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Determination of Some Trace Elements in Aquatic Samples from Khabur River-Iraq by Using Inductively Coupled Plasma Optical Emission Spectroscopy and some other Parameters

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Abstract: This research aims to examine heavy metals contents and environmental risk in the Khabur river water in Zakho-Iraq. Ten different locations were selected on the Khabur River from the beginning of its entrance into the Kurdistan region until it overlapped with the Tigris River at the triple border point (Iraq, Surya, and Turkey). Temperature, pH, electrical conductivity, dissolved oxygen, total dissolved salts, and turbidity were tested locally in the field. Inductively coupled plasma optical emission spectroscopy (ICP-OES), flame photometer, and titration methods were used to analyses twenty-five metals in water samples. It was found that some heavy metals are undetectable such as Boron, Cadmium, Beryllium, Nickel, antimony, and selenium. Chromium was found in only one location with a concentration of 0.002 mg/L. Aluminum was found at higher than the acceptable levels in two areas with concentrations (0.215 and 0.1893 mg/L). Also, in two other points, Iron was found to be higher than the permissible level (0.397 and 0.311 mg/L). According to Iraqi and World Health Organization standards, other heavy metals were less than the affected value. The Water Quality Index (WQI) was calculated to evaluate water quality; the results shown water in one of the locations of the Khabur river was poor in quality, yet in other locations, it was good.

KEYWORDS: Khabur River, Heavy Metals, ICP-OES, Chemical Characterization, water quality index.

1. INTRODUCTION

Water is a natural resource that is required for many people's survival, and for all living organisms to carry out their biological functions. Because water is used for a variety of reasons, it is critical to consider the long-term advantages of water resources for future generations (Hering and Ingold 2012). River water is one of the most common sources of water; rivers are crucial components of the hydrological cycle and vital habitats for people; rivers offer water for humans to use in various activities such as farming, fishing, industry, and residential use. A river ecosystem's potential advantages include agricultural irrigation, fisheries, mineral water raw resources, rainwater and wastewater drainage, and river tourist objects (River et al. 2021).

Heavy metal ions (HMIs) are a micropollutant that is becoming more prevalent in the environment, affecting aquatic and terrestrial life. HMIs are present in cosmetics, by-products, fertilizers, and other industrial or household waste substances. These HMIs do not break down and accumulate in living organisms, causing various disorders and issues in the neurological, hormonal, immunological, and digestive systems. Since these HMIs are not biodegradable, they can persist in the environment for decades or even centuries. Among the most toxic heavy metals include mercury, cadmium, chromium, arsenic, and lead. Even trace levels of these very poisonous metals can severely affect the environment and human health. People are exposed to metal ions primarily via food, drink, and air (Gumpu et al.

2015b).

HMIs are also among the most common water and soil contaminants. It is vital to identify heavy metal ions in ambient and drinkable water and determine their quantities. As a result of environmental concerns, several international organizations, such as the World Health Organization (WHO), the European Union (EU), the United States Environmental Protection Agency (EPA), the Center for Disease Control (CDC), and the Combined Food and Agricultural Organizations (FAO), have designated HMIs as essential materials to be monitored and have defined acceptable levels for their concentrations in water and soil. (Gumpu et al. 2015a; Reiling, Roberrson, and Cromwell III 2009; SANGWIJIT 2019; WHO 2011).

Recently studies on excessive levels of dissolved metals in aquatic environments have gotten a lot of press across the world (Alsaffar, Suhaimi Jaafar, and Ahmad Kabir 2016; Bingöl et al. 2010; Koesmawati, Tanuwidjaja, and Nurachman 2021; Roberto Gutiérrez et al. 2008).

inductively coupled plasma optical emission spectroscopy (ICP-OES), Atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectroscopy (ICP-MS), neutron activation analysis (NAA), and x-ray fluorescence spectroscopy (XFS) are examples of highly sensitive spectroscopic techniques, in terms of determining HMI concentrations for a variety of samples at the same time, these methods are useful. Furthermore, these methods have a low detection limit (LOD) in the femtomolar range (Pujol et al. 2014).

to determine heavy metals in environmental samples, the most common techniques used nowadays involve highly sensitive spectroscopic techniques, such as atomic absorption spectrometry (Alves, Correia dos Santos, and Trancoso 2009; Carril, Corbillón, and Madariaga 1997; Jindy, Qasim, and Mohamad 2020; Sastre et al. 2002; Trancoso, Correia dos Santos, and Simões Gonçalves 2003). inductively coupled plasma mass spectrometry (ICP-MS)(Chaves et al. 2010; Chudzinska, Debska, and Baralkiewicz 2012), and inductively coupled plasma optical emission spectrometry (ICP-OES)(Abdulla, Jamil, and Aziz 2020; Al- Barwary 2021; Asare, Assim, and Wahi 2020; Ghannam et al. 2014; Kumar and Acharya 2021).

In the current study, waters of the Khabour River from Zakho city in the Kurdistan region of Iraq were studied. ICP-OES instrument was used for the analysis of these elements (Pb, As, Fe, Zn, Sb, Ni, Cu, Co, Cr, V, Ti, Tl, Se, Mg, Al, Mn, Ba, Be, B, Cd, Mo, and, Sr). (Na and, K) by flame photometer. However, anions such as NO_3^-, Cl^-, and, SO_4^{2-} have been measured with different methods; NO_3^- and SO_4^{2-} by using UV-visible spectroscopy, and Cl^- by Mohr's method which is the titration method. Also, some measurements were made in water samples such as dissolved oxygen (DO), turbidity, conductivity, total dissolved solids (TDS), temperature, and pH, by using portable devices.

Water quality indexes (WQI) have been calculated to determine how suitable water is for a wide range of purposes. WQI is based on a contrast between a water quality parameter and the corresponding regulatory limits (Soaded Alsaqqar, Hashim, and Mahdi Ali 2015). For reliable communication to managers and the general public, (WQI) condenses enormous volumes of data about water quality into simple phrases (such as bad, good, Excellent, etc.)(Boyacioglu 2010). WQI may be used as a tool for evaluating the water quality of various sources and it provides the general public with an overview of any potential water issues in a given area. The indices are among the best tools for communicating water quality trend data for management purposes (Jagadeeswari and Ramesh 2012).

There are several common formulas for measuring WQI including

I. Cumulative formulation

this formula was developed by (Horton 1965), who made the notion of water quality index suggestion, and it served as the foundation for creating the index. This formula is written as follows:

$$WQI = \frac{\sum_{i=1}^{n} Ci.Wi}{\sum_{i=1}^{n} Wi} \qquad (1)$$

Where:

WQI: water quality index

n: number of determinants.

Ci: the rating for the ith determinants.

M1, M2: additional determinant parameters.

Wi: the weighting for the determinants.

II. Arithmetic Weighted Formula

This formula was developed by (Brown et al 1974), (Couillard and Lefebarre, 1986), (Brown et al. 1972),(Alsaqqar, Hashim, and Mahdi 2015) and It is as follows:

$$WQI = \frac{\sum_{i=1}^{n} Ci.Wi}{\sum_{i=1}^{n} Wi} \qquad (2)$$

Where:
n: number of determinants.
Qi: the rating for ith determinants, this value varies from (0-100).
Wi: the weighting for the ith determinant, this value varies between (0-1) and the $\sum Wi$ =1.

III. Geometric Weighted Mean

The multiplicative weighted formula was derived by (Brown et al., 1970) using the same symbols as the arithmetic weighted formula. The formula is written as follows:

$$WQI = \pi \sum_{i=1}^{n} Qi\,.Wi \qquad (3)$$

IV. Modified Arithmetic Weighted

A modified arithmetic weighted formula was proposed in 1976 by the Scottish Development Department (SSD). The following is the formula, which was deemed to be sufficiently sensitive for the Scottish water quality conditions:

$$WQI = 1/100 \sum_{i=1}^{n} (Qi\,.Wi)^2 \qquad (4)$$

2. MATERIALS AND METHOD

2.1 STUDY AREA

Khabur, also recognized as the Little Khabur (in Kurdish: Xabîr, Xabûr, Turkish: Habur, Khabir, or Habur Suyu or, AvaXbûr. In Arabic: Nahr Al-Khabur (Al-Khabur River)). The length of Khabur river is 90 kilometers it originates in Turkey and flows through Iraq to link to the Tigris River at the tripoint of Iraq, Turkey, and Syria. The river rises in turkey's louder district from a series of small rivers that flow off the Taurus Mountains to the southeast of Hakkari. From there, it normally runs south, passages the Turkish-Iraqi border into Iraqi Kurdistan before rotating west to the Tigris. Zakho is a significant town along the river, where the historic Delal Bridge spans it. The Little Khabur is joined by its main branch, the Hezil River a few kilometers west of Zakho, The Khabur River and the Tigris form a border of about 20 km between the countries of Iraq, Turkey and Syria (Ibrahim Galalaye 2019). The study area is located in the Zakho District; the study region is located around 55 kilometers north of Duhok Governorate figure 1.

2.2 SAMPLING

Water samples were collected from ten different locations along the Khabur River in September 2021. Figure 1 shows the distribution of sampling points and more information about samples are presented in table 1. samples were collected into plastic washed buttle by HNO_3 Sampling bottles were washed with 10% HNO_3 and deionized water. from more than 10 cm waters depth samples were taken and, were acidified to approximately to pH = 2 using pure nitric acid to prevent metal absorption into the wall of the bottles and avoid precipitation of metals (Federation 2012)

(Alsaffar et al. 2016) Before acidification, at the sampling sites, the same parameter has been read such as temperature pH, dissolved oxygen, total dissolved salt, electrical conductivity, and turbidity at the sample area. All collected samples were then transported to the laboratory.

TABLE.1
characteristic of the sampling area

Stations	Name of area	Major activity	Location
W1	Kesta	Before the Khabur River reaches the Begova complex	37°14'46.2"N 43°10'06.5"E
W2	Govke	After the Khabur River pass through the Begova complex	37°06'45.5"N 43°04'26.6"E
W3	Gondkosa	After the Khabur River pass through Gondkosa village	37°05'07.8"N 42°56'17.5"E
W4	Beraka	The village before the Tawke oil field operated by DNO	37°06'50.6"N 42°46'25.4"E
W5	Chamsirmo	Before Zakho city	37°07'58.4"N 42°42'45.2"E
W6	Ashechame	Inside the city of Zakho	37°08'41.2"N 42°40'48.5"E
W7	Bedar	Near Ibrahim Khalil border crossing	37°09'10.9"N 42°38'34.7"E
W8	Hezil River	Another River sample was taken before it overlapped with Khabur (it's the Turkey and Iraq border), the Durnax area	37°12'24.2"N 42°37'06.3"E
W9	Khabur & Hezil rivers	After overlapping Hezil and Khabur river	37°08'27.7"N 42°31'20.4"E
W10	Khabur & Hezil & Tigris rivers	After overlapping Khabur and Hezil with the Tigris River Near the triple point of Turkey, Surya and Iraq border	37°02'42.5"N 42°22'39.8"E

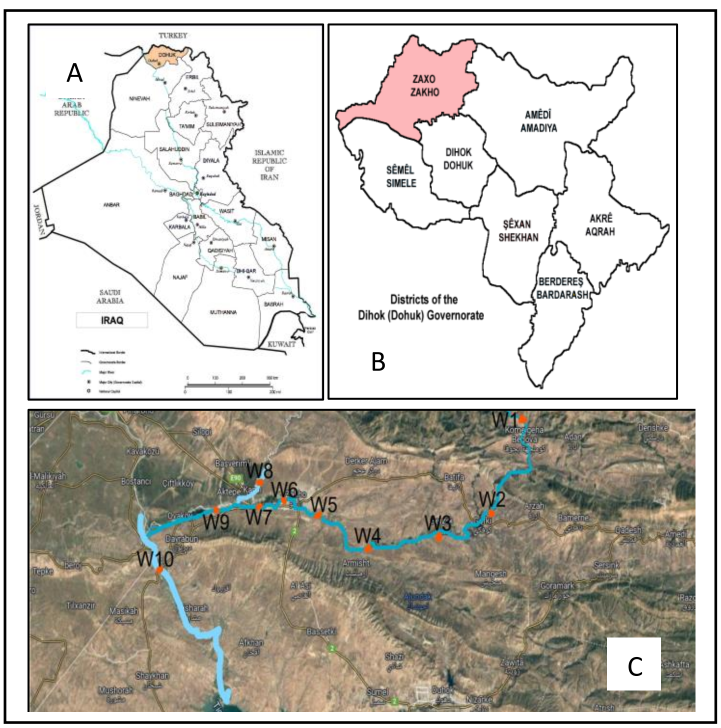

Fig.1. A; Iraq government, B; Duhok distract-Zakho, C; location of the samples taken by GPS source google map

2.3. ANALYTICAL METHODS

2.3.1 IN SITU ANALYSIS

The physical and chemical variables that were measured directly in samples stations by using portable instruments such as; Temperature, pH (Anecity pen type), dissolved oxygen (HANNA HI 9146), total dissolved solids, electrical conductivity EC (Wagtech conductivity/TDS/℃ meter), and turbidity (LaMotte 2020i).

TABLE 2
Parameter and accessories of ICP-OES instruments

Parameter	Conditions
Carrier gas	Argon
UV exposure time (sec)	15
Plasma viewing	Axial
RF power (kW)	1.15
Plasma gas flow rate (L /min)	15
Nebulizer gas flow rat (L/min)	0.5
Auxiliary gas flow rat (L/min)	0.5
VIS exposure time (sec)	5
Number of replicates	3
Detector Type	High-performance solid-state CID86 chip

2.3.2 IN VITRO ANALYSIS

All of the chemicals used are of the highest purity and quality which made by many companies and countries, including Sigma-Aldrich in China, Biochim in France, Alfa Aeser in Germany, ALPHA CHEMICA in India, Merck in Germany, and Scharlau in Spain. Multi elements ICP-OES standard solution 27 E from ChemLab in Belgium. The different methods used to determine the concentration of heavy metals in water samples. Flame photometer (Jenway PfP7, UK) used for determination of Na and K. also, Pb, As, Fe, Zn, Sb, Ni, Cu, Co, Cr, V, Ti, Tl, Se, Mg, Al, Mn, Ba, Be, B, Cd, Mo, and, Sr elements were determined by using inductively coupled plasma optical emission spectrometry (ICP-OES) (by instrument Thermo Scientific iCAP 7000 SERIES, Germany) in Parwezxan-Kalar by lox agency Company for quality control in advance chemistry Lab. Validation of analysis shown in table 3. The emission wavelength of each element is shown in table 4. ICP-OES parameters and accessories are shown in table 2. Sulphate was measured by turbidimetric method 9038 (with mobile device LaMotte 2020i). by putting the sample to the flask for the formation of barium sulphate then adding conditional reagent with mixing then add barium chloride, stirring for one minute put the solution into absorbance cells for measuring turbidity prepare calibration carve calculate sulphate concentration (APhA 2005) figure 2. Nitrate concentration was measured by using an instrument UV-visible spectrophotometer (Perkin Elmer Lambda 25) the absorption value of nitrate ion at the wavelength of 220 nm is used to calculate the amount of nitrate present. However, since the dissolved organic matter was absorbed in both 220nm and 275nm but not nitrate ion, a second measurement at 275 nm is taken to correct this ($A=A_{220}-2A_{275}$) (Wei 2002) depending on calibration curve of standard concentration with wavelength nitrate concentration has been determined figure 3. Chloride ion concentration was measured by titration method (Mohr's method), chloride ion concentration of the given solution is determined by titrating with silver nitrate, silver. nitrate precipitate was formed, and potassium chromate was used as an indicator to observe the endpoint of titration (Korkmaz 2011). Calcium concentration in water samples was determined by the complexometric titration method using EDTA as titrant and murexide indicator. Magnesium was estimated from calcium and total hardness titrations (Megh R. Goyal 2017).

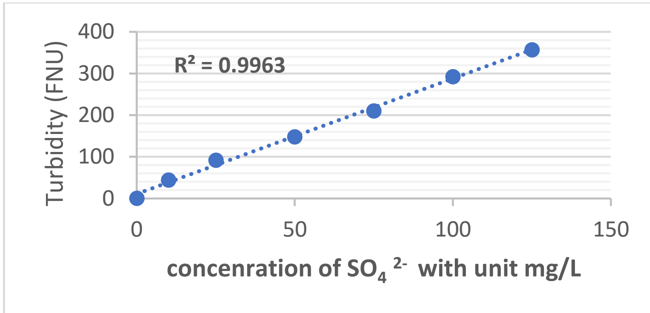

Figure 2. calibration curve of Sulphate.

TABLE 3
Method validation results of ICP-OES for metal measurement

Metals	Al	Ba	Cu	Fe	Pb	Mn	Mo	Sr	Ti	Tl	V	Zn	As	Co
Coefficient of correlation (r2)	0.9965	0.9994	0.9997	0.9999	0.9996	0.9993	1	0.9991	0.9988	1	0.9998	0.9997	0.9998	0.9999
%RSD	2.389	2.309	3.2925	1.434	3.183	3.216	2.994	0.813	2.225	2.92	1.888	2.06	3.1	2.039
MQL	0.007	0.001	0.01	0.009	0.004	0.006	0.002	0.0001	0.0002	0.02	0.017	0.001	0.018	0.001
LOD (mg/)	0.0022	0.0004	0.0031	0.0027	0.0013	0.0018	0.0007	0.0001	0.0001	0.0059	0.0052	0.0002	0.0054	0.0004
LOQ (mg/L)	0.0066	0.0012	0.0093	0.0081	0.0039	0.0054	0.0021	0.0003	0.0003	0.0177	0.0156	0.0006	0.0162	0.0012
BEC (mg/L)	0.021	0.005	0.021	0.03	0.007	0.013	0.0001	0.0003	0.001	0.005	0.110	0.008	0.006	0.002

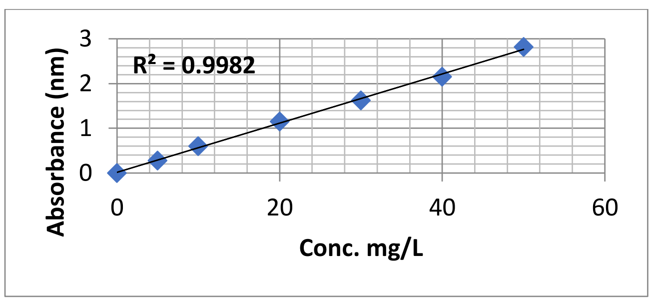

Figure 3. Calibration curve of nitrate.

TABLE 4
Detection wavelength of ICP-OES for each element

Elements	Wavelength (nm)/order	Measure mode
Pb	220.353 {453}	Axial
Sb	206.833 {463}	Axial
As	189.042 {478}	Axial
Zn	213.856 {458}	Axial
Cu	324.754 {104}	Axial
Ni	221.647 {452}	Axial
Co	228.616 {447}	Axial
Fe	259.940 {130}	Axial
Mn	257.610 {131}	Axial
Cr	283.563 {119}	Axial

V	309.311 {109}	Axial
Ti	334.941 {101}	Axial
Tl	190.856 {477}	Axial
Se	196.090 {472}	Axial
Mg	279.553 {121}	Axial
Al	167.079 {502}	Axial
Sr	407.771 {83}	Axial
Ba	455.403 {74}	Axial

3. RESULTS AND DESICCATION

3.1 TURBIDITY

Turbidity refers to water clearly. In some locations, water was colorless with very low turbidity especially in W1 and W5, on another hand in W8 water the turbidity was at a very high level, also in W2 turbidity is at a high level due to the sand mining process table 5. The maximum acceptable concentration of turbidity according to Iraqi and WHO is 5 FNU, results of turbidity are unacceptable in all locations except W1 and W5. The results are significantly higher than those obtained by (Ibrahim, Al-Tawash, and Abed 2018)

3.2 ELECTRICAL CONDUCTIVITY

Conductivity in all samples was between (388 – 555 $\mu S/cm1$) and these results are considered at an acceptable level according to Iraqi and the World Health Organization table 5. The results are significantly like those obtained by (Al- Barwary 2021) in the same river.

3.3 POWER OF HYDROGEN (pH)

standard concentration of pH is (6.5-8.5) for drinking water maximum value was recorded was 8.2 and the minimum value was 7.8 as represented in table 5. that means at all sites the value of pH is an acceptable level. They have a significant Same result (Yousif 2016).

TABLE 5
Physical Parameter of Khabur's Water

Samples	pH	Temperature (℃)	Conductivity ($\mu S/cm$)	TDS mg/L	Dissolved oxygen mg/L	Turbidity (FNU)	Total hardness mg/L	Alkalinity As CaCO3 mg/L
W1	8.1	18.5	420	240	7.3	2.25	210	*165*
W2	8	19	457	260	7.1	68.9	224	*170*
W3	8.1	19.8	449	233	7.4	11.6	226	*155*
W4	8.3	21.7	430	229	6.5	8.87	214	*155*
W5	7.8	24	398	213	7.8	1.75	204	*135*
W6	7.8	25	427	268	7.3	6.87	236	*137*
W7	8.2	24.5	415	224	7.20	8.84	228	*141*
W8	7.9	22.4	555	279	6.71	190	270	*135*
W9	8	23	468	255	7.00	38	232	*138*
W10	8.2	20	388	220	7.13	25.6	230	*133*
Average	8.0	21.8	440.7	242.1	7.1	36.27	210	146.4
Iraqi specification	6.5-8.5	Not specified	2000	1000	Not specified	5	500	*125-200*
WHO specification	6.5-8.5	Not specified	600	1000	5-8.6	5	500	600

3.4 TOTAL DISSOLVED SOLIDS

Total Dissolved Solids (TDS) are the total quantity of transportable charged ions, counting minerals and salts (Al-heety, Turky, and Al-othman 2011). TDS is directly correlated to water purity. In this study TDS values ranged between 213-270 mg/L. Iraqi and WHO standard is lower than 1000 mg/L, meaning water quality is at an acceptable level.

3.5 TOTAL HARNESS

the concentration of total hardness in all locations were between (204-270 mg/L) as $CaCO_3$. acceptable value of total hardness according to Iraqi and WHO (World Health Organization 2017) (Herschy 2012) standard is 500 mg/L results shown in table 5 Khabur water with acceptable level for drinking. This work results are very close to the results obtained by (Toma 2006).

3.6 TOTAL ALKALINITY

For surface water, the alkalinity values ranged from (133-170) mg/l as $CaCO_3$. The maximum value found was (170) mg/L as $CaCO_3$ at position W2, while the minimum was (133) mg/Las $CaCO_3$ at location W10. In general, the alkalinity values were within Iraqi and WHO drinking water requirements table 5. This work results are very close to the results obtained by (Barbooti et al. 2010)

3.7 . HEAVY METALS

Table 10 shows the results of heavy metals analysis by using ICP-OES, Chromium is only found in W8 with a concentration of 0.002 mg/L also, it is an acceptable level according to Iraqi and WHO guidelines. The amount of aluminum present in all locations was below the required level according to Iraqi and, WHO, which is (0.01 - 0.02 mg/L) except for W6 and, W8 0.215 and 0.277 mg/L which are a little higher than the acceptable level. The maximum acceptable concentration of copper is (2 mg/L) according to WHO, all samples are below this ratio and the maximum value is 0.095 mg/L in the W5 sample Copper is not found in the location. Recommended or healthy level of Iron in drinking water is less than (0.3 mg/L) according to Iraqi and WHO, only W8 and, W9 are higher than the acceptable levels which are (0.397 and, 0.311 mg/L) consecutively. The guideline value of barium in drinking water is (0.7 mg/L in WHO and 0.3 in Iraqi) in all locations considered with the guideline. Lead as a toxic element was found in all samples but with levels less than guidelines according to Iraqi and, WHO. Molybdenum is also, found in acceptable levels in all locations below 0.07 mg/L which is an acceptable level according to WHO and is not specified in Iraqi guidelines (Organization 2003) (Quality 1996). The maximum permitted content of titanium in drinking water is thought to be 0.1 mg/L according to (Dong et al. 1993), but it is not mentioned in Iraqi and WHO guidelines. In general, drinking water sources have low levels of titanium in all locations it was between (0.004-0.014 mg/L) lowest concentration in W10 and higher concentration of titanium found in W1 and, W4. Strontium concentration was found between (0.4-1.7 mg/L) highest concentration found in W8 and lowest in W10 locations. Strontium high concentration in drinking water causes bone softening or weakening, inhibits growth, and causes bone abnormalities, but WHO, the European Union, and Australia have not set health-based strontium limitations in drinking water. In another hand One of the first nations to create health-based guidelines for strontium in drinking water was Canada's acceptable value according to Canada guideline is (7 mg/L)(Talk et al. 2019). Manganese can cause test and smell bad of water, in this study the level of manganese was less than harmed level for humans (0.4 mg/L) according to Iraqi and, WHO guidelines, in locations W1, W4, W5, and W6 it does not detect. Thallium has a maximum contamination limit (MCL) in drinking water of 0.002 mg/L according to Canadian guideline (Environment 2002), W2, W3, W4, W5, W6, W8, higher than the acceptable value which causes nerve damage and gastrointestinal irritation, water with a high level of thallium should be treated to remove thallium (Xu et al. 2019). The value of vanadium concentrations was between (0.013-0.04 mg/L), the highest value obtained was (0.04 mg/L) in W7 and, the lowest value was (0.013 mg/L) in W6. Vanadium concentration is not specified by Iraqi and WHO standardization, it has been proposed that vanadium may operate as a regulator for enzymatic activities in mammalian tissues, which could have a substantial impact on human nutrition. Vanadium deficiency has been linked to reduced growth, impaired reproduction, and changes in lipid metabolism. Numerous enzymes are effectively inhibited by vanadium (Nielsen 1987). Cobalt concentration ranged from (0.001 to 0.002 mg/L). cobalt concentrations were very similar to those in (Gokalp and Mohammed 2019) findings for the Heshakaro River in Duhok-Iraq, the results are with the acceptable value of cobalt according to Iraqi Specification, Cobalt level is not specified by WHO. Also, ICP-OES analysis data shows that in all stations some heavy metals are below LOD (not detected) in Khabur water such as Boron, Cadmium, Antimony, Selenium, and, nickel.

As presented in table 11. concentrations of Potassium and, in all locations with guidelines according to Iraqi and WHO guidelines. On another hand, Magnesium was found in all locations with a concentration between (12-19 mg/L), which is a very low value according to Iraqi and WHO specifications. The value of calcium concentrations was between (53-80 mg/L), the highest value obtained was (80 mg/L) in W8 and, the lowest value was (53 mg/L) in W6, according to Iraqi specifications in all stations it is an acceptable value, but according to WHO specification W8 and, W9 was in unacceptable value.

TABLE 10
Elements concentration measured by ICP-OES with unit mg/L

	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	Average	Iraqi specification	WHO specification
Al	0.02	0.018	0.001	0.008	0.008	0.215	0.024	0.227	0.1893	0.082	0.0792	0.2	0.2
Ba	0.068	0.082	0.089	0.091	0.088	0.088	0.084	0.056	0.0857	0.054	0.0786	0.7	0.3
Fe	0.079	0.15	0.078	0.06	0.025	0.1	0.048	0.397	0.3107	0.101	0.1349	0.3	0.3
Pb	0.0089	0.005	0.004	0.004	0.005	0.003	0.006	0.006	0.0058	0.005	0.0053	0.01	0.01
Mn	ND*	0.011	0.001	ND*	ND*	ND*	0.006	0.01	0.014	0.003	0.0045	0.1	0.1
Sr	0.742	0.771	0.706	0.708	0.656	0.643	0.639	1.233	0.78	0.454	0.733	Not specified	Not specified
Mo	0.0015	0.001	0.001	0.001	0.001	0.001	0.001	0.005	0.0025	0.003	0.0018	Not specified	0.07
Ti	0.014	0.011	0.011	0.014	0.01	0.012	0.011	0.011	0.012	0.004	0.011	Not specified	Not specified
Cu	0.003	0.004	0.003	0.002	0.095	ND*	0.025	0.003	0.0036	0.006	0.0161	1	2
V	0.026	0.029	0.035	0.033	0.037	0.013	0.04	0.035	0.029	0.023	0.03	Not specified	Not specified
Zn	0.004	0.005	0.007	0	0	0.003	0.005	0.008	0.007	0.002	0.0051	3	Not specified
As	0.0029	0.003	0.003	0.003	0.001	0.003	0.002	0.002	0.002	0.002	0.0024	0.01	0.01
Co	0.001	0.001	0.001	0	0.001	0.001	0	0.002	0.001	0.001	0.0011	0.05	Not specified
Cr	ND*	ND*	ND*	ND*	ND*	ND*	ND*	0.002	ND*	ND*	0.002	0.05	0.05
Tl	0.002	0.004	0.003	0.003	0.004	0.004	0.002	0.003	0.002	0.002	0.0029	Not specified	Not specified

TABLE 11
Elements were detected by flame photometer and titration methods, with unit mg/L

	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	Average	Iraqi specification	WHO specification
K	2.07	1.17	1.26	3.62	1.44	1.62	2.25	2.89	2.53	2.53	2.14	10	10
Na	11.17	12.09	12.09	13.01	13.01	17.63	20.4	21.32	20.4	23.17	16.43	50	50
Ca	56	59	60	61	54	53	54	80	75	62	61.4	150	75
Mg	15	12	15	15	14	17	19	10	11	15	14.3	100	125

3.8 ANIONS CONCENTRATION

Sulphate is found in arrange between (47.7-100.8 mg/L) table 6. it was acceptable values according to Iraqi and WHO specifications in drinking water. Sulphate sensitivity is greater in children than in adults. Water with a Sulphate level greater than 400 mg/L should not be used in the making of infant food as a precaution (WHO directives). After a few days, older children and adults become accustomed to high sulphate levels. In any case, high sulphate water should be side-stepped while rehydrating diarrhea patients (Barbooti et al. 2010). The results of this study are less than the results of a study that were carried out by (Al-Shujairi, Sulaiman, and Najemalden 2015) on the Tigris river. Nitrate is found in very low concentration levels which are between (0.4-4.2 mg/L) table 6, it was an acceptable value according to Iraqi and WHO permission values. When nitrate is consumed under circumstances that promote the creation of N-nitroso compounds, there may be an elevated risk of some cancers and birth problems (Ward et al.

2018). The results of this study are less than the results of a study that was carried out by (Kadhem 2013). Chloride concentration in all sites of Khabur River were within the Iraqi and WHO drinking water Standard, which is represented in table 6. The concentrations were between (12.5 to 30 mg/L). The results of this study are less than the results of a study that was carried out by (Ewaid, Abed, and Kadhum 2018).

3.9 WATER QUALITY INDEX (WQI)

In the current study arithmetic weighted formula method has been used which was had developed by (Brown et al. 1972). The value of twenty parameters is used to calculate water quality index, and WHO guidelines standards are used table 7. Classification of water as quality index according to weighted formula method (Boah, Twum, and Pelig-Ba 2015) shown in table 8. WQI results were obtained by some complex and accurate calculations, in the W1 site recorded the largest value, and it mean the water in this site is good in terms of quality, while the rest of the sites have a lower value of WQI and poor in quality table 9.

TABLE 6
Concentration of Anions

Samples	SO_4^{2-} mg/L	NO_3^- mg/L	Cl^- mg/L
w1	47.7	0.9	18.0
w2	52.7	1.1	17.5
w3	52.0	0.9	17.0
w4	50.2	0.8	30.0
w5	48.4	0.4	12.5
w6	50.2	0.7	21.5
w7	54.2	1.0	20.0
w8	110.8	1.4	14.0
w9	72.2	1.4	19.0
w10	57.8	4.2	24.5
Average	59.62	1.28	19.4
Iraqi specification	400	50	250
WHO specification	250	50	350

TABLE 7
WQI CALCULATION FOR LOCATION W1

parameters	Mean of Observed Value In W1 location	Sn	K=1/∑(1/Sn)	Wi=K/Sn	Ideal value	Vn/Sn	Qn=Vn/Sn*100	Wn.Qn
pH	8.100	8.500	0.004	0.001	7.000	0.733	73.333	0.038
Conductivity	420.000	300.000	0.004	0.000	0.000	1.400	140.000	0.002
TDS	240.000	500.000	0.004	0.000	0.000	0.480	48.000	0.000
Dissolved oxygen	7.300	5.000	0.004	0.001	14.600	0.760	76.042	0.067
Turbidity (FNU)	2.250	5.000	0.004	0.001	0.000	0.450	45.000	0.040
Total hardness mg/L	210.000	300.000	0.004	0.000	0.000	0.700	70.000	0.001
Alkalinity	165.000	200.000	0.004	0.000	0.000	0.825	82.500	0.002
Al	0.020	0.200	0.004	0.022	0.000	0.100	10.000	0.221
Ba	0.068	0.300	0.004	0.015	0.000	0.227	22.667	0.333
Fe	0.079	0.300	0.004	0.015	0.000	0.263	26.333	0.387
Pb	0.009	0.010	0.004	0.441	0.000	0.890	89.000	39.267
Mo	0.002	0.070	0.004	0.063	0.000	0.021	2.143	0.135
As	0.003	0.010	0.004	0.441	0.000	0.290	29.000	12.795
K	2.070	10.000	0.004	0.000	0.000	0.207	20.700	0.009
Na	11.170	50.000	0.004	0.000	0.000	0.223	22.340	0.002
Ca	56.000	75.000	0.004	0.000	0.000	0.747	74.667	0.004
Mg	15.000	125.000	0.004	0.000	0.000	0.120	12.000	0.000
SO42-	47.700	250.000	0.004	0.000	0.000	0.191	19.080	0.000
NO3-	0.900	50.000	0.004	0.000	0.000	0.018	1.800	0.000
Cl-	18.000	250.000	0.004	0.000	0.000	0.072	7.200	0.000
				∑=1.000				∑=53.305

Qi: the rating for ith determinants. Wi: the weighting for the ith determinant, this value varies between (0-1) and the $\sum Wi$ =1. Sn: Standard value by WHO. $WQI = \sum_{i=1}^{15} Qi.\ Wi \,/ \sum_{i=1}^{15} Wi$ = 53.305/1 =53.305

TABLE 8
Classification of water quality according WQI

WQI value	Status
0-25	Excellent
26-50	Good
51-75	Poor
76-100	Very poor
WQI>100	Unsuitable for uses

source: (Brown et al. 1972),(Boah et al. 2015)

TABLE 9
WQI for all locations in Khabur river

Location	WQI	Status
W1	53.38	Poor
W2	38.13	Good
W3	32.2	Good
W4	32.15	Good
W5	27.34	Good
W6	30.1	Good
W7	36.6	Good
W8	43.9	Good
W9	39.47	Good
W10	33.2	Good

4. CONCLUSION

The current study a to assess how the discharge of untreated wastewater from the Khabur River will affect the quality of the river water. The result of this study demonstrated several chemical and physical parameters, including pH, dissolved oxygen, total alkalinity, conductivity, and total dissolved salt. Nitrate, sulphate, and chloride concentration, were within the generally accepted range. The turbidity of water in all sample was over acceptable value according to Iraqi and WHO specification. Also, all heavy metal concentration were within acceptable value excepted aluminium at W6 is 0.215 and, at W8 is 0.277 mg/L little higher than WHO specifications, iron only in W8 and, W9 higher than the acceptable level which is 0.397 and, 0.311 consecutively shown in table 3. Thallium has a maximum contamination limit (MCL) in drinking water of 0.002 mg/L according to Canadian guideline in W2, W3, W4, W5, W6, W8, table 3 was higher than acceptable value which causes nerve damage and gastrointestinal irritation, water with high level of thallium should be treatment to remove thallium. The WQI values represented that quality of water at the Khabur river is good except W1 location.

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REFERENCE

Abdulla, S. M., D. M. Jamil, and K. H. H. Aziz. 2020. "Investigation in Heavy Metal Contents of Drinking Water and Fish from Darbandikhan and Dokan Lakes in Sulaimaniyah Province-Iraqi Kurdistan Region." *IOP Conference Series: Earth and Environmental Science* 612(1). doi: 10.1088/1755-1315/612/1/012023.

Al- Barwary, Musher R. A. 2021. "Seasonal Assessment of Chemical and Physical Characterization of Khabur River, Zakho District, Kurdistan Region/Iraq -A Case Study." *Science Journal of University of Zakho* 9(3):149–57. doi: 10.25271/sjuoz.2021.9.3.814.

Al-heety, Emad A., Ahamed M. Turky, and Eethar M. Al-othman. 2011. "Physico-Chemical Assessment of Euphrates River between Heet and Ramadi Cities , Iraq." 2011(November):812–23. doi: 10.4236/jwarp.2011.311091.

Al-Shujairi, Sabah Obaid Hamad, Sadeq Oleiwi Sulaiman, and Mohamed A. Najemalden. 2015. "Variations of Major Ionic Composition and Salinity of Tigris River within Iraq." *Sulaimani Journal for Engineering Sciences* 2(2):64–73. doi: 10.17656/sjes.10025.

Alsaffar, M. S., M. Suhaimi Jaafar, and N. Ahmad Kabir. 2016. "Evaluation of Heavy Metals in Surface Water of Major Rivers in Penang , Malaysia." *International Journal of Environmental Sciences* 6(5):657–69. doi: 10.6088/ijes.6062.

Alsaqqar, Awatif Soaded, Athraa Hashim, and A. Mahdi. 2015. "Water Quality Index Assessment Using GIS Case Study: Tigris River in Baghdad City." *International Journal of Current Engineering and Technology* 5(4):2515–20.

Alves, Sheila, Margarida Maria Correia dos Santos, and Maria Ascensao Trancoso. 2009. "Evaluation of Measurement Uncertainties for the Determination of Total Metal Content in Soils by Atomic Absorption Spectrometry." *Accreditation and Quality Assurance* 14(2):87–93.

APhA, WPCF. 2005. "Awwa." *Standard Methods for the Examination of Water and Wastewater, 21st Ed., American Public Health Association (APHA), Washington, DC.*

Asare, Ebenezer Aquisman, Zaini Bin Assim, and Rafeah Binti Wahi. 2020. "Geochemistry Examination of Surface Sediments from Sadong River , Sarawak , Malaysia : Validation of ICP-OES Assessment of Selected Heavy Metals." (December).

Barbooti, M. .., G. Bolzoni, I. .. Mirza, M. Pelosi, I. Barilli, R. Kadhum, and G. Peterlongo. 2010. "Evaluation of Quality of Drinking Water from Baghdad, Iraq." *Science World Journal* 5(2):35–46. doi: 10.4314/swj.v5i2.61512.

Bingöl, Mehmet, Gülderen Yentür, Buket Er, and Aysel Bayhan Öktem. 2010. "Determination of Some Heavy Metal Levels in Soft Drinks from Turkey Using ICP-OES Method." 28(3):213–16.

Boah, Douglas Kwasi, Stephen Boakye Twum, and Kenneth B. Pelig-Ba. 2015. "Mathematical Computation of Water Quality Index of Vea Dam in Upper East Region of Ghana." *Environmental Sciences* 3(February):11–16. doi: 10.12988/es.2015.4116.

Boyacioglu, Hülya. 2010. "Utilization of the Water Quality Index Method as a Classification Tool." *Environmental Monitoring and Assessment* 167(1):115–24.

Brown, Robert M., Nina I. McClelland, Rolf A. Deininger, and Michael F. O'Connor. 1972. "A Water Quality Index—Crashing the Psychological Barrier." Pp. 173–82 in *Indicators of environmental quality*. Springer.

Carril, M. Paz, M. Soledad Corbillón, and J. Manuel Madariaga. 1997. "Validation of an Analytical Method to Determine Trace Metal Impurities in Fluoride Compounds by Flame Atomic Absorption Spectroscopy." *Accreditation and Quality Assurance* 2(6):301–8.

Chaves, Eduardo S., Eder José dos Santos, Rennan G. O. Araujo, José Vladimir Oliveira, Vera Lúcia A. Frescura, and Adilson J. Curtius. 2010. "Metals and Phosphorus Determination in Vegetable Seeds Used in the Production of Biodiesel by ICP OES and ICP-MS." *Microchemical Journal* 96(1):71–76.

Chudzinska, Maria, Anna Debska, and Danuta Baralkiewicz. 2012. "Method Validation for Determination of 13 Elements in Honey Samples by ICP-MS." *Accreditation and Quality Assurance* 17(1):65–73.

Dong, S. Z., C. Z. Chen, D. M. Li, and Y. S. Sun. 1993. "[A study of hygienic standard for titanium in the source of drinking water]." *Zhonghua yu fang yi xue za zhi [Chinese journal of preventive medicine]* 27(1):26–28.

Environment, Canadian Council of Ministers of the. 2002. *Canadian Environmental Quality Guidelines*. Vol. 2. Canadian Council of Ministers of the Environment.

Ewaid, Salam Hussein, Salwan Ali Abed, and Safaa A. Kadhum. 2018. "Prediction the Tigris River Water Quality within Baghdad , Iraq by Using Water." *Environmental Technology & Innovation*. doi: 10.1016/j.eti.2018.06.013.

Federation, Water Environment. 2012. "APHA, AWWA, WEF. 'Standard Methods for Examination of Water and Wastewater.'" *Anales de Hidrología Médica* 5(2):185-186–186.

Ghannam, Hala E., A. S. Talab, S. E. Gaber, and H. S. Jahin. 2014. "Assessment of Heavy Metals Distribution in Some Freshwater Fish Organs Using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)." *Ecology, Environment and Conservation* 20(2):467–78.

Gokalp, Zeki, and Dilshad Mohammed. 2019. "Assessment of Heavy Metal Pollution in Heshkaro Stream of Duhok City, Iraq." *Journal of Cleaner Production* 237:117681. doi: 10.1016/j.jclepro.2019.117681.

Gumpu, Manju Bhargavi, Swaminathan Sethuraman, Uma Maheswari Krishnan, and John Bosco Balaguru Rayappan. 2015a. "A Review on Detection of Heavy Metal Ions in Water–an Electrochemical Approach." *Sensors and Actuators B: Chemical* 213:515–33.

Gumpu, Manju Bhargavi, Swaminathan Sethuraman, Uma Maheswari Krishnan, and John Bosco Balaguru Rayappan. 2015b. "A Review on Detection of Heavy Metal Ions in Water - An Electrochemical Approach." *Sensors and Actuators, B: Chemical* 213(July):515–33. doi: 10.1016/j.snb.2015.02.122.

Hering, Janet G., and Karin M. Ingold. 2012. "Water Resources Management: What Should Be Integrated?" *Science* 336(6086):1234–35.

Herschy, Reginald W. 2012. "Water Quality for Drinking: WHO Guidelines." *Encyclopedia of Earth Sciences Series* 876–83. doi: 10.1007/978-1-4020-4410-6_184.

Ibrahim Galalaye, Mohammed. 2019. *Zakho In the Perspective on Nineteenth Travelers*.

Ibrahim, Shatha Amer, Balsam Salim Al-Tawash, and Mahmood Fadhil Abed. 2018. "Environmental Assessment of Heavy Metals in Surface and Groundwater at Samarra City, Central Iraq." *Iraqi Journal of Science* 59(3):1277–84. doi: 10.24996/IJS.2018.59.3A.16.

Jagadeeswari, P. Bhuvana, and K. Ramesh. 2012. "Water Quality Index for Assessment of Water Quality in South Chennai Coastal Aquifer, Tamil Nadu, India." *International Journal of ChemTech Research* 4(4):1582–88.

Jindy, Jindy M., Amin K. Qasim, and Sagvan A. Mohamad. 2020. "Evaluation of Soil Pollution by Some Heavy Metals Via Atomic Absorption

Spectrophotometer (AAS) Technique in Zakho District, Kurdistan Region - Iraq." *Science Journal of University of Zakho* 8(4):145–48. doi: 10.25271/sjuoz.2020.8.4.765.
Kadhem, Abbas J. 2013. "Assessment of Water Quality in Tigris River-Iraq by Using GIS Mapping." *Natural Resources* 04(06):441–48. doi: 10.4236/nr.2013.46054.
Koesmawati, T. A., S. Tanuwidjaja, and A. Nurachman. 2021. "Method Validation of As, Cd, Cr, Cu, Mn, Ni, Se, and Zn Metals in Citarum River Sediment Using Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES)." *Journal of Physics: Conference Series* 1764(1). doi: 10.1088/1742-6596/1764/1/012030.
Korkmaz, Deniz. 2011. "Determination of Chloride Ion Concentration by Titration (Mohr's Method)." *University of Cantearbury* 1–2.
Kumar, Vikash, and Ashok K. Acharya. 2021. "Analysis the Amounts of Heavy Metals and Trace Elements in Water of Different Sources of Ranchi City by Using ICP-OES Technique Analysis the Amounts of Heavy Metals and Trace Elements in Water of Different Sources of Ranchi City by Using ICP-OES Technique." (December). doi: 10.13140/RG.2.2.31931.54569.
Megh R. Goyal, R. K. Sivanappan. 2017. *Engineering Practices for Agricultural Production and Water Conservation: An Interdisciplinary Approach*. Vol. 3. first edit. edited by R. K. S. Megh R. Goyal. Canada: Apple academic press.
Nielsen, Forrest H. 1987. "Vanadium." *Trace Elements in Human and Animal Nutrition: Fifth Edition* 3(V):275–300. doi: 10.1016/B978-0-08-092468-7.50013-2.
Organization, World Health. 2003. *Molybdenum in Drinking-Water: Background Document for Development of WHO Guidelines for Drinking-Water Quality*. World Health Organization.
Pujol, Luca, David Evrard, Karine Groenen-Serrano, Mathilde Freyssinier, Audrey Ruffien-Cizsak, and Pierre Gros. 2014. "Electrochemical Sensors and Devices for Heavy Metals Assay in Water: The French Groups' Contribution." *Frontiers in Chemistry* 2:19.
Quality, Drinking-water. 1996. "Molybdenum in Drinking-Water." *WHO Guidelines for Drinking-Water Quality* 2:7.
Reiling, Stephen J., J. Alan Roberrson, and John E. Cromwell III. 2009. "Drinking Water Regulations: Estimated Cumulative Energy Use and Costs." *Journal-American Water Works Association* 101(3):42–53.
River, Talawaan, North Minahasa District, North Sulawesi Province, Alfa Winny Pongoh, and Fadillah Putra. 2021. "Indonesian Journal of Environmental Management and Sustainability The Study of River Water Quality in Water Pollution Control : Case Study Of." (1).
Roberto Gutiérrez, L., Hector Rubio-Arias, Ray Quintana, Juan Angel Ortega, and Melida Gutierrez. 2008. "Heavy Metals in Water of the San Pedro River in Chihuahua, Mexico and Its Potential Health Risk." *International Journal of Environmental Research and Public Health* 5(2):91–98. doi: 10.3390/ijerph2008050011.
SANGWIJIT, CHONYITREE. 2019. "Comparative Study on the Determination Methodology of Total Suspended Solids by Using the Microwave and the Laboratory Standard Methods." *International Journal of Environmental and Rural Development* 10(1):82–87.
Sastre, J., A. Sahuquillo, M. Vidal, and G. Rauret. 2002. "Determination of Cd, Cu, Pb and Zn in Environmental Samples: Microwave-Assisted Total Digestion versus Aqua Regia and Nitric Acid Extraction." *Analytica Chimica Acta* 462(1):59–72.
Soaded Alsaqqar, Awatif, Athraa Hashim, and Amal Mahdi Ali. 2015. "Water Quality Index Assessment Using GIS Case Study: Tigris River in Baghdad City." *2515 | International Journal of Current Engineering and Technology* 5(4):2515-20.
Talk, Water, Strontium July, Health Canada, and Health Canada. 2019. "Strontium in Drinking Water Health Effects of Strontium in Drinking Water Guideline Value for Strontium in Drinking Water in Canada How to Reduce Your Exposure to Strontium in Drinking Water Removing Strontium from Drinking Water If You Are Pregnant , Bre."
Toma, Janan Jabbar. 2006. "Physical and Chemical Properties and Algal Composition of Derbendikhan Lake, Sulaimania, Iraq." *Current World Environment* 1(1):17–27. doi: 10.12944/cwe.6.1.02.
Trancoso, Maria A., Margarida M. Correia dos Santos, and Maria L. Simões Gonçalves. 2003. "Quality Assurance Program for the Chemical Characterization of Soils." *Accreditation and Quality Assurance* 8(7):323–33.
Ward, Mary H., Rena R. Jones, Jean D. Brender, Theo M. de Kok, Peter J. Weyer, Bernard T. Nolan, Cristina M. Villanueva, and Simone G. van Breda. 2018. "Drinking Water Nitrate and Human Health: An Updated Review." *International Journal of Environmental Research and Public Health* 15(7):1–31. doi: 10.3390/ijerph15071557.
Wei, F. S. 2002. "Monitoring and Analysis Methods of Water and Wastewater." *China Environmental Science Press, Beijing*.
WHO, Geneva. 2011. "Guidelines for Drinking-Water Quality." *World Health Organization* 216:303–4.
World Health Organization. 2017. "WATER QUALITY AND HEALTH - REVIEW OF TURBIDITY: Information for Regulators and Water Suppliers." *Who/Fwc/Wsh/17.01* 10.
Xu, Haiyin, Yuanling Luo, Ping Wang, Jian Zhu, Zhaohui Yang, and Zhiming Liu. 2019. "Removal of Thallium in Water/Wastewater: A Review." *Water Research* 165:114981. doi: 10.1016/j.watres.2019.114981.
Yousif, Kamil M. 2016. "EFFECTIVENESS OF CHLORINE TREATMEN WATER SUPPLIES FOR."