

Some Heavy Metals Status and Water quality parameters of Darbandikhan Dam, Sirwan and Tanjaro rivers

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Abstract

Three stations were used for this study, including the Darbandikhan Dam at coordinates $35^{\circ}7'16"N$, $45^{\circ}43'18"E$, the Sirwan River at coordinates $35^{\circ}7'17"N$, $45^{\circ}50'54"E$, and the Tanjaro River at coordinates $35^{\circ}14'22"N$, $45^{\circ}51'58"E$, to examine the concentration of heavy metals there over a six-month period. The studied heavy metals include Hg, Cd, Pb, Cu, Co and Cr analyzed by ICP-OES (Spectro acros). Temperature values range between 13-30.9 C°, Dissolved Oxygen value ranged between 4.82- 9.5 mg L^{-1} , pH values varied between 6.11-7.97, Total Hardness level exceed (100mg L⁻¹), The sulphate value was between 51 and 145 mg L⁻¹, Nitrate values ranged from 3.01 to 14.7 mg L⁻¹. The range of electrical conductivity of this study was 191 to 595 µs cm⁻¹, The concentration of calcium ions (Ca²⁺) was between 48-104 mg L⁻¹, Magnesium concentration was between 12.6-40 mg L⁻¹. Hg, Cr and Cd were below detectable level, the Pb was higher in August 2021, Cu in September 2021 in Darbandikhan Dam. In Tanjaro River Site each of Cd and Hg were below detectable level, the Cr, Co, Cu and Pb were higher in August 2021.

Key words: Heavy Metals, Water quality, Darbandikhan Dam, Sirwan, Tanjaro rivers

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Introduction

Water pollution define is the presence of excessive amounts of a hazard (pollutants) in water in such a way that it is no longer suitable for other uses, it includes all of the waste materials that can't be naturally counteracted by water, Water pollution can be caused by a variety of different, diffuse, and human-related sources, either directly (point source pollution), where the source of the pollution is known, or indirectly (nonpoint source pollution), where the source of the contamination is unknown. Environmental dumping grounds have been part created. in or entirely. by industrialization and human activities. As a result, many water supplies are now contaminated and dangerous for people and other living things [1].

Heavy metals (HM), which are defined as any metallic or metalloid chemical elements with relatively high densities larger than 5 g cm-3 and are poisonous even at low concentrations, are a component of the earth's crust. Heavy metal pollution of aquatic ecosystems is mostly caused by anthropogenic activities and natural sources. Due to their endurance, toxicity, and capacity to bind to organic components in the body, these metals pose a major hazard to aquatic life. They also cause cell dysfunction by obstructing transport mechanisms via the cell wall [2]. Additionally, they have an impact on human existence due to bioaccumulation, bioaugmentation in the food chain, and their non-biodegradable nature in ecosystems [3];[4] and [5].

Darbandekhan lake in the Kurdistan region is located 60km southeast of Sulaimani city. This lake is mainly fed by two rivers as supplying sources including, Tanjaro It rises in the city of Sulaymaniyah at the meeting of the rivers Kiliasan and Kani-Ban, and after 58 kilometers, it enters the

Darbandikhan Dam reservoir and Sirwan a river and tributary of the Tigris that originates in Iran as the Sirwan River then runs mainly through Eastern Iraq Other supplying sources such as precipitation of rain and snow, also ground waters from springs around the lake are also fed into this lake, it is an important source of food [6]. Numerous studies have been conducted on the water quality of water and the accumulation of heavy metals in water, sediments, and fish in the Kurdistan region generally and in Darbandikhan lake especially [7]; [8]; [9].

The main objectives of the study are to determine physical parameters such as Temperature, electrical conductivity (EC), pH, Dissolved Oxygen, Total Hardness, and soluble cation and anion that influence metal concentration in water. (Cd, Co, Cr, Cu, Pb, and Hg) in Water.

2. Materials and Methods

Study Area: The Darbandikhan is a large freshwater reservoir created bv the Darbandikhan Dam. The Darbandikhan lake is located at 35° 6' 35" N ,N , 45° 41' 20" E , the altitude is 485 m, about 60 km southeast of Sulaymaniyah City in the Kurdistan Region, northern Iraq. The lake is fed by two main rivers, the Tanjero in the north and the Sirwan in the east [6] besides other supply sources of precipitation such as rain, snow, ground waters from springs around the lake, [10]. The lake is surrounded by hills covered with grass and small shrubs and mountains (including Bashari, Zmnako and Zawaly) that are covered in oak forests. During (1956-1961) Darbandikhan Dam was built for irrigation, electricity production, controlling excessive precipitations, and recreation purposes. Due to problems after construction, there have been several slope failures upstream and repairs required of the dam. Water levels

decline in summer after the spring melt due to dam release and rise again when winter rains return in the late fall.

The Kurdistan climate characteristic of a semi-arid region is described as Mediterranean with hot and dry weather in Summer, and cool with relatively moist conditions in winter [11]. The area of the lake is about 114.30 Km² with a maximum depth of 75m. The volume of the Darbandikhan lake approximately ranges from 1.3-1.4 Km³ [12]; [7]. As a result, Darbandikhan can be categorized as a limnetic water body because it is warm and monomictic, has just one wintertime circulation period, and never experiences below-freezing temperatures in its water. Marine-derived sedimentary rocks make to the region's geology. The collection decision of 9 regarding the climate of the studied area is a dry-summer approach Irano-Turanian type characterized by the occurrences of three seasons: a cold winter, a mild growing period of spring, and hot-dry summer.

Location of sampling: Three sites have been studied in Darbandikhan lake: the first site is Mid-Darbandikhan lake Side, which is located behind the dam directly with a 40-50m depth average in the area (35°7'16'' N 45°43'18'' E). The second site is Tanjaro

River Side, the area in which Tanjaro river reaches the lake, that located at (35°14'22" N 45°51'58" E). Most of the trash from Sulaymaniyah is dumped directly into the Tanjaro River in the Tanjaro region. Domestic, industrial, transportation, mining, and agricultural wastes make up this garbage. The majority of the toxins and pollutants were released into the river as a result, which subsequently passed through several cities and neighborhoods before merging with other rivers or tributaries and draining into Darbandikhan Lake. The third site is Sirwan River Side: The area in which the Sirwan river reaches the lake, located at (35°7'17" N 45°50'54" E). This area is rich in fishes and a source of life for many fishermen not only from Darbandikhan but also coming from Halabja city for fishing, the level of the water in this area depends on how much water follows from Iran throw the Sirwan river which will decrease especially during summer time as there is no feed from Iran to the river Figure (1). Preparation of sample containers: All of the high-density glassware and plastic containers underwent a complete detergent wash, distilled water rinse, three-day soak in analytical grade HNO3, and deionized water rinse.



Figure 1: Map of the study area the sampling sites.

Samples and Sampling procedure: Water samples were collected into acid pre-cleaned plastic bottles. Surface water was collected during different periods of discharge. Six sampling campaigns were conducted from August 2021 to January 2022. Two samples in 300 ml bottles were collected at each site. One sample was for heavy metal analysis and the other sample was for dissolved oxygen (DO) modification of the Winkler method was used to fix oxygen on-site for dissolved oxygen (DO) analysis. Water samples for physicochemical determination were collected into 1.5 L plastic bottles, according to the procedure described by [13].

All the sample containers and corks used in the sampling were rinsed three times with the sample water before being filled to the brim to expel air which leads to preventing iron deposition and consequent loss of phosphate and carbon dioxide with consequent calcium precipitation and then covered with cork and labeled [14]. The samples were filtered through 0.45 µm filters and done analyzed, while some parameters such as temperature, EC, DO and pH were measured on site, using the portable instrument. Samples collected for heavy metals analysis were filtered and preserved with dilute nitric acid (2 ml) in 300 ml before transporting to the laboratory for analysis. The bottles were kept in the refrigerator at (4-6 C°) temperature for subsequent analysis.

Water sample analysis:

Temperature (C°) On-site thermometer measurements of the water sample temperatures were made. The water sample was measured at about 100 ml and put into a beaker with a capacity of 250 ml. According to the field procedure, the thermometer was submerged in the water [13].

Active hydrogen: Hydrogen ion concentration (pH): The water pH was measured on-site using a portable pH meter (Multi 340i/SET multiparameter instrument WTW Company-Germany), equipped with pH probes, the probe was calibrated using appropriate standard solutions (buffer solutions of pH 4.01 and 7.00) before sampling as described by [13].

Electrical Conductivity (EC): The water Electrical Conductivity was measured in the field by electrometric method, using a portable EC-meter (Cond 330i, 82362 Weilheim WTW Company-Germany). The final result was corrected at (25 C°) and expressed in dS\m bbb [13].

Dissolved Oxygen (DO): Dissolved oxygen was measured in the field using a special oxygen-sensitive membrane electrode (InoLab.OXi730, WTW Company-Germany). The readings were allowed to stabilize and DO read in mg L-1, as described in the [13].

Total hardness: The determination of total hardness and calcium hardness was done by using an accurate method. The measurements of total hardness were done depending on the mathematical model below:

(mg L⁻¹ Ca⁺² + × 2.496) + (mg L-1 Mg⁺² × 4.115) = mg L⁻¹ Total hardness as CaCO³ Calcium and magnesium (Ca⁺² and Mg⁺²) and Nitrate and Sulphate (NO⁻³ and SO4⁻²) according to (Mati, 2004). Sodium and potassium (Na⁺ and K⁺), Chloride ion (Cl⁻), Alkalinity as bicarbonate contents (HCO⁻³) as described by [13].

Heavy metals analysis: The heavy metals analyzed by using analytical were methodologies as per [13]. The collected samples were filtered with filter paper (pore size 0.45 µm) and to minimize adsorption and precipitation of metals on the walls of the bottles the samples were preserved by correcting the pH below 2 with nitric acid as described the standard procedure. The heavy metals concentration copper (Cu), chromium (Co), iron (Fe), lead (Pb), manganese (Mn), Nickel (Ni), Selenium (Se), and zinc (Zn)

were determined using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) multi-element system, which is powered by Argon gas and nebulizer gas flow (L min⁻¹). At 14–16 C°, ICP-OES analysis begins with three samples replicating.

Statistical analysis: The data obtained in this study were subjected to statistical analysis (basic statistics) and tabulated by using the XLSTAT computer program, version (2016). The means were compared by ANOVA Duncan test at the significance levels of 95% (p < 0.05). the water quality data were compared with WHO (2018).

3.Results

Water Physic-Chemical Properties: Water quality data records for six months' worth of can be seen as a network of interconnected variables, such as pH, oxygen content, temperature, etc. The quantities of metals in the aquatic system can be impacted by changes in these physical and chemical factors in a number of different ways [15].

Temperature: Temperature values range between 13-30.9 C° as shown in the Table (1) and charts (1-3). The temperature of the water has profound effects on dissolved oxygen in polluted water. Therefore, the temperature has a significant impact on the rate of chemical processes, the metabolic rate of organisms, and the distribution of aquatic species. Season, location, sampling timing, and temperature of effluents entering the lake are the factors that affect the variation in lake water temperature [16]

Many environmental conditions, like the water's current, depth, beneath materials, temperature of effluents entering the water stream, exposure to direct sunlight, and amount of shade, are responsible for the basic variations [17]. The results of water temperature in this study agreed with results of [18] who found the temperature of water 9.8-34 C° Tigris River southern Baghdad city. [19] found in their studies water

temperature values were ranging between 11-30 C° Tigris River at Baghdad city and this result agrees with our records.

Dissolved Oxygen (DO): Dissolved Oxygen value ranged between 4.82- 9.5 mg L^{-1} as seen in Table (1) and Charts (4-6). The most crucial factor in fish production is dissolved oxygen because most fish cannot survive when DO level drop to less than 3 ug L^{-1} . Fish metabolic rates increase with food availability, however the process of absorption is impacted by reduced concentrations of dissolved oxygen, which is a need necessary for fish. Fish growth is influenced by feeding rates, food quality, and environmental changes that occur. [20]. The variations in the amount of dissolved oxygen in water are influenced by a variety of causes. Along with respiration of aquatic organisms and photosynthesis, the amount of dissolved oxygen is influenced by temperature [21].

pH: pH values varied between 6.11-7.97 as shown in Table (1) and Charts (7-9), The pH of the aquatic ecosystem is impacted by chemical and biological activity in the water. Natural water typically has a pH greater than 7 [22].It is crucial because many biological processes have short window of opportunity, and any deviation from this window could be lethal to a particular organism [23].

Generally, the geology and atmosphere influence the pH of natural waters and thus most freshwaters within Iraq are relatively well buffered with pH ranges between 7 and 8 and mainly tend to be slightly alkaline [24]. The pH values during this study were within the normal range for living of fish. Iraqi waters have slightly alkaline nature that is due to the presence of calcium bicarbonate [25], whereas the water in the study area was natural because it is a component of Darbandikhan Lake. The pH of the water, the kind and concentration of ligands that the metal could adsorb to, the oxidation state of the mineral components, and the redox are the primary factors that affect the solubility of heavy metals in surface waters. At alkaline pH, the metals typically precipitate as insoluble oxides and carbonates. [26] found that the pH levels in the Al-Gharraf River in southern Iraq ranged from 6.9 to 8.2. [27] and [28] discovered that the pH levels in the Tigris River at Baghdad City ranged from 7.1 to 8.4 and 7.1 to 8.2 respectively.

Total Hardness (TH): Total Hardness level in our study exceed 100mg L⁻¹ as shown in Table (1) and Charts (10-12) which exceeded the maximum level of total hardness limit according to (WHO, 2004) which is 100mg L⁻¹. A key indicator of water quality is water hardness. The range of total hardness was 196-340 mg L⁻¹. due to flooding; TH content is high throughout this investigation. It is influenced by the presence of the ions Mg⁺² and Ca⁺², and it also displays the total of carbonate and noncarbonate hardness [22].

In Iraq, hardness concentrations rise with heavy rainfall; this rise may be caused by the caules's nature of Iraqi soils. In contrast, hardness concentrations fall in the spring and rise again in the summer due to dust storms and the precipitation of large amounts of dust that are rich in minute CaCO3 and high concentrations of salts and this is consistent with what was mentioned by [15].

Sulphate (SO⁻⁴): The sulphate value was between 51 and 145 mg L⁻¹ as shown Table (1) and Charts (13-15). Water evaporation from catchment regions with high mineral and organic content the main source of sulphate is sulfur. There was seasonal variation of the sulfate value within the different study location. It was discovered that it peaked in the rainy season and lowed in the summer [29] With 250 mg L⁻¹ (WHO, 2004) limit for sulphate the ranges show in the below table (1) that the concentration of sulphate within the study area and for the six months duration of the study was within the limit.

Nitrates (NO⁻³): Nitrate values ranged from 3.01 to 14.7 mg L^{-1} as shown in Table number (1) and Charts (16-18), the Tanjaro river inlet to the lake station marked as (N) in the below table number (1) Nitrates results are exceeded the (WHO, 2004) limit which is 10 mg L^{-1} . Nitrate is the most highly oxidized form of nitrogen compounds usually seen in waterways because it is produced by the anaerobic decomposition of organic nitrogenous waste. Nitrification of ammonia decreases at relatively low dissolved oxygen levels, the sediments' capacity to absorb oxygen is diminished, and a noticeable increase in the discharge of NH⁻⁴N from the sediments follows.

Electrical conductivity (EC): The range of electrical conductivity of this study was 191 to 595 µs/cm as shown in Table (1) and Charts (19-21). The Investigations have found EC values that may be related to snowmelt, rock quality, and water flow rates. These result in diluted water and decreased EC measurements (WHO, 2004). Conductivity is used to calculate the mass of dissolved salts in a given mass of solution which is called salinity. Conductivity evaluates the total quantity of salts in a sample of water in addition to the water's capacity to conduct an electrical current since salty water transmits electricity more readily than clean water. Consequently, utilizing electrical conductivity to evaluate salinity is a frequent technique. The chlorides, sulphates, and carbonates of sodium, magnesium (Mg), calcium, and potassium are commonly responsible for conductivity [30]. In comparison with standards (WHO, 2004) the maximum value allowable for electrical conductivity is 750 $mg L^{-1}$.

Calcium: The concentration of calcium ions (Ca^{+2}) in our study was between 48-104 mg

 L^{-1} as shown in table (1) and chart number (22-24). One of the most common inorganic cations, or positive ions, in both freshwater and saltwater is calcium in the form of the Ca⁺² ion. It might develop from the dissociation of salts in water, like calcium chloride or calcium sulfate. The majority of the calcium in surface water comes from streams that pass over calcium-containing rocks and minerals such gypsum, calcium carbonate, limestone, and CaCO³. When there is a high amount of dissolved carbon dioxide in the water, calcium carbonate dissolves more easily. A level of 50 mg L^{-1} is recommended as the upper limit for drinking water. (WHO, 2004) allowable limit for Ca⁺² Concentration in water is (75 $mg L^{-1}$).

Magnesium: Magnesium concentration in our study was between 12.6-40 mg L^{-1} as shown in table (1) and chart number (25-27) Additionally, it is assessed using a complex metric titration method using an EDTA standard solution and an Eriochrome black T indicator under buffering conditions of pH 10.0. Mg^{+2} is the most prevalent aqueous species. The carbonate equilibrium reactions for magnesium are more complex than those for calcium, and it is uncommon for dolomite to directly precipitate in natural waters. Magnesium salts, which play a significant role in water hardness. decompose when heated. Magnesium and

associated hardness are reduced to acceptable levels using chemical softening, reverse osmosis, or ion exchange. Magnesium is a crucial component of red and chlorophyll. blood cells Some magnesium salts are poisonous when consumed or inhaled. A cathartic and diuretic effect may also occur at concentrations higher than 125 mg L^{-1} [13]. As for the (WHO, 2004) limit for Magnesium it is (30mg L^{-1}) , in the Sirwan river inlet location of the study the magnesium concentration has exceeded the WHO, (2004) limit for August 2021 and January 2022 as shown in Table 9 and Chart 9.

Sodium and potassium: Slightly high concentrations of sodium may be found in brines and hard water which is softened by the sodium exchange process. Agriculture and human pathology both depend on the sodium to total cation ratio. A high sodium ratio can be detrimental to soil permeability. Certain disorders call for water with reduced concentrations salt for the patients. or the hydrogen-exchange Distillation technique can be used to remove sodium. Potassium is a crucial component of plant and human nutrition and enters groundwater as a result of the breakdown of minerals [13]. The limit for sodium and potassium concentration in water is 55 and 200

#	Month – Parameters	Locations	Temp C ^o	$\frac{DO}{mg L^{-1}}$	pН	TH mgL ⁻¹	Sulphate mg L ⁻¹	Nitrates mg L ⁻¹	EC µscm ⁻¹	Calcium mg L ⁻¹	Magnesium mg L ⁻¹	Potassium mg L ⁻¹	Sodium mg ⁻¹ L ⁻¹
1	August 2021	D	30.9	8.5	7.64	196	84	8.03	191	48	18.4	0.72	38
		Ν	30.9	7.7	7.41	254	51	12.4	345	54.4	28.6	0.48	32
		А	30.8	9.5	7.38	302	130	7.1	557	65.6	33.5	0.76	40
2	September 2021	D	29.6	8.85	7.82	226	91	6.4	380	68	13.6	0.72	45
		Ν	30	7.82	7.6	292	62	12.4	450	72	27.2	0.60	42
		А	28.3	9.4	7.97	202	145	5.8	375	48	19.9	0.68	51
3	October 2021	D	23.6	6.75	7.83	222	82	3.4	356	54	21	1.80	26
		Ν	24.5	6.6	7.91	322	61	12.9	491	88	24	1.28	23
		А	23	7.2	7.76	262	100	3.5	395	58	28	1.96	28
4	November 2021	D	20	7.38	7.6	240	78	3.01	304	64	19	2.16	36
		Ν	20.3	8.55	7.71	260	92	9.1	256	72	19.1	2.64	42
		А	20.5	7.74	7.53	260	93	3.5	335	56	29	2.68	37
5	December 2021	D	13.6	8.04	7.6	220	70	3.5	399	76	12.6	2.30	32
		Ν	13	7.03	7.71	248	96.1	14.7	497	67	13	4.08	33
		А	14.5	7.25	7.53	240	69	3.7	395	56.8	23	2.40	32
6	January 2021	D	15.2	4.82	7.31	320	62	3.2	436	72	34	2.08	52
		Ν	15	7.2	7.11	324	55	11.6	595	104	23.2	2.80	70
		А	15.3	7.5	7.46	340	68	3.7	510	68.8	40	2.04	51

Table (1) Water parameter data from studied location during the study period

D = Darbandikhan dam area; DO = Dissolved Oxygen; N = Tanjaro river site area, EC = Electrical Connectivity; A = Sirwan river site area; TH = Total hardness; Temp.= Temperature



Chart 1-3: Water Temperature in °C in (Darbandikhan, Tanjaro River side, Sirwan River side) from (August2021 till January2022)



Chart 4-6: Dissolved Oxygen in mg L⁻¹ in (Darbandikhan, Tanjaro River side, Sirwan River side) from (August2021 till January2022)



Chart 7-9: Water pH in in (Darbandikhan, Tanjaro River side, Sirwan River side) from (August2021 till January2022)



Chart 10-12: Total Hardness in mg L-1 in (Darbandikhan, Tanjaro River area, Sirwan River area) from (August2021 till January2022)



Chart 13-15: Sulphate Concentration in mg L-1 in (Darbandikhan, Tanjaro River Side, Sirwan River Side) from (August2021 till January2022)



Chart 16-18: Nitrates Concentration in mg L⁻¹ in (Darbandikhan, Tanjaro River area, Sirwan River area) from (August 2021 till January 2022)



Chart 19-21: EC in µs cm⁻¹ in (Darbandikhan, Tanjaro River area, Sirwan River area) from (August2021 till January2022)



Chart 22-24: Calcium concentration in mg L⁻¹ in (Darbandikhan, Tanjaro River side, Sirwan River side) from (August2021 till January2022).



Chart 25-27: Magnesium concentration in mg/L in (Darbandikhan , Tanjaro River side , Sirwan River side) from (August2021 till January2022).

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Chart 28-30: Potassium concentration in mg L⁻¹ in (Darbandikhan, Tanjaro River side, Sirwan River side) from (August2021 till January2022).



Chart 31-33: Na concentration in mg L⁻¹ in (Darbandikhan, Tanjaro River area, Sirwan River area) from (August2021 till January2022)



Chart 1-3: Water Temperature in C° in (Darbandikhan, Tanjaro River area, Sirwan River area) from (August2021 till January2022)



Chart 4-6: Dissolved Oxygen in mg L° in (Darbandikhan , Tanjaro River area , Sirwan River area) from (August2021 till January2022)



Chart 7: Darbandikhan Dam area

Chart 8: Tanjaro River area

Chart 9: Sirwan River Area

Chart 7-9: Water pH in (Darbandikhan, Tanjaro River area, Sirwan River area) from (August2021 till January2022)







Chart 12: Sirwan River Area





Chart 13: Darbandikhan Dam area

Chart 14: Tanjaro River area

Chart 15: Sirwan River Area

Chart 13-15: Sulphate Concentration in mg L⁻¹ in (Darbandikhan, Tanjaro River area, Sirwan River area) from (August2021 till January2022)



Chart 16: Darbandikhan Dam area

Chart 17: Tanjaro River area

Chart 18: Sirwan River Area

Chart 16-18: Nitrates Concentration in mg L⁻¹ in (Darbandikhan, Tanjaro River area, Sirwan River area) from (August2021 till January2022)



Chart 19: Darbandikhan Dam area C

Chart 20: Tanjaro River area

Chart 21: Sirwan River Area





Chart 22: Darbandikhan Dam area Chart 23: Tanjaro River area Chart 24: Sirwan River Area Chart 22-24: Ca in mg L⁻¹ in (Darbandikhan, Tanjaro River area, Sirwan River area) from (August2021 till January2022).



Chart 25: Darbandikhan Dam area Chart 26: Tanjaro River area Chart 27: Sirwan River Area Chart 25-27: Mg in mg L⁻¹ in (Darbandikhan, Tanjaro River area, Sirwan River area) from (August2021 till January2022).



Chart 28: Darbandikhan Dam area Chart 29: Tanjaro River area Chart 30: Sirwan River Area





Chart 31: Darbandikhan Dam area

Chart 32: Tanjaro River area

Chart 33: Sirwan River Area

Chart 31-33: Na in mg L⁻¹ in (Darbandikhan, Tanjaro River area, Sirwan River area) from (August2021 till January2022)

4. Discussion

[31] found the low values were found during spring, autumn, and early stage of summer, which may be due to effect of dilution factor. Whereas, the values of TDS increase in August month because the high temperature evaporates the river water therefore, the TDS value will be high and this agree with results of present study. In comparison with standards (WHO, 2004) the maximum level of total hardness was slightly favorable limit and the mean value of total hardness was found within permissible limit, which was 500 mg L^{-1} , and according to that the studied area water regarded as hard water. The concentration of nitrate increases during this study because of the agricultural wastewater flow to Ranya lakelet, nitrogen presence in this waste water and this may be the reasons of the results of water parameters of the recent study. Nitrate is the most highly oxidized form of nitrogen compounds commonly found in waters, as it is the product of anaerobic decomposition of organic nitrogenous waste.

[32] suggest being of several sources of pollution in the Tanjaro River. Much of the sewage comes from the Sulaymaniyah City center. This includes: raw influent (sewage), which comes from household waste liquid such as toilets, baths, showers, kitchens, disposed via sewers, sinks, etc. and municipal wastewater, which originates as residential, commercial, and industrial liquid waste and includes storm water runoff. In addition, the Tanjaro River was polluted from sewage sources (Nature Iraq, 2008) originating from Oalawa, Oiliasan, Wluba, Bakrajo, Kani Goma, Shekh Abbas, Tanjaro villages, and both legal and illegal factories located on the Tanjaro River. Other potential sources of contamination are runoff from excess irrigation on fields that have applied with pesticides and fertilizers and leachate from the Tanjaro landfill and all these may be a reason of the polluted with the studied

heavy metals in the recent study. They are all together discharged through sewer pipelines and they combine with rain water to dispose away to Tanjaro River. Sewage systems for Sulaimani city are not capable of handling storm water. Heavy storms contribute more flows causing over flows, finally forming of seasonal pollution as seen in the results of the recent study in increasing the heavy metals concentrations in summer and autumn, and according to WHO (2006), cadmium is released to environment in wastewater and diffuse pollution is caused the bv contamination from fertilizers and local air pollution.

Iran has recently started a well-planned project, called Tropical Water Project (TWP), to build more dams, tunnels, and canals on the main tributaries of the Diyala River (Sirwan and Zmkan) to irrigate agricultural areas inside and outside the Divala River basin. One task in the TWP project is diverting a large volume of the water flowing through the Sirwan and Zmkan rivers through a series of tunnels. From the results, it was found that the TWP project consists of 14 dams constructed on Sirwan and Zmkan rivers and their tributaries with a total storage capacity of 1.9 Milliard cubic meters and of about 150 km long tunnels to divert more than one Milliard m3 of water to another basin. In addition, it has been found that after the full operation of the TWP project, the catchment area of Darbandikhan dam will lose 77% of its original one [33] and these clearly seen in the results of the recent study in which the high concentrations of the different studied heavy metals and the differences in the some of the water quality parameters due to the decreased in water levels.

Metals with a density of over 5 g cm⁻³ are considered heavy metals. Some metals are crucial to live cells as micronutrients (Fe, Mo, Mn). Even some substances that are beneficial to live cells can be harmful in excess of minuscule amounts (Zn, Ni, Cu and Cr) [34]. Some metals are poisonous to living organisms and serve no purpose as nutrition such as As, Hg, Ag, Sb, Cd, Pb [35]. Water samples in different locations had varying concentrations of the heavy metals. thus, water quality monitoring is crucial specially for the lakes that are impacted by pollutants cities, atmospheric discharged from precipitation, and industrial residential sewage, which represent the main source for water contamination [36].

According to [37] One of the five main categories of harmful pollutants that are frequently found in surface waters is heavy metal pollution; at certain concentrations, it may be toxic to aquatic life. heavy metal concentrations in the environment are a major cause for concern because of their detrimental impact on animal and human health across the food chain [38]. chemicals become more soluble at higher temperatures, the concentrations were at their maximum during the hot and warm seasons [39] Iraq's point sources of pollution take many different forms, including home waste and industrial effluents [40]. The hazardous metal cadmium coexists with zinc in nature and is found naturally in fish and water.

The study of [31] results showed that the mean concentrations heavy metals (Cd, Zn, Ni, Cr, Cu and Pb) were below detection limit (1µg L⁻¹) except Zn, which it was 8.18 µg L⁻¹ in filtered water in Ranya Lakelet in Sulaimani Governorate. The study of [41] on Euphrates River recorded that the dissolved Zn concentration values ranged from 26 to 55.6 g L⁻¹. Zinc metal concentrations also

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demonstrated a general decline as a result of runoff's dilution effect as well as the river's plants and sediments absorbing it [42].

Ni concentration in water that was below the detection threshold based on three measurements is probably unhealthy for the environment. The same is true for other fundamental components. Ni is similarly poisonous to fish when present in sufficient amounts [43]. [25]. found that Heavy metals such as (Cd, Cr, Cu, Ni, Pb, and Zn) in the Euphrates River were within the WHOreported acceptable range of values, but they were more than that recorded by [44] in Al-Hilla River.[45] studied the average of Cd, Cu, Mn, Ni, Zn, and Fe values were found to be high in spring and summer when heavy metal concentrations in water, sediment, and fish were measured at specific sites along the Turkey bank of the Tigris River and this agree with the recent results in increasing heavy metals levels in summer. The findings indicated that Cu levels have gradually dropped over the past few years, and that the benthic biota, particularly fish, form in a sequence with Cu, Fe, Mn, and Zn. [46] Cu, Cd, Zn, Pb, and Cr enrichment values in the sediments of the inner Izmir Bay were found to be particularly less than 5 while Zn, Pb, and Cr were significantly enriched in the study area.

5. Conclusions: According to the obtained results the water quality parameters were within the normal ranges according to the IQS (2009) guideline value [47] guideline value. Most of the heavy metals were in high ranges in August and September.

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