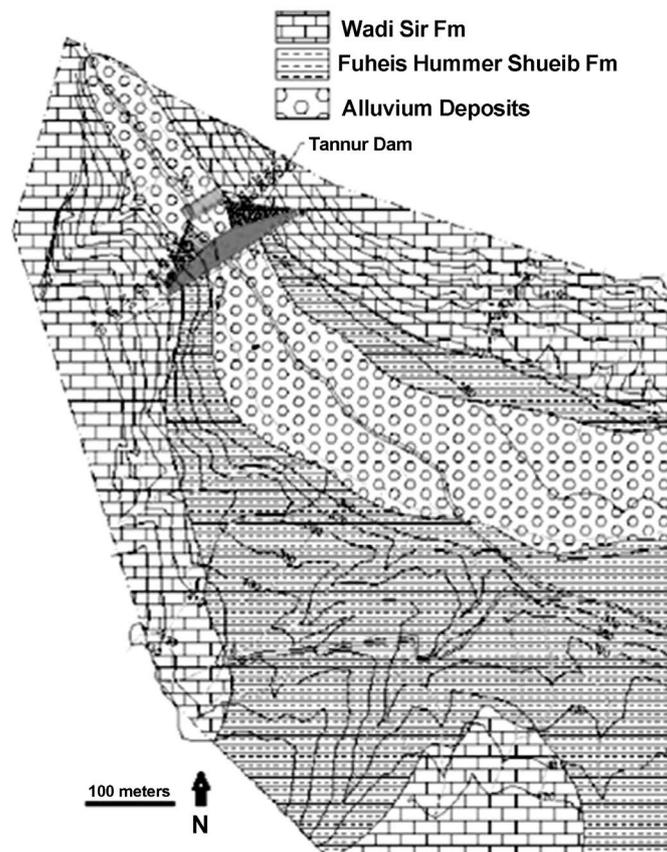


Figure 3. A simplified geological map of the Tannur dam area (slightly modified from El Naqa and Al Kuisi [2]).

consist of thin to moderately thick bedded (5 - 55 cm thick) limestone, marlstone, marl and clayey marl with gypsum bands [11]. The limestone is moderately hard and moderately weak, and these strata contain small bands of marl and fossiliferous limestone up to 70 cm thick [10]. The Wadi As-Sir Limestone (WSL) formation (A7) is exposed over the whole of the study area. This formation is characterized by predominant hard buff dolomitic limestone, thickly and thinly bedded limestone with nodules of chert interbedded with marly limestone and dolomite wackstone [12]. The alluvium and wadi sediments comprise recent sub rounded to rounded, poorly sorted gravels ranging in size from pebbles to boulders. The clastic materials are composed of regional bedrock, mostly limestone, chert and sand grains [10] [12] [13] [14].

Structurally, the area is intensively faulted and folded as a result of various tectonic activities. The Wadi El Hasa fault is the major E-W faults in the study area. In the west it trends ENE and curves eastwards to the N-W and ESE direction. At the western side it branches into two faults. The Wadi El Hasa fault strikes generally E-W from the Dead Sea fault, which is about 25 km west of Tannur dam location [10] [12]. The minor faults at the eastern end of the Wadi El Hasa fault are considered to be dextral strike-slip faults as indicated by the peripheral small scale folding. Along the Wadi El Hasa fault, a volcanic plug has erupted.

1.3. Hydrogeology

The aquifer systems in the study area can be divided into three main aquifers; they are Kurnub Sandstone system (lower aquifer), middle aquifer systems (Wadi Es Sir Limestone aquifer) and shallow aquifer systems (upper aquifer).

1.3.1. Kurnub Sandstone Aquifer

The Kurnub aquifer consists of massive, white and varicolored sandstone reaching inn total thickness about [10] [15]. The Kurnub group composed primarily sandstone long the rift of the study area. The sequences jointed, well cemented to friable and highly permeable, hence possessing good aquifer properties [16]. The hydraulic parameters of this aquifer were derived from the pumping test data. The permeability of the aquifer is 4.5×10^{-5} m/s [17]. On the other hand, the storage coefficient and the transmissivity of the Kurnub aquifer were estimated to be 0.002 and 1.31×10^{-3} , respectively [2] [18].

1.3.2. Ajlun and Belqa Group Aquifer System

This aquifer system consists of Ajlun and Belqa group of the Upper Cretaceous sediments. There are only main aquifer systems (A4, A7, B2, and B4) out of twelve rock units in both groups [19]. Wadi Es Sir Formation (A7) is considered to be one of the most important groundwater reservoirs in the study area as well as in Jordan [20]. This formation consists of alternating marl, marly limestone, crystalline limestone, dolomitic limestone and chert nodules. It has an excellent potentiality of water bearing and has a permeability ranges between 2×10^{-8} and

1.49×10^{-5} m/s, with an average value of 5.5×10^{-6} m/s [17]. It is noticed that the permeability of middle aquifer (A7) is quite similar to that of lower aquifer (Kurnub Sandstone Aquifer).

1.3.3. Alluvium Aquifer System

This shallow aquifer system of Quaternary age extends along the wadi floor and consists of conglomerate, gravels and fragments of limestone, chert, basalts and sandstone of elevated terraces and old mantle rock. The total thickness of these water bearing sediments is estimated at 170 m [15]. The permeability of the aquifer ranges between 6.5×10^{-4} and 1.3×10^{-2} m/s, with an average value of 6.6×10^{-3} m/s [17].

The majority of the aquifers in the study area are limestone, sandstone, dolomitic limestone and Silicified limestone. Secondary permeability is controlled by the structure and tectonic effects [21].

2. Methodology

2.1. Sampling and Experimental Work

Reservoir water samples were collected from thirty six locations in the dam, as shown in **Figure 4**.

The water samples were collected in two periods, the first during May 2015 and the second during September 2015. The collected water samples were stored in polyethylene bottles. The bottles were washed previously with deionized water and diluted hydrochloric acid. Before filling the bottle with the samples, the bottles were rinsed with the samples water and transported to a lab in cold storage.

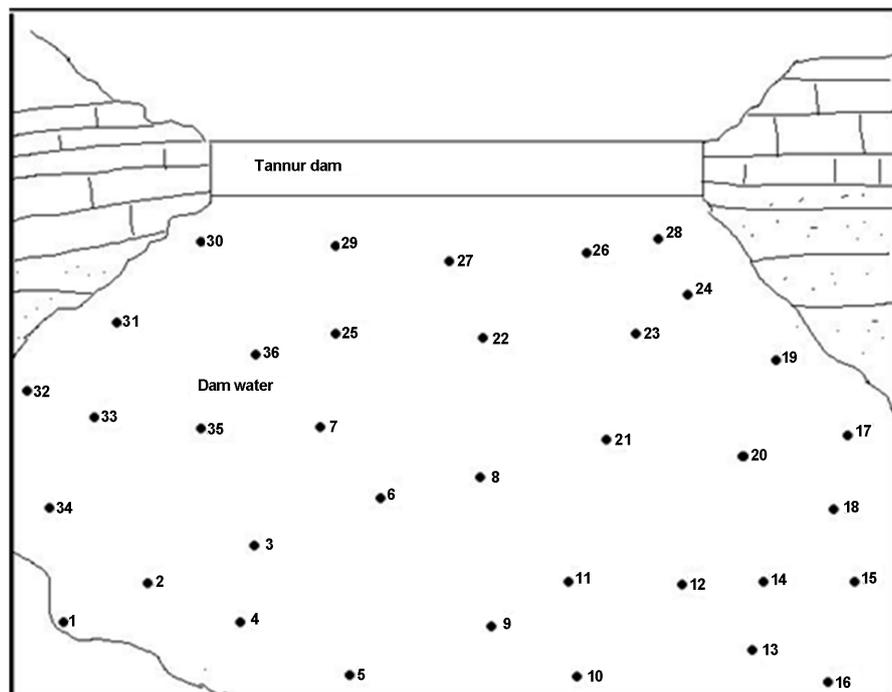


Figure 4. Location map of sampling sites.

After collection the water samples were transferred from polyethylene containers (1 L) into polyethylene bottles (250 mL), and then filtered through a 45- μm cellulose nitrate membrane filter using a vacuum pump in order to remove insoluble particles. Each sample was divided into two polyethylene bottles one for major anion analyses and the other was acidified the samples to $\text{pH} < 2$ for cation analysis and all samples were kept in refrigerator at 4°C until the time of chemical analysis, which was usually performed within one week after bottling. Electrical conductivity, pH, temperature and dissolved oxygen (DO) of the water samples were measured on site by using portable pH meter, EC meter, dissolved oxygen meter and temperature meter. All glassware and polyethylene bottles were soaked in 20% HNO_3 for 1 day and rinsed several times with deionized water before use. Conductivity measurements were carried out with 470 JENWAY conductivity meter with temperature compensation, while the pH values were measured in the field using 370 JENWAY pH-meters equipped with a combination glass electrode. Calibration was always carried out before measurement using standards buffer solutions of pH 4.00 and 7.00. Dissolved oxygen values were measured in the field using field DO-meter (WTW equipment). TDS was measured by the conductivity measurements. The calculation is carried out by the following equation: $\text{TDS (mg/l)} = \text{EC } (\mu\text{s/cm}) \times 0.64$, where EC is the electrical conductivity (Howari *et al.*, 2005). The bicarbonate concentration was determined by titration of the water samples with 0.02 H_2SO_4 using methyl orange as indicator. Major anions (Cl^- , NO_3^- and SO_4^{2-}) were analyzed by 100 Dionex Ion Chromatography instruments equipped with AG4A-SC guard column, AS4ASC separating column, SSR1 anion self-regeneration suppresser and conductivity detector. The samples were injected through 25 MI sample loop and eluted at 2.0 ml min⁻¹ using 1.7 m μ NaHCO_3 and 1.8 m μ Na_2CO_3 . The system was calibrated with a certified standard from Dionex. Major cations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) were measured by 800 Varian flames Atomic Absorption Spectrophotometer. The concentrations of cations were determined using a CS12 analytical column, CG 12 guard column, using 20 m μ CH_4SO_3^- . The concentration of bicarbonate was determined by titration with 0.01 hydrochloric acid using methyl orange as indicator. The standard solutions of the anions and cations as well as blank samples were prepared with different concentrations. All standard solution were made daily by diluting the stock solutions with 0.01 M HNO_3 [22], which was prepared from analytical grade HNO_3 solution obtained from Merck. A quality control procedure, including, recalibration of the instruments, analysis of triplicate samples and recovery test of standard reference material was used to control data quality [23]. All chemicals and reagents used in this study were of analytical grade unless otherwise stated. Deionized water (Milli-Q 18.2 $\mu\text{s/cm}$) was used for all dilutions. Standard solution was prepared by diluting the stock solutions.

To prevent the sample contamination with any source of pollution, all the glassware, Pyrex and plastic containers were washed several times with soap, deionized water and treated with 0.01 M HNO_3 and finally rinsed with ul-

tra-pure water. After analysis the accuracy of these standards were within $\pm 7\%$. The numerical simulation model PHREEQ was used to set up the hydrological components of the groundwater, especially the saturation indices of minerals (calcite, dolomite, gypsum, anhydrite and halite) to test the saturation of minerals.

2.2. Hydrochemical Evaluation and Water Quality Indices

To assess water quality and hydrochemistry of water samples, the parameters such as; Total Hardness ($TH_{mg/L}$), Sodium Adsorption Ratio (SAR), Percent Sodium (Na%), Residual Sodium Carbonate (RSC) and Permeability Index (PI) were calculated based on the chemical characteristics of water samples beside the hydrochemical parameters which include hydrochemical evaluation and Saturation Index (SI). These parameters and assessment indices will be defined later.

3. Results and Discussion

3.1. Chemical Characteristics of Water

Thirty six water samples were collected from reservoir water in Tannur dam during the studying period, May 2015 and September 2015. Statistical summary of volume-weighted mean concentrations of physical and chemical parameters are presented in **Table 2**.

The ratio of total anions to that of cations ($(\sum \text{anions})/(\sum \text{cations})$) was an indicator for the completeness of measured parameters [24]. The average equivalent sum of cations to that of anions ($(\sum \text{anions})/(\sum \text{cations})$) was 0.89 ± 0.32 . Also, for the set of samples considered in this study, linear regression of cation sum on anion sum gave value $R^2 = 0.93$ indicating that the quality of the data was good. The *in-situ* measured temperature for the water samples in the wet season (May 2015) ranged between 9.0°C and 12.8°C , with an average value of 10.6°C . On the other hand, the temperature of water samples in the dry season (September 2015) varied between 11.0°C and 18.1°C , with an average value of 13.8°C . Dissolved oxygen (DO) in water samples in wet season ranged from 3.4 and 6.6 mg/l, with an average value of 5.8 mg/l, but in dry season ranged from 4.1 mg/l to 6.9 mg/l, with an average value 5.41 mg/l. The water samples of the study area have pH values varied from 6.8 to 8.2 (alkaline type) with an average values in wet and dry seasons 7.6 and 7.9, respectively. The high value of pH content has resulted from the increase of calcite from carbonate rocks in the study area. In the water samples, the EC in wet season ranged between 1210 and 1910 $\mu\text{s/cm}$, with a mean value of 1501 $\mu\text{s/cm}$, while, in the dry season EC varied from 1800 and 1968 $\mu\text{s/cm}$, with a mean value of 1903 $\mu\text{s/cm}$. However, the high conductivity of the water samples in Shoubak basin corresponding to the highest of dominant ions, which is result by ion exchange and solubility of rocks in aquifer [22] [25]. TDS values in water varied from 772 mg/l to 1241 mg/l in wet season, with a mean value of 942 mg/l but in dry season it ranged from 1155 mg/l to 1264 mg/l, with a mean value of 1218 (**Table 2**). The increase of salinity in water

Table 2. Summary of chemical analysis of water samples in Tannur dam.

Parameters	Wet season (May, 2015)				Dry season (September, 2015)			
	Min	Max	Mean	St.dev	Min	Max	Mean	St.dev
T (°C)	9.0	13.1	10.5	0.41	11.0	18.1	13.8	0.32
pH	6.8	8.2	7.6	0.26	7.1	8.2	7.9	0.19
EC (µs/cm)	1210	1910	1501	180.0	1800	1968	1903	37.1
DO (mg/l)	3.4	6.6	5.8	0.18	4.0	6.9	5.4	0.11
Ca ²⁺ (mg/l)	102.1	150.3	126.3	0.6	150.6	182.3	166.3	0.2
Mg ²⁺ (mg/l)	43.6	71.4	54.8	0.6	66.9	79.6	73.9	0.3
Na ⁺ (mg/l)	71.3	135.7	92.1	0.8	103.2	135.7	131.1	0.4
K ⁺ (mg/l)	15.7	35.2	23.5	0.1	36.2	47.3	43.1	0.1
HCO ₃ ⁻ (mg/l)	262.3	475.8	341.6	1.1	451.4	481.9	475.8	0.17
Cl ⁻ (mg/l)	50.2	195.3	163.5	0.4	184.6	215.6	209.2	0.20
NO ₃ ⁻ (mg/l)	130.2	198.4	161.5	0.3	179.8	243.6	223.3	0.23
SO ₄ ²⁻ (mg/l)	91.2	187.2	110.4	0.6	188.6	154.8	191.5	0.21
TDS (mg/l)	772	1241	942	136.2	1155	1264	1218	34.21

samples can be explained by the chemical reactions that take place during water-rock interaction and through long period of contact with rocks. Dissolved Oxygen (DO) varied in the range from 3.4 mg/l to 6.6 mg/l in the wet season, with a mean value of 5.8 mg/l, but in dry season it ranged from 4.0 mg/l to 6.9 mg/l, with a mean value of 5.4. The chemical composition of the water in Tannur dam was variable. The chemical parameters including statistical measures were shown in **Table 2**. The abundance of the major ions in water samples is in the following order: $\text{HCO}_3^- > \text{Ca}^{2+} > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$. The concentration of calcium ion in wet season ranged from 102.1 mg/l to 150.3 mg/l, with a mean value of 126.3 mg/l but in dry season varied from 150.6 mg/l and 182.3 mg/l, with a mean value of 166.3 mg/l. Higher value of calcium in the wet season was due to release of calcium from the sedimentary carbonate rocks and soils to the aquifer (Al-Khashman, 2006). Calcium often comes from carbonate minerals such as calcite and dolomite, which commonly occurs in sedimentary and volcanic rocks, surrounded the study area. In wet season the concentration of Mg²⁺ in water ranged from 43.6 mg/l and 71.4 mg/l with a mean value of 54.8 mg/l but in dry season the concentration of Mg²⁺ varied from 66.9 to 79.6 mg/l, with a mean value of 73.9 mg/l. The maximum content of Mg²⁺ exists on the eastern side of the study area is related to the dissolution of volcanic rock which is present in this area and from chemical fertilizers [26]. The source of Ca²⁺ and Mg²⁺ in the water dam is believed to be limestone, dolomite, gypsum and anhydrite in the Wadi Es Sir and FHS formations [2]. The presence of HCO₃⁻ in the water samples is derived from carbon dioxide in the atmosphere, soils and by dissolution of carbonate rocks. The increasing of bicarbonate in the

dry season is attributed to the dissolution of carbonate rock in the study area (Figure 5). Sodium is the most abundant cation in the hydrosphere and present in natural water. The common source of sodium in the water samples is gypsum in sedimentary rocks, weathering of plagioclase and feldspar, which are typical constituents of volcanic rock surround the study area and evaporate deposits. Nitrate in water generally originates from several natural and human sources on the earth surface [27]. Also, nitrogen value in groundwater is derived from the biosphere [28]. The nitrate content in the water of Tannur dam in wet season ranged from 130.2 mg/l to 198.4 mg/l with a mean value of 161.5 mg/l, whereas, the nitrate in dry season varied from 179.8 mg/l to 243.6 mg/l with a mean value of 223.3 mg/l. The main source of nitrate in the water samples is related to the intensive use of nitrogen fertilizers in the nearby agricultural lands in the eastern and northern side of the Tannur dam, where most of the farms are located and manure and plant decomposition [1] [29].

3.2. Hydrochemical Evaluation of the Water Samples

Human activities near the Tannur dam site have had direct and indirect effects on the rate of water contamination. The direct effects on water include dissolution and transport of excess quantities of fertilizers with associated materials and hydrological alteration related to agriculture activities. While, the indirect effects include changes in water-rock reactions in soils and aquifers caused by increased concentration of major ions [30] [31]. Groundwater chemistry exchange matter with the various minerals and gases within the aquifer which it resulting from dissolution and precipitation of minerals [32]. Saturation indices of minerals in the water samples can be expressed by the saturation index (SI). The SI is defined as the logarithm of the ratio of the ion activity product of the mineral equilibrium constant at a given temperature [33]. When $SI < 1$ the water is undersaturated and the minerals will dissolve. If the ratio of saturated indices greater than 1; the water is supersaturated and the minerals tend to be precipitated [32] [33]. On the other hand, if SI is equal to 1, the water is in equilibrium with the

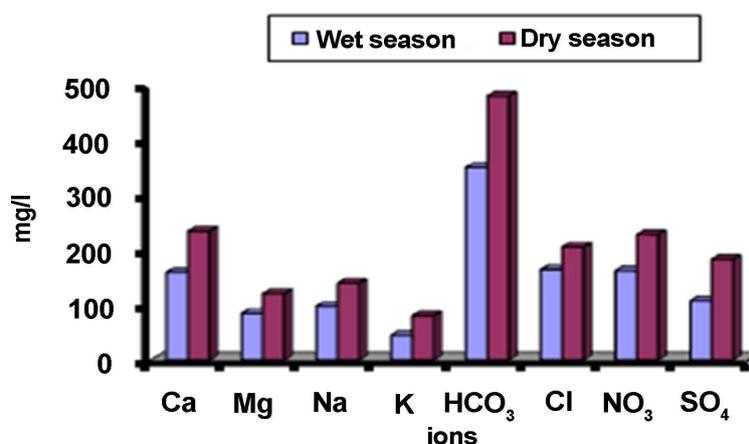


Figure 5. Mean concentration of ions in water samples.

mineral. The statistical of saturation indices of water samples were presented in (Table 3). All water samples have positive calcite and dolomite indices; indicate that the water was oversaturated with respect to calcite and dolomite. On the other hand, all the water samples indicate negative value for gypsum, halite and anhydrate indices; which means that all of the water samples below the saturation state with respect to the gypsum and anhydrate and they are able to dissolve additional amount of these minerals. The saturation indices at different water sampling locations in the study area were plotted in Figure 6. It is noticed that the water samples are oversaturated with respect to calcite and dolomite, slightly under saturated with respect to anhydrate and gypsum, but highly under saturated with respect to halite.

The geochemical evolution of water samples can be understood by plotting the concentrations of major ions on the trilinear diagram of Piper [34] (Figure 7) to determine the water type according to the Langguth classification [35]. Figure 7 shows that most of water samples analyzed during May 2015 and September 2015 in the field of mixed $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-Cl}^-$ type of water, whereas some samples are representing $\text{Ca}^{2+}\text{-Cl}^-$ and $\text{Na}^+\text{-Cl}^-$ types. From the Figure, alkaline earths (HCO_3^- , Ca^{2+} and Mg^{2+}) significantly exceed the alkalis (Na^+ and K^+) and strong acids chloride and sulfate. Water chemistry originates from dissolution of carbonate rocks. However, the water was generally classified as Ca-HCO_3 water with low salinity. The hardness of water samples was classified according to Sawyer and McCarty [36]. The hardness of water resulted from the presence of calcium, magnesium, bicarbonate and sulfate concentrations that are the most abundant ions. (Table 4) shows the classification of the water samples based on their hardness. The calculated of hardness of the water samples as CaCO_3 in mg/L according to Todd [27]:

$$\text{TH} = 2.5\text{Ca}^{2+} + 4.1\text{Mg}^{2+} \quad (1)$$

It was clearly shown from Table 4 that the water samples in wet season can be classified as hard water, 29 water samples show relatively very hard water. However, in the dry season two water samples are classified as hard water while the most of water samples were considered as very hard water. The general increase of water hardness from wet to dry season can be attributed to the dissolution of carbonate rocks that also includes traces of evaporate deposits and percolation of rainwater to the saturation zone [20].

Table 3. Statistical analyses of saturation indices of water samples.

Para	Wet Season (May 2015)				Dry Season (September 2015)			
	Min	Max	Mean	St.dev	Min	Max	Mean	St.dev
$\text{SI}_{\text{calcite}}$	0.07	1.03	0.32	0.37	0.53	1.06	0.87	0.13
$\text{SI}_{\text{dolomite}}$	0.66	1.93	1.33	0.41	0.79	1.84	1.16	0.22
$\text{SI}_{\text{anhydrate}}$	-1.61	-0.45	-1.03	0.32	-1.06	-0.39	-0.80	0.20
$\text{SI}_{\text{gypsum}}$	-1.69	-0.83	-1.29	0.26	-1.69	-0.75	-1.10	0.15
$\text{SI}_{\text{halite}}$	-7.92	-4.32	-5.78	1.14	-8.92	-4.09	-6.32	0.62

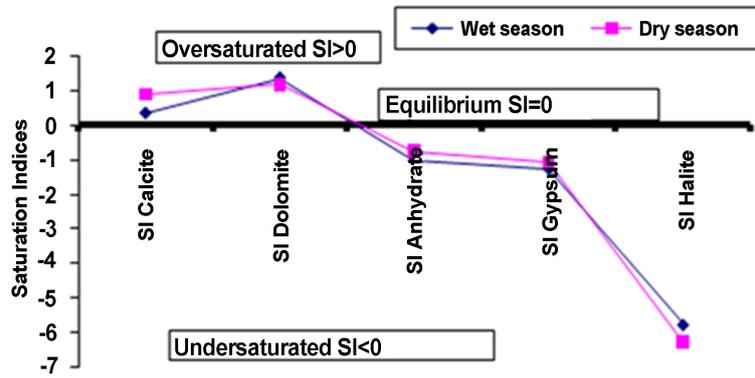


Figure 6. Saturation indices of minerals in water samples.

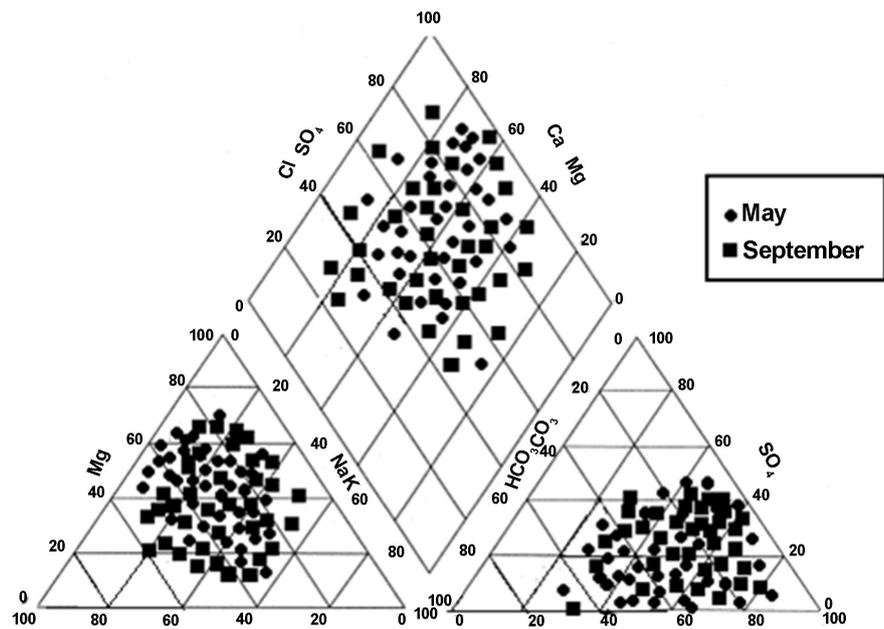


Figure 7. Piper diagram of water samples in Tannur dam.

Table 4. Classification of the water samples on the basis of the total hardness.

Total hardness (mg/l)	Water class	Wet season		Dry season	
		No. of samples	Samples %	No. of samples	Samples %
0 - 75	Soft	-	-	-	-
75 - 150	Moderate	-	-	-	-
150 - 300	Hard	7	19.4	2	5.6
>300	Very hard	29	80.6	34	94.4

3.3. Hydrochemical Coefficient

The ratio of Ca^{2+}/Mg^{2+} , Na^+/Cl^- , $Mg^{2+}/Ca^{2+} + Mg^{2+}$, SO_4^{2-}/Cl^- and Ca^{2+}/Na^+ were calculated for water samples (Table 5). In the water samples, Ca^{2+}/Mg^{2+} equivalent ratios were >1.0 , the Ca^{2+}/Mg^{2+} was higher in water samples due to higher carbonate concentration in the water. High correlation was found between

Table 5. Hydrochemical coefficient of water samples.

Ionic ratio	Wet season (May 2015)				Dry season (September 2015)			
	Min	Max	Mean	St.dev	Min	Max	Mean	St.dev
Ca/Mg	1.23	1.60	1.41	0.10	1.20	1.66	1.33	0.12
Na/Cl	0.58	1.11	0.85	0.14	0.82	1.25	1.10	0.10
Mg/Ca + Mg	0.35	0.65	0.44	0.09	0.35	0.76	0.52	0.09
SO ₄ /Cl	0.40	0.82	0.62	0.12	0.45	0.86	0.66	0.08
Ca/Na	1.15	1.76	1.48	0.14	1.22	1.82	1.52	0.18

calcium and magnesium of water ($R^2 = 0.81$), suggesting that the common source of these ions from carbonate dissolution in the water. While the median Na^+/Cl^- equivalent ratios were <1 , the lower ratio of Na^+/Cl^- in water can be due to dissolution with clay minerals exchanging Na^+ for Ca^{2+} . On the other hand, strong correlation was found between sodium and chloride of water ($R^2 = 0.91$) (Table 6), suggesting that the common source of these ions from salt dissolution. The possible sources of these ions were anthropogenic sources and natural sources. The median $\text{Mg}^{2+}/\text{Ca}^{2+} + \text{Mg}^{2+}$ ratios were <1 indicating weathering of limestone and dolomite, while the median $\text{Ca}^{2+}/\text{Na}^+$ equivalent ratios in two periods varied between 1.48 to 1.82, this ratio is high in water as a result of solubility of carbonate in the study area. The median $\text{SO}_4^{2-}/\text{Cl}^-$ ratios were <1 indicating the dissolution of gypsum and limestone in the water. Chloride ion is highly correlated with sodium ($R^2 = 0.91$), while they are better correlated with HCO_3^- , SO_4^{2-} and Mg^{2+} ($R^2 = 0.74, 0.72$ and 0.68) respectively.

3.4. Irrigation Water Quality

The suitability of water for irrigation is dependent on the effects of its mineral constituents on both plants and the soil [27] [37]. The quality of water for irrigation water is based on the total salt concentration of the water, the concentration of specific ions that may be toxic to plants. Sodium adsorption ratio (SAR) is an important parameter for determining the suitability of water for irrigation because it is a measure of alkali and sodium hazard to plant [38]. The sodium adsorption ratio (SAR) is defined as follows where the concentrations of the constituents are expressed in milliequivalent per liter (meq/l).

$$\text{SAR} = \text{Na} / \left\{ \sqrt{(\text{Ca} + \text{Mg}) / 2} \right\} \quad (2)$$

The SAR values ranged from 1.48 to 2.29 with a mean value of 1.75 during the wet season (May 2015) and 2.08 to 2.44 with a mean value of 2.20 during dry season (September 2015). The dam water of Tannur was classified with respect to SAR (Richards, 1954). All analytical data plotted on the US salinity diagram [39] shows that most of water samples classified in the field of C3S1, indicating high salinity with low sodium water. This type of water is suitable for irrigation on almost all types of soil (Figure 8). Another parameter can be used for classification of irrigation water is the sodium percentage while, sodium reacts with

Table 6. Correlation matrix for different water quality parameters, cells show the Pearson correlation coefficient and the corresponding *P*-value.

	Ca	Mg	Na	K	HCO ₃	Cl	NO ₃
Ca							
Mg	0.811						
Na	0.401	0.310					
K	0.661	0.351	0.132				
HCO ₃	0.681	0.462	0.021	0.521			
Cl	0.742	0.685	0.910	0.644	0.523		
NO ₃	0.341	0.470	0.521	0.426	0.463	0.331	
SO ₄	0.640	0.720	0.701	0.601	0.592	0.741	0.294

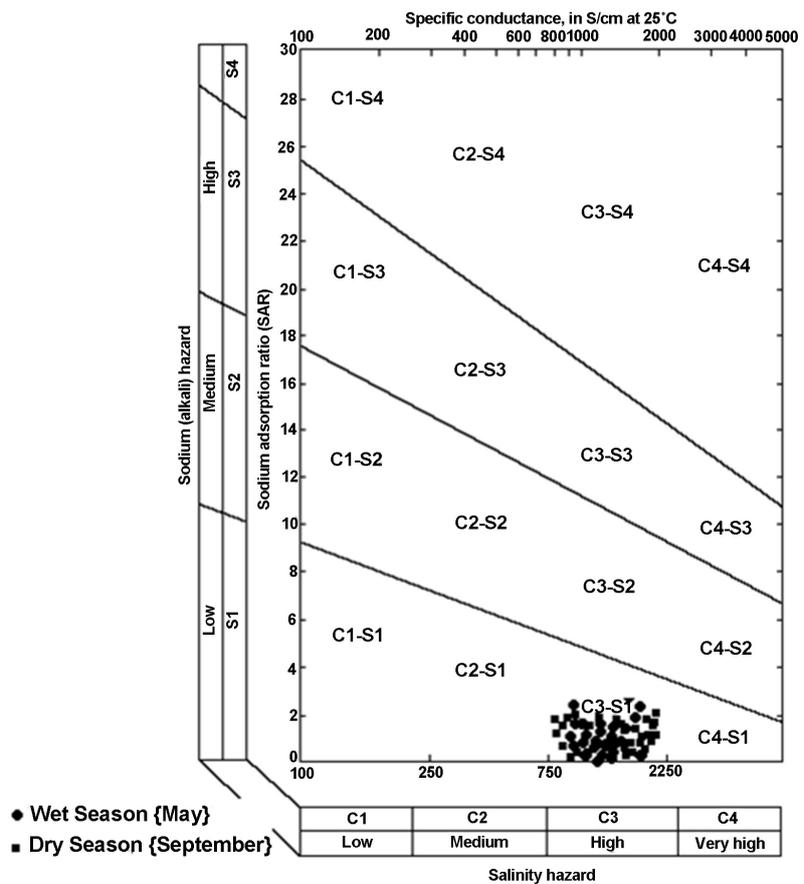


Figure 8. Classification of dam water for irrigation purposes.

soil to reduce its permeability. The sodium percentage (Na%) is calculated using the formula given below:

$$Na\% = \left\{ \frac{Na + K}{Ca + Mg + Na + K} \right\} \times 100 \quad (3)$$

where all of the concentrations are expressed in meq/l.

The sodium percentage indicates that the water is good to permissible for irrigation (Table 7). All samples in the wet season are classified as good water for irrigation, while in dry season 69.4% of water samples are classified as good water, and others are classified as permissible water for irrigation (Table 7). When the concentration of sodium is high value in irrigation water, sodium ions tends to be adsorbed by clay minerals, displacing Mg^{2+} and Ca^{2+} ions. This exchange process of sodium in water calcium and magnesium in soil reduced the permeability and eventually results in soil with weak internal drainage [18] [28].

In addition to the sodium adsorption ratio (SAR) and sodium percentage (%Na), the residual sodium carbonate (RSC) represents the excess sum of carbonate and bicarbonate over the sum of calcium and magnesium also influences the unsuitability of water resources for irrigation. The residual sodium carbonate (RSC) is calculated by the following equation:

$$RSC = (HCO_3^- + CO_3^{2-}) - (Ca^{2+} + Mg^{2+}) \quad (4)$$

where the concentration of ions is expressed in meq/l.

The classification of irrigation water in the Tannur dam according to the residue sodium carbonate (RSC) values is shown in Table 8. The first category has (RSC) < 1.25 epm (good quality). The second category has ranged from 1.25 to 2.5 epm (doubtful), while the third category has more than 2.5 epm (unsuitable). Table 8 shows the samples in two time periods and their relevant class. Results shown in this table indicate that the water of Tannur dam is mostly of good quality.

The permeability index (PI) values also indicate that the water of Tannur dam is suitable for irrigation. The permeability index is shown in the following equation:

$$PI = (Na^+ + \sqrt{HCO_3^-}) \times 100 / (Ca^{2+} + Mg^{2+} + Na^+) \quad (5)$$

where all values of ions are expressed in meq/l.

The permeability index (PI) in water from Tannur dam ranged from 34% to 43% during May 2015. On the other hand, in dry season the PI varied from 45% to 60% during September 2015, which found under class-1 of Doneen's chart [40].

Table 7. Suitability of dam water for irrigation based on the %Na.

%Na	Water class	Wet season		Dry season	
		No. of samples	Samples %	No. of samples	Samples %
<20	Excellent	-	-	-	-
20 - 40	Good	36	100	28	77.8
40 - 60	Permissible	-	-	8	22.2
60 - 80	Doubtful	-	-	-	-
>80	Unsuitable	-	-	-	-

Table 8. Water quality based on residual sodium carbonate (Na_2CO_3).

RSC (meq/l)	Remark on quality	Wet season		Dry season	
		No. of samples	Samples %	No. of samples	Samples %
<1.25	Good	30	83.3	22	61.1
1.25 - 2.5	Doubtful	6	16.7	14	38.9
>2.5	Unsuitable	-	-	-	-

4. Conclusion

In this study water samples of the Tannur dam were collected to evaluate the hydrochemical characteristics of water and suitability for domestic, irrigation and industrial purposes. Physical and chemical parameters of water were determined; such as temperature, pH, conductivity, dissolved oxygen, total dissolved solid (TDS), total hardness (TH), cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) and anions (HCO_3^- , Cl^- , NO_3^- and SO_4^{2-}). Results show that water samples in the study area were hard to very hard in nature. The PHREEQC hydro-geochemical modeling was used to obtain the saturation indices of specific mineral phases, which might be related to interaction with water and aquifer, and to identify the chemical species of the dissolved ions. The thermodynamic calculations indicate that most of the water samples are undersaturated with respect to halite, gypsum and anhydrite, and are saturated and oversaturated with respect to calcite and dolomite. The hydrogeochemistry behavior is rather complicated and is affected by anthropogenic and natural sources. The abundance of the major ions in water samples is in the following order: $\text{HCO}_3^- > \text{Ca}^{2+} > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$. Water samples of the Tannur dam are generally very hard, high to very high saline and medium alkaline in nature. High total hardness (TH) and total dissolved solids (TDS) in some samples identify the permissible for domestic and irrigation purposes. According to the residual sodium carbonate, sodium adsorption ratio, and sodium percentage values, the dam water can be used for irrigation purposes. The inorganic constituents of the water were influenced by lithology, anthropogenic activities. Some water samples are highly affected by human activities and agricultural activities around the dam. The integrated management of water samples for domestic, irrigation and industrial purposes to solve the water scarcity is not only in the studied area but also in other watershed. This study recommends continuous monitoring of the Tannur dam water, and protection of the dam from pollutants that originate from human activities and chemical fertilizers used in agricultural activities beside the dam.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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