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ESTIMATION AND CORRELATION ANALYSIS OF HEAVY METALS OF SOME WELL WATER IN ZAKHO CITY, IRAQ

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ABSTRACT:
This study was carried out to examine the concentrations of major heavy metals in fifteen different well water in Zakho City, Kurdistan Region, Iraq. The studied heavy metals were iron, copper, chromium, aluminum, cadmium, cobalt, nickel, manganese, zinc and lead. The results obtained in the studied area showed that copper, chromium, cobalt, zinc, manganese, aluminum, iron and lead were within the acceptable limits as recommended by WHO for water drinking. However, in all studied areas, cadmium and nickel were mostly founded to exceed the maximum permissible limit set by WHO. It is found that zinc and copper possess a very good positive correlation between each other. The results obtained in this study confirmed the groundwater pollution and hence it is not suitable for consumption without any prior treatment.

KEYWORDS: Zakho City, Water Quality, Heavy metals, Water Pollution, Well Water.

1. INTRODUCTION

The global population growth and accelerated industrialization process in combination with agricultural activities has brought the risk of rising the population index is natural environments, for instance air, soil, water, etc. (Assubaie, 2015; Dawson & Macklin, 1998; Ekpo & Ibok, 1998; Morrison, Revitt, & Ellis, 1990). Since of their persistence and accumulation in different environmental compartments, heavy metals are considered as one of the most serious environmental pollutants. More attention has been devoted to the investigation of heavy metal pollutants in the environment because of the increasing anthropogenic contribution by these pollutants (Edmunds, Shand, Hart, & Ward, 2003; Marengo et al., 2006). The main sources of pollution, which are responsible for producing significant load of heavy metals to the environment, are low efficiency in industrial production processes (petrochemical, energy power plants and chemical industries etc.) and the unsuitable management and handling of industrial wastes (Banat, Howari, & Al-Hamad, 2005; Charlesworth & Lees, 1999; Kuang, Neumann, Norra, & Stüben, 2004; Mireles et al., 2004; Namaghi, Karami, & Saadat, 2011).
Groundwater is considered as the healthiest drinking water source, but agricultural, domestic and industrial activities led to the degradation of water quality in different parts of the world. In developing countries like Iraq, groundwater pollutants are responsible for waterborne and water related diseases. Since natural filtration through sediments and soils, generally, water supplies from groundwater are free from suspended and organic contaminants (Karanth, 1989). Regional geology, geochemical processes and land use patterns are main factors for controlling the chemistry of groundwater (Kumar, Ramanathan, Rao, & Kumar, 2006; Liu, Jang, Chen, Lin, & Lou, 2008; Rajesh, Brindha, Murugan, & Elango, 2012; Zhu & Schwartz, 2011).
Availability of groundwater as well as quality is deteriorating at a faster rate in response to developmental activities. Storage and flow of groundwater in hard rock regions have always been a main issue for general public, water managers and researchers either with respect to water quality and water quantity (De Silva & Weatherhead, 1997; Gupta & Singh, 1988; Négrel, Lemière, Machard de Grammont, Billaud, & Sengupta, 2007; Robins & Smedley, 1994). Also, the limitation of groundwater aquifers and resource and long term sustainability is a major issue (Foster & Bank, 2002; Singhal, Niwas, & Singhal, 1988).
The main aim of this study was to assess the quality of well water sources in Zakho City in northern Iraq, Kurdistan Region. With the aid of Atomic Absorption Spectrophotometer (AAS) the presence and concentration of ten heavy metals (Iron, Aluminum, Cadmium, Manganese, Copper, Chrom, Nickel, Zinc, Cobalt and Lead) were determined and the results compared to the maximum contaminant level specified by the World Health Organization (WHO).

2. MATERIALS AND METHODS

2.1 Digestion and Analysis of Water Samples

Water sample, 100 ml of well mixed acid preserved, was transferred into a beaker and 5 ml of concentrated nitric acid was added. The beaker was placed on a heater and allowed to evaporate to about 5 ml without boiling. Then diluted to 100 ml in a volumetric flask and was ready for analysis. For all water samples, these procedures were adopted for all water samples (Nouri, Mahvi, Jahed, & Babaei, 2008). Thereafter, metals of interest (Mn, Pb, Ni, Cd, Cu, Fe, Al, Cr, Co and Zn) were assayed using Flam Atomic Absorption Spectrophotometer, Shimadzu AA7000, Japan.

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2.2 Water sample Collecting and Studied Area

According to standard procedure by (Clesceri et al., 1998), groundwater samples were collected in January 2013 from 15 different well waters from Zakho City, Duhok Governorate, Kurdistan Region. The sampling locations and coordinates for sampling sites are shown in Table 1. The map of Zakho City and locations of sampling sites are shown in Figure 1.

Table 1. Sampling Locations and GPS Coordinates for sampling sites.

Well ID	Coordinates	
W1	37°10'42.36"N	42°48'36.03"E
W2	37°10'1.21"N	42°43'31.82"E
W3	37° 9'57.00"N	42°43'41.82"E
W4	37°10'1.51"N	42°43'12.83"E
W5	37° 8'30.14"N	42°34'35.93"E
W6	37° 8'29.43"N	42°34'21.01"E
W7	37° 9'24.07"N	42°41'32.14"E
W8	37° 8'15.23"N	42°41'17.53"E
W9	37° 9'42.55"N	42°40'41.03"E
W10	37° 9'25.35"N	42°40'6.40"E
W11	37°14'30.90"N	43° 9'46.65"E
W12	37°14'20.06"N	43° 9'43.23"E
W13	37°14'4.57"N	43° 9'43.81"E
W14	37°07'51.3"N	42°53'37.5"E
W15	37°11'29.5"N	42°51'12.6"E

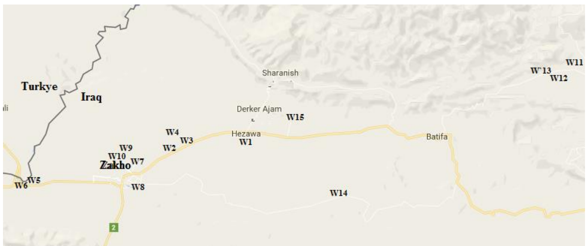

Figure 1. Map of Zakho City showing the locations of sampling sites.

3. RESULTS AND DISCUSSION

The results obtained for the metal ion concentrations (Mn, Pb, Ni, Co, Cd, Cu, Fe, Al, Cr and Zn) in the water samples collected from various sites was compared with the maximum permissible limit of WHO. The physical and chemical properties of water samples from the selected sites is shown in Table 2. The concentrations for analyzed metals are summarized in Table 3.

The maximum tolerance limit by WHO for iron, copper, manganese and zinc are 0.2, 1, 0.5 and 4 mg/L, respectively. As shown in Table 3, these metals in all well water samples were observed to be below the maximum permissible limit set by WHO. Although these metals are considered as an essential nutrient, but at high doses they have been reported to cause damage to the kidneys and can become fatal, as well as, they may cause a decrease in fetal growth (Cassat & Skaar; Mattison et al.; Olmedo et al., 2013; Salgueiro et al., 2000; Schaible & Kaufmann, 2004).

Table 2. Physical and chemical properties of water samples from the selected sites

Parameters	WHO	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14	W15
Turb. (NTU)	5	0.3	0.4	0.2	0.5	0.2	0.4	0.3	0.1	0.2	0.2	0.4	0.2	19.7	0.8	0.6
pH	6.5-8.5	7.48	7.87	7.97	8.08	7.86	8.02	8.08	8.15	8.06	8.11	7.94	8.06	8.88	8.07	8.43
EC (μs/cm)		600	556	468	498	649	496	517	471	574	659	615	562	479	551	800
TDS (mg/L)	1000	384	355	299	319	415	317	331	301	367	422	393	359	307	353	512
NO_3^{-1}(mg/L)	50	44.7	42.4	19.9	27.6	40.4	28.4	36.3	29.5	54.7	74.4	2.44	7.58	2.92	17.7	2.26
TAl (mg/L)	125-200	274	292	270	282	330	278	268	270	280	296	334	306	282	334	508
TH (mg/L)	100-500	324	372	304	324	412	316	328	300	356	388	392	332	340	380	544
Ca^{+2} (mg/L)	75-200	83.2	94.4	76.8	83.2	110	78.4	83.2	76.8	91.2	99.2	96	92.8	59.2	70.4	84.8
Mg^{+2} (mg/L)	30-150	28.3	33.1	27.3	28.3	33.1	29.2	29.2	26.3	31.2	34.1	37.0	24.4	46.8	49.7	81.0
Cl^- (mg/L)	250	18	26	20	22	40	30	28	26	36	46	24	20	12	20	18
Na^+ (mg/L)	200	12	11	10	10.3	16.5	12	10	6.5	17	20	4.8	13.5	3	11.3	22
K^+ (mg/L)	2-3	1	2	2	2	3	2	2	2	2	2	1	1	1	2	2
SO_4^{-2} (mg/L)	250	9	14	4	9	23	9	8	8	14	19	46	22	29	2	29

Lead is considered as the most significant toxin of the heavy metals, and the inorganic forms are absorbed through ingestion by food and water, and inhalation (Jaishankar, Tseten, Anbalagan, Mathew, & Beeregowda, 2014). The permissible limit of Pb concentrations by WHO for drinking water. The maximum concentration found to be 0.00153 mg/L in W 1 for Pb.

The permissible limit of Co, Al and Cr concentrations by WHO are 0.005, 0.2 and 0.05 mg/L, respectively. As shown in Table 3, Co, Al and Cr ions in all samples were observed to be below the maximum permissible limit set by WHO for drinking water except in well W5, in which the level of Co and Cr were 0.00705, 0.350 and 0.0614 mg/L, respectively. It has been reported that metals such as cobalt (Co) and chromium (Cr) are essential nutrients that are required for various biochemical and physiological functions; however, these elements , at high doses, are considered to be toxic industrial pollutant that is classified as human carcinogen by several regulatory and non-regulatory agencies (Tchounwou, Yedjou, Patlolla, & Sutton, 2012).

At extremely low levels, Cd is a toxic and non-essential heavy metal and high exposure can cause obstructive lung disease (Khaled et al.). The maximum allowable concentration of Cd by WHO is 0.003 mg/L. It was found that Cd concentration in all wells was above the acceptable concentration set by WHO for drinking water. The maximum concentration for Cd found to be 0.089 and 0.085 mg/L in W 6 and w5, respectively.

Table 3. Concentration of metals ion in five different sites compared to WHO for drinking water.

Well ID	Fe (mg/L)	Cu (mg/L)	Mn (mg/L)	Zn (mg/L)	Co (mg/L)	Ni (mg/L)	Pb (mg/L)	Cd (mg/L)	Cr (mg/L)	Al (mg/L)
WHO	0.2	1	0.5	4	0.005	0.02	0.01	0.003	0.05	0.2
W1	0.0096	0.01096	0.0009842	0.0240000	0.0000533	0.0454150	0.0015357	0.0055638	0.0088144	0.0559242
W2	0.0044	0.0322	0.0002314	0.0009000	0.0000022	0.0277000	0.0000000	0.0059000	0.0185000	0.0107415
W3	0.0087	0.029	0.0018922	0.0073000	0.0001035	0.0277000	0.0000000	0.0076000	0.0214000	0.0099024
W4	0.0277	0.0322	0.0001000	0.0769000	0.0000668	0.0323000	0.0000000	0.0072000	0.0204000	0.0155855
W5	0.0321	0.0322	0.0000160	0.0132000	0.0070517	0.0693000	0.0000000	0.0085000	0.0614000	0.3506665
W6	0.0131	0.0387	0.000200	0.0082000	0.0000000	0.0416000	0.0000000	0.0089000	0.0156000	0.0308656
W7	0.0233	0.0226	0.0005312	0.0450000	0.0000000	0.0139000	0.0000000	0.0051000	0.0195000	0.0147340
W8	0.0175	0.0258	0.0002404	0.0043000	0.0000603	0.0300000	0.0000000	0.0055000	0.0224000	0.0151182
W9	0.0335	0.0258	0.0007109	0.0039000	0.0000108	0.0323000	0.0000000	0.0051000	0.0214000	0.0278475
W10	0.0292	0.0322	0.0003000	0.0006000	0.0003158	0.0346000	0.0000000	0.0059000	0.0234000	0.0122277
W11	0.0350	0.0258	0.0005322	0.0026000	0.0000409	0.0231000	0.0000000	0.0068000	0.0195000	0.0237992
W12	0.03210	0.0258	0.0004000	0.0099000	0.0000776	0.0323000	0.0000000	0.0076000	0.0214000	0.0072117
W13	0.12530	0.0548	0.0009591	0.0078000	0.0000474	0.0277000	0.0000000	0.0080000	0.0195000	0.0153915
W14	0.08975	0.0580	0.0004657	1.3066000	0.0000108	0.0208000	0.0013065	0.0055000	0.0097000	0.0160974
W15	0.170	0.0226	0.0026199	0.054500	0.0000108	0.0139000	0.0000000	0.0051000	0.0078000	0.0180394

Table 4. Correlation matrix among different heavy metals in water wells of Zakho City.

	Fe	Cu	Mn	Zn	Co	Ni	Pb	Cd	Cr	Al
Fe	1									
Cu	0.411	1								
Mn	-0.102	-0.189	1							
Zn	-0.245	0.617	-0.038	1						
Co	0.096	-0.046	-0.178	-0.168	1					
Ni	0.067	-0.082	-0.429	-0.225	0.165	1				
Pb	-0.280	0.045	0.071	0.605	-0.118	0.077	1			
Cd	0.380	0.333	-0.279	-0.216	0.032	0.543	-0.311	1		
Cr	0.369	-0.01	-0.491	-0.462	0.418	0.207	-0.693	0.307	1	
Al	-0.126	-0.380	0.097	-0.084	-0.215	0.298	0.616	-0.135	-0.525	1

Nickel represents a good example of a metal whose use is widening in modern technologies. As the result of accelerated consumption of nickel-containing products nickel compounds are released to the environment at all stages of production and utilization. Their accumulation in the environment may represent a serious hazard to human health. Among the known health related effects of nickel are skin allergies, lung fibrosis, variable degrees of kidney and cardiovascular system poisoning and stimulation of neoplastic transformation (Denkhaus & Salnikow, 2002). The maximum acceptable concentrations set by WHO is 0.02 mg/L for Ni ions. As shown in Table 3, Al metal ion in all wells, except W 7 and W 15, was observed to be above the maximum permissible limit set by the WHO for drinking water. The maximum concentrations of Ni found to be 0.0693 mg/L.

To measure and establish the relationship between two variables, the correlation coefficient is commonly used. It is a statistical tool to show the dependency degree of one variable to the other (Stigler, 1989). The correlation matrix of analyzed metals has been represented in Table 4. As shown, copper ion metal exhibit high positive correlation with Zn (r = 0.6174). However, Zn exhibit high correlation with Pb (r = 0.6055) and Pb metal exhibit high correlation with Al metal (r = 0.6168). Nickel ion exhibit high positive correlation with Cd (r= 0.5434). Cu and Zn possess a very good positive correlation (r = 0.6174) between each other. According to the results shown in this investigation, the water from well in Zakho City is not suitable for consumption without any prior treatment.

4. CONCLUSION

The results obtained in the studied area of Zakho City well water showed that iron, copper, zinc, manganese and lead were within the acceptable limits according to WHO for water drinking. However, chromium, cobalt and aluminum were mostly founded, at some studied area, to exceed the maximum permissible limit as recommended by WHO. Cadmium and nickel, in all well water in Zakho City found to be above the maximum permissible set by WHO. It is also found that Cu and Zn possess a very good positive correlation between each other. Rock mineral dissolution with the groundwater is a possible reason for contamination. The results obtained in this study confirmed the high groundwater pollution and hence it is not suitable for consumption without any prior treatment.

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کورتیا لێکولینێ:

ئەڤ ڤەکۆلینە هاتە ئەنجامدان بۆشـیکارکرنا خەسـتیا کانزایێن قورسـێن سـەرەکی د پازدە بیرێن جیاواز ل باژێرێ زاخو، هەرێما کوردسـتانێ، عیراق. کانزایێن گران ئەوێن هاتینە خاندن پێکهاتیە ژ ئاسن ومس وکرۆم وئەلەمنیۆم وکادمیوم وکۆباڵت ونیکل ومەنگەنیز وتوتیا وقورقوشم. ئەنجامێن هاتینە بدەسـتڤەئینان دیارکر کو ئاسـن ومس وکرۆم وئەلەمنیۆم وکۆباڵت ومەنگەنیز وتوتیا وقورقوشـم د ناڤ سـنوورێ پەسـەندکری یێ ڕاسـپێرای ژ لایێ ڕێکخراوا تەندروسـتیا جیهانی بو ئاڤ ڤەخوارنێ. هەرچەندە لگشـت ناوچەیێن ڤەکۆلین هاتیە ئەنجامدان دیارکر کو وکادمیوم ونیکل رێژا وان تێپەڕی ژ سـنوورێ پەسـەندکری یێ ڕاسـپێرای ژ لایێ ڕێکخراوا تەندروسـتیا جیهانی بو ئاڤ ڤەخوارنێ. هەروسـا ئەڤ ڤەکۆلینە ڤە دبینت کو توتیا ومس هاوپەیوەندیەکا گەلەك باش یا پۆزەتیڤانە هەیە ناڤبەرا ئێکدا. ل دیڤ ئەنجامێن بدەستڤەئینای پشتڕاست دکەت ئاڤا ژێر زەڤی نەیا شیاوە بو بکارئینانێ بێ چارەسەریا پێشتر.

خلاصة البحث:

أجريت هذه الدراسة لفحص تركيزات المعادن الثقيلة الاساسية في خمسة عشر بئر ماء مختلفة في مدينة زاخو، إقليم كوردستان، العراق. المعادن الثقيلة التي درسـت في هذا البحث هم الحديد والنحاس والكروم والألومنيوم والكادميوم والكوبالت والنيكل والمنغنيز والزنك والرصـاص. وأظهرت النتائج التي تم الحصول عليها في منطقة الدارسة أن النحاس والكروم والكوبالت والزنك والمنجنيز والألومنيوم والحديد والرصاص كانت في حدود مقبولة على النحو الموصـى به من قبل منظمة الصـحة العالمية لمياه الشـرب. ومع ذلك، في جميع المناطق التي تمت دراسـتها، الكادميوم والنيكل تم ايجاد معظمها يتجاوز الحد الأقصى المسموح به الذي حددته منظمة الصحة العالمية. تبين أن الزنك والنحاس تملك علاقة إيجابية جيدة جدا بين بعضها البعض. وأكدت النتائج التي تم الحصول عليها في هذه الدراسة على تلوث المياه الجوفية، بأنه ليست مناسبة للاستهلاك دون أي معالجة مسبقة.