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RESEARCH PAPER

Heavy metals compositions in springs and streams from Shaqlawa district, Erbil Province, Kurdistan region of Iraq.

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A B S T R A C T:

This study was conducted to determine some heavy metals concentration (Fe, Mn, Ni, Cr, Cd, Al, Zn, Cu and Pb) in 18 springs and streams from Shaqlawa district, Erbil governorate from September-2019 till August-2020. The results indicated that higher value of Fe was 660.0 µg/L and 450.0 µg/L recorded in October-2019 in site 17 (Azarian spring) and site 8 (along stream). Mn concentration value varied between 1.0-39.0 µg/L in some springs and streams sites. While, Ni and Cr values was ranged between 7.0--47.0 µg/L and 1.8-24.3 µg/L respectively. The Cd, Al and Zn concentrations were ranged between 2.0-6.50 µg/L, 1070-3380 µg/L and 10-320 µg/L respectively. Finally, Cu and Pb concentration was never exceeded 67.8 µg/L and 50.0 µg/L in site 2 (Piawan spring) and site 16 (Benwan spring) during July-2020 respectively. According to world Health Organization (WHO) all heavy metals in studied sites were within allowable level. Except concentrations of Al in all sites, Ni in many sites and Fe only in site 17(Azarian spring) was above the permissible level for drinking purposes. Relying on the heavy metal pollution index (HPI) the results was varied between 65.66 to 87.75 which mean that all the studied sites lower than 100 which considered as critical number for drinking water purposes. This means all springs and streams sites in this investigation were not polluted by the heavy metals. But according to single factor pollution index of Fe,Mn, Cr, Cd, Zn, Cu and Pb was less <1 means uncontaminated while, pollution index for Al was > 3 and Ni more than one in most sites which polluted.

KEY WORDS: Heavy metals; Springs; Streams; Shaqlawa; Erbil
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1.INTRODUCTION :

important source of water for life of human, and agricultural output. With the continuous evolution of human society and economy, anthropogenic activities cause serious contamination to water sources(Liang et al., 2019). Once too much heavy metals enter the water body, it will directly or indirectly impacts to the human health, and even dangerous to the aquatic ecosystem(Fan et al., 2016). The term heavy metals is worldwide utilized and indicate to metals and metalloids with an atomic density more than 5 g cm^{-3}(Liang et al., 2019). Heavy metals availability to living organisms depended on physical factors such as temperature, sequestration and adsorption. Chemical factors that effects complexation kinetics and solubility in lipids or water. Biological factors like characteristics of species, trophic levels interact, physiologically and biochemically adaptation (Verkleji, 1993). They are found in two important types, first one is essential elements which have vital role in organisms activity like copper, chromium, iron, manganese, molybdenum, nickel, selenium, and zinc which named microelement or essential trace element because they need for different function like biochemical and physiological, inadequately they cause disease, also higher level of these metals become toxic almost organisms(Ametepey et al., 2018). The second type of heavy metals are with unknown functions like cadmium, lead and mercury which cause severe effects or damage in living organisms at trace concentration(Ametepey et al., 2018). Heavy metals may add to environment either nature through geological

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activity like erosion of soil, sediments or rocks or volcanoes which cause pollution through acid rain that carry heavy metals and also cause erosion of earth crust then enter heavy metals to aquatic system. Fertilizers, pesticides, urban runoff, industrial waste, waste of households and others factors belonging to anthropogenic activity(Deng et al., 2020). Assessment of drinking water by utilizing some index is very useful tool to solve quality of water to related problems(Naqeeb and Jazza, 2020). This study objective to determined heavy metals levels in some springs and streams sites within Shaqlawa district and estimate their availability for the drinking purposes through using heavy metal pollution index and single factor pollution index

2.MATERIALS AND METHODS

2.1. MATERIALS

2.1.1 The case study:

In the current study were selected 18 sites within Shaqlawa district which include 6 stream sites and 12 springs sites, the first five springs are located in within Aquban khwaru named (Sard, Piawan, Zhnan, Darmanawa and Mink), and six sites are located along streams started from Shaqlawa till Sarkand village. Finally the remaining 7 springs located within Sarkand, Razga and Azarian villages includes (Nawkand, Prenga, Chemma, Sarkand, Benwan Razga, Azarian), generally the spring and stream waters are used for many purposes including irrigation, agriculture and domestic uses Figure(1).

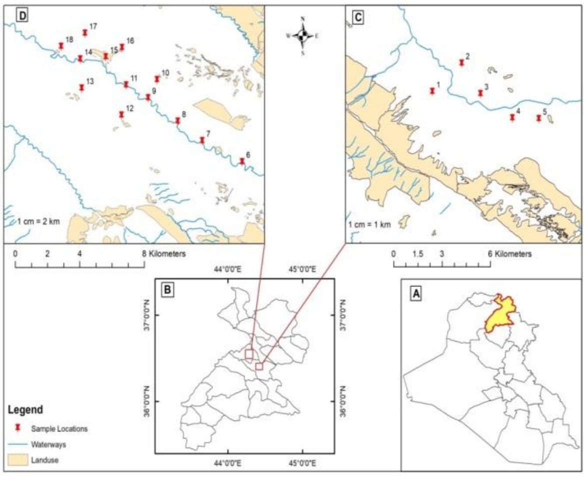

Figure 1. A- Map of Iraq and Erbil shaded B- Erbil Governorate C- Aquban village D- Sarkand village

2.2 Sample collection

A For this study, in order to cover all monthly variations in the studied area, samples of water were being collected from eighteen sites for a year starting from September 2019 until August 2020. The water samples were collected in pre-washed with de-ionized water polypropylene bottles. The samples were brought to the laboratory in cooled ice box (4°C) they filtered (Whatman 0.45 μm) and acidified with nitric acid in order to arrive a pH below 2.0, to reduce precipitation and adsorption on the walls of the container(Abdulla, 2013).

2.3. Samples analysis

The collected samples were analyzed for the concentrations of heavy metals include (Fe, Mn, Ni, Cr, Cd, Al, Zn, Cu and Pb) by atomic absorption spectrophotometer (A A 700 Perkin Elmer USA), according to Standard Method for Examination of Water and Wastewater(APHA, 1999)

2.4. Heavy metals Pollution indices

A heavy metal pollution index (HPI) is a mechanism of assessment that supplies the composite effect of individual heavy metal on the total quality of water. The rating is a value between 0 and 1 and which reflect the importance of individual quality considerations. (Milivojević et al., 2016, Chiamsathit et al., 2020).

Estimation of HPI includes the next steps**:**

1. Estimation of the unit weight for each variable.
2. The determination of the sub-index values.
3. The sum of sub-indices.

The weightage of each variable can be determined by applying Equation (1):

$Wi = k/Si$ -------------------- (1)

Where, Wi is the unit of weight and Si is the allowable value that found in the standard for each variable and k is the stable of proportionality. The singles quality rating is given by the expressing

$\mathbf{Qi = 100\ Vi / Si}$ ------------------- (2)

Where Qi is the sub index of ith variable, Vi is the monitoring value of the ith variable and Si the standard or allowable limit for the ith variable.

The Heavy Metal Indices (HPI) is then determined as the follow:-

HPI= $\sum_{i=1}^{n}$ Qi Wi / $\sum_{i=1}^{n}$ Wi

Where, Qi is the sub-index of ith variable, Wi is the unit weight for each variable, n is the number of parameters. The critical pollution indices value is 100. For the present study the Si value was taken from the WHO drinking water guidelines (WHO, 2004). .

2.5 Single factor pollution index way

The single-factor pollution index way is an estimation method depended on the environmental quality standards utilized by contamination.

Its benefits are simple operation and easy application; but it is only utilized to reverse the contamination degree of every heavy metal element in the sampling area. And cannot reverse the overall pollution value caused by the combination of various pollution factors(Cheng and Li, 2017).

See formula (1) for calculation.

Pi =Ci/Si …………… (3)

Pi means the single factor indice of heavy metal element i .

Ci means the actual concentration level of heavy metal i in water resource, and

Si represents to the evaluation standard value utilized for heavy metals in ground and surface water. The classification standard of single factor contamination indice is explained in Table 1.

Table 1:- Single factor contamination index

Index	Range	Contamination Degree
Single	$Pi \leq 1$	Uncontaminated
factor	$1<Pi \leq 2$	Light pollution
index	$2<Pi \leq 3$	Moderately polluted
	$Pi >3$	Heavy pollution

2.7. 2. RESULTS AND DISCUSSION

Iron concentrations in the current study were ranged between (42-660µg.l^{-1}) for springs and (50-450 µg.l^{-1}) in stream sites were recorded in autumn and winter seasons respectively Figure (2). Iron commonly found through soil erosion and during rocks weathering. The maximum concentration of Iron in summer and the minimum in winter seasons, possibly related to evaporation during to high temperature and dilution of water to rainfall(Rasheed, 2008). Iron get to the environment by nature during weathering of different rocks including sulfide minerals, sedimentary, metamorphic and igneous. Anthropogenic sources of iron play the significant role to increase the concentration of iron in the environment(WHO, 2004). Iron in drinking water depending to the guideline of(WHO, 2004) was 0.3mg/L, thus, which all streams and springs are considered as safe water for drinking purposes according to iron levels except in the site 3, 6, 8,11 and 17 in autumn months. Similar conclusion observed by (Toma, 2008, Toma, 2011, Goran, 2014). Manganese in the studied springs and stream were ranged between (1.00-39.00 µg.l^{-1}) and (1.00-36.00 µg.l^{-1}) respectively Figure (3). This variation of manganese concentration probably, due to the characteristics of soil, rocks type, sources of water, weathering and erosion of rocks(WHO, 2004). Similar concentrations were observation was reported by (Rasheed, 2008, Toma, 2008, Goran, 2014). The highest desirable concentration of manganese in drinking waters is 0.5 mg/L (WHO, 2004), subsequently all studied sites are considered as safe water for drinking purposes Nickel is a toxic element to health for human , when it presents in levels more than in the standard guideline or concentration of 0.02mg/L(WHO, 2004).

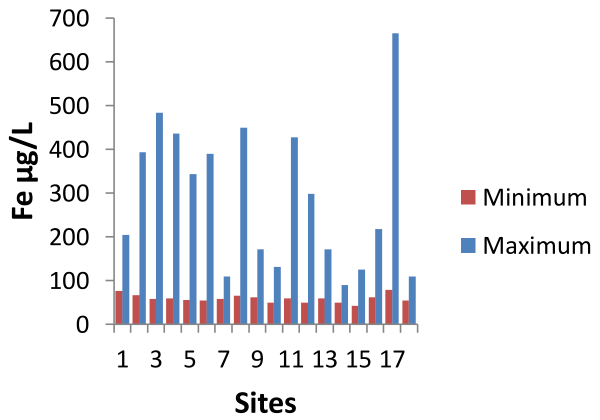

Figure 2: Minimum and maximum value of Iron concentration (µg.l^{-1}) in studied sites during the studied period

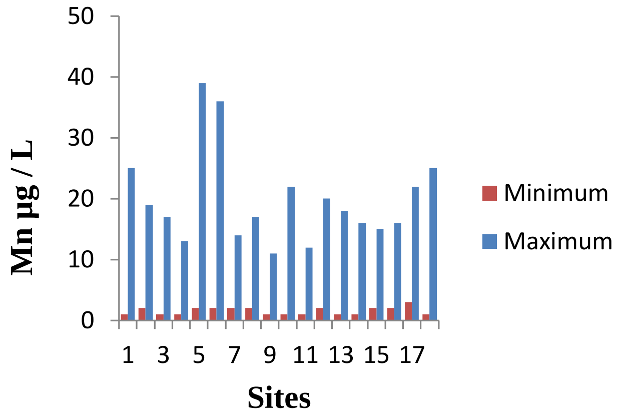

Figure 3: Minimum and maximum value of Manganese concentration (µg.l-1) in studied sites during the studied period

Nickel level in the current study was varied between (7-47 µg.l^{-1}) and (9-36 µg.l^{-1}) in springs and stream sites respectively Figure(4), and they were within the allowable values for inland surface waters and accepted with results reported by researchers on Inland waters. Researches indicate that increasing nickel levels more than (5 ppm) in drinking water lead to infection with cancer in various areas of human body(Al-Manharawi and Hafiz, 1997). Slight variation of Nickel concentration in the studied area, may be due to the geological formation in the studied area are which poor in nickel, low utilization of nickel in industrial activity in Arbil province, nickel ability to moving and transformed for a long area and it is absorbed strongly by Fe and Mn(Gassama et al., 1994).. Chromium concentration measured in streams and springs were variation between (1.80-24.30 µg.l^{-1}) and (1.70-14.30µg.l^{-1}) respectively, in springs and stream Figure (5).

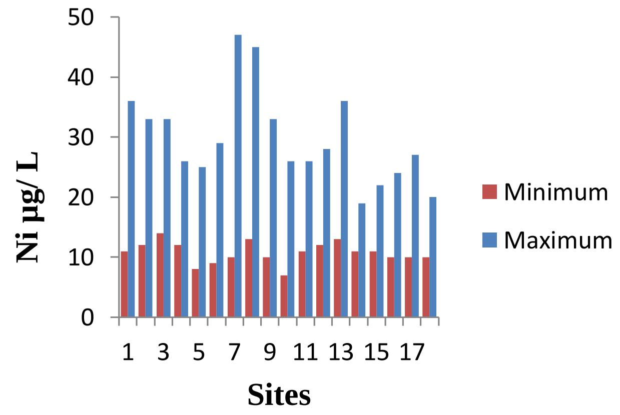

Figure 4: Minimum and maximum value of Nickel concentration (µg.l^{-1}) in studied sites during the studied period

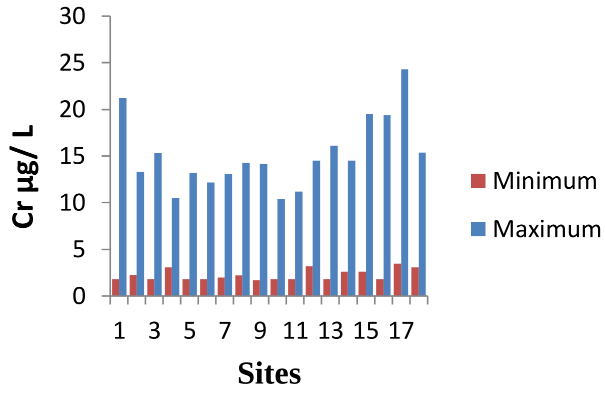

Figure 5: Minimum and maximum value of Nickel concentration (µg.l^{-1}) in studied sites during the studied period

In general, their levels were higher in summer than in autumn and winter at all sites. The high levels of metals through the summer may be due to the increase in the electrical conductivity and pH values, which accelerates or raises the adsorption process and the accumulation of the metal ions in the water(Al-Asadi et al., 2019). Depending to the WHO standard, chromium concentration in this investigation within permissible level(WHO, 2004). Cadmium level Figure (6) in the current study varied from (2.00-6.30µg.l^{-1}) in springs and (2.10-6.50 µg.l^{-}1) in stream and higher concentration were recorded in autumn and summer seasons while, lower values were reported in winter months .The higher concentration of cadmium was lower than the acceptable limit of WHO guideline for drinking water and within the acceptable limit (1 mg.l^{-1}) for public sewer(Weast, 1989). The high levels of cadmium through the summer possibly may due to the increase in the electrical conductivity and pH values, which accelerates or raises the adsorption process and the accumulation of the metal ions in the water(Al-Asadi et al., 2019). The lowest level of aluminum was 1070 and 1100µg.l^{-1} and the highest levels were 3380 and 3100 µg.l^{-1} Figure (7) detected in the in springs and streams sites respectively. All of the water samples was contained aluminum more than the specified maximum contaminant level (0.2mg.l^{-1}) (WHO, 2004). The toxicity of aluminum linked with continuous low concentration exposure, this can finally lead to dangerous health effects as several epidemiological studies have supplied clear explanation about the possible link between Aluminium in drinking water and dementia as well as Aluminium exposure being an factor cause in Alzheimer's disease(Toma and Othman, 2011).

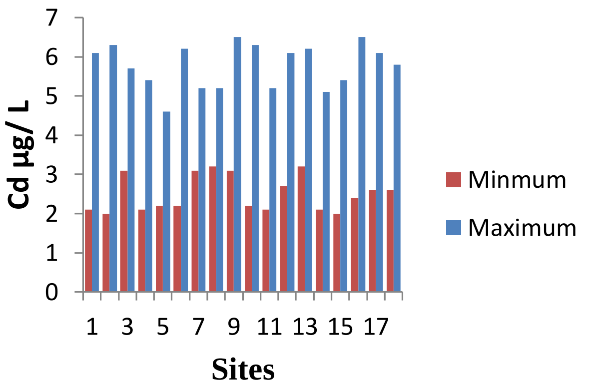

Figure 6: Minimum and maximum value of Chromium concentration ($\mu g.l^{-1}$) in studied sites during the studied peroid

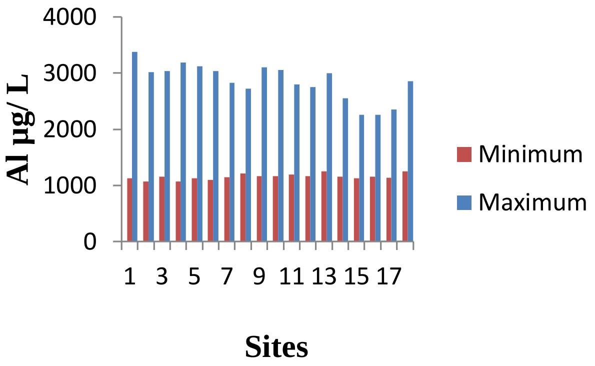

Figure 7: Minimum and maximum of Aluminium concentration ($\mu g.l^{-1}$) in studied sites during the studied peroid

Concentrations of zinc were fluctuated in springs and stream among (10.0-320.0$\mu g.l^{-1}$) and (10.0-184.0$\mu g.l^{-1}$) respectively, in which the highest values were recorded in summer and the lowest values were measured in winter seasons Figure (8). Generally as the water level was increases, the recorded zinc levels were decreased. This is basically related to the dilution effect and partly may be possibly due to the adsorption of zinc ions by the dense suspended material that are found in water through this period. Suspended sediments are famous for their high ability to adsorb the zinc from solution and concentrate them on their out surfaces due to their precise size and large surface areas(Al-Ani et al., 2014). These results came in coincided with (Rasheed, 2008, Toma, 2008, Goran, 2014). The permissible concentration of zinc in drinking water is less than 3$mg.l^{-1}$(WHO, 2004), therefore all studied sites through this study were within the allowable level and are safe for drinking purposes. In the current study the highest value of copper was 28.00$\mu g.l^{-1}$ and 67.00$\mu g.l^{-1}$ recorded in springs and streams sites during summer season. While lower value was 2.00$\mu g.l^{-1}$ recorded in both sites springs and streams through autumn and winter seasons Figure (9). This foundation was within maximum permissible levels for Iraqi standard for aquatic systems 100$mg.l^{-1}$(Al-Saadi et al., 1995), and it's also lower than value of 1$mg.l^{-1}$ in accordance to WHO guideline for drinking water(WHO, 2004). The current variation of copper probably may due to in acidity, alkalinity (pH), content of mineral (hardness), and availability of copper in the water system(Araya et al., 2004). The high concentrations in summer probably related to impact of temperature and low algal activity to consume or use copper in this period(Hellawell, 1998). The concentration of Pb were fluctuated between was (09-50$\mu g.l^{-1}$) in springs sites and (10-37$\mu g.l^{-1}$) streams sites. However, all the values including the average concentration (22.08 $\mu g.l^{-1}$) were much lower than standard (0.01 $mg.l^{-1}$) provided by(WHO, 2004) for drinking purposes. In general, low levels of dissolved lead are present in surface and ground water this may due to the trend of lead to adsorbs onto surface of sediment and form compounds that are insoluble with sulfate, hydroxides, sulfide, carbonates and various oxides(Drever, 1997). High lead values in water may come from fuels and oil which used for car and also during the formation of coal in the area of current study. A small variation was observed among studied locations and sampling periods. The fluctuation in the results were slight they may have related precipitation, dilution and the geology of the studied area and may be contributed to the industrial and agricultural discharge(Nordberg et al., 2007). The HPI levels of this study of water samples in eighteen sites were ranged between 65.660 to 87.756 in Mink and Sard springs respectively, which was lesser than 100 the standard level for drinking water purposes Table(2), this shows the water is not seriously polluted with regarding to studied heavy metals(Sahoo and Swain, 2020). This means all springs and streams sites in this investigation were not polluted with heavy metals. The results HPI in the current study are in line with the conclusions of (Eldaw et al., 2020, Jazza et al., 2021). Single factor rate index of Fe and Ni was less than 1 in most sites were considered uncontaminated except site 17 and half of sites Ni was recorded more than 1 which considered light pollution. Single factor pollution index of Mn, Cr, Cd, Zn, Cu and Pb was less than one which means uncontaminated water while, pollution index for Al was more than 3 which means it was polluted as seen in Tables (3).

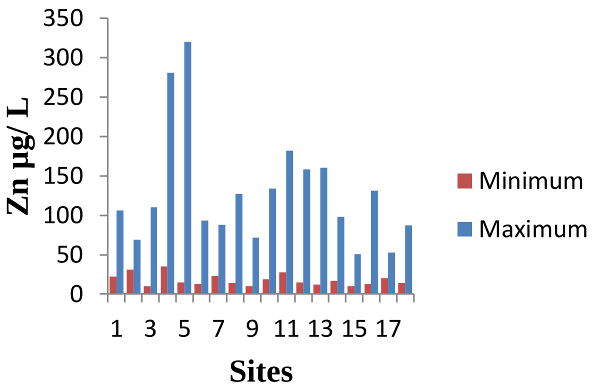

Figure 8: Minimum and maximum value of Zinc concentration (µg.l^{-1}) in studied sites during the studied peroid

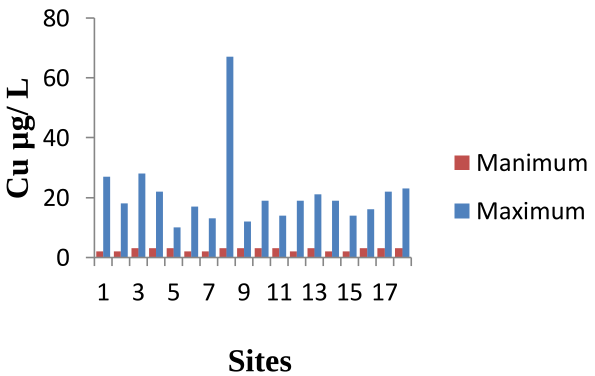

Figure 9: Minimum and maximum value of Copper concentration (µg.l^{-1}) in studied sites during the studied peroid

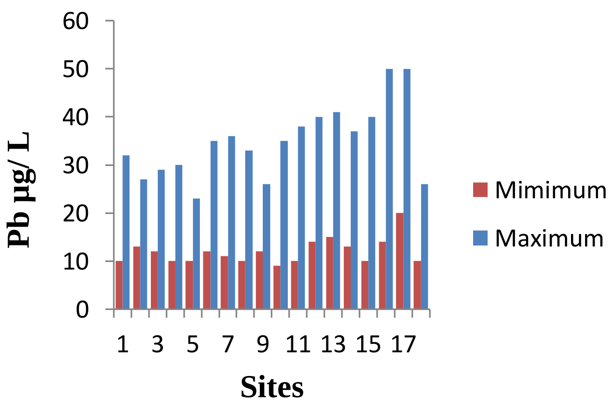

Figure 10: Minimum and maximum of Lead concentration (µg.l^{-1}) in studied sites during the period of study

Table 2:- Heavy Metals Pollution Index in studied sites during the period of study

Sites	Name of site	Value of HPI index	Status
1	Sard Spring	86.55377201	Not seriously polluted
2	Piawan Spring	87.7564081	Not seriously polluted
3	Zhnan Spring	79.05440877	Not seriously polluted
4	Darmanawa Spring	81.41179658	Not seriously polluted
5	Mink Spring	65.66044445	Not seriously polluted
6	Along stream	80.25556707	Not seriously polluted
7	Along Stream	77.13411156	Not seriously polluted
8	Along Stream	80.77170254	Not seriously polluted
9	Along Stream	75.88269248	Not seriously polluted
10	Prenga Spring	77.51255468	Not seriously polluted
11	Along Stream	75.51991544	Not seriously polluted
12	Nawkand Spring	86.23503724	Not seriously polluted
13	Chemma Spring	86.60746163	Not seriously polluted
14	Along Stream	70.60430913	Not seriously polluted
15	Sarkand Spring	72.8498349	Not seriously polluted
16	Benwan Spring	79.38083242	Not seriously polluted
17	Azarian Spring	86.3566698	Not seriously polluted
18	Razga Spring	72.68642236	Not seriously polluted

Table 3:- Assessment results of single factor pollution index

Element Sites	Fe	Mn	Ni	Cr	Cd	Al	Zn	Cu	Pb
1	0.501	0.014	0.887	0.140	0.792	9.42	0.019	0.010	0.34
2	0.629	0.017	1.062	0.127	0.774	8.63	0.017	0.010	0.448
3	0.720	0.014	1.059	0.115	0.856	8.960	0.023	0.010	0.398
4	0.542	0.013	0.929	0.126	0.776	9.025	0.033	0.009	0.537
5	0.400	0.018	0.800	0.120	0.646	8.655	0.033	0.006	0.328
6	0.447	0.021	1.084	0.113	0.866	8.655	0.018	0.007	0.427
7	0.275	0.012	1.104	0.122	0.766	8.545	0.014	0.006	0.388
8	0.554	0.015	1.167	0.136	0.836	8.495	0.018	0.019	0.408
9	0.356	0.011	0.984	0.112	0.808	9.495	0.012	0.006	0.362
10	0.298	0.015	0.992	0.106	0.802	9.055	0.013	0.008	0.418
11	0.713	0.011	0.996	0.127	0.688	8.685	0.012	0.007	0.422
12	0.524	0.017	1.029	0.147	0.908	8.880	0.013	0.009	0.550
13	0.379	0.014	1.071	0.156	0.866	9.135	0.015	0.008	0.537
14	0.232	0.013	0.779	0.136	0.726	8.355	0.016	0.008	0.432
15	0.284	0.011	0.842	0.164	0.698	8.210	0.014	0.006	0.458
16	0.344	0.012	0.879	0.151	0.822	8.085	0.012	0.007	0.547
17	1.014	0.017	1.017	0.200	0.760	8.285	0.015	0.010	0.621
18	0.260	0.017	0.909	0.145	0.796	9.505	0.012	0.010	0.328

4. CONCLUSIONS

All heavy metals levels in studied sites lie within permissible level for drinking purposes except Fe in Azarian spring, Ni in most sites and Al in all location exceeded the permissible level according to WHO guidelines. Depending on HPI of springs and streams sites in this investigation were water not polluted in respect to heavy metals but according to Single factor pollution index of Mn, Cr, Cd, Zn, Cu and Pb which less than one means uncontaminated while, Ni was recorded more than 1which considered light pollution and Al was more than 3 which means it was heavy pollution.

Declaration of conflicting interests

-Conflicts of Interest: None.

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

-The project has been approved by the local ethical committee in Salahaddin University, Erbil-Kurdistan Region of Iraq.

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