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Evaluation of Some Heavy Metals in well water within Sulaimani City , Kurdistan Region- Iraq.

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Abstract

In the present study, from April to August 2010, twelve sites of groundwater within Sulaimani Governorate (Sharawany, Mama Yara, Peshasazy, Twi Malik, and Ibrahim Pasha) were selected in order to evaluate some physico – chemical characteristics and seasonal analysis (Spring, Summer, and Autumn) for heavy metals (Cr, Zn, Ni, Cd, and Pb). The results showed the range of studied parameters as following: 19.6 °c-24.4 °c for water

temperature. pH value of the study sites range from 7.14-8.48 and 201, 50 - 943 μ s.cm⁻¹ for Electrical conductivity.

Heavy metals content of Chrome (Cr), Zinc (Zn), Nickel (Ni), Cadmium (Cd), and Lead (Pb) for each seasons (Spring , Summer and Autumn) in groundwater determined, Chrome concentration in water samples were $0 - 0.002 \text{ mg.l}^{-1}$, $0 - 0.003 \text{ mg.l}^{-1}$ and $0 - 0.002 \text{ mg.l}^{-1}$ for all seasons respectively . On the other hand Zinc was ranged in water samples during Spring , Summer ,and Autumn from $0 - 3.759 \text{ mg.l}^{-1}$, $0 - 1.887 \text{ mg.l}^{-1}$ $0 - 0.026 \text{ mg.l}^{-1}$ respectively While Nickel concentration were ranged between $0 - 0.002 \text{ mg.l}^{-1}$ in Spring, $0 - 0.004 \text{ mg.l}^{-1}$ in summer below detectable level (BDL) in Autumn. Cadmium in the water samples ranged between $0 - 0.001 \text{ mg.l}^{-1}$ for all seasons. Lead is the other metal was determined in groundwater ,it was below detectable level (BDL) during Spring , and $0 - 0.001 \text{ mg.l}^{-1}$, $0 - 0.007 \text{ mg.l}^{-1}$ for Summer and Autumn respectively.

Key words: Well water, heavy metals, Sulaimani city

1- Introduction

Ground water is water saturating the voids, pores, fractures holes in the soil & rock at some depth below the earth's surface. Groundwater is generally a very important source for drinking water, because over 98 % of the available fresh water on earth is ground water (Samuel et al., 2002), and of the purification properties of the soils; and it is also used for irrigation and spraying. The main source of water, an aquifer constitutes a natural reservoir of usually high-quality water. Although it is more protected than surface water, groundwater appears to be pollution. The subject to usage of groundwater has gradually increased because of the increase of water demand and the shortage of surface water during growth of population. In many cases groundwater is polluted by the inflow of pollutants such as sewage and industrial wastewater (Freeze and Cherry, 1979). Because groundwater is primarily used for drinking water, pollution from untreated sewage, intensive agriculture, solid waste disposal, and industry can cause serious human health problems (Khanfar, 2008). Due to the rapid growth of urbanization and industrialization, there is an increasing pressure on land, water and environment, particularly like these metropolitan cities. Concentration of human population in urban areas has resulted in increase of buildings, roads, vehicles, factories, urban sewage and storm drains,

smoke and dust, and garbage hazards which leads to severe water and air pollution (Swarna and Rao, 2007).

Heavy metals are elements with atomic weight between 63.5 and 200,5, and specific gravity greater the 4,5-Living organisms require trace amounts of some heavy metals, including cobalt, copper, iron, molybdenum, vanadium, strontium and zinc (Momodu and Anyakora., 2010). Although many heavy metals are necessary in small amounts for the normal development of the biological cycles, most of them become toxic at a high concentration (Hani, 1990).

Heavy metals in subsurface environments come from natural and arthropogenic sources The weathering of minerals is one of the major natural sources, include fertilizers, industrial effluent, and leakage service pipes (Leung and Jiao., 2006). Heavy metals are biodegradable and they non can be accumulated in living tissue and causing various diseases and disorders (Wan Ngah and Hanafiah., 2008).

This study was carried out in order to get enough information about water quality of some wells in Sulaimani city,through analyzing some heavy metals as an important part of public health study and comparing results with international specification to know how long it is beneficial for different purposes or multiple usages.

2-The study area:

Sulaimani is located on Northeastern part of (West, East, North, S)Iraq between altitudes 35° 31' 26" – 35` 35' of Sulaimani city 37" North and 45` 22' 10"- 45` 28' 48" East (Sharawani, Pishasaz covering an area 90.95 km2,cited form(Al-Manmi, 2002). Well water samples were yara).Table(1). **Table (1) show direction, coordinates and description of each site.**

collected from (12) wells in directions (West, East, North, South) around the center of Sulaimani city including sites of (Sharawani, Pishasazy, Twi malik, Ibrahim Pasha, Kareza weshk and Mama yara).Table(1).

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Sites	Coordinates North(N) East (E)	Site description
Sharawani	35°33'4.20" 045° 22'15.9"	South of center city
Mama yara	35° 33'10.0" 045°27'26.1"	South East of city center
P eshasazy	35° 33'41.9" 045°23'15.9"	South west of city center
Kareza weshk	35° 34'38.9" 045°25'44.9"	East of city center
Twi malek	35°34'24.3" 045°27'05.8"	North east of city center
Ibrahim Pasha	35° 34'37.8" 045° 22'15.8"	East of city center



Fig. (1): the location of the Sulaimani city and the study sites.(Google earth,2011 and Master plane of Sulaimani city).

3- Material and methods

Water samples were collected among three seasons (Spring, Summer and Autumn 2010, coordinates were recorded by using Geographical position system (GPS) model Etrex, Garmin. (A.P.H.A, 2005).

Water temperatures (C°) was measured in the field using multi meter model TPS90FL-Т Field lab Analyzer, (Goltermon, 1975).Hydrogen ion concentration (pH)Hydrogen ion concentration of samples was recorded by using a Multi meter model Tps90FL_Tfield lab analyzer after the calibration by using standard buffers of 4,7,and 9 (Lind, 1979). Electrical conductivity (E.C) in μ S.cm⁻¹ EC. was recorded by using multi meter model TPS90FL-T Field lab Analyzer in (us.cm⁻¹) samples in accordance to (APHA, 2005).

Heavy metals were measured according to the methods described by (APHA,2005). Heavy metals (Cr, Zn, Ni, Cd, and Pb) of water samples were determined using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) model Optima 2100 DV.(APHA, 2005). Results were statistically analyzed according to the statistical program of statistical package for the social science (SPSS), Version 15, data were treated with analysis of Variance (ANOVA) and (Duncan) to detect the variation of different variables at sites and sampling period. The mean, Standard Deviation, and the significant differences at the probability (%5)(Al-Rawi and Abdul Al-Aziz 1985).

4-Result:

Water Temperature Ground water temperatures at different sites and during the sampling periods are showed in Fig. (2). The maximum value of 24.4 C° was recorded in site 9 during August. While the minimum value of 19.6 C° was recorded in site⁻¹2 The of during April. values water temperature slight up rising through study period were evident.

Statistical analysis tables (2 a) and (2 b) reveal the significant differences among April and May with June, July and August studied months, (P<0.05).



Fig. (2): Water Temperature (C^o) value recorded for the studied during April to August 2010.

Table (2): water temperature (C^o) : a- For the studied months. b- For the studied sites

Mon	Mean± Std.	Mini	Maxi.
Apri	20.3208±.48451a	19.60	21.15
May	21.0833±.92622b	19.70	22.75
June	21.9250±.64403c	21.10	23.15
July	22.1667±.54952c	21.45	23.00
Aug	21.8583±1.05072c	20.3	24.40

St.	Mean± Std.	Minim.	Maxim.
1	21.1400±.66087a	20.50	22.05
2	21.5200±1.01094a	20.30	22.05
3	21.6250±1.14755a	20.30	23.00
4	21.9000±1.28647a	20.15	23.15
5	20.9200±.80125a	20.10	22.20
6	22.1500±.64614a	21.10	22.75
7	22.0200±.82280a	20.60	22.50
8	21.7600±.35951a	21.15	22.10
9	21.6700±1.96138a	19.70	24.40
10	21.0600±.59937a	20.00	21.45
11	21.1200±.74213a	19.80	21.55
12	21.0300±1.03296a	19.60	22.00

Hydrogen Ion Concentration (pH): Generally, hydrogen ion concentration at all the sites was more than 6. The recorded values were ranged between 7.14 and 8.48 during study the sites, the minimum pH value was recorded in st.3 (7.14) during July, while the maximum pH value (8.48) was recorded in St.6 during July.

Statistical analysis in table (4 a), and (4 b) show significant differences among sites and months of July and August with April, May and June (P<0.05).

Electrical conductivity (EC) µs.cm⁻¹:

The results of EC in the water samples showed that variations in all sites and they ranged between (201,5-968) μ s.cm⁻¹ mostly the maximum value of 968 μ s.cm¹ was recorded in site 3 during May, while the minimum value 201 μ s.cm⁻¹ was recorded in site (well) 9 during August.

Heavy metals concentration during spring: The Concentration of heavy metals (Cr, Zn, Ni, Cd, and Pb) arranged between BDL and within permissible level according to the guide line of WHO (2004) during spring, While maximum concentration of Zn was (3.759) mg.1⁻¹, above permissible level was recorded at site 3. and the maximum concentration of (Cr, Ni, and Cd 0.02 mg.1⁻¹ at site 12, 0.002 mg.l⁻¹ at site 5,10 and 0.001 mg.l⁻¹ in sites 1, 2, 6,7, 9,10 and site 12.

Concentration of heavy metals during summer: The minimum concentration of (Cr, Zn, Ni, Cd, and Pb) in groundwater during summer was below detectable level BDL, while maximum concentration of heavy metals was (0.003, 1,887, 0.004, 0.001 and 0.001) mg.l⁻¹ respectively. On the another hand the concentration of Zn> Ni> Cr> Cd and Pb, and according to this investigation all value of (Cr, Zn, Ni, Cd, and Pb) in groundwater during summer was within permissible level according to the guide line of (WHO,2004).

Concentration of heavy metals during autumn The minimum and maximum concentration of (Cr, Zn, Ni, Cd, and Pb) in autumn was arranged between (0- 0.002, 0-0.026, BDL, 0- 0.001 and 0- 0.007 mg.l⁻¹ respectively, the maximum concentration for Cr recorded at site 10, for Zn recorded at site 11, for Cd recorded at sites 1, 5 and 11 while the maximum concentration for Pb recorded at site 1.

Statistical analysis Tables (3 a) and (3 b) revealed the significant differences between studied months, (April, May, June) difference (July, August) (P<0.05).



Fig. (4): pH value recorded for the studied site during April to August 2010. Table (4) pH value: a-For the studied months b- For the studied sites

Months	Mean± Std. Deviation	Minimum	Maximum
April	7.7296±.25751ab	7.38	8.15
May	7.6679±.16302a	7.45	7.99
June	7.6704±.16070a	7.45	7.99
July	7.9275±.37640 bc	7.14	8.48
August	8.1008±.28102c	7.49	8.47

Sites	Mean± Std. Deviation	Minimum	Maximum	
1	7.6700±.14912 abc	7.46	7.85	
2	7.6180±.19071 ab	7.45	7.91	
3	7.4600±.19445 a	7.14	7.61	
4	7.9200±.24915 bc	7.79	8.37	
5	7.9420±.36699 bc	7.66	8.43	
6	8.0520±.25784 c	7.87	8.48	
7	7.9190±.33611 bc	7.69	8.47	
8	7.6490±.32933 ab	7.38	8.16	
9	8.0040±.02945 bc	7.98	8.05	
10	7.7290±.28166 abc	7.45	8.10	
11	7.8110±.29250 abc	7.57	8.24	
12	8.0520±.33865 c	7.72	8.48	



Fig. (3): Electrical Conductivity (µs.cm⁻¹) value recorded for the studied sites during April – August 2010

Table (3) Electrical Conductivity μ s.cm⁻¹ for the studied sites during the studied period a- For the studied months.

Months	Mean± Std. Deviation	Mini.	Maxi.
April	728.8750±162.53631b	434.50	894.00
May	758.2500±161.95180b	462.50	894.00
June	709.5417±172.84773b	427.50	943.00
July	375.2083±108.12250a	209.00	835.00
Aug.	361.6940±90.85532 a	201.50	892.00

Site	Mean± Std. Deviation	Minimum	Maximum
1	703.8000±230.48660bc	828.00	897.00
2	696.3000±230.15962 bc	789.00	886.00
3	812.6250±207.40401c	828.00	968.00
4	567.5000±137.63766abc	329.00	662.50
5	551.6000±230.87589 abc	299.50	737.50
6	432.0000±160.94409ab	253.50	564.50
7	693.1000±231.76184bc	434.00	878.00
8	698.2000±237.59330bc	428.50	894.00
9	352.1000±134.79030a	201.50	462.50
10	581.5000±274.70530abc	284.00	855.00
11	586.4000±221.94521abc	335.00	767.00
12	434.0000±124.65452ab	306.00	560.50

b- For the studied sites

Table (5): Heavy metals concentration mg.l⁻¹ (ppm) value in the studied sites during spring(season) 2010.

No.	site	Concentration (PPm)				
		Cr	Zn	Ni	Cd	pb
1	sharawani a	BDL	0.003	0.001	0.001	BDL
2	sharawani b	BDL	0.001	0.001	0.001	BDL
3	sharawani c	BDL	3.759	0.01	BDL	BDL
4	Mama yara a	0.001	0.003	0.001	BDL	BDL
5	Mama yara b	BDL	0.016	0.002	BDL	BDL
6	Mama yara c	BDL	0.002	0.001	0.001	BDL
7	Peshasazy a	0.001	0.003	0.001	0.001	BDL
8	Peshasazy b	0.001	BDL	BDL	BDL	BDL
9	Twi malik	0.001	0.001	BDL	0.001	BDL
10	Kreza wshk a	0.001	0.003	0.002	0.001	BDL
11	Kreza wshk b	0.001	0.009	0.001	BDL	BDL
12	Ibrahim pasha	0.002	0.003	0.001	0.001	BDL

BDL = Below Detectable Level

	Concentr	ration (PPm))			
No	site	Cr	Zn Ni		Cd	Pb
1	sharawani a	0.001	0.003	BDL	BDL	BDL
2	sharawani b	0.001	0.007	0.001	0.001	BDL
3	sharawani c	0.001	1.887	0.004	BDL	BDL
4	Mama yara a	0.003	BDL	BDL	0.001	BDL
5	Mama yara b	BDL	0.003	BDL	0.001	BDL
6	Mama yara c	BDL	0.04	0.002	0.001	BDL
7	Peshasazy a	BDL	0.008	BDL	0.001	BDL
8	Peshasazy b	BDL	0.019	0.003	BDL	BDL
9	Twi malik	BDL	BDL	BDL	BDL	BDL
10	Kreza wshk a	0.001	0.016	0.001	BDL	BDL
11	Kreza wshk b	0.001	0.004	0 BDL	BDL	BDL
12	Ibrahim pasha	0.002	0.003	0.001	0.001	0.001

Table (6): Heavy metals concentration mg.l⁻¹ (ppm) value in the studied sites during summer (season) 2010.

BDL = Below Detectable Level

Table (7) : Heavy metals concentration mg.l⁻¹(ppm) value in the studied sites during autumn (season) 2010.

		Concentration (ppm)				
No	Site	Cr	Zn	Ni	Cd	Pb
1	sharawani a	BDL	0.004	BDL	0.001	BDL
2	sharawani b	BDL	BDL	BDL	BDL	0.007
3	sharawani c	-	-	-	-	-
4	Mama yara a	BDL	BDL	BDL	BDL	0.004
5	Mama yara b	BDL	BDL	BDL	0.001	BDL
6	Mama yara c	0.001	BDL	BDL	BDL	0.003
7	Peshasazy a	0.001	BDL	BDL	BDL	BDL
8	Peshasazy b	BDL	BDL	BDL	BDL	BDL
9	Twi malik	BDL	BDL	BDL	BDL	BDL
10	Kreza wshk a	0.002	BDL	BDL	BDL	BDL
11	Kreza wshk b	0.001	0.026	BDL	0.001	BDL
12	Ibrahim pasha	0.001	BDL	BDL	BDL	BDL

BDL = Below Detectable Level

5-Discussion:

Ground water temperature basically important for its effects on other properties, example, speeding up of chemical reaction .reduction in solubility of gases, amplification of tastes and odors. (Tebbutt, 1973). Groundwater temperature depends on several factors such as depth of layers contain water, and reactions that occurred in rocks (Todd, 1980). The maximum value of groundwater temperature 24.4 co was recorded in site (9) (karez) during June, while the minimum value was 19 .6 c° recorded in site 12 (karez) during April. According to this, the temperature of earth Cortex increase about 2.9c every 100m. when we recorded the result of water temperature showed that is normal results in groundwater temperature, and the slight increase in temperature due to depth and hot seasons. The slight differenced temperature, also due to the hot seasons and it is related to its abundant temperature In this seasons and shallow wells near to the (karez) surface is effected by air temperature, the similar results were realized by (Al.Manmi, 2002).

In the study area pH of the water sample varies from 7.14-8.48 the pH level where within WHO optimum limits of between 6.5-8.5. pH value lower than 6.5 are considered too acidic for human consumption and cause

health problems such as acidosis. The pH value grater than 8.5 is considered to be too alkaline for human consumption, (Nkansah, et al. 2010). The result It in this investigation is near with the range 7.6-7.7 recorded by(Khorshid, 1981) in sulaemani city and the pH range between 7.11 to 8.54 recorded by (Khodapanah, et al.2009). In Eshtehard District, Tehran. Iran well. In Iraqi Kurdistan regio n, the pH of water characterized by shiftingtoward the alkalinity duo to the geological formation of the area which composed mainly of CaCo3 (Nabi, 2005).

Electrical Conductivity . EC is an important factor in water quality measurement because its gives a good idea of the amount of dissolved materials in the water (Muhammad, 2004). The lowers value of EC was recorded in June was $201.5 \mu s.cm^{-1}$ at site 9 during August, while the highest value was 943 μ s.cm⁻¹ at site 3 during June .E.C. depending on water temperature, that the increasing water temperature one degree causes the increase of E. C.2% (Hem, 1985). Also E.C.depends on concentration of dissolved salt (Detay, 1997). The conductivity value in water system related to climate season and geological information of the area (Hynes, 1976, Goldman & Horne, 1983). The highest value of E.C .in this study recorded in the Sharawani site

including well 1,2,3, the average rang was between (828-897), (789-886) and (828-968) µs.cm⁻¹ respectively during the study sites ,this result in the same station may be related to geological information of the area. The value E.C. for (karez) is less than wells, Electrical conductivity value in the present investigation was ranged between 201.5-943 us.cm⁻¹. The Maximum acceptable level of conductivity as indicated by USEPA (2004) is 1000 µs.cm⁻¹ Table (5-2). According to all studies, well & karez lie within permissible range for drinking purposes, since this value was near to that recorded by (Toma,2006 b) in shaqlawa ground water which was arranged between 610-840 µs.cm⁻¹ and (Toma 2006 a). In Ainkawa groundwater (530-790) µs.cm⁻¹ while (AlManmi 2002) recorded in sulaimani city for karez (440-902) μ s.cm⁻¹ and shallow wells (473-1065) μ s.cm⁻¹, and (Umadevi *et al.*, 2010) in India recorded EC arrange was between (380-910) $\mu s.cm^{-1}$.

The main anthropogenic sources of Cd are the use of phosphate fertilizers, land application of municipal sewage sludge, atmospheric deposition, and mining and smelting activities. (McLaughlin and Tiller, 1994). As shown in the present study the Cd ranged between 0 to 0.001 mg.l⁻¹.The acceptable levels of Cd in drinking water is less than 0.003 mg.l⁻¹ according (WHO.2006). Accordingly all study sites during this survey were within permissible concentration and are in safe side for drinking purposes. (AL_Manmi, 2002) recorded Cd in well water ranged between(0.08 to 0.012) mg.l⁻¹, and(0-0046) mg.l⁻¹ Cd in spring water in sulaimani city recorded by (Ibrahim , 1981) and(0.01 to 0.001) mg.l⁻¹ recorded by (Hashem ,1992).from different place in Saudi Arabia (Abha, Arar,Dammam, Gizan, Hail, Madinah, Riyadh, Tabouk) .

Chromium (Cr) is an essential element in animal and human nutrition (Rajappa et al., 2010). The concentration of Cr in the study area was ranged between minimum of below detectable level (BDL) to 0.003 mg.l⁻¹ present results agree with the observation obtained by (Siddique 2006)in the Karachi, Pakistan recorded concentration of Cr in groundwater investigated under study are lower that the recommended value (WHO 2006) . on the other hand (Iqbal and Gupta, 2009) reported the concentration of Cr ranged between maximum (0.010) mg.l⁻¹ and minimum (0.006) mg. l^{-1} in (India) are during winter and (Al_Manmi ,2002) in sulaimani groundwater. However Cr concentration in present study comes within the normal range that must be present in drinking water 0.05 as suggested by (WHO, 2006 and BIS, 2003).

Lead (Pb) value of all study karezes and wells during the study period was ranged between a minimum of BDL to 0.007 mg. 1⁻¹ .The values of Pb in all groundwater studied during this investigationwas within the safe limit by (WHO,2006).Concentration of Pb in all well and Karez was BDL except wells 2,4 and 6, during July but also it was lie within permissible level .Lead in drinking water primarily comes from dissolution from plumbing material and Pb pipes and solders (Harrison , 2001).The result agree with the results of (AL_Manmi , 2002) ,who was recorded(0.01 to 0.016)mg. 1^{-1} ,(0.012 to 0.016) mg. 1^{-1} for karez and well respectively in Sulaimani city , and that of (Toma , 2010d) who recorded values ranged from (0.010 to 0.039) mg. 1^{-1} in Shaqlawa well water.

Nickel (Ni): The main sources of Ni in the environment are from mining and smelting, from sewage sludge, and from fuel oil and coal combus (Rajappa et al., 2010). The Ni concentration in groundwater of the study area were ranged between BDL to 0.004 mg. 1^{-1} . The values of Ni are showed within the limit of drinking Water standard . WHO limit for Ni is 0.02 mg. 1^{-1} . The result in this investigation agree with the result (0.01 to (0.02) mg.l⁻¹recorded by (Toma , 2010d) in Shaqlawa well water and other study recorded BDL by(Rajappa et al., 2010) in Groundwater of Hakinaka Taluk, India. and the concentration of Ni in all well was in permissible limits and suitable for drinking recorded by (Bhaskar, et al., 2010) in Tumkur, Karnataka, India

Zinc (Zn) is a metal shows fairly low concentration in surface water, which is due

to is restricted mobility from place of rock weathering or from the natural Sources (BIS,2003). The permissible level of Zn in drinking water is less than 3 mg. 1⁻¹ (WHO, 2006 and National Health, 2004). Results of Zn in this study was within the normal range (National Health 2004:WHO.2006), also was agreed with the results of studies done by (Ibrahim, 1981; and Al Manmi,2002), were the values of (0.016 to 0.024 mg. l^{-1}) and (0.022 to 0.4 mg. l^{-1}) were recorded for springs and karezes respectively in Sulaimani City, (Borah, et al. 2009) revealed that the ground water of the area (Tea Garden Belt of Darrang District, Assam, India, concentration of Zn were within the guide line values of WHO. In the present study, the concentration of Zn arranged between a minimum of BDL and. maximum of 3.759 mg. l^{-1} at site 3 during April and Spring seasons. The values of Zn are showed within the limit of drinking water Standard except site 3 located in Sharawani, among all metal studied during this investigation, the concentration of Zn was high, this may be due to use of fertilizers.

Conclusion and Recommendation:

1-It was observed that the pH is neutral to slightly alkaline in the study area.

2-EC in all water sample was in a permissible level for drinking water according to WHO (2004).

3-The concentration of heavy metals (Cr, Cd, Zn, Ni, and Pb) in all groundwater samples during spring, summer, autumn, lie within permissible level except Zn is above permissible level at site 3 according to WHO(2006)and all water samples were safe for drinking and other purposes.

4-Aware people to monitor well water monthly or even seasonally and study area before digging.

5- More studies for more physicochemical characters and trace metals concentration in groundwater are to be conducted due to important sources for drinking water must be carrying out

6- Prevent contamination of groundwater especially by sewage water.

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