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Major and Trace Elements of Water and Sediments of Dibb's Dam -Iraq

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ABSTRACT

The main objective of this work is to analyze the water quality for the possible pollution of the Dibb's Dam through determining the major elements (Ca^{+2}, Mg^{+2}, Na^{+}, K^{+} ,SO_4^{-2}, Cl^{-}, HCO_3 , CO_3^{-2})and trace elements (Zn, Cu, Mn, Ni, Co, Cr, Pb) in the water and soil of the Dibb's Dam and the Lesser Zab river. The Dibb's Dam is considered the most important supply source of water to the rural population, agricultural and industrial activities at Kirkuk city.

The geochemical analysis of water and sediments samples from Dibb's Dam showed abnormal concentration in some trace elements. Twenty one samples of water and nine samples from recent sediments at Dibb's Dam was analyzed. The analysis showed that some of the trace elements are more than the standard in the earth crust while others within the standards.

Keywords: Contamination, Major Elements, Trace Elements and Dibb's Dam

1. INTRODUCTION

The Dibbs dam was constructed in the year 1965 on Lesser Zab River at a distance 40 Km NW- Kirkuk city and about 4.7 km from Dibbs town center. The Dam and the reservoir located at latitude (35^{0} 40^{-} $48^{=}$- 35^{0} 41^{-} $24^{=}$) and longitude (44^{0} 05^{-} $24^{=}$ - 44^{0} 06^{-} $36^{=}$),see Fig.1. The present study including determination some of the major elements such as (Ca^{+2}, Mg^{+2}, Na^{+}, K^{+} ,SO_4^{-2}, Cl^{-}, HCO_3^{-} , CO_3^{-2})and the trace elements such as (Zn, Cu, Mn, Ni, Co, Cr, Pb) in the water and soil of the reservoirs which leads to indicate any pollution within these elements.

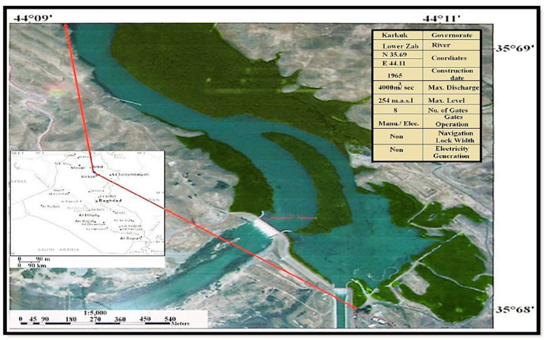

Figure 1: The study area location

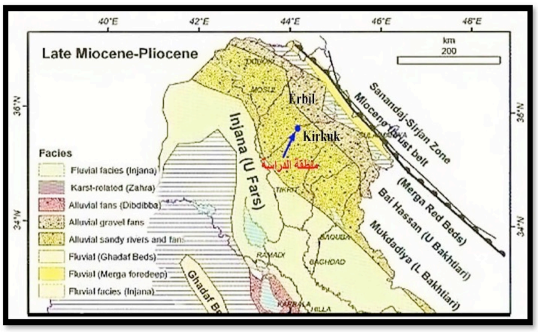

Figure 2: Geologic map of the study area.

From geologic point the area of study located in the low folded zone of Iraq and characterized by series of hills and mountains extends northeast-southwest which represent anticlines forming Kani Domaline mountain series and inter bedded by broad synclines in the unstable platform of Iraq(Jassim and Goff, 2006 , Azawi ,2003, Buday and Jassim,1987) see fig. 2. The field study is including sampling from the water reservoir and from the soil at the bottom of the reservoir in addition to sampling of the sediment from Injana formation which outcrops in the area surrounding the reservoir The most outcropped formation in the area: 1. Injana Formation (Late Miocene): Formed of clastic sediments of layers of sandstone with grey to reddish color alternated with red mudstone. The lower contact of the formation represented by the appearance of greenish clay layers of Fatha formation while the upper contact represented by gradual appearance of gravel layers related to Magdadia Formation. 2. Magdadia Formation (Lower Pliocene): formed of gravelly alluvial thick layers alternated with pebbly sandstone and mudstone (Jassim and Goff,2006). 3. Quaternary and recent sediments: Formed of molasses clastic sediments accumulated in the synclines and lower areas with different thickness and derived from many sources with lenses of sandy pebbles or gravels (Jassim and Goff, 2006).

2. METHODOLOGY

Soil samples have been collected from the bottom of the reservoir and the surrounding area which represents the recent sediments and Injana Formation. Also water samples were collected from the reservoir and Lesser Zab .Grain size analysis of the (19) samples of sediments have been carried out to indicate the nature of the sediments (Figure 3), also clay fraction separated and examined by XRD to recognize the clay mineral types. Hydrochemical and geochemical studies have been carried out to indicate the concentration of major and trace elements.

Climate of the area characterized by semi- arid and arid condition with very hot and dry summer, concentration of the elements are highly affected by precipitations, evaporation and humidity. The annual monthly precipitation according to Kirkuk station for the period (1992-2011) ranges between (0-74.5)mm. during the wet period (Nov.-Apr.) with average (74.5)mm monthly, while during the dry season (June-September) with no precipitation. Evaporation is depending mainly on the temperature and ranging between (50.59-315.77) mm with increasing for the period from May to October proportional with average temperature rising.

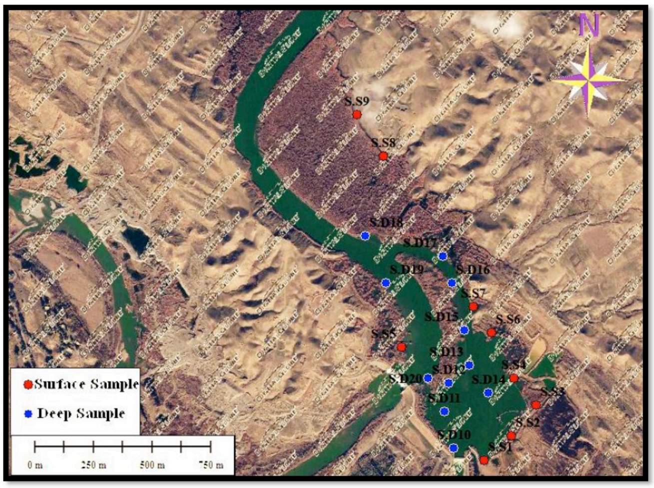

Figure 3: Sampling point location

3. RESULTS AND DISCUSSIONS

3.1. Distributions and concentration of cations and anions in water:

The hydrochemistry of twenty one water samples collected from the reservoir and from the Lesser Zab river have been studied chemically to indicate the major ions (Table 1).The source of these ions in the water are mostly from chemical weathering of rocks and soil (Singh et.al.,1980) in addition to the effect of temperature and flow character (Ibrahim,2009). The abundance of the major ions is as follows: $Ca^{+2}>Mg^{+2}>Na^{+}+K^{+}$; $HCO^{-}_{3}>SO^{=}_{4}>Cl^{-}$. The major hydrochemical facieses were $Ca–HCO_3$, $Ca–SO_4$ types (Al-Kuzachi, 2012). The recognized cations and anions are: 1- Ca^{+2} and Mg^{+2} : formed from dissolving of limestone or evaporates (Kadem, 1990) indicated that the concentration of Ca^{+2} in river water is about 15 ppm.Ca^{+2} in the present study is about 60 ppm and that may due to the presence of chemical rocks in the basin of Lesser Zab river while the Mg^{+2} concentration in the river water is (1-40)ppm (Apodaca et.al.,2006).concentration of Mg^{+2} in the present study is (5.8-13.5)ppm which is less than the international standards (WHO, 2009). 2. Na^{+} and K^{+}: These ions are below the international standards (WHO, 2011) and the increasing in some samples may due to the high evaporation (Table 1).

Table 1: Water sample analysis

Sample	**Cations (ppm)**				**Anions (ppm)**		
	Ca^{+2}	Mg^{+2}	Na^{+1}	K^{+}	Cl^{-1}	HCO_3^{-1}	SO_4^{-2}
1	62	7.5	4.5	1.5	13.31	177.19	7
2	56	7.8	4.2	1.4	13.31	146.64	22
3	60	9.2	4.9	2.4	13.31	198.58	27
4	59	7.6	3.8	1.5	13.31	155.81	16
5	55.6	9.3	8.5	2.5	17.75	189.41	29
6	57	7.6	4.2	1.1	13.31	152.75	24
7	56	7.4	3.8	1.2	13.31	177.19	26
8	64	8.3	7.6	1.4	17.75	171.08	27
10	52.4	5.7	3.6	1.3	13.31	137.48	12
11	65	6.4	4.2	1.1	13.31	171.08	21
12	64	6.5	3.8	1.0	13.31	152.75	28
13	63	7.6	3.6	1.0	13.31	168.03	36
14	71	6.9	4.3	1.0	13.31	177.19	22
15	72	6.8	3.8	1.4	13.31	171.08	25
16	72.5	6.9	3.7	1.1	13.31	171.08	12
18	73.7	5.8	3.1	1.1	13.31	168.03	23
19	68.2	7.6	3.2	1.3	17.75	168.03	13
20	66	6.8	3.5	1.3	17.75	164.97	16
21	63	7.1	3.6	1.2	13.31	158.86	14

3. SO_4^{-2}, Cl^{-}, HCO_3^{-}, and $CO3^{-2}$ Anions: Most of these anions formed from the dissolving of evaporate such as SO_4^{-2} while Cl^{-} is originated from halite or sulfate or from irrigated water (WHO, 1996). HCO_3^{-}, CO_3^{-2} are formed from the carbonate rocks. All the anions are less than the international standards (WHO, 2011).

3.2. Trace elements in water samples:

The concentration of the following trace elements have been determined and as follows; Zinc (Zn) characterized by low dissolving in water and effect by pH(Boyd,2000) and the source of Zn is from sphalerite or smithsonite minerals (Emsley, 1980) and present with Cd, Cu and Mn(Aljubory ,2004) . Zinc ranges between (5.9-12.2) ppm with average (9.66) ppm which mostly higher than the international standards. Copper (Cu): mostly present low concentration in water because absorbed with clay and organic materials (Hem, 1985) also maturely the Cu is low in earth crust which is about (550) ppm (Kabata, 2011). The concentration is very low in the present study (Table 2). Manganese (Mn): the concentration of Mn in the studied water samples are range (0.11-0.54)ppm with average (0.3)ppm which consider higher than the standards(WHO,2011) which range between 0.02-0.05)ppm and that may due to the nature of soil and the agricultural activities in the area. Nickel (Ni): The concentration of Ni is mostly depends on Ph (Siebielec, et.al, 2007) and concentration of Ni is less than (0.1) ppm in the present water samples. Cadmium (Cd): The Cd is present with some minerals such as Greenockite, olarite (Emsley, 1998) also present within Fertilizing materials .the concentration of Cd in the present water samples are less than (0.02) ppm which the international standard (WHO, 2011) ranging (0-0.005) ppm. Cobalt (Co): Cobalt formed as Ni geochemically formed as hydroxides and carbonates and concentrated with clays and find in water by the effect biologic and biochemical activities. The Co concentration in the present study is less than (0.1) ppm. Lead (Pb): It is found that the Pb concentration is very low (0.01) ppm in the present water less than international standards (WHO, 2011).

Table 2: Trace elements in water samples.

Sample N	Trace elements							
	Mn	Pb	Cd	Co	Cr	Cu	Zn	Ni
1	0.11	<0.01	<0.02	<0.1	<0.1	0.72	11.50	<0.1
2	0.12	<0.01	<0.02	<0.1	<0.1	0.68	10.20	<0.1
3	0.32	<0.01	<0.02	<0.1	<0.1	0.93	8.60	<0.1
4	0.31	<0.01	<0.02	<0.1	<0.1	0.55	5.90	<0.1
5	0.29	<0.01	<0.02	<0.1	<0.1	0.63	7.60	<0.1
6	0.28	<0.01	<0.02	<0.1	<0.1	0.52	11.30	<0.1
7	0.31	<0.01	<0.02	<0.1	<0.1	0.78	10.70	<0.1
8	0.41	<0.01	<0.02	<0.1	<0.1	0.49	10.60	<0.1
9	0.44	<0.01	<0.02	<0.1	<0.1	0.53	11.10	<0.1
10	0.39	<0.01	<0.02	<0.1	<0.1	0.52	8.60	<0.1
11	0.12	<0.01	<0.02	<0.1	<0.1	0.63	7.90	<0.1
12	0.14	<0.01	<0.02	<0.1	<0.1	0.62	7.30	<0.1
13	0.22	<0.01	<0.02	<0.1	<0.1	0.67	7.10	<0.1
14	0.28	<0.01	<0.02	<0.1	<0.1	0.54	10.20	<0.1
15	0.32	<0.01	<0.02	<0.1	<0.1	0.68	10.40	<0.1
16	0.42	<0.01	<0.02	<0.1	<0.1	0.93	11.40	<0.1
18	0.54	<0.01	<0.02	<0.1	<0.1	0.86	8.60	<0.1
19	0.19	<0.01	<0.02	<0.1	<0.1	0.52	12.20	<0.1
20	0.32	<0.01	<0.02	<0.1	<0.1	0.76	11.60	<0.1
21	0.45	<0.01	<0.02	<0.1	<0.1	0.63	10.40	<0.1

3.3. Major oxides of soil and sediment:

The percentage of AL_2O_3, SiO_2, Fe_2O_3, MgO, P_2O_5, CaO, K_2O and Na_2O (Table 3).The high concentration of AL_2O_3,CaO and K_2O related to the nature of the sediment which is mostly fine and the clays forming the main part of it while the SiO2 forming the main part of the fine sand and mud. The oxides of P_2O_5 and Fe_2O_3 related to the organic nature and the plant cover in the area of the reservoir and the surrounding.

Table 3: Major oxides in the sediments samples.

Sample N.	MgO %	Al_2O_3 %	SiO_2%	P_2O_5%	K_2O%	CaO%	Na_2O%	Fe_2O_3%
2	5.49	13.84	44.37	0.18	2.20	11.59	0.094	9.5
5	4.01	12.91	42.80	0.73	2.33	14.43	0.097	7.88
7	6.30	12.56	40.81	2.98	1.79	15.82	0.376	9.00
11	4.89	12.16	44.80	0.27	2.10	14.84	0.091	7.95
12	5.08	12.91	45.84	0.13	2.74	12.81	0.088	7.85
13	5.75	12.99	43.78	0.38	2.03	15.19	0.092	7.71
15	5.13	12.53	47.86	0.13	2.37	11.08	0.093	8.70
17	4.40	12.51	45.19	0.11	2.54	10.78	0.098	9.81
19	4.86	13.83	43.90	0.12	2.36	11.54	0.089	9.18

3.4. Trace elements in soil and sediments:

From the study of trace elements or heavy metals found that the source of these elements are mostly due to the source rock or as a result of soil pollution by manufacturing or heavy waters. The concentration of these elements increased as a result of adsorption or absorption of on the sediments (Sumnar, 2000). Also the organic and fertilizing materials increased the concentration of these elements. The following are most important elements which considered most pollutant, have been determined in the soil and sediment in the Dibbs area (Table 4). Cobalt (Co): The sources of cobalt are mostly from the basic rocks (200) ppm (Kabala, 2011), while in the upper earth crust (10-12) ppm and increased in the fine sediments. In the present study the Co ranging (31-62.4) ppm with average (42.8) ppm. The pollution of soil by Co may due to the heavy uses of fertilizers in the Lesser Zab basin and also may due to the decomposition of rocks in the area. Nickel (Ni): The Ni considers one of the dangerous pollutants in the soil and sediment and originated from the human being activities. Concentration of Ni ranging (118-218.6) ppm with average (177.87) ppm, which is more than the standards in the earth crust (WHO, 2011). Copper (Cu): The Cu in the earth crust between (25-75) ppm (Kabata, 2011) and the concentration depending mainly on the factors forming the soil and sediment. The concentration of Cu in the studied samples ranging between (36.8-63.2) ppm with average (45.51) ppm, which is within the standards of the earth crust. Zinic (Zn): Zinic in the earth crust is about (70) ppm while in the soil rich in organic is about (120) ppm (Kabata, 2011). The Zn in the present study ranging (86.9-140.5) ppm with average (99.51) ppm and that high concentration may due to the high organic content and the fine nature of sediment. Galina (Ga) and Arsenic (As): these elements mostly within the standards of the earth crust (Table 4) and originated from the source rocks and the nature of the fine sediments in addition to local artificial pollutants. Bormline (Br), Rubidium (Rb), Strontium (Sr), Zircon (Zr), Thallium (Ti),Lead (Pb), Uranium (U) and Thorium (Th):The concentration of these elements mostly are within the standards of the earth crust or slightly more and that because the heavy using of fertilizers in addition to the human being activities in the basin of Lesser Zab River (Table 4).

Table 4: Sediment analysis

Sample	**Trace elements (ppm)**													
	Co	**Ni**	**Cu**	**Zn**	**Ga**	**As**	**Br**	**Rb**	**Sr**	**Zr**	**Ti**	**Pb**	**U**	**Th**
2	52.5	214	63.2	140.5	17.9	9.1	5.2	71.2	196.1	115.9	1.4	29.9	6.4	3.0
5	35.9	118	38.8	104	18.8	13.6	6.2	91.9	297.4	123.4	1.6	20.5	5.9	8.6
7	37.6	218.6	61.7	98.5	13.4	10.6	7.4	55.2	379.7	100.5	1.5	28.1	7.6	2.5
11	51.7	159.4	43.1	88	17.5	9.5	2.6	83.9	201.7	110.7	1.0	17.9	7.3	5.3
12	39.2	171	36.8	86.9	16.7	9.2	2.6	81.7	191.2	103.3	1.4	19.4	10.3	6.3
13	32.3	182.4	40.9	102.4	16.5	8.9	3.9	67.8	226.5	102.6	1.5	20.5	9.9	4.6
15	31.0	181.2	42.2	89.5	16.6	9.6	3.1	83.4	181.8	118.6	1.4	20.9	7.2	5.1
17	42.9	182.5	42.8	93.9	18.3	11.2	2.6	93	182.4	127.1	1.4	19.4	5.9	5.7
19	62.4	173.8	40.1	91.9	18.5	11.2	3.2	86	181.9	110.8	1.4	19.2	5.8	6.1

4. CONCLUSION

From this study it's concluded that the trace elements such as Co, Ni, Cu, Zn, Rb, Zr and Sr exist in the samples represent a threaten to the water and the soil quality in the area of the Dam and the river. This high concentration of contaminates is due to uncontrolled uses of fertilizers in the area where are many agriculture activities around. This pollution may cause harm to the human and to the environment. Treatment is recommended to remove these elevated traces of elements. Chemical treatment is recommended.

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