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RESEARCH PAPER

Assessment of Some Physico-Chemical Parameters and Heavy Metals in The Greater Zab River Path from Bekhma to Al Guwayr District in Erbil Province-KRI.

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A B S T R A C T:
Fifteen physico-chemical parameters with heavy metals were evaluated from the Greater Zab River path within Erbil province in twelve sites over a period of 10 months (from April 2021 to January 2022). In the field, Air and water temperature measured by thermometer, Electrical conductivity, total dissolved solids, potential of hydrogen measured by portable EC and pH meter, While, the laboratory measurement included total hardness, calcium ion, magnesium ion, total alkalinity, chloride measured by titration method, nitrate, nitrite, phosphorus and sulfate measured by spectrophotometric method. Water Quality calculated by using Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI). Heavy metals were analyzed by (AAS Perkins Elmer USA 1100D). The results of the present study shows that electrical conductivity, total alkalinity and phosphorus mean values were higher than the limits of WHO standards, While all remaining mean parameters were found in agreement for drinking purposes for WHO standards. The studied sites were classified under the hard waters. CCME WQI status for all sites located under the category of "Fair" (65-79) except for site 12 was located under the category of "Marginal" (45-64) water quality. The decreasing trend of heavy metals were observed in the water as Si > Fe > Cr > Zn > Mn > Pb > Ni > Co > Cu > Cd.

KEY WORDS: Physico-chemical; Heavy metals; Rivers; Springs; Ponds; Erbil.
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1.INTRODUCTION:

Aquifer acting important roles in the maintain the physical, chemical and biological properties of ground water and surface water (lakes, ponds, spring outflow and streams) (Plants, 2007). Compared to groundwater, surface water is more accessible to humans and more exposed to environmental variables, making it more prone to contamination. According to the distribution of water on Earth, only around 3% of it is fresh, and of that, only 0.8% is reachable or usable, with the remainder frozen in the polar ice caps (Owusu-Boateng et al., 2022). Nearly 80% of the world's population relies on groundwater as a supply of drinking water, making it the most dependable source of freshwater or/and surface water (Hanrahan, 2012). Water's physical and chemical properties have a significant role in the distribution and production aquatic life since they can directly or indirectly impact the water's quality (Moses, 1983). Water contaminants are largely such as geological conditions, industrial, and agricultural activity (Nollet and De Gelder, 2000). The pollution of potentially hazardous substances divided in to two categories anthropogenic (mine, agricultural, and industrial) and natural (bedrock weathering and erosion) activities (Antoniadis et al., 2017). Water quality is a water body's chemical,

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physical, and biological characteristics based on its intended use (Abdul Hameed M Jawad et al., 2010). One of the most enduring contaminants in water is heavy metals, which are defined as elements with an atomic density more than 6 $g.cm^{-3}$. They are slow to breakdown, unlike other contaminants, and can build up throughout the food chain, potentially endangering human health and causing ecological disruption. Copper, cadmium, lead, chromium, nickel, and zinc are some of the typical heavy metals that have been found in contaminated water (Akpor and Muchie, 2010). Iron (Fe), zinc (Zn), copper (Cu), and manganese (Mn) are necessary for basic bodily activities and are important elements. However, if it is used in excess or exceeds their threshold limitations, it is harmful to health (Ullah et al., 2017). However, some heavy metals, such as cadmium (Cd), chromium (Cr) and lead (Pb) can be hazardous to living things (Kurnaz et al., 2016). There were many studies on Greater Zab River on physical and chemical water properties lead by (Al-Nimma, 1982, Shekha, 2016) . The aim of this study is determining the evaluation of the physico-chemical characteristics of the water in springs, ponds, and rivers. as well as degree of heavy metal content in water from Bekhma village to Al Guwayr district.

2. MATERIAL AND METHODS

2.1. Description of the study area

The present study was carried out in Erbil governorate which is locates between the latitude of 35^{o} 40' and 30^{o} 30' N, and longitude 43^{o} 20' and 44^{o} 20' E. Greater Zab River situated between 36o-37o north latitudes and 43^{o}-44^{o} east longitude (Hassan, 1998). Greater Zab River locates about 35 km southwest of Erbil city. Generally, Erbil city climate is similar to other parts of Iraq. The climate is semi-arid and classified as continental subtropical, with large seasonal and yearly temperature variations. The climate is thought to closely resemble that of Irano-Turanian type and is distinguished by a mild spring growing season and a scorching summer (Zohary, 1950). Twelve sites (rivers, springs and ponds) a long Greater Zab River path were selected to some physico-chemical parameters and heavy metal study from Bekhma to Al Guwayr district in Erbil province (Table 1). All the studied sites are about 95 km long (Figure 1).

Table 1. Locations of sampling sites within studied areas.

Sites	Places	Habitat type	X - Field	Y - Field
1	Ruwandiz	River	436082	4063343
2	Ble-Barzan	River	435941	4063509
3	Behkma	River	434498	4060141
4	Gomi Gali	Pond	434390	4060135
5	Chami Raza	Spring	431080	4057123
6	Qandil	Spring	428770	4054650
7	Prdisarkawr	Spring	425862	4052589
8	Ifraz	River	386628	4020974
9	Aski Kalak	Pond	378459	4016213
10	Aski Kalak	River	377990	4014307
11	Al Guwayr	Pond	369444	3999202
12	Al Guwayr	River	368132	4000218

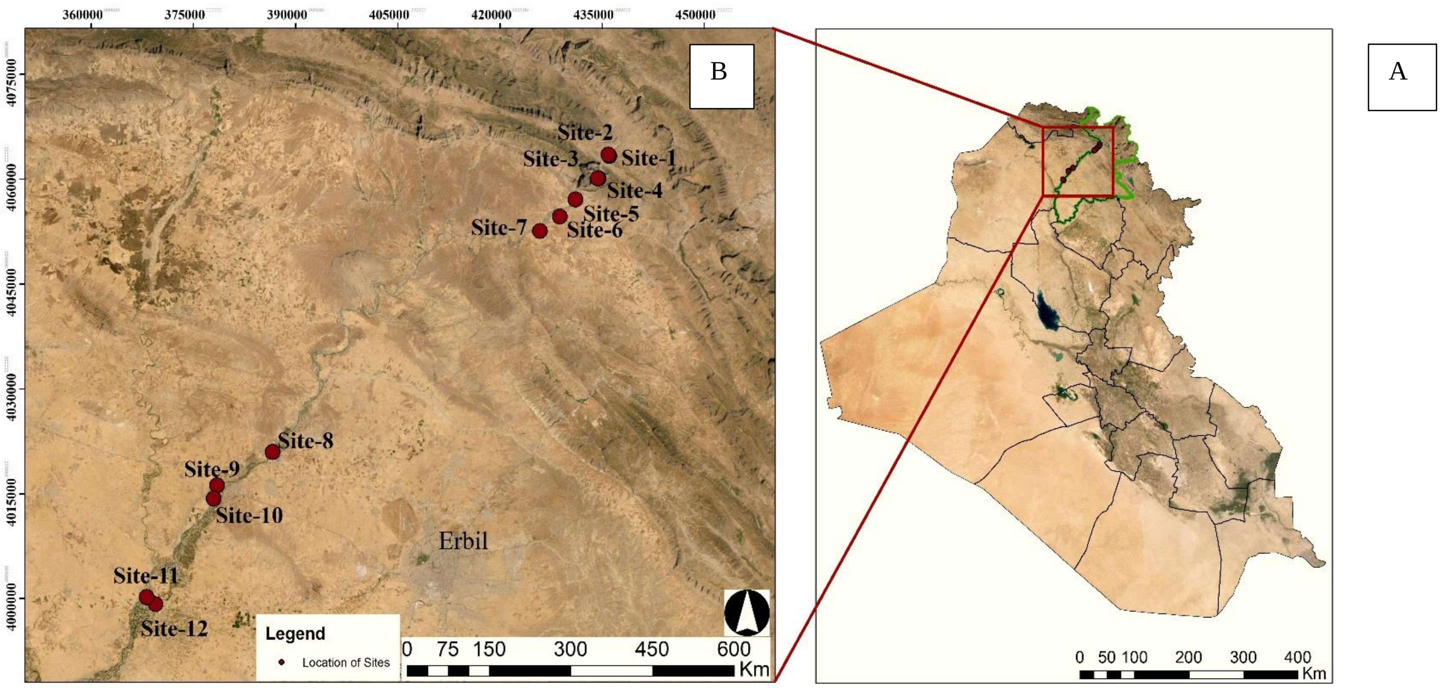

Figure 1. A- Map of Iraq and Erbil province B- Map of studied area and the sampling sites

2.2. Methods of sampling and analysis

Water samples were collected at 12 sites in Greater Zab River path for 10 months from April 2021 to January 2022. Use a pre-washed polyethylene bucket for physical, chemical, and analysis purposes. The bucket was rinsed twice with a water sample before being filled. A precise glass mercury thermometer (0-100 °C) was used in the field to measure the Air and water temperatures. Electrical conductivity was measured in the field by (HANNA instruments, HI98303). Total Dissolved Solids was calculated by using the formula below: TDS=Ke x EC (Ke is correlation factor =0.64). Using a portable pH meter (JENWAY 3505) to measure potential of hydrogen. Total hardness, calcium ion concentration, magnesium Ion concentration, total acidity and total alkalinity were measured by titrimetric method. Chloride was determined by Argentometric (colorimetric) method. Each parameter of nitrate, nitrite, reactive phosphorus was measured by spectrophotometric method. Turbidimetric method used to determine the sulfate ions. The Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI) was used for estimate water quality of studied sites within Greater Zab River Path. The CWQI equation is calculated using three factors (Cash and Wright, 2001).

$$\mathrm{CCMEWQI} = 100 - \frac{\sqrt{F1^{2} + F2^{2} + F3^{2}}}{1.732}$$

F1 represents Scope: The percentage of parameters that exceed the guideline

F1 = (Number of failed variables) / (Total number of variables) × 100

F2 represents Frequency: The percentage of individual tests within each parameter that exceeded the guideline

F2 = (Number of failed tests)/(Total number of tests) × 100

F3 represents Amplitude: The extent (excursion) to which the failed test exceeds the guideline. This is calculated in three stages. First, the excursion is calculated

excursion = failed test value/Objective - 1

Second, the normalized sum of excursions (nse) is calculated as follows:

nse = "∑ excursion" /Total number of tests

F3 is then calculated using a formula that scales the nse to range between 1 and 100:

F3 = "nse" /(0.01 "nse " +0.01)

The index equation generates a number between 1 and 100, with 1 is the poorest and 100 indicating the best water quality. Within this range, designations have been set and classify water quality as poor, marginal, fair, good or excellent (Table 5).

Water samples for heavy metals were taken in summer and winter during studied period. First, acid digestion was done by HNO_3. Then samples were analysis by (AAS Perkins Elmer USA 1100D) (Rice et al., 2012).

Table 2. Heavy metal standard solution with company.

Elements	Concentration (mg. L^{-1})	Name of company
Fe	1000	CARLO ERBA – EU
Ni	1000	CARLO ERBA – EU
Co	1000	Merck company- Germany
Cr	1000	CARLO ERBA – EU
Pb	1000	Merck company- Germany
Cd	1000	Merck company- Germany
Cu	1000	CARLO ERBA – EU
Zn	1000	CARLO ERBA – EU
Mn	1000	Merck company- Germany
Si	1000	Merck company- Germany

2.3 Statistical analysis

Using a software program Statistical Product and Service Solutions (SPSS Statistics for Windows). Version 24. Released 2016. One-Way ANOVA was used for multiple comparison for means of parameters by (Tukey test) between sites to know significant or not. Pearson correlations was adopted to analyses the relationship between physic-chemical characteristics of the Greater Zab River path. P< 0.05 was used as the significant level.

3. RESULTS AND DISCUSSION

3.1. Physico-chemical parameters

Air temperature is a standard physical characteristic which is important directly or indirectly for concentration determination of same chemical properties of water (Shaw, 1998). Air temperature fluctuated between a minimum mean value of 23.4 °C was noted at site 2, and the highest mean value was 31.3 ºC recorded at site 12, with significant differences between studied sites (P<0.05). As affected by geographical, topographical, altitude and climate of Iraq and Kurdistan temperature was highly varied between summer and winter (Abed et al., 2014). The results of this investigation was come in accordance with (Bilbas, 2014).

Water temperature either directly or indirectly affects numerous biotic and abiotic elements of an aquatic ecosystem (Singh, 2014). Water temperature data revealed the minimum mean value of temperatures was 17.3 ºC in site 1, while the maximum mean value of 21.0 ºC was recorded at site 11 and 12. A statistical analysis determined that there were insignificant differences (P<0.05) between studied sites. Throughout the study period, it was evident that air temperature may have an impact on monthly variations in water temperature. This phenomenon was also seen in other water systems in the Kurdistan region of Iraq (Aziz, 1997). The similar results were obtained by (Aziz, 1997 and Bilbas, 2004).

Electrical conductivity mean value of the present study was ranged from 408.6 to 776.0 µs.

cm^{-1}. The highest mean value was recorded at site 12 and the lowest mean value was at site 2. The result of EC was high due to high precipitation and soil leaching processes or effluent loaded by salts and dissolved material during rainy season causes increase in EC value the same comments were made by (Jacoby and Welch, 2004). Conductive ions are produced by inorganic substances including alkalis, chlorides, sulfides, and carbonate complex as well as dissolved salts (Al-Ani et al., 2019). The electrical conductivity of water samples revealed a wide range of variations with significant differences ($P<0.05$) between studied sites. Correlation analysis shows that EC has a positive correlation with water temperature, TDS and SO_4 but there was negative correlation with NO_2 and PO_4 (Table 4). The maximum acceptable level standard of conductivity is 1500 $\mu s.cm^{-1}$ (WHO, 2004) and accordingly all results in studied sampling sites were in permissible range of WHO standards. Result came in agreement with work done by (Aziz and Abdulwahed, 2012).

Total dissolved solids are a measurement of the amount of dissolved minerals in a sample of water. It is made up primarily of inorganic salts (such as calcium, magnesium, potassium, bicarbonates, chlorides, and sulfates) and very minute amounts of organic matter, according to the WHO standard for drinking water permissible level of TDS is 500-1500 mg. L^{-1} (WHO, 2004). Total dissolved solids were revealed to follow the similar trend as the EC, with mean values in the current study ranging from 261.50 to 496.64 mg. L^{-1}, where site 2 provided the lowest value and site 12 provided the highest. The statistical analysis revealed distinct patterns ($P<0.05$) between the investigated sites. The highly positive correlation between TDS and EC were noticed (Table 4). The variation of TDS levels among sites were found in the trend of the EC, increasing and decreasing TDS values possibly related to the differences in climatic conditions, rock weathering, lithology and geological formations within catchments basin (Goldman and Horne, 1983). Total dissolved solids (TDS) indicate that the concentrations of dissolved ions in water (Alhadithi, 2018). The recorded mean value of TDS was within the limits of WHO standards (Table 4). This result higher than results of (Aziz, 2008).

The pH of water is referring to the measure of hydrogen ions concentration in water. The pH showed the lower mean value of 7.428 was observed at site 4, while the highest mean value of 7.822 was noted at site 8, it was slightly alkaline side to ward neutrality for most studied site. Statistical analysis of pH concentrations showed a significant difference ($P<0.05$) for studied sites. It was negatively correlated with water temperature (Table 4). All of the examined water samples contain concentrations that are within the permissible range set by the WHO of 6.5 to 8.5 for drinking water. Low levels of carbon dioxide may be caused by an increase in the rate of decomposition of the organic waste deposited during the summer, which speeds up the production of carbonic acid and the release of more free carbon dioxide as a result of microbial respiration at hot temperatures (Hussain et al., 2021). Due to the region's geological formation, the pH of the water in the Kurdistan Region of Iraq fluctuates toward the alkaline side of neutrality (Guest and Townsend, 1966), and because of the land development of the territory, which is mostly made from calcium and magnesium carbonate (Al-Naqishbandi, 2002). The mean value of pH was within the limits of WHO standards (Table 5) Also the result agrees with results of pH values reviewed by (Aziz and Samiaa, 2012).

Total hardness is the ability of water to precipitate soap (Lind, 1974). Total hardness content reached its minimum mean value 165.6 mg $CaCO_3$. L^{-1} and its maximum mean value was 285.4 mg $CaCO_3$. L^{-1}, it was classified under hard water (150-300) according to type of hard water (WHO, 2004). Total hardness results indicated a significant difference ($P<0.05$) between studied sites. The current study found that there was significant degree of positive correlation between total hardness and pH, EC, TDS, SO_4^{-2} and PO_4^{-3} (Table 4). Although higher values encountered, in general, in winter season is related to runoff and leaching of surrounding cations (Goran, 2014). In general, sedimentary rocks, the most prevalent of which are limestone and chalk, are the source of the hardness brought on by the presence of calcium and magnesium (WHO, 2004). The presence of calcium and magnesium along with carbonate, bicarbonate, sulfate and chloride causes the hardness in water (Bashkin, 2003). The mean value of TH was within the limits of WHO standards (Table 5). The result is lower than result recorded by (Goran, 2010).

Calcium ion is one of the major inorganic substances present in nearly all water systems attributable to its easy solubility from all rocks especially in areas with limestone, dolomite and gypsum (Bartram and Ballance, 1996). Magnesium is a necessary element for plants as it is an important component in chlorophyll molecules which is needed in the process of photosynthesis (Rice et al., 2012). Calcium mean values 20-63 mg Ca^{+2}. L^{-1} was much higher than magnesium mean values 10.86-25.11 mg Mg^{+2}.$^{L-1}$. According to (WHO, 2004) guidelines, the acceptable concentrations of calcium and magnesium ranged from 75 to 200 mg. L^{-1} and 30 to 150 mg. L^{-1}, all studied sites occurred below these limits. Significant difference of calcium and magnesium were obvious in all studied sites ($P<0.05$). Calcium and magnesium was positively correlated to pH, EC and TDS (Table 4). Variation in calcium concentrations in the studied sampling sites because of the addition of surface runoff from agricultural and other catchment regions, the region's geology, variations in the climate and seasons, diverse biogeochemical activities in the water environment, and human activities and water demands, among other factors (Kumar et al., 2006). Calcium ion is one of the major inorganic substances present in nearly all water systems attributable to its easy solubility from all rocks especially in areas with limestone, dolomite and gypsum (Bartram and Ballance, 1996). Magnesium is a necessary element for plants as it is an important component in chlorophyll molecules which is needed in the process of photosynthesis (Rice et al., 2012). The mean value of Ca^{+2} and Mg^{+2} were within the limits of WHO standards (Table 5). The results of the present study are in agreement with those of (Aziz, 2008).

Water acidity is the expression of the concentration of hydrogen ions that determine the quantitative capacity of water to neutralize bases (Rice et al., 2012). The lowest mean value of total acidity was 4.1 mg $CaCO_3$ L^{-1} site 6 and 7, and a maximum mean value was 23.0 mg $CaCO_3$ L^{-1} site 12. Total acidity values showed a significant difference ($P<0.05$) between the studied sites. In addition, total acidity was found to be positively correlated with water temperature (Table 4). Ingeneral the main factor for water acidity is the presence of dissolved carbon dioxide from atmosphere and strong mineral acids (Sawyer et al., 2003). Total acidity was increased in the hot season and decreased during winter perhaps related to the nature of the geological formation of the drainage basin and total degree to which they are weathered (Muhammad, 2004). The mean value of total acidity was within the limits of WHO standards (Table 5).

Alkalinity is referred to the buffering capacity of water to resist changes in pH and total alkalinity is a measure of the amount of strong acid needed to neutralize alkalinity (Bartram and Ballance, 1996). The mean values of total alkalinity fluctuated between 193 mg $CaCO_3$ L^{-1} at site 2 and 239 mg $CaCO_3$ L^{-1} at site 5. Total alkalinity values revealed an insignificant difference ($P<0.05$) between studied sites. Alkalinity has a positive correlation with pH, EC and TDS (Table 4). Total alkalinity is mainly produced by carbonate (CO3=), bicarbonate (HCO_3) and hydroxyl (OH-) anions (Boyd and Tucker, 1998). Higher values of alkalinity were measured during rainy months (Starks and Champion, 2001). When rainfall as it moves through the soil layers, reacting with carbon dioxide to create carbonic acid and limestone to create dissolved calcium and bicarbonate (HCO_3) (Al-Barzingy et al., 2009). The mean value of total alkalinity was higher than the limits of WHO standards (Table 5). The results of this study were in disagreement with those of (Goran, 2010).

The chloride ion is an important component of both surface waters and groundwater (Mullaney et al., 2009). The lowest mean value of chloride 7 mg. L^{-1} was recorded at site 7 and the highest mean value of 55 mg. L^{-1} was detected at site 11. The chloride value for studied sites showed seasonal variations with significant differences ($P<0.05$) between studied sites. Chloride was found to be positively correlated with water temperature, but negatively with pH (Table 4). A rapid rate of evaporation followed by rising air and water temperatures may be the source of the relative increase in chloride concentrations during the hot weather (Mohamed, 2005). The concentration declined which might be due to the rainfall which lead to water dilution (Birkle and Alvarado, 2010). The standards of chloride in both ground and drinking water should not exceed 250 mg. L^{-1} (WHO, 2004). Mean value of Cl^- was within the limits of WHO standards (Table 5). The result of chloride in this study disagree with the results of (Aziz, 2008 and Goran, 2010).

3.2. Nutrients

The most stable and oxidized form of nitrogen in a body of water is measured by nitrate. It is the main form of nitrogen used by plants and algae as a nutrient to promote growth, and it is produced by the full oxidation of nitrogen molecules (Langmuir, 1997). Nitrate mean concentration levels over the time of this study varied between 6.62 and 13.53 mg. L^{-1} in Site 3 and Site 9, respectively. There was a fluctuation between studied sites ($P<0.05$). Correlation analysis showed that nitrate has a negative correlation temperature (Table 4). The relative increasing of nitrate in winter may be related to the rainfall (Al-Nimma, 1982) and direct effect of the agriculture runoff (Fathi and Al-Kahtani, 2009). The acceptable concentration of nitrate is 50 mg. L^{-1} (WHO, 2008). Mean value of NO_3^- was within the permissible level of WHO standards (Table 5). The results of the present study were higher than those observed by (Goran, 2010 and Al-Naqishbandi, 2002).

The minimum nitrite mean value for the present study was 0.014 in site 3, while the highest value was 0.134 mg. L^{-1} in site 11, with significant differences ($P<0.05$) between studied sites. Correlation analysis showed that nitrite has a negative correlation with water temperature (Table 4). High concentration of nitrite in January may be attributed to secretions of phytoplankton, but decrease in the nitrite contents during summer, autumn and spring periods, this is may be due to the reduction into ammonia during those periods. Additionally, they are absorbed by the water's phytoplankton (Hutchinson, 1967). In most cases, bacteria's oxidation of ammonia in water results in the formation of nitrite, which are easily converted to nitrates (Verma and Saksena, 2010). Mean value of NO_2^- was within the limits of Iraqi and WHO standards (Table 5).

Reactive phosphorus is a measurement of soluble phosphorus in its inorganic oxidized state (Langmuir, 1997). The minimum mean value of phosphate was 0.62 determined at site 9, while the maximum result was 3.53 mg. L^{-1} recorded at site 12. Statistical analysis reveal significant differences ($P<0.05$) between the studied sites. Phosphate has a positive correlation with pH but negatively with water temperature, EC and TDS (Table 4). Decreasing of PO_4^{-3} in spring could be attributed to the vigorous uptake by the plankton (Fathi and Al-Kahtani, 2009). Phosphorus in surface water mostly comes from runoff of soil particles since it is a byproduct of the aerobic breakdown of organic nitrogenous materials. Due to the geochemical scarcity of phosphorus in many drainage basins, phosphorus is one of the common elements that restrict phytoplankton growth (Goldman and Horne, 1983). Mean value of PO_4^{-3} was higher than the limits of WHO standards (Table 5).

Inland waters in the Iraqi Kurdistan Region typically include considerable amounts of sulfate (Al-Naqishbandi et al., 2008). Sulfate minimum mean concentration was 136.3 mg. L^{-1}. In contrast, the highest mean value observed at site 5 was 228.2 mg. L^{-1}. There were significant variations ($P<0.05$) among the research sites. Correlation analysis shows that sulfate has a positive correlation with EC and TDS (Table 4). Because of the high evaporation rate during the summer months, there may be a relative increase in sulfate concentrations (Mohamed, 2005). SO_4^{-2} mean value was within the permissible level of WHO standards (Table 5). Results of the present study are lower than the results of (Al-Naqishbandi, 2002).

Table 3. Mean ± SE for parameters at selected sampling sites with minimum and maximum value.

Parameters \ Sites	S1	S2	S3	S4	S5	S6
Air temp.	23.3±0.57	23.4±1.12	24.3±0.75	24.2±0.58	25.6±0.94	25.9±0.92
Water temp.	17.3±0.57	18.1±0.86	19.0±1.21	20.1±0.11	19.5±0.18	19.4±0.15
EC	416.1±14.82	408.6±16.40	416.7±16.55	517.2±14.19	531.0±10.59	691.5±18.63
TDS	266.30±9.49	261.50±10.50	266.69±10.59	331.01±9.08	339.84±6.77	442.56±11.92
pH	7.752±0.08	7.768±0.08	7.752±0.08	7.428±0.02	7.563±0.04	7.487±0.07
T. hardness	208.2±12.80	194.5±14.11	203.3±12.76	165.6±9.83	265.5±6.32	263.4±7.38
Ca^{+2}	35±1.26	34±1.04	33±1.07	20±1.10	47±3.48	55±3.67
Mg^{+2}	16.46±0.57	16.80±1.12	17.64±0.75	10.86±0.58	21.94±0.94	19.13±0.92
T. acidity	19.5±0.90	18.2±1.01	17.9±1.30	6.8±0.36	9.2±0.57	4.1±0.27
T.alkalinity	194±5.48	193±5.54	197±5.77	225±13.35	239±14.30	235±15.20
Cl^{-}	27±1.60	30±2.41	29±2.36	21±1.23	8±0.96	8±1.24
NO_3^{-}	7.03±0.73	7.03±0.50	6.62±0.65	7.22±0.70	8.80±0.66	8.73±0.62
NO_2^{-}	0.131±0.005	0.128±0.005	0.134±0.005	0.025±0.002	0.057±0.003	0.036±0.003
PO_4^{-3}	2.42±0.06	2.56±0.09	2.59±0.08	1.27±0.02	1.03±0.08	1.05±0.11
SO_4^{-2}	172.6±5.08	137.9±3.27	155.7±4.89	136.3±4.96	228.2±7.81	178.5±4.59

Table 3. Continued

Parameters \ Sites	S7	S8	S9	S10	S11	S12
Air temp.	26.1±1.17	27.4±0.82	28.6±0.57	28.8±1.09	30.9±0.56	31.3±0.89
Water temp.	20.1±0.24	19.7±1.20	19.8±0.22	20.1±1.22	21.0±1.51	21.0±1.33
EC	609.5±27.06	416.8±21.12	589.7±15.85	409.3±20.10	636.3±19.03	776.0±29.40
TDS	390.08±17.32	275.06±11.92	377.41±10.14	261.95±12.87	407.23±12.18	496.64±18.82
pH	7.531±0.07	7.822±0.07	7.618±0.05	7.812±0.09	7.637±0.10	7.796±0.09
T.hardness	258.9±6.50	202.8±13.14	193.7±16.10	205.9±13.79	196.5±14.36	285.4±11.59
Ca^{+2}	58±3.83	36±1.22	45±3.58	40±1.30	63±2.75	59±3.81
Mg^{+2}	18.19±1.17	16.21±0.82	20.44±0.57	16.76±1.09	25.11±0.56	21.46±0.89
T. acidity	4.1±0.35	20.6±1.05	8.6±0.54	22.6±0.73	8.6±0.83	23.0±1.35
T.alkalinity	231±14.69	200±7.15	218±13.66	201±5.33	208±18.26	210±6.50
Cl^{-}	7±0.87	30±2.28	35±2.56	29±2.64	55±5.01	47±3.05
NO_3^{-}	9.47±0.83	7.36±0.64	13.53±1.40	7.07±0.64	12.70±1.37	7.53±0.57
NO_2^{-}	0.066±0.026	0.126±0.003	0.018±0.001	0.128±0.005	0.014±0.002	0.127±0.006
PO_4^{-3}	1.04±0.11	2.57±0.06	0.62±0.03	3.48±0.16	0.64±0.06	3.54±0.14
SO_4^{-2}	143.6±3.79	164.4±5.60	156.2±4.49	161.2±6.28	178.9±5.05	207.0±13.52

Table 4. The correlation between the various physico-chemical properties of water during the study period.

Parameters	Water Temp.	pH	EC	TDS	SO_4^{-2}	PO_4^{-3}
Water Temp.	1					
pH	-0.645	1				
EC	0.178	-0.068	1			
TDS	0.172	-0.069	1	1		
SO_4^{-2}	0.388	-0.203	0.333	0.334	1	
PO_4^{-3}	-0.083	0.472	-0.243	-0.242	0.027	1
NO_2^-	-0.198	0.45	-0.413	-0.411	-0.039	0.804
NO_3^-	-0.226	0.262	0.375	0.366	-0.132	-0.379
T. hard	-0.417	0.464	0.490	0.487	0.149	0.098
Ca^{+2}	-0.101	0.297	0.621	0.625	0.177	-0.187
Mg^{+2}	-0.198	0.364	0.374	0.367	0.228	-0.193
T. acidity	0.161	-0.255	-0.365	-0.360	0.181	0.849
T. alkalinity	-0.354	0.379	0.356	0.352	-0.212	-0.227
Cl^-	0.459	-0.062	0.095	0.098	0.177	0.221

Table 4. Continued

Parameters	NO_2	NO_3	T. hard	Ca^{+2}	Mg^{+2}	T. acidity	T. alkalinity	Cl^-
NO_2	1							
NO_3	-0.372	1						
T. hard	0.120	0.376	1					
Ca^{+2}	-0.203	0.579	0.679	1				
Mg^{+2}	-0.122	0.534	0.573	0.775	1			
T. acidity	0.728	-0.430	-0.220	-0.318	-0.231	1		
T. alkalinity	-0.290	0.715	0.535	0.549	0.342	-0.467	1	
Cl^-	0.058	-0.064	-0.451	-0.042	0.076	0.504	-0.366	1

Table 5. The concentration of water quality of studied areas with standards of Kurdistan, Iraq and WHO.

Parameters	Mean of studied sites	Kurdistan	Iraq	WHO
EC	534.892	400	600-1200	100-500
TDS	343.023	842	100-500	500-1500
pH	7.664	7.7	6.5-8.5	6.5-8.5
T.hardness	220.308	204	100-500	100-300
Ca^{+2} ions	43.750	51	50	75
Mg^{+2} ions	18.417	22	20	30
T.alkalinity	212.583	205	100-200	100-200
Cl^-	27.167	150	250	250
NO_3^-	8.591	44	50	50
NO_2^-	0.083	0.1	3	3
PO_4^{-3}	1.901	1.9	0.25	0.25
SO_4^{-2}	168.375	184	250	250

3.3. The Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI) for drinking purposes

From this study, (CCME WQI) values showed that the maximum level was 76.699 at site 9, while the minimum value was 61.863 at site 12 (Table 6). The results indicated that CCME WQI status for all sites located under the category of "Fair" (65-79) except site 12 was located under category of "Marginal" (within range 45-64) water quality (Table 7). The results were supported by (Aziz and Samiaa, 2012). Which were suitable after conventional treatment for a variety of uses.

Table 6. Calculation of (CCME WQI) for drinking purpose

Sites	WQI	Water Quality
Ruwandiz River	71.797	Fair
Ble-Barzan River	71.051	Fair
Behkma River	70.858	Fair
Gomi Gali pond	72.984	Fair
Chami Raza spring	74.245	Fair
Qandil spring	73.337	Fair
Prdisarkawr spring	73.860	Fair
Ifraz River	70.937	Fair
Aski Kalak pond	76.699	Fair
Aski Kalak River	66.776	Fair
Al Guwayr pond	76.444	Fair
Al Guwayr River	61.863	Marginal

Table 7. Designation and description of CCME- WQI according to (Cash and Wright, 2001).

Designation	Index value	Description
Excellent	95-100	All measurements are within objectives virtually all of the time
Good	80-94	Conditions rarely depart from natural or desirable levels
Fair	65-79	Conditions sometimes depart from natural or desirable levels
Marginal	45-64	Conditions often depart from natural or desirable levels
Poor	0-44	Conditions usually depart from natural or desirable levels

3.4. Heavy metals

Iron due to its abundance in the earth's crust, iron is a necessary and non-conservative trace element that is present in large quantities in drinking water (Oyeku and Eludoyin, 2010). Fe value was high during August 2021 specifically at site 10 (1.138 mg. L^{-1}) and lower during February 2022 particularly at site 5 (0.167 mg. L^{-1}). The result appeared that there were no significant differences among the studied sides ($p<0.05$). The present study showed that Iron has a positive correlation with other elements except for Ni (Table 10). The higher content during dry season (August) may be the result of high temperature due to evaporation in dry season (Rasheed, 2008). Anemia is a condition caused by a lack of iron, and haermosiderosis, a liver condition, may result from drinking water with a high iron content over an extended period of time (Rajappa et al., 2010). According to guidelines (WHO, 2011), the limit for iron is less than (0.3 mg. L^{-1}) in drinking water. Mean value of Fe for all sampling sites were higher than standard (Table 11). Results of the present study were higher than those observed by (Salah et al., 2015, Toma and Aziz, 2022) (0.340 and 0.660 mg. L^{-1}).

Nickel can be found naturally in rocks and soils. Natural processes such as weathering of rocks and soils as well as mineral leaching cause nickel to naturally enter water bodies (Gautam et al., 2014). Site 12 showed the highest concentration of Ni at summer (0.015 mg. L^{-1}) and the lowest concentration of Ni is at site 3 and site 4 at winter (0.006 mg. L^{-1}). The statistically there were significant differences between 12 with other studied sites ($p<0.05$). Ni has positive correlation with Co, Cr, Pb, Cd and Cu, but natively with Zn, Mn and Si (Table 10). Mean value of Ni was higher than standard (Table 11). The results of present study disagreed with results of (Salah et al., 2015, Toma and Aziz, 2022).

Cobalt is a substance that is extremely hazardous to the environment. The minimum level of cobalt level was recorded at site 4 and site 9 (0.003 mg. L^{-1}) in winter and the maximum value was recorded at site one (0.018 mg. L^{-1}) in summer. The result appeared that there were significant differences between site 7 with other studied sites ($p<0.05$). There was positive correlation between Co with all elements except Pb (Table 10). Numerous health issues, including paralysis, diarrhea, low blood pressure, lung irritation, and bone deformities, may be impacted by high cobalt levels (Manohar et al., 2006). The concentration of Co for all sampling sites is higher than drinking water recommendation (Table 11). The result was lower than result obtained by (Sultan et al., 2018).

Chromium is very dangerous to human life (Sultan et al., 2018). Cr concentration was between 0.004 mg. L^{-1} during August 2021 particularly at site 5 and 0.399 mg. L^{-1} during February 2022 at site 3, Chromium has a negative correlation with Pb and Mn and positively with Cd, Cu, Zn and Si (Table 10). The higher Cr content during the winter season may be the result of considerable rainfall which washed down wastes, a similar conclusion was drawn by (Obasohan et al., 2006). The natural sources of chromium are the geological weathering of rocks, soils, and sediments, whereas anthropogenic sources of chromium include the burning of fossil fuels, the production of chromates, the manufacture of plastics, the electroplating of metals, and extensive use in the leather and tannery industries (Gautam et al., 2014). The maximum amount of chromium that could be present in drinking water was 0.05 mg. L^{-1} as stated by (WHO, 2011). Mean value of Cr was higher than standard (Table 11). The concentration of Cr was observed to be higher than the result recorded by (Othman, 2020).

lead is a general toxin that accumulates in the skeleton and is damaging to both the central and peripheral nervous systems, it can have an adverse effect on the brain and behaviors (WHO, 2008). The highest concentration of Pb 0.027 mg. L^{-1} was recorded during August 2021 at site 10 and site 12, while the lowest value 0.003 mg. L^{-1} was recorded during February 2022 at site 4. Pb has significant positive correlation with Cd and Mn but negatively with Cu, Zn and Si (Table 10). The higher value in summer may be the outcome of a slow water that causes particles to settle. Additionally, as temperatures rise, water evaporates more quickly, increasing the concentration of trace metals in watery environments throughout the summer (Amteghy, 2014). Pb may come from commercial in agricultural fertilizers and residential effluents (Micó et al., 2006). Mean value of Pb was higher than WHO standard, but lower than Iraqi standards (Table 11). The similar results were recorded by (Salah et al., 2015, Toma and Aziz, 2022).

Cadmium is one of the most dangerous heavy metals (Cd), which is regarded as non-essential for living things (Bazrafshan et al., 2016). Cadmium results of this study showed that cadmium concentration was ranged from 0.003 to 0.006 mg. L^{-1} the highest value during February 2022, while the lowest value was recorded during August 2021. Cd has a negative correlation with Zn and Mn, but positively with Cu and Si (Table 10). Waste disposal and phosphate fertilizers are two ways that cadmium can enter the environment. Even at its low quantity in the food chain, cadmium is the most hazardous metal. Cadmium, in contrast to other heavy metals, is not necessary for biological processes (Gautam et al., 2014). Mean value of Cd was lower than standard (Table 11). The results of present study agreed with results of (Toma and Aziz, 2022).

Copper is a necessary trace element that biological systems need to activate some enzymes during photosynthesis, but at greater amounts, it has negative effects on the human body (Gautam et al., 2014). Site 1 displayed greater levels of copper in the surface water during the winter (0.016 mg. L^{-1}), may be a result of considerable rainfalls which washed down wastes in to the river similar conclusion was drawn by (Obasohan et al., 2006). When compared to other stations. Station 6 had the lowest concentration of copper at summer (0.001 mg. L^{-1}). The statistical analysis showed significant differences between site 7 with other studied sites ($p<0.05$). The result showed positive correlation between Cu and all other heavy metal except Pb (Table 10). Mean value of Cu was less than standard (Table 11). The results of the present study are higher than the results recorded by (Al-Alem et al., 2013).

Zinc is a vital trace element for healthy animal and human development, correct plant growth and reproduction, and many biological activities. (Cakmak, 2008). Results of the current study showed that the highest value of zinc was 0.189 mg. L^{-1} was recorded at site 12 during February 2022, while the lowest value 0.004 mg. L^{-1} was recorded at site 9 during summer 2021. Zn has negative correlation with Mn and Si (Table 10). Increase concentration of Zn during February 2022 may be ascribed to high rain and erosion during the rainfall season in the study area which gives rise to flow of the water in the river. Zn is also present in surface and groundwater, and it enters the environment through a variety of channels, such as mine drainage, municipal and industrial waste, urban runoff, and mostly through the erosion of Zn containing soil particles (Noulas et al., 2018). The result showed there were no significant differences between studied sides ($p<0.05$). Mean value of Zn was less than standard (Table 11). The results of the present study agreed with the results of (Balasim et al., 2013).

Manganese in drinking water may come from bedrock's natural sources and from external environmental contamination (Frisbie et al., 2012). The result was ranged between 0.003 and 0.037 mg. L^{-1}. Mn has positive correlation with Fe, Co, Pb, Cu and Si but negatively with Ni, Cr, Cd and Zn (Table 10). Numerous research has revealed a link between excessive manganese (Mn) in water and kids' neurodevelopment, behavior, and academic success (Khan et al., 2011, Oulhote et al., 2014). According to guidelines all studied sites was located under limited level (Table 11). Similar concentrations were observation was reported by (Salah et al., 2015, Toma and Aziz, 2022).

Silica is one among the earth's most significant elements and an essential element for all living organisms. It is the basic nutrient of plants and promotes toughness of roots, and is also important in the process of growth and plant resistance to disease (Putko and Kwaśny, 2019). The value was fluctuated between 1.607 and 5.895 mg. L^{-1}. Si has a positive correlation with Fe, Co, Cr, Cd, Cu and Mn and negatively with Ni, Pb and Zn (Table 10). The mean value of Si was lower than drinking water standard (Table 11).

Table 8. Heavy metal concentration (mg. L^{-1}) in freshwater during summer / August in studied sites.

Sites	Metals									
	Fe	Ni	Co	Cr	Pb	Cd	Cu	Zn	Mn	Si
S1	1.028	0.009	0.018	0.077	0.011	0.004	0.032	0.034	0.012	4.796
S2	1.211	0.011	0.008	0.123	0.011	0.005	0.002	0.031	0.012	4.774
S3	1.118	0.007	0.005	0.021	0.016	0.005	0.003	0.025	0.014	4.216
S4	0.782	0.007	0.007	0.021	0.012	0.004	0.002	0.038	0.004	3.427
S5	0.791	0.009	0.004	0.004	0.012	0.003	0.002	0.075	0.005	1.607
S6	0.713	0.009	0.004	0.004	0.016	0.004	0.002	0.008	0.004	4.204
S7	0.924	0.009	0.007	0.018	0.011	0.005	0.001	0.008	0.011	4.986
S8	0.960	0.007	0.007	0.107	0.011	0.003	0.001	0.014	0.008	4.156
S9	0.520	0.008	0.004	0.004	0.005	0.003	0.001	0.004	0.008	4.395
S10	1.138	0.008	0.005	0.004	0.027	0.003	0.003	0.009	0.037	4.028
S11	1.119	0.008	0.005	0.011	0.011	0.003	0.002	0.014	0.006	4.112
S12	0.772	0.015	0.005	0.008	0.027	0.004	0.002	0.009	0.004	3.5
Mean	0.923	0.009	0.007	0.034	0.014	0.004	0.004	0.022	0.01	4.017

Table 9. Heavy metal concentration (mg. L^{-1}) in freshwater during Winter / February in in 2021-2022.

Sites	Metals									
	Fe	Ni	Co	Cr	Pb	Cd	Cu	Zn	Mn	Si
S1	0.934	0.009	0.01	0.21	0.012	0.006	0.016	0.065	0.013	5.229
S2	0.87	0.007	0.004	0.189	0.012	0.004	0.006	0.062	0.048	5.024
S3	1.09	0.006	0.004	0.399	0.006	0.005	0.005	0.043	0.044	4.778
S4	0.572	0.006	0.003	0.112	0.003	0.003	0.013	0.045	0.028	4.764
S5	0.167	0.011	0.007	0.119	0.012	0.004	0.004	0.121	0.003	5.037
S6	0.586	0.008	0.004	0.112	0.006	0.004	0.002	0.019	0.003	4.849
S7	0.658	0.008	0.007	0.074	0.006	0.004	0.002	0.011	0.019	5.895
S8	0.833	0.008	0.004	0.137	0.006	0.006	0.002	0.042	0.014	5.005
S9	0.17	0.008	0.003	0.004	0.006	0.004	0.002	0.014	0.006	5.136
S10	0.934	0.012	0.005	0.011	0.012	0.005	0.003	0.014	0.023	4.226
S11	0.806	0.008	0.004	0.029	0.006	0.003	0.002	0.118	0.012	4.561
S12	0.49	0.011	0.004	0.021	0.006	0.003	0.002	0.189	0.014	4.3
Mean	0.676	0.009	0.005	0.118	0.008	0.004	0.005	0.062	0.019	4.9

Table 10. Correlation of heavy metals of studied sites in August (Summer) and January (Winter) in 2021-2022.

Elements	Fe	Ni	Co	Cr	Pb	Cd	Cu	Zn	Mn	Si
Fe	1									
Ni	-0.101	1								
Co	0.312	0.006	1							
Cr	0.476	0.010	0.555	1						
Pb	0.203	0.475	-0.208	-0.305	1					
Cd	0.296	0.236	0.231	0.250	0.005	1				
Cu	0.195	0.011	0.925	0.298	-0.102	0.073	1			
Zn	0.057	-0.086	0.166	0.104	-0.211	-0.039	0.195	1		
Mn	0.524	-0.200	0.060	-0.010	0.471	-0.074	0.094	-0.212	1	
Si	0.317	-0.071	0.404	0.393	-0.176	0.452	0.258	-0.699	0.238	1

Table 11. Heavy metal concentration(mg. L^{-1}) of studied areas with Iraq and WHO standards (WHO, 2011) (Standard, 2009).

Elements	Mean of studied sites	Iraq	WHO
Fe	0.799	0.3	0.3
Ni	0.009	0.07	0.02
Co	0.006	-	0.005
Cr	0.076	0.1	0.05
Pb	0.011	0.015	0.01
Cd	0.004	0.005	0.005
Cu	0.005	1.3	2.0
Zn	0.042	5.0	3.0
Mn	0.015	0.05	0.5
Si	4.459	-	25

4. CONCLUSION

According to the results of the physico-chemical parameters of the water. The quantity of several investigated physico-chemical factors, such as (EC, Total alkalinity and PO_4^{-3}) were above the permissible limit for drinking purpose standards WHO. The EC values was high (850 µS.cm^{-1}) in site 12 in compared to other studied sites. The pH value in all sites were constantly on alkaline site of neutrality. The calcium ion level dominates on magnesium ion level. According to CCME WQI, water quality in all studied sites within Greater Zab River path considered as a Marginal and Fair. The concentration of Fe, Co, Pb and Cr for all sampling sites was higher than drinking water recommended by WHO. Correlation studies between the variables of the physico-chemical parameters and heavy metals showed that there were significant differences between studied sites.

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Conflict of Interest

-Conflicts of Interest: None.

-We hereby emphasize that every Figures and Tables in the manuscript are mine.

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