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An evaluation of waste and well water quality for agriculture production around Erbil city, Iraq

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Abstract:

Erbil city is located in the northern Iraq with a population of over one million people. Due to water crises farmers usually use wastewater and well water for the agricultural production. In this study six stations were designed to sample waste water and three from well water to define waste water and ground water characteristics. In this study, Residual Na^+ Carbonate, Mg^{++} hazard, salinity hazard, Kelley index, %sodium, total hardness, permeability index, potential salinity, sodium adsorption ratio, and Irrigation Water Quality Index (IWQI) were determined. The order of average cation concentrations in water was $Mg^{2+} > Ca^{2+} > Na^+ > K^+$. While the proportion of main anions in water were $HCO_3 > SO_4 > Cl$. The highest concentrations of Ca^{2+}, Mg^{2+} and Na^+ were found in well water, while the highest concentration of K^+ was found in wastewater. The maximum concentration of HCO_3 and Cl recorded in well water, while the highest concentration SO_4 recorded in wastewater. Moreover, the order of trace elements was Pb > Al > Fe > Cd > As > Mn >Cr > Ag > Ni. Keeping in mind metal concentration set by US EPA and FAO (1999) and (1994) guidelines the levels of Pb, Al, Fe, Mn, Cr, Ag and Ni in the waste and well water were within the admissible limitations for irrigation schemes. Moreover, limitations of As and Cd were beyond permissible limitation need to be reduced. The IWQI ranged from 88.92 to 95.09 in the waste water samples. Overall assessment reveals that cultivated agriculture plants were secured from toxic compounds.

Keywords: Agriculture land, Irrigation wastewater and well water, Trace elements, Water quality indices.

Introduction:

Water elements are one of the virtually important factors due to the fact that they have a direct bearing on human health and other living things [1]. Excessive water usage, together with population and economic expansion, will reduce each person's water supply and threaten the global ecosystem's fauna [2]. Water quality assessment is a crucial tool for long-term success and provides valuable information for water executives. In a number of countries with severe or semi-hard climates, the quality of surface water is a sensitive and critical issue [3].Farmers are compelled to utilize wastewater for agriculture due to rising urbanization and a scarcity of freshwater globally, particularly in developing nations. It provides substantial advantages to farmers who lack access to treated wastewater [4].This farmland will treble due to population growth according to [5], Wastewaters ninety nine point ninety eight percent water, 0.02-0.03% hanging particles, and soluble biotic and abiotic components. Biotic and abiotic pollutants degrade water quality aquatic structure and abundance have improved [6, 7]. Erbil's sewer system handles storm and grey water. Cesspools and septic tanks treat toilet black water. Erbil City has neither integrated nor separated sewers. In newly built communities and villages in Erbil City, small-scale wastewater treatment plants are required under investment legislation to treat wastewater. Erbil wastewater is often utilized for irrigation directly and enters the Greater-Zab River near Gwer without treatment [8]. Researchers must analyze the fluctuation of trace elements and content in the pair surface water and groundwater to reduce pollution and improve water quality. Trace elements, unlike organic contaminants, are non-biodegradable and aggregate in living being's; in addition, many ions of trace metals are poisonous or carcinogenic [7, 9]. Heavy metal bioaccumulation in food chains and their toxicity as concentrations rise have hampered their separation and purification. Due to stricter regulations, toxic metals are a major ecological problem [10]. Furthermore, composition and amount of soluble salts used to test water quality (for human and livestock consumption, crop irrigation, and so on). Sodicity, salinity, and ion toxicity are key irrigation fluid factors. It's salty. Sodicity degrades soil structure. Toxicity is the concentration at which CO_3^{2-}, HCO^-_3, Cl^-, Na^+, Mg^{2+}, and other trace ions harm plant development [11]. Horton [12] was the first to propose employing the WQI, and since then several researches have been published for various aquatic systems [2], an irrigation water quality index (IWQI) is a single, unit less value obtained from a complex computational technique using numerous hydrochemical factors [13], as well as well-known indices like as potential salinity (PS), permeability index (PI), Kelley index (KI), etc. [14]. In this study a comparative analysis of waste and well water quality is provided to understand whether the use of both waters for agriculture is safe. In addition, vegetable qualitative analysis is given to determine if human consumption will have no health risk. In this study a comparative analysis of waste and well water quality is provided to understand whether the use of both waters for agriculture is safe. In addition, vegetable qualitative analysis is given to determine if human consumption will have no health risk.

Materials and Methods:

Erbil is the capitol of Iraq's Kurdistan region. The studied area is located southwest of Erbil city till Demhat region, between 36^o 16' 95'38" E to 36^o 10' 07'62" E and longitude 43^o 92' 97'34" N to 43^o 81'22'71" N, by using GPS (Garmin type), three sites (vegetable field) were selected along Erbil wastewater channel or irrigated with Erbil waste water with three sites (vegetable field) irrigated with well water the location of well waters near the Erbil wastewater channel in general all studied sites is located on Turaq region, Table. 1 and Fig. 1.

Table 1. Sampling locations and use of water for agriculture production.

Site No.	location	Longitude X(UTM)*	Latitude Y(UTM)	Z(altitude) m.a.s.I	Type of Irrigated water
1	Turaq 1	36.169538	43.929734	379	Waste water
2	Turaq 2	36.155158	43.917439	365	Well water
3	Jmka 1	36.126431	43.855755	323	Waste water
4	Jmka 2	36.129563	43.860852	327	Waste water
5	Daleguly khwarey	36.120052	43.855984	325	Well water
6	Dhemat	36.100762	43.812271	307	Well water

GPS*: Global positioning system, UTM*: Universal Transverse Mercator projective system, m.a.s.l: meter above sea level

Water samples were obtained over the summer, fall of 2020, and winter, spring of 2021, with each site's samples preserved in acid-washed plastic bottles for analysis after that, 0.45µ membrane filters were used to filter the samples. During the collection and handling of samples, all precautions were taken to avoid contamination.

Data collection in the field

Portable pH, EC and TDS meter with two different models (Hanna instruments, HI98107 and Hanna 9025), a glass sensor calibrated with buffer solutions of pH 4, 7 and 9 and for EC prepared standard solutions given by the same instrument company.

Laboratory analysis

Both CO_3 and HCO_3 were decisive by the titration method of [15]. Flame photometry was used to determine the concentrations of cations (Na+ and K+) using a model PFH 70B Biologie Spectrophotometer[15]. The sulphate content of the water samples was estimated gravimetrically by (Jenway Company, Filsted, UK).[14].The value of Cl was calculated using an $AgNO_3$ titration technique [15].Calcium and Magnesium ion was determined using EDTA- titrimetric method as described by [15]. Trace elements in each water sample were determined by ICPE-9820 Shimadzu. The method was conducted according to (ICP multi – element standard solution IV) at Bashmakh quality control lab, following condition spectrophotometer chosen for the determination of Cr, As, Cd, Cu, Fe, Zn, Ni, Hg, Al and Pb. To prevent mineral binding on the container walls, 4 mL of conc. HNO^-_3 was added to a (1-liter) retention filtered water. The levels of measurement were (milligrams per liter).

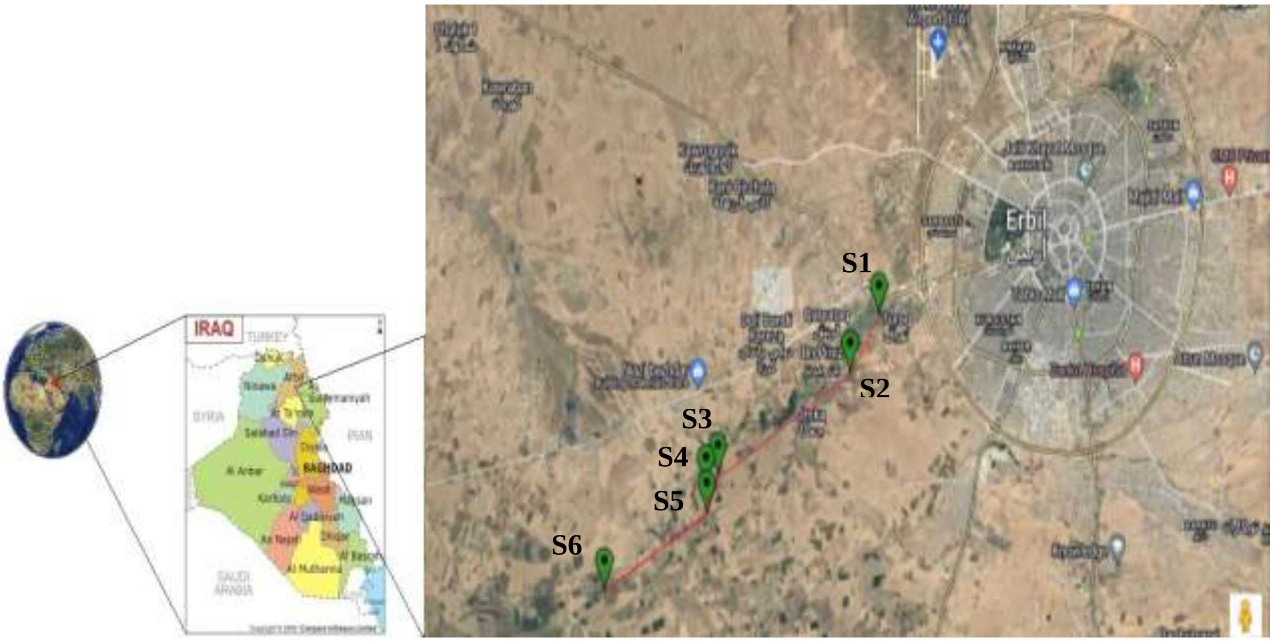

Figure 1. A map of the study area shows the locations of the several research sites (S1–S6).

Irrigation Water Quality:

Presence of undesired attenuated salts or components is a key criterion for determining irrigation water appropriateness [14].Sodium - Adsorption- Ratio (SAR), Permeability Index (PI), Magnesium Hazard (MH), Sodium percent (Na%), Total Hardness (TH), Potential salinity (PS), Kelly's index (KI), Residual Sodium Carbonate (RSC), Tables. 2 and 3, illustrate the irrigated agriculture water quality index (IWQI) and its categories. The formulae in Table. 2 are used to transform the analytical data of several qualities of water metrics into a single number.

Table 2. Indicators of water quality in the Erbil wastewater channel and well waters.

Quality Index	Formula	References
Permeability Index (PI)	$\mathrm{PI} = \frac{\mathrm{Na^+} + \sqrt{\mathrm{HCO3^-}}}{\mathrm{Na^+} + \mathrm{Mg^{2+}} + \mathrm{Ca^{2+}}} \times 100$	[16]
Sodium Adsorption Ratio (SAR)	$\mathrm{SAR} = \frac{\mathrm{Na^+}}{\sqrt{\frac{\mathrm{Mg^{2+}} + \mathrm{Ca^{2+}}}{2}}}$	[17]
Sodium percent (Na%)	$\mathrm{Na\%} \frac{\mathrm{Na^+} + \mathrm{K^+}}{\mathrm{Na^+} + \mathrm{K^+} + \mathrm{Mg^{2+}} + \mathrm{Ca^{2+}}} \times 100$	[18]
Residual Sodium Carbonate (RSC)	$\mathrm{RSC} = (\mathrm{CO3^{2-}} + \mathrm{HCO3^-}) - (\mathrm{Mg^{2+}} + \mathrm{Ca^{2+}})$	[17]
Magnesium Hazard (MH)	$\mathrm{MH\%} \frac{\mathrm{Mg^{2+}}}{\mathrm{Mg^{2+}} + \mathrm{Ca^{2+}}}$	[19], [20]
Kelly's Index (KI)	$\mathrm{KI} = \frac{\mathrm{Na^+}}{\mathrm{Mg^{2+}} + \mathrm{Ca^{2+}}}$	[21, 22]
Total Hardness (TH)	$\mathrm{TH} = (\mathrm{Mg^{2+}} + \mathrm{Ca^{2+}})$	[23]
Potential Salinity (PS)	$\mathrm{PS} = \left(\mathrm{Cl^-} + \frac{1}{2}\mathrm{SO4^{2-}}\right)$	[16, 19]

Table 3. Categories of indices for water quality and irrigation water qualities were used in the current study.

Quality Index	Range	Water Quality	References
Permeability Index (PI)	PI > 75% PI = 25–75% PI < 25%	Suitable Moderate Unsuitable	16
Sodium Adsorption Ratio (SAR)	SAR < 10 SAR = 10–18 SAR = 19–26 SAR > 26	Excellent Good Doubtful/Fair Poor Doubtful/Fair Poor Unsuitable	17, 24
Sodium percent (Na%)	Na% < 20 Na% = 20–40 Na% = 40–60 Na% = 60–80 Na% > 80	Excellent/Safe Good/Safe Permissible/Safe Doubtful/unsafe Unsuitable/unsafe	19, 25
Residual Sodium Carbonate (RSC) (meq L^{-1})	RSC < 1.25 RSC = 1.25–2.50 RSC > 2.50	Good Medium Unsuitable	25
Magnesium Hazard (MH)	MH < 50% MH > 50%	Suitable Unsuitable	21
Kelly's Index (KI)	KI < 1 KI > 1	Suitable Unsuitable	22
Total Hardness (TH)(meq L^{-1})	0–60 61–120 121–180 >181	Soft Moderate Hard Very	23
Potential Salinity (PS)(meq L^{-1})	PS < 3.0 PS = 3.0–5 PS > 5.0	Excellent to good Good to injurious Injurious to unsatisfactory	16

The Design of (Irrigation Water Quality Index IWQI)

The (IWQI) design given by [26] is implemented in three steps:

1- Identifying the parameters that have the greatest influence on the quality of irrigation water.

2- The Eq.1 was used to determine quality measurement (Qi) and aggregate weights (wi) for each parameter based on irrigation water quality parameters suggested by the University of California committee of consultants (UCCC) and recommendations specified by [27]. It was designed in accordance with the criteria of water quality were expressed by a non-dimensional numeric; the greater the score, the more appropriate the water qualities.

$$Q_i = q_{i\,max} - [(X_{ij} - X_{inf}) * q_{iamp} / X_{amp}] \quad \ldots\ldots.\ 1$$

Where;

q_{imax} : the class's maximum qi value (unit less).
x_{ij}: the parameter's actual value.
x_{inf}: the value corresponding to the lower limit of the class to which the parameter corresponds
q_{iamp} : x_{amp} denotes the class amplitude where the parameter relates.

To assess x_{amp} in the final class of every parameter, the upper limit was deemed to be the largest value achieved by physical-chemical and chemical examination of the water samples.

3- Establishing the weight value (wi) to every parameter according with Table.4 As indicated, the variables are transformed so that their total equaled one.

Table 4. weights assigned to each of the IWQI characteristics [26].

Parameters	w_i
EC	0.211
Na^{+1}	0.204
HCO_3^{-1}	0.202
Cl^{-1}	0.194
SAR	0.189
Total	1.000

4- Performing the calculations necessary to determine the irrigation water quality index as:

$$IWQI = \sum q_i w_i \quad \ldots\ldots\ldots..\ 2$$

IWQI is a dimensionless parameter with a range of 0 to 100, qi is the quality of the ith parameter and has a number from 0 to 100, which is a function of its concentration or measurement, and wi is the normalized weight of the ith parameter, which is a function of its significance and illustrates water quality fluctuations. The recommended water quality index is utilized to categorize the categories into their appropriate groupings. The classifications provided by summarize the hazards of water salinity, slow soil water penetration, and plant toxicity. [28, 29].

Statistical analysis and software used:

A one-way analysis of variance (ANOVA) was performed on the data of physicochemical parameters, trace metals, and quality indices that were managed to gather from the six sites. The ANOVA analysis, along with the various water parameters and trace elements from six different locations, were subjected to Pearson's correlation testing. Additionally, the data of water chemical parameters and trace elements were analyzed using the (PAST 4.03) program for principal component analysis (PCA). On the basis of cation and anion data, the piper plot was created using the Diagrammes software. The sampled sites were plotted and classified using Doneen [16], Wilcox [24], and US salinity Richards [17] diagrams.

Results and Discussion:

Waste and well water characteristics

The hydrochemical characteristics of surface water and well water samples were determined, collected from six sites are listed in Table. 5. Three sites along Erbil's wastewater and three sites on well water were monitored, with the water from six sites being used for vegetable irrigation. The pH fluctuated from 7.63 in S5 to 7.92 in S6, with an average of 7.80, indicating that the waters were neutral to alkaline. pH changes are connected to changes in conductivity and bicarbonate content [18]. EC ranges from 809 to 1078 S/cm. EC may be used to determine the total quantity of dissolved salts in water. Temperature, concentration, and ion types affect outcomes. [30] All examined locations have satisfactory EC ratings [31]. TDS concentrations ranged from 517.76 to 689.92 mg/l, with a mean of 586.13 mg/l. The fundamental hydrochemical characteristics of surface water are mostly determined by the main ions that are present [32]. All samples exceeded the 500 mg/l TDS limit [32]. Major cations make up around 60% of the total dissolved solids (TDS). Magnesium and calcium are the most frequent cations, accounting for 33% and 17% of TDS, respectively. Major ion concentrations control the basic hydrochemical characteristics of surface water. Except for Mg^{2+}, the mean of the examined anions and cations is below permissible limits, the amount of Mg^{2+} in three sites especially the well water samples are over acceptable limits [33] leaching of rocks into well water may contribute, [34] as well as the soil containing a high quantity of dolomite, which is high in magnesium, or it might be owing to the higher quantities of magnesium coming from fertilizer used by farmers to boost output, and then the magnesium ion seeping into ground water, although high concentrations of magnesium may also cause dispersion with some clays, while K$^+$ ions in three sites of waste water are over acceptable limits [33], as shown in Table. 5, may be as material disintegration as a consequence of the decomposition of plant material and the runoff from agricultural activities [10]. In surface water, the main cations were Mg^{2+} (58.95), Ca^{2+} (40.11), Na$^+$ (33.68), and K$^+$ (3.55).

Table 5. Physico - chemical properties of water samples gathered from a study sites.

Sites	pH	EC (μS/cm)	TDS (mg/l)	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Cl (mg/l)	SO_4 (mg/l)	CO_3 (mg/l)	HCO_3 (mg/l)
S1	7.63	809	517.76	40.25	6.16	38.47	34.99	9.217	99.33	0.00	409.92
S2	7.86	1078	689.92	32.49	0.53	72.14	65.61	32.61	30.67	0.00	390.4
S3	7.84	839	536.96	29.66	6.01	36.87	44.71	9.92	100.67	0.00	441.64
S4	7.65	865	553.6	30.46	6.60	37.87	45.07	11.34	102.76	0.00	445.3
S5	7.89	941	602.24	26.84	0.83	40.08	89.91	59.55	36.67	0.00	529.48
S6	7.92	963	616.32	42.37	1.20	15.23	73.38	55.3	24.67	0.00	439.2
Mean	7.80	915.83	586.13	33.68	3.55	40.11	58.95	29.66	65.79	0.00	442.66
SE	0.05	40.44	25.88	2.54	1.21	7.45	8.53	9.49	15.79	0.00	19.46
CV%	1.61	10.82	10.82	18.48	83.69	45.47	35.43	78.40	58.79	0.00	10.77
Permissible limits worldwide											
WHO[31]	6.5–8.5	1500	500	200	12	75	50	250	250	0	500
FAO [33]	6.5–8.6	700-<3000	0–2000	0–920	0–2	0–400	9.4–13.5	70	575	-	-

SE: Standard error; CV: Coefficient of variation, Permissible limits are those provided by Food and SE: SE:Standard error; CV: Coefficient of variation, Permissible limits for irrigation water are set by the Food and Agriculture Organization (FAO) and the World Health Organization (WHO).

The domains of magnesium ion on other cations documented in this research are partly attributable to the local soil and watershed's geology. Well water has more magnesium than waste water due to Clay minerals, a source of magnesium ion in water and ferromagnetic igneous rocks. It's possible that the low amount of K^+ in comparison to Mg^{2++}, Ca^{2++}, and Na^+ is related to the fact that clay minerals may easily fix it [35]. In studied samples the sequence of major anions were HCO_3^- (442.66 mg l^{-1}) > SO_4 (65.79 mg l^{-1}) > Cl^- (29.66mg l^{-1}) > CO_3^{2-} (0.00 mg l^{-1}). The most common dissolved ions are bicarbonate, sulphate and chloride. It contributes for 82 %, 12%, and 6 %, sequentially, of the total anions. Table. 4 Water samples has chloride and sulphate concentrations wide ranging from 9.92 to 59.55 mg l^{-1} and 24.67 to 102.76 mg l^{-1}, respectively, based on the values' mean of 29.66 and 65.79 mg l^{-1}. In the corresponding unit, the chloride concentration provides 5.5 percent of the total anionic concentration. All Cl^- scores are below those recommended by WHO. [32] The recommended limit of 250 mg l^{-1} while HCO_3^- concentrations are within the WHO except Site 5 well water are above the WHO's recommended levels., 500 mg l^{-1} [32]. It's possible that this is due to the presence of natural produce in the aquifer, which is oxidized to create carbon dioxide and encourages mineral dissolution [36]. Half of the HCO3 ions would come from the fossilized carbon in the calcite and dolomite in the aquifer. The amount of calcium, magnesium, and bicarbonate ions in the groundwater goes up because of the process of weathering. When silicate minerals break down over time, bicarbonate ions may be made [37]. The concentration of CO_3 all studied samples was 0.00 mg.l^{-1} the reason is due to the pH value is less than 8.2 [14].

Hydrochemical Deposition:

To demonstrate the chemistry of a rock, soil, or water sample, the principal chemical compositions in three portions of a ternary diagram are plotted in a Piper plot. Cations are depicted on the left, while anions are depicted on the right, with a diamond-shaped region to represent a joined placement of cations and anions. Hydrochemical depositions, which are various zones, characterize the predominant cations and anions that affect the hydrochemistry of groundwater [38, 39]. The Piper diagram's diamond-shaped region is split into four primary portions, each representing and describing a different form of cation and anion variation or dominance Fig 2.

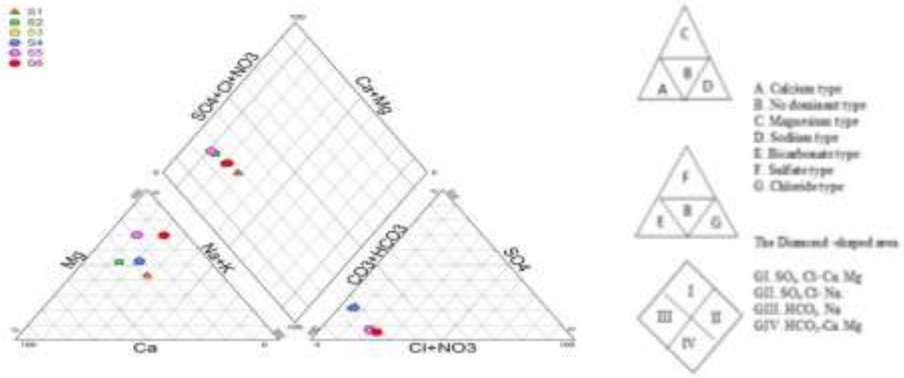

Figure 2. Piper plot showing the hydrogeochemical characteristics of water at the six sites where Erbil wastewater and well waters were studied.

According to this diagram, HCO_3. Na was found to be the most prevalent water type across the research sites. The hydrochemical surfaces of six distinct water sources were affected by ion exchange, evaporation, and concentration [40]. With respect to major anions, water belonging to HCO_3 dominant Fig.2. The highest SO_4^- concentrations are found at the sites of S1, S2 and S3. Regarding the major cations, the water belonging to Mg dominant type except for at S1 where it was no dominant. The above results may be due to the type of soil,, ,the nature of sewage discharge and the solubility of calcite rock which is abundant in the study area is more rapidly than dolomite or visversa. [12]

Trace elements concentration

The mean concentrations of Ag, Al, Cd, Cr, Fe, Mn, Ni, Pb, Zn, As, in the surface water samples collected on three sited of wastewater channel and three well water are shown in Table 6. The following is the sequence of mean metals concentrations in water: (in mg l^{-1}) Pb (1.2933)> Al (0.9872) >Fe (0.5389)>As 0.3303) >Cd (0.3302) > Mn(0.1318) > Cr (0.0807) > Zn (0.0385) > Ag (0.0292) >Ni (0.0124).

Table 6. Concentrations of metals in waste water sampled from six locations.

Sites	Ag (mg/l)	Al (mg/l)	Cd (mg/l)	Cr (mg/l)	Fe (mg/l)	Mn (mg/l)	Ni (mg/l)	Pb (mg/l)	Zn (mg/l)	As (mg/l)
S1	0.0367	1.240	0.265	0.083	1.090	0.189	0.0116	1.220	0.071	0.294
S2	0.0326	1.160	0.447	0.088	0.319	0.088	0.0137	1.470	0.061	0.434
S3	0.0269	1.000	0.260	0.071	0.635	0.181	0.0120	1.170	0.015	0.321
S4	0.0248	0.987	0.289	0.091	0.783	0.193	0.0142	1.490	0.016	0.365
S5	0.0290	0.769	0.395	0.077	0.209	0.073	0.0121	1.270	0.035	0.208
S6	0.0254	0.767	0.325	0.074	0.197	0.067	0.0108	1.140	0.033	0.360
Mean	0.0292	0.9872	0.3302	0.0807	0.5389	0.1318	0.0124	1.2933	0.0385	0.3303
SE	0.0019	0.0796	0.0310	0.0033	0.1468	0.0252	0.0005	0.0618	0.0095	0.0312
CV%	15.8345	19.7475	22.9647	9.9581	66.7406	46.9187	10.5036	11.7023	60.4299	23.1347
Permissible limits worldwide										
USEPA [41] and FAO[33]	0.1	5	0.01	0.1	5	0.2	0.2	5	2	0.1

In general, most metals had larger concentrations in waste water sites, with the exception of Cd and As, which had high concentrations in site 2 (well water). The causes for this may be traced back to the fact that waste waterways take massive volumes of agricultural drainage and sewage, as well as industrial wastewater [10, 42]. The quick movement of contaminants and the ability of metals to attach onto clays, biological matter, iron, and manganese oxides, as well as other particles in water [43, 44].Other causes include the hydrogeological and geochemical features of the examined region of well may impact metal transport in groundwater [44, 45]. According to the US EPA and FAO [33, 45], Ag, Al, Cr, Fe, Mn, Ni, Pb, and Zn concentrations in all analyzed locations are below the recommended limit for irrigation, however Cd and As concentrations are greater than those reported by US EPA and FAO. The reason is that oil refineries and iron production plants are only a few kilometers away from the study site. This means that the amount of cadmium in each water sample is getting higher. Cadmium can get into water systems through the movement of groundwater and the release of chemicals from the materials that contain it. Pesticides are used by farmers to safeguard their crops and maximize yields. Arsenic appears to be extremely widespread since it was once used in pesticides. Arsenic may get into water systems through runoff from nearby farms, making the amount of arsenic in the water go up [41].

Correlation among Chemical Characteristics of Water and Trace elements:

To investigate their effect on the kinetics of trace elements in the water body, a Pearson correlation matrix was employed. Table. 7 Correlation analysis may be used to determine the strength of a link between any two variables [46]. There are many things, both natural and man-made, that can change the pH of water. Most natural changes happen when things touch the earth's crust. In aquatic systems, salinity may show how much land imports affect water streams to some degree [47]. pH and Mg^{2+} exhibited a positive connection with a value of r = 8.00. TDS had a positive connection with EC and Cd, with r = 1 and 0.926, respectively. (Table 9). The concentration, distribution, and transit of trace elements throughout the estuary were affected by pH, temperature, dissolved oxygen, and salinity [48, 49].

The principal replaceable ions at the sites that were investigated had substantial connections with a wide variety of cations and anions. Table 7. K-SO$_4$ and Mg-Cl exhibit a substantial positive correlation with values of r equal to 0.988 and 0.964, respectively, indicating a significant relationship between the two variables. K-Fe, K-Mn, Fe- SO$_4$ and Mn- SO$_4$ showed positive correlation with value of r = 0.895, 0.983, 0.895 and 0.990, respectively. Distinct behaviors, as well as varied sources and sinks of metals, result in different correlations between dissolved metals. Cr showed a significant positive correlation with Ni and Pb (r = 0.813 and 0.905, respectively).

Table 7. Pearson's correlation matrix showing a variety of water characteristics and trace elements from six different sites

	pH	EC	TDS	Na	K	Ca	Mg	Cl	SO4	CO3	HCO3	Ag	Al	Cd	Cr	Fe	Mn	Ni	Pb	Zn	As
pH	1.00																				
EC	0.65	1.00																			
TDS	0.65	1.00	1.00																		
Na	-0.11	-0.06	-0.06	1.00																	
K	-0.81	-0.88	-0.88	-0.01	1.00																
Ca	-0.05	0.50	0.50	-0.43	-0.21	1.00															
Mg	0.80	0.67	0.67	-0.23	-0.90	-0.02	1.00														
Cl	0.78	0.61	0.61	0.03	-0.89	-0.19	0.96	1.00													
SO4	-0.80	-0.86	-0.86	-0.13	0.99	-0.10	-0.88	-0.91	1.00												
CO3	-	-	-	-	-	-	-	-	-	1.00											
HCO3	0.31	-0.13	-0.13	-0.53	-0.21	-0.35	0.61	0.54	-0.17	-	1.00										
Ag	-0.34	-0.01	-0.01	0.26	0.00	0.49	-0.26	-0.22	0.06	-	-0.40	1.00									
Al	-0.64	-0.16	-0.16	0.16	0.44	0.59	-0.74	-0.75	0.48	-	-0.76	0.74	1.00								
Cd	0.56	0.93	0.93	-0.27	-0.87	0.62	0.74	0.64	-0.81	-	0.09	0.15	-0.14	1.00							
Cr	-0.60	0.19	0.19	-0.08	0.15	0.56	-0.27	-0.33	0.16	-	-0.38	0.25	0.52	0.25	1.00						
Fe	-0.93	-0.78	-0.78	0.18	0.89	-0.01	-0.92	-0.88	0.90	-	-0.39	0.42	0.71	-0.72	0.33	1.00					
Mn	-0.84	-0.81	-0.81	-0.07	0.98	-0.03	-0.93	-0.95	0.99	-	-0.30	0.11	0.58	-0.78	0.25	0.92	1.00				
Ni	-0.36	0.24	0.24	-0.57	0.16	0.68	-0.18	-0.36	0.22	-	-0.19	-0.08	0.34	0.30	0.81	0.14	0.27	1.00			
Pb	-0.33	0.38	0.38	-0.43	0.00	0.69	-0.06	-0.21	0.04	-	-0.21	0.02	0.33	0.44	0.91	0.06	0.11	0.96	1.00		
Zn	-0.19	0.24	0.24	0.46	-0.25	0.44	-0.07	0.01	-0.23	-	-0.47	0.93	0.61	0.33	0.31	0.20	-0.15	-0.12	0.06	1.00	
As	-0.01	0.47	0.47	0.28	-0.05	0.37	-0.27	-0.26	-0.11	-	-0.82	-0.08	0.39	0.19	0.45	-0.04	0.01	0.44	0.47	0.10	1.00

Ag showed appositive correlation with Zn, r = 0.927. Fe and Ni had a 0.923 and 0.964 correlation with Mn and Pb, respectively. Even though pH is thought to be a key factor in determining how much metal is available [50], the present data demonstrated a negative correlation between pH and the examined trace elements, with the exception of Cd, for which no significant correlation was seen. PCA was used to link the trace elements with the investigated locations, Principal Component Analysis waste water and well waters had PC1 described 42.21% of the components in waste water and well waters, PC2 explained 26.89 %, five Principal Components were required to describe 95% of the overall variation, as seen on the screen plot of Fig. 3. The large proportion of PC1 indicates that the variables are substantially connected already

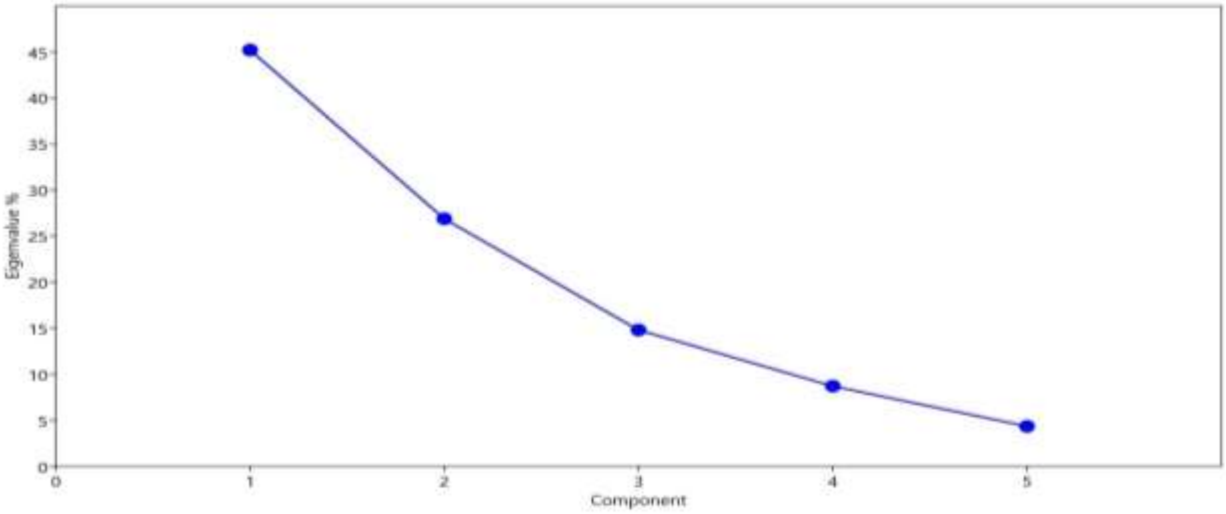

Figure 3. Scree plots explaining variability of first four components.

Principal Components having an eigenvalue > 1 were selected for further analysis using the Kaiser criteria [51]. Table 8's eigenvalues supply this information, and PC1 and PC2 will be utilized depending on it. It disregards PC5 since its eigenvalue is less than 1, the eigenvalue of PC3 and PC4, is much smaller than PC1 and PC2, and shows few variables.

Table 8. Eigenvalues of each principal component

PC	Eigenvalue
PC1	9.04
PC2	5.37
PC3	2.96
PC4	1.74
PC5	0.87

Bi plots can be seen in (Fig. 4) PC1 mostly characterizes (TDS, EC, Cd, Ca, K, SO_4 and Mn). The second PC mainly loads (Mg, Cl, HCO_3, Ag, Al, Cr, Fe, Ni, Pb, Zn and As,). It is clear that sites S2 were segregated on the right side where they showed positive correlation between TDS, EC, and Ca with heavy metal especially Cd, This result reconfirm that the amount of Cd in the site 2 is higher than other sites. However, sites S5 and S6 were separated on the right lower side of the plot and they showed no correlation between cation and anion with trace elements Fig. 4. On the left upper side, site 1 and site 4 where they showed the positive correlation between eight trace elements, this might be due to the release of industrial waste or the runoff of pesticides used by farmers into the water. It is evident that most pesticides contain trace elements. Site 3 on the lower left side of the figure revealed a Mn-K-SO_4 association.

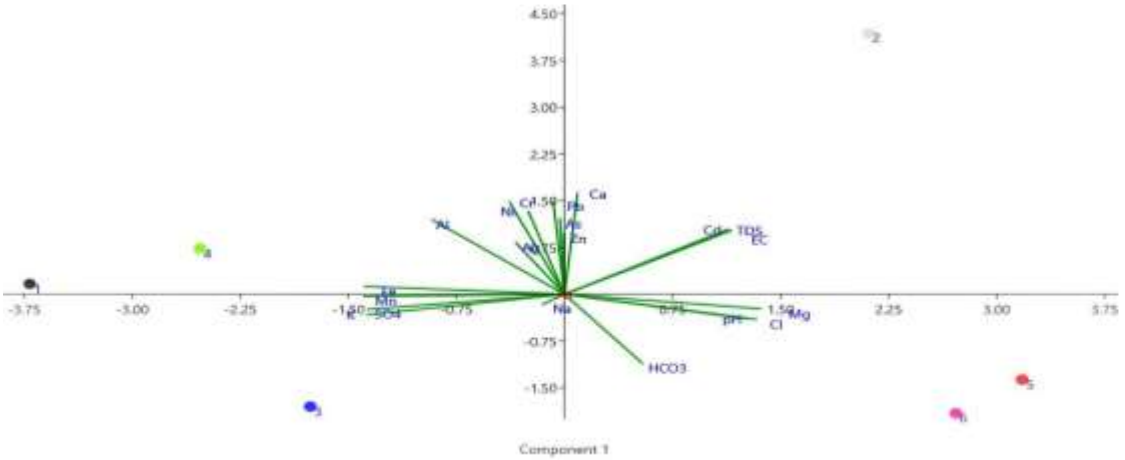

Figure 4. Biplots of PC1 × PC2 for S1, S2, S3, S4, S5 and S6.

Cd and As exhibited a strong association in our study Fig. 4, indicating that they posed health hazards. Using polluted water to irrigate leads to heavy metal contamination of the soil, which is then transferred to the crops or plants. There are two ways trace elements which may enter vegetables: first, they can be absorbed from polluted soils; second, they can be deposited on the surfaces of vegetables that are exposed to polluted surroundings [52]. When consumed on a consistent basis, trace elements may lead to a variety of adverse health effects in humans as well as in other species[53]. A number of different malignancies have been linked to long-term exposure to very small levels of carcinogenic trace elements [54]. According to the criteria set by the International Agency for Research on Cancer (IARC), arsenic, cadmium, and chromium are all "carcinogenic to humans" [55]. Because of this, these three cancer-causing substances were analyzed to determine the chronic health hazards they posed, both carcinogenic and non-carcinogenic.

Irrigation Suitability Assessment:

Permeability Index (PI)

Doneen [16] presented a PI-based classification scheme for irrigation water. This takes into account the soil's concentrations of Na^+, Ca^{++}, Mg^{++}, and HCO_3. The PI scores in the research region vary from 37.86 % in S2 to 66.30 % in S1, as shown in Fig. 5 and Table. 9. Water samples having a PI more than 75% (PI > 75 percent) are classified as acceptable, moderate (25–75 percent), and unsuitable (25 percent) according to Doneen's chart [16]. The PI may also be used to determine whether or not the water is suitable for use in irrigation [30].

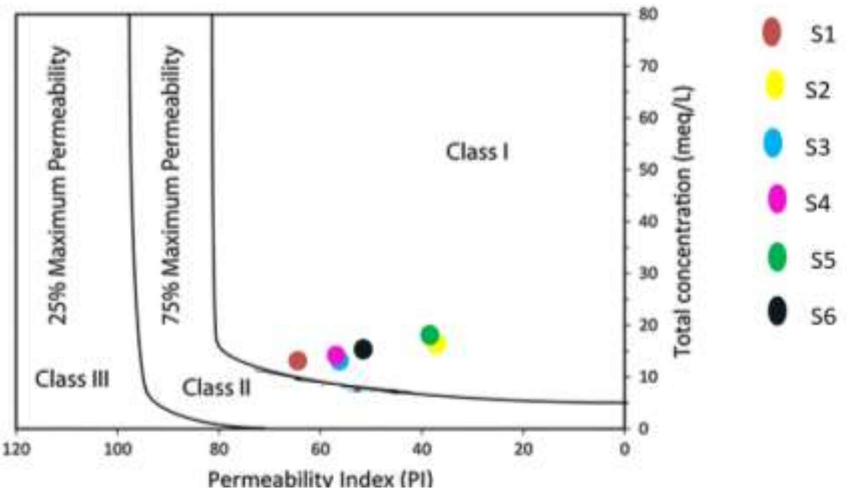

Figure 5. Displays the categorization of the permeability index used by Doneen [16] to categorize the irrigation water from each of the six sample sites.

Table 9. The water indices are the results of water samples gathered from a study sites.

Sites	PI (%)	SAR	%Na	%MH	RSC (meq L^1)	KI	TH (meq L^1)	PS (meq L^1)	IWQI
S1	66.31	6.64	38.71	47.63	1.92	6.64	4.80	1.29	94.61
S2	37.87	3.91	19.33	47.63	-2.60	3.91	9.00	1.24	91.60
S3	58.47	4.64	30.42	54.80	1.72	4.64	5.52	1.33	93.18
S4	58.16	4.73	30.87	54.34	1.70	4.73	5.60	1.39	94.01
S5	38.93	3.33	17.54	69.17	-0.72	3.33	9.40	2.06	93.77
S6	52.38	6.37	32.96	82.81	0.40	6.37	6.80	1.82	93.96
Mean	52.02	4.94	28.31	59.40	0.40	4.94	6.85	1.52	93.52
SE	4.67	0.54	3.35	5.68	0.73	0.54	0.79	0.14	0.34

PI: permeability index, SAR: sodium adsorption ratio, KI: Kelly's index, MH: magnesium hazard, PS: potential salinity, RSC: residual sodium carbonate, TH: total hardness, IWQI: Irrigation water quality index, SE: standard error..

Most of the samples used in this research had PI levels that were about moderate. hence they were deemed suitable for irrigation based on PI values Table. 10. High amounts of Na^+ and HCO_3 have been associated to high PI values, which may be the result of carbonate breakdown and cation interchange in minerals like calcite and dolomite [56].

Table 10. Classification of water for irrigation based on different parameters and indexes.

Sites	PI	SAR	Na	RSC	MH	KI	TH	PS	IWQI
S1	Moderate	Excellent	Good/ Safe	Medium	Suitable	Unsuitable	Soft	Excellent to good	No Restriction
S2	Moderate	Excellent	Excellent/ Safe	Good	Suitable	Unsuitable	Soft	Excellent to good	No Restriction
S3	Moderate	Excellent	Good/ Safe	Medium	Unsuitable	Unsuitable	Soft	Excellent to good	No Restriction
S4	Moderate	Excellent	Good/ Safe	Medium	Unsuitable	Unsuitable	Soft	Excellent to good	No Restriction
S5	Moderate	Excellent	Excellent/ Safe	Good	Unsuitable	Unsuitable	Soft	Excellent to good	No Restriction
S6	Moderate	Excellent	Good/ Safe	Good	Unsuitable	Unsuitable	Soft	Excellent to good	No Restricti

PI: permeability index, SAR: sodium adsorption ratio, RSC: residual sodium carbonate, MH: magnesium hazard ,KI: Kelly's index, TH: total hardness , PS: potential salinity, IWQI: Irrigation water quality index

Sodium Adsorption Ratio (SAR):

Irrigation water with high extents of salt is of particular concern because sodium has negative impacts on soil, bearing a sodium hazard. Additionally, the SAR categorizes salt threats, which may lessen the soil's permeability and hinder plants from taking up water [57]. Soil particles absorb sodium and become bonded to it. Whenever the soil is dried, it dries out and becomes hard and tight. Making water penetration more difficult. Soils having a fine texture, particularly those that include a significant amount of clay, are more vulnerable to the effects of this activity. For the preservation of soils with high SAR levels, certain amendments could be necessary. If appropriate concentrations of Ca^{++} and Mg^{++} are present in the soil, they will work to mitigate the consequences of Na^{+} exposure and contribute to the upkeep of good soil properties [58, 59]. SAR is used to categorize surface water into four categories: excellent (SAR < 10), good (10 < SAR < 18), doubtful (18 < SAR< 26), and unsuitable (SAR > 26). Water samples' SAR ranged from 3.33 to 6.34, with an average of 4.94. Table 9. As a result, according to Wilcox [24] and Richards [17], all studied samples are excellent Table 10. By comparing the SAR to the EC on a USSL diagram, one might get more insight into whether or not water should be used for irrigation [17]. All of the water samples in Fig. 6a are of the high salinity/low sodium type (C3–S1, acceptable for irrigation; S1).

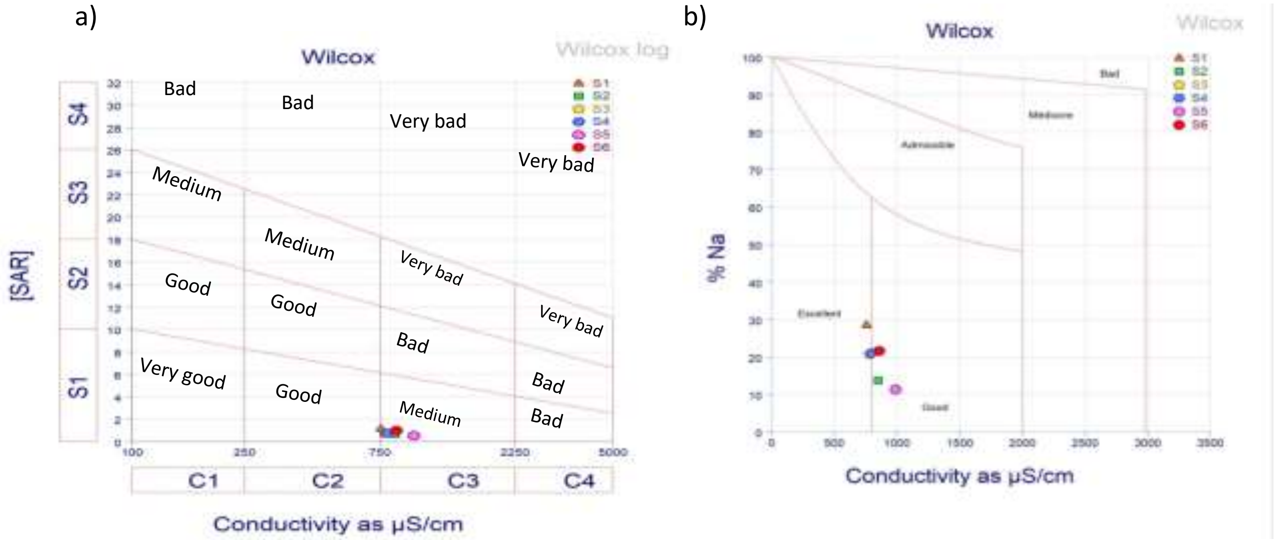

Figure 6. The acceptability of the water quality at each of the six selected sites for agricultural irrigation based n (a) The salinity diagram for the US shows the relationship between SAR and EC (µS cm−1) [31] and (b) The Wilcox diagram [24]

Sodium Percentage (Na%):

The amount of sodium that is soluble in surface water is expressed as a percentage called the Na percent. This measurement is also used in calculating the risk of sodium exposure. Na^{+} percent is a common statistic used in the determination of the viability of natural waters for irrigation because sodium interacts with the soil and reduces permeability [24] Water with an Na percent concentration is more than 60%, according to [58]. This may create salt accumulations and soil deterioration. Alkali soils arise when sodium combines with carbonate; saline soils form when sodium combines with chloride. The percent Na^{+} in the study area's surface waters ranges from 17.54 percent in S5 to 38.71 percent in S1, with an average value of 28.31 percent, Table. 9. Therefore, according to Ravikumar, *et al.* [19] and Eaton [25], the sampling sites of the Erbil wastewater Canal and well water are good/safe for S1, S3, S4 and S6 sites and Excellent/safe for S2 and S5 sites, Table 10. The Wilcox [24] diagram linking sodium percent and EC shows the sites S1, S3 and S4 wastewater samples fall in the "excellent" region While the sites S2, S5 and S6 well water samples fall under the "Good" region Fig. 6b.

Residual Sodium Carbonate (RSC)

Because it determines whether or not there is a correlation between the amount of carbonate and bicarbonate present and the overall concentration of calcium and magnesium, RSC is a good measure for analyzing the adequacy of irrigation water [39]. When the water content of the soil becomes more concentrated, waters that include high concentrations of HCO$_3$ have a greater propensity to precipitate Ca^{2+} and Mg^{2+}. As a consequence of the formation of sodium carbonate, soils that are watered with water that has a high RSC risk becoming unproductive [46]. When the RSC levels are lower than 1.25 meq L^{-1}, it is deemed safe to conduct irrigation. The usage of water with a relative salinity concentration (RSC) ranging from 1.25 to 2.5 meq L^{-1} is regarded marginal and may be done so with proper irrigation planning and laboratory soil salinity testing. RSC concentrations that are higher than 2.5 meq L^{-1} are regarded as being inappropriate for irrigation [24, 25]. The analysis found that all of the samples could be used for irrigation, with the RSC of the well water being excellent and that of the wastewater being medium. Table. 10.

Magnesium, Hazard(MH):
In most waterways, calcium and magnesium are in a condition of balance. Soil alkalinity is caused by a high level of MH (>50%) in a water sample; also, a significant amount of water is adsorbed among magnesium and clay particles, decreasing the soil's infiltration potential and consequently damaging crop yields [19,39]. Water samples had an MH ranging from 47.63 to 82.81 percent (mean = 59.40 percent), Table9. Except for S1 and S2, which are below 50%, all of the samples are over 50%, making S1 and S2 suitable for irrigation and S3 to S6 unsuitable Table 10, may be as a result of the presence of magnesium in ground water and wastewater that has been in interaction with particular of geological materials, particularly limestone and gypsum. Magnesium is released as a byproduct of the dissolution of these materials. [39]

Kelly's Index (KI):
Kelly [34] introduced Kelly's index as an important criterion for assessing irrigation water quality. This value is calculated using the Na, Ca, and Mg levels in the water. When it comes to irrigation, water that has a KI value that is higher than one (KI > 1) is seen as unsuitable, while water that has a KI value that is lower than one (KI 1) is regarded as being appropriate. Throughout the course of this inquiry, the KI of the water sample varied anywhere from 3.33 to 6.64, with a mean value of 4.94 Table. 9. As a result of Kelly's ratio Table. 10, all of the analyzed locations are declared inappropriate for irrigation, which might be owing to high cation exchange, which supplies sufficient Na^+ [60].

Total Hardness (TH):
The distinctive flavor and texture of hard water is due to the natural buildup of calcium, magnesium ions, and salts, or both. The total hardness equals the product of calcium and magnesium hardness. The total hardness (TH) categorization of groundwater categorized all wastewater canal and well water samples as soft water. After examining the samples, this conclusion was reached. The hardness values vary from 4.80 meq L^{-1} to 9.40 meq L^{-1}, with the mean value being 6.85 meq L^{-1} Table. 9. According to Durfor and Becker [23], the maximum amount of TH permitted for use irrigation is 60 meq L^{-1}, while 120 meq L^{-1} is deemed to be the most appropriate limit. Table 10 indicates that the study locations are all deemed soft.

Potential Salinity (PS):
The potential salinity of a water body is equal to the concentration of Cl^-, 50 % of the concentration of SO4- (PS). The PS value is a parameter-based water quality indicator that is used for categorizing irrigation water. [16]. Salts with limited solubility are known to precipitate and concentrate in the soil, making them suitable for irrigation. In contrast, salts with hydrophilic properties tend to increase soil salinity [61].This analysis found that the amounts of PS in the water samples varied from 1.24 to 2.06 meq L^{-1}. with a mean of 1.52 meq L-1 Table 9. That is to say, all samples are rated Excellent to Good Table. 10.

Irrigation Water Quality Index (IWQI)
IWQI defines irrigation water quality as a single number, eliminating the requirement for huge data intervals. IWQI compares water quality measurements to criteria [21]. The irrigation water quality index is calculated using water consumption restrictions for each soil type. Ionic composition estimates irrigation water quality [62]. The categorization of the water's quality according to the IWQI measurements is indicated in Table. 9, which shows the WQI calculation for water samples. The IWQI value in water samples in this investigation ranged from 91.60 to 94.61, with a mean of 93.52. All of the places that were investigated were sampled (No restriction) [28, 29] indicating that most plants and soils have negligible toxicity concern, with a low likelihood of generating salinity and sodicity problems. With the exception of soils that have an exceptionally low permeability, it is suggested that irrigation strategies include leaching [28, 29].

Conclusion:

Based on the overall assessment, it is concluded that anions and cations examined in this study are within the permissible limits. The domains of magnesium ion on other cations recorded in present study as well as the level of magnesium in well water are larger than in wastewater. The sequence of major anions is bicarbonate, sulphate and chloride. The ternary diagram is plotted in a piper plot, and the results showed that the most common kind of water is HCO_3.Na in all the studied sites, Ag, Al, Cr, Fe, Mn, Ni, Pb, and Zn levels in all studied sites are within allowable limits reviewed for irrigation purposes, according to the US EPA and FAO. However, the levels of two carcinogenic metals, including Cd and As, are discovered in higher concentrations than those documented in the US EPA and FAO; this is the case even though the permissible limit is within the acceptable range. Most metals have larger concentrations in waste water sites, with the exception of Cd and As, which had high concentrations recorded in site 2 (well water).The positive correlation found among pH with Mg^{2+} ,TDS - EC and Cd, K - SO_4, Mg- Cl, K - Fe, K - Mn, Fe - SO_4 and Mn- SO_4 , Cr shows a significant positive correlation with Ni and Pb , Ag showing a positive correlation with Zn and Fe and Ni is in a positive correlation with Mn and Pb. According to PI, SAR, Sodium percent, RSC, TH,PS and IWQI indexes the studied sites water is suitable for irrigation purpose for depend on KI index water of the studied sites which is unsuitable. According to MH index S3,S4,S5 and S6 is unsuitable for irrigation

Authors' Declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Besides, the Figures and images, which are not ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in Salahaddin University, Erbil, Iraq.

Author's contributions:

D A.D. conceived of the presented idea and The process of auditing the search, AM.Y. took the samples, make sample analysis, statistical analysis and wrote the research.

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الحساب الهيدروكيميائي لنوعية مياه الري قناة الصرف الصحي في أربيل وبعض الآبار

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الخلاصة:

تقع مدينة أربيل في شمال العراق ويبلغ عدد سكانها أكثر من مليون نسمة. بسبب أزمات المياه ، يستخدم المزارعون عادة مياه الصرف الصحي ومياه الآبار للإنتاج الزراعي. في هذه الدراسة تم تصميم ست محطات لأخذ عينات من مياه الصرف وثلاث محطات من مياه الآبار لتحديد خصائص مياه الصرف الصحي والمياه الجوفية. في هذه الدراسة تم تحديد متبقي الصوديوم , كربونات ، مخاطر المغنيسيوم ، مخاطر الملوحة ، مؤشر كيلي ،٪ صوديوم ، عسر كلي ، مؤشر النفاذية ، الملوحة المحتملة ، نسبة امتصاص الصوديوم ، مؤشر جودة مياه الري .(IWQI) كان ترتيب متوسط تركيزات الكاتيون في الماء $Mg_2{}^+ > Ca_2{}^+ > Na{}^+ > K{}^+$. بينما كانت نسبة الأنيونات الرئيسية في الماء $HCO^-_3 > SO4 > Cl$. تم العثور على أعلى تركيزات Ca^{2+} و Mg^{2+} و Na^+ في مياه الآبار ، بينما تم العثور على أعلى تركيز من K^+ في مياه الصرف الصحي. سجل أقصى تركيز لـ HCO^-_3 و Cl^- في مياه الآبار ، بينما سجل أعلى تركيز SO^{2-}_4 في مياه الصرف الصحي. علاوة على ذلك ، كان ترتيب المعادن الثقيلة هو $Pb > Al > Fe > Cd > As > Mn > Cr > Ag > Ni$. مع الأخذ في الاعتبار تركيز المعادن الذي حددته وكالة حماية البيئة الأمريكية ومنظمة الأغذية والزراعة (1999) و (1994) المبادئ التوجيهية لمستويات Pb و Al و Fe و Mn و Cr و Ag و Ni في مياه الصرف الصحي ومياه الآبار كانت ضمن الحدود المسموح بها لبرامج الري. علاوة على ذلك ، كانت قيود As و Cd خارج الحدود المسموح بها تحتاج إلى تقليلها. تراوح IWQI من 88.92 إلى 95.09 في عينات مياه الصرف. يكشف التقييم العام أن النباتات الزراعية المزروعة تم تأمينها من المركبات السامة

الكلمات المفتاحية: أرض زراعية، الري ومياه الآبار، معادن ثقيلة، مؤشرات جودة المياه.