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Environmental assessment of heavy metals in surface and groundwater at Samarra City, Central Iraq

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Abstract

Urban Samarra City is characterized by high population density and wide variation in land use, has led to many environmental problems, for this purpose the environmental assessment became an urgent need for surface and ground water at study area. Three water samples from Tigris River and six groundwater samples were collected and analyzed for heavy metals as Fe, Mn, Zn, Cd, Cu, Co ,Pb, Ni, Cr, As, Mo, Hg, Al, Li, Be, Se, V, U, Sr. Most heavy metal concentrations have shown higher level than standards, such as Fe, Mn, Cd, Pb, Ni, Cr, As, Mo, Hg, Al ,Li ,Be, Se, V, that might be due to anthropogenic activities such as agricultural and the heavy use of fertilizers, besides other activities among them industrial .

All water samples have higher concentration level of Uranium except (SW1, SW2, SW3, GW1) might be due to military activity. On the other hand all samples were polluted in Co except SW2, GW4, high value of Co may be caused by industrial processes and oil product spills.

Physical and chemical properties values which have obtained in this study are pH, EC, TDS, TSS, DO, BOD,COD and turbidity. Water analyses reveal unacceptable values for physical and chemical parameters according to WHO standard and IQS2009 limits for drinking water, BOD, EC have shown high values in all surface and groundwater samples. Whereas, high values of TDS, COD and turbidity only in ground water samples.

The water is not drinkable according to Water Quality Index (WQI) all values are above 100 and, in the sequence (GW1>GW5>GW4>GW3>GW6>GW2), the water quality index of surface water (SW3>SW2>SW1). Mixing of the shallow groundwater and Tigris River water show various patterns affected by other factors such as the aquifer recharge and evaporation, especially at the shallowest parts.

Keywords: Heavy metal, Drinking water, Water pollution, Samarra City.

التقييم البيئي للعناصر الثقيله في المياه مدينة سامراء ،وسط العراق

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الخلاصه

تتميز مدينه سامراء الحضريه بالكثافه السكانيه العاليه وتفاوت الكبير في استخدام الاراضي والانشطه البشريه المتنوعه , التي ادت الى العديد من المشاكل البيئيه ولغرض تقييم البيئي للمنطقه و نوعية المياه السطحيه والجوفيه تم تحليل عدد من النماذج لهذا الغرض، حيث تم جمع وتحليل ثلاث عينات من المياه

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السطحيه وسته عينات من المياه الجوفيه لغرض تحديد التراكيز للعناصر الثقيله وهي النيكلNi والرصاصPb والنحاسCu والكاديميومCd والزنكZn والمنغنيز Mn والحديدFe والكروم Cr والزرنيخ As والموليبوديوم Mo والزئبق Hg والالمنيومAl والبيريليوم Br والفيناديوم V وسنتروتيومSr وسيلينيوم Se واليورانيوم U.حيث وجد بان معظم المعادن الثقيله تواجدت بتراكيز اعلى من المعدلات المسموح بها .ان هناك تلوث حقيقي في العناصر التاليه الرصاص والحديد والمنغنيز والكاديميوم والنيكل والكروم والزرنيخ والموليبدينيوم والزئبق والالمنيوم واليثيوم والفيناديوم والسيلينيوم والسنترونتيوم والبيريليوم. بسبب النشاط الزراعي واستخدام المكثف للاسمده والانشطة البشريه الاخرى في المنطقه ومنها الصناعيه . ان جميع العينات المياه ملوثه باليورانيوم عدا (SW1,SW2,SW3,GW1) بسبب ان مدينه سامراء قد يعود الى النشاط العسكري. ان جميع العينات ملوثة بالكوبلت Co عدا SW2,GW4 بسبب النشاط الصناعي واستخدام وتسرب المنتجات النفطيه. ان قيم الخواص الفيزيائيه والكيميائيه التي تم احتسابها في هذه الدراسه هي العكوره Turbidity والتوصيليه الكهربائيه EC والداله الحامضيه pH ونسبه الاملاح الذائبه TDS ونسبه الاملاح الصلبه TSS والاوكسجين المذاب DOوطلب الاوكسجين الاحيائي BOD وطلب الاوكسجين الكيميائي COD, حيث وجد بان هناك قيم عاليه في جميع النماذج للتوصيليه الكهربائيه وطلب الاوكسجين الاحيائي .اما بالنسبه للمياه الجوفيه فان القيم العاليه فقط العكوره ونسبه الاملاح الذائبه وطلب الاوكسجين الكيميائي.

المياه غير صالحه للشرب وفقا لمعيار الصحه العالميه ومعامل جوده المياه (WQI)حيث ان جميع القيم اعلى من 100 للمياه السطحيه والجوفيه .

حيث ان تتابع المياه الجوفيه حسب قيم معامل نقاوة المياه (WQI) هي كالاتي (GW1>GW5>GW4>GW3>GW6>GW2) والمياه السطحيه (SW3>SW2>SW1) .حيث ان خلط المياه الجوفيه الضحله مع مياه دجله تتاثر بعوامل اخرى مثل تغذيه المياه الجوفيه والتبخر وخصوصا في الاجزاء الاكثر ضحاله.

1. Introduction

Any physical, biological, or chemical change in water quality that adversely affects living organisms or make water unsuitable for desired uses can considered pollution .There are natural source of water contamination ,such as poison springs ,oil seep ,and sedimentation from erosion [1], but in this research is going to focused primarily on human-caused changes that affect water quality or usability. Releasing of untreated effluents from agriculture runoff, domestic sewage, industries waste led to increasing of chemical compound from solute in surface and ground water which in turn has affected on water quality at the study area. Heavy metal pollution in water (both surface water and groundwater) is a serious environmental problem, threatening not only the aquatic ecosystems but also human health, through contamination of drinking water. Sources of heavy metals are either naturally by weathering of rocks, or by human activities [2]. Water sample (surface and ground) of study area are analyzed to determine the concentration of heavy metal and compare the results with international and local standard to found it suitability to different utilization (e.g. human drinking water).

In this study nine water samples are collect in winter 2017 three surface water samples (Tigris River) and six ground water samples at different locations by drilled well. All the water samples (surface and ground) are analyzed for their physical, chemical properties and heavy metals analyses.

2. Study Sites

The study area is located in Samarra City (120) km north of Baghdad central Iraq, between (34°11'22"- 34°12'50" N) and (43°52'30"- 43°55'20" E) .The work focusing on the north part of the City which can represents the left bank of Tigris River near the great Samarra Bridge (Figure-1).

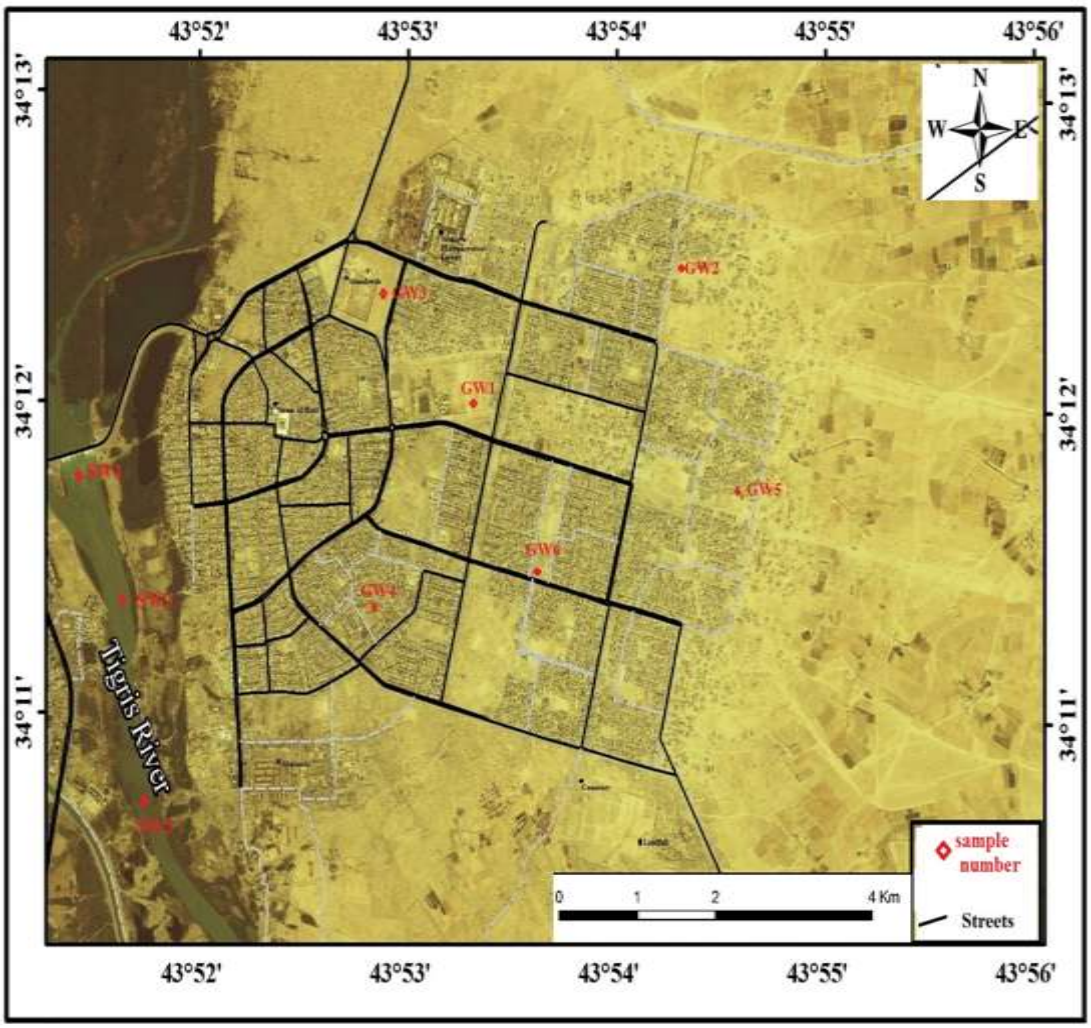

Figure 1: Map of study area with sampling stations

Table 1 : Location Of The Water Samples (Surface And Groundwater)In Samarra City

Water samples	Site names	Coordinates	
		N	E
Sw 1	Samarra Dam Bridge	34°11'65"	43°51'79.1 "
Sw 2	After Abu- Nisan Drainage	34°11'1.5"	43°51'0.17"
Sw 3	Samarra Bridge Road	34°10'70.75"	43°51'34.56"
Gw *1*	A Park Well Al -Shiratih	34°12'08.1"	43°53'18.15"
Gw 2	Al-Qadisih	34°12'63.88"	43°54'19"
Gw 3	Near Mawliah Samarra	34°12'86.45"	43°53'19.94"
Gw 4	Al -Sikak	34°11'93.49"	43°53'05.28"
Gw 5	Al -Muthanna	34°11'43.61"	47°54'16.73"
Gw 6	Al-Jabiriuh 2	34°11'73.14"	43° 53'94.71"

3. Material and method

The water samples were collected from three samples from Tigris River and six samples from ground water (Quaternary aquifer) during October 2017.The surface and ground water were collected polyethylene bottles 50 ml containers for heavy metals analysis after filtering the samples by0.45 µm filters and acidify the samples by ultrapure nitric acid to avoid unpredictable change in characteristic as per standard procedures. All surface and groundwater was analyzed for their physical and chemical properties and heavy metal analyses.

4. Physical and Chemical Parameters

Physical and chemical parameters are measured in the environmental laboratories of Iraqi science and technology using specialized devices. Properties have been measured in the study area are hydrogen number (pH), electrical conductivity (EC),total dissolved solid (TDS), total Suspended Solid TSS, Dissolved Oxygen DO, biological oxygen demand BOD, chemical oxygen demand COD, Turbidity. And then correlated the results with Iraqi standard and international standard.

Water analyses reveal higher values for most of physical and chemical parameter for all groundwater and some of surface water samples, according to [5] and [4] limits for drinking water ,the higher values in all samples for BOD and EC. higher value of TDS, COD,BOD found only in ground water samples Table-2. The increase of BOD in all samples because chemical include industrial wastes, sewage water, pharmaceutical or medical wastes, sanitizers in food processing or commercial cleaning facilities

Table 2- Physical And Chemical Parameter Of Laboratory Measurements Of Surface And Ground Water Samples Comparing With Iraqi Standards [3] And WHO Standards [4].

Parameters	**Surface water**		**Ground water**		IQS, 2009	WHO, 2008
	Range	**Mean**	**Range**	**Mean**		
pH	7.46-7.61	7.54	7-10.3	7.865	6.5-8.5	6.5-8.5
EC (dS/m)	387-396	387	245-315	2895	-------	250
TDS (mg/l)	243-251	245	1568-2009	1831	1000	1000
BOD (mg/l)	5.88-8.77	8.44	4.1-8.6	7.9	<5	--------
COD (mg/l)	52-88	75	100-257	161	-------	100
Turbidity (NTU)	2.65-7.15	4.91	10.5-16.81	14.45	5.0	5.0
DO mg/l	7-10	7.95	4-7	6	**8.3	--------
TSS	0.2-0.6	0.4	0.6-1	0.8	-------	-------

5. Heavy metal in water and drinking water standards

The samples analyzed in the environmental laboratories of Iraqi Science and Technology by using Atomic - Absorption Spectroscopy (AAS).For the purpose of evaluating the suitability of Samarra City water for human drinking .Twenty heavy metals which are Fe, Mn, Zn, Cd, Cu, Co, Pb, Ni, Cr, As, Mo, Hg, Al, Li, Be, Se, V, U, Sr. and then compared with [3-5],The heavy metal concentration level are higher than standard for according to the standard in Fe, Mn, Cd, Pb, Ni, Cr, As, Mo, Hg, Al, Li, Be, Se, V. Uranium concentration levels are higher than standard except (SW1, SW2, SW3, GW1) . Cobalt concentration are higher than standard in most of samples except SW2, GW4 Table-3.

Table 3-Heavy Metal Concentrations Of Water Samples With Standards

	Units	SW1	SW2	SW 3	GW1	2 GW	GW3	4 GW	GW 5	GW 6	EPA	*IQS
Fe	µg/l	4880	2000	108 0	4760	2350	3120	496	921	730	300	300
Mn	µg/l	300	980	911	3160	2080	2340	461	513	263	100	50
Zn	µg/l	1900	870	860	1415	2601	933	690	743	592	300	5000
Cd	µg/l	164	124	127	160.2	96.5	131	54.5	82	68. 6	3	5
Cu	µg/l	844	587	510	822	636	745	193	382	269	1000	1300
Co	µg/l	154	45	83	157	91	129	40	63	58	***5	--------
Pb	µg/l	898	800	891	950	1133	1664	178	933	567	10	15
Ni	µg/l	197	99	91	193	126	152	51	96	78	20	*** 70
Cr	µg/l	580	198	195	586	378	751	219	83	106	50	100
As	µg/l	94	71	78	98	86	93	59	83	71	10	10
Mo	µg/l	139	145	118	148	96	158	81	94	78	*** 70	-------- -
Hg	µg/l	170	160	165	188	176	181	70	51	40	1	2
Al	µg/l	702	300	265	730	516	468	81	112	90	200	100
Li	µg/l	288	80	89	265	311	105	4	7	3	700	------
Be	µg/l	100	74	79	103	91	86	75	57	68	4	-------
Se	µg/l	0.2	0.4	0.44	0.2	0.1	0.5	0.8	**40.**	0.7	50	10
V	µg/l	79	90	86	94	78	84	62	73	56	1000	------
U	µg/l	13	12	11	17	60	40	40	65	45	30	------
Sr	µg/l	1.4	2	1	3	1	4	5	4	10	4000	-------

*Maximum contaminant level (MCL) EPA, U.S. Environmental Protection Agency (EPA, 2009and 2002).
** IQS, Iraqi standards 2009.
** *WHO, 2008, Guidelines for drinking water quality

6. Water Quality Index (WQI)

Water quality index for surface and groundwater are calculated as in the first step, unit weight (Wi) for various parameters is inversely proportional to the recommended standard
(V standard) for the corresponding parameter.Wi values were calculated by using the following formula proposed by [6].

$$Wi = K/ Vstandard \quad (1)$$

where K = proportionality constant, V standard = world- widely accepted drinking water quality standard pre- scribed by WHO 2004.
The constant of proportionality K in the above equation can be determined from the following condition,

$$Wi = K (1/Vstandard) \quad (2)$$

In the second step, Quality rating (Qi) is calculated as,

$$Qi = 100 V actual/ V standard \quad (3)$$

While, the quality rating for pH (QpH) was calculated on the basis of,

$$(QpH) =V actual – V ideal /(V standard- V ideal) \quad (4)$$

where, V actual = value of the water quality parameter obtained from the laboratory analysis.

V ideal = the ideal value of pH considered as equal to (7.00).
V standard = value of the water quality parameter obtained from recommended WHO standard of corresponding parameter.
This equation ensures that Qi = 0 when a pollutant is totally absent in the water sample and Qi = 100 when the value of this parameter is just equal to its permissible value. Thus the higher the value of Qi is, the more polluted is the water.
Then, the overall WQI was calculated using the method proposed by [7] and Harkins [8] on the basis of weighting and rating of the different physical and chemical properties.

$$WQI = Wi\ Qi \quad (5)$$

Based on the calculated WQI showed in Table- 4, the classification of water quality types is given according to [9].

Table 4-Water Quality Index Classification And Grading.

WQI Value	Rating of Water Quality	Grading
0-25	Excellent water quality	A
26-50	Good water quality	B
51-75	Poor water quality	C
76-100	Very Poor water quality	D
Above 100	Unsuitable for drinking purpose	E

Table 5-Water Quality Index Of Water Sample (WQI)

Water Sample	Water Quality Index	Classification
SW1	262.3592	Not suitable for drinking
SW2	294.2695	Not suitable for drinking
SW3	317.644	Not suitable for drinking
GW1	1301.319	Not suitable for drinking
GW2	1056.952	Not suitable for drinking
GW3	1227.796	Not suitable for drinking
GW4	1239.172	Not suitable for drinking
GW5	1294.335	Not suitable for drinking
GW6	1144.423	Not suitable for drinking

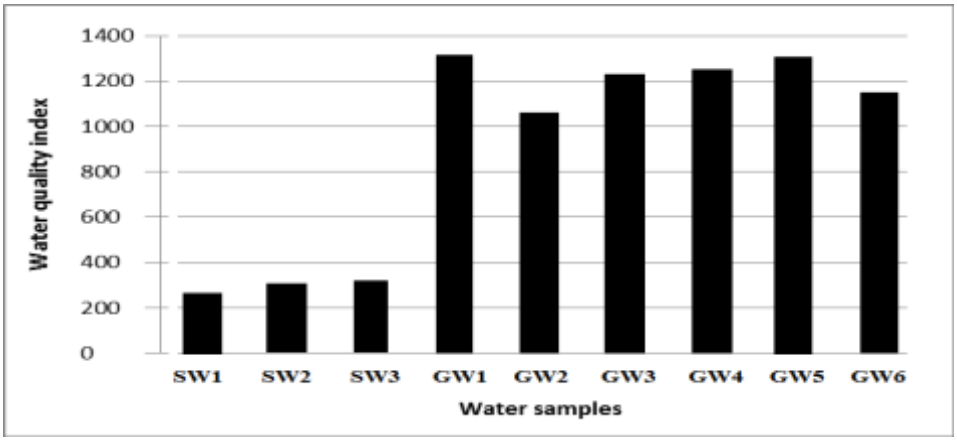

Figure 4-Water Quality Index Values Of Water Samples.

The equations are applied on the results of the surface and groundwater analysis. The water quality index values are all higher than 100, that's mean that the groundwater and surface water in Samarra is not suitable for drinking and grading E according (Table- 4) of water quality index classification [5] as its shown in Figure -4.

According to water quality index results the polluted stations are arrange from higher to lower for ground water as (GW1>GW5>GW4>GW3>GW6>GW2),the water quality index of surface water (SW3>SW2>SW1).

6. Results and discussion

Physical and chemical properties value which found in this study is pH, EC, TDS, TSS, DO, BOD, COD, turbidity. The highest for pH value is the range value of surface and ground water greater than 7 to that's mean Samarra City water is nearly alkaline, 8.10 detected in ground water in GW_3 and considered as out of the limit.

Water analyses reveal unacceptable values for physical and chemical, according to WHO standard and IQS 2009 limits for drinking water ,the higher values in all samples for BOD, EC. And higher value of TDS, COD, and turbidity only in ground water samples.

The ground water TDS higher than the standard which is 1000. The increase of BOD in all samples because chemical include industrial wastes, pharmaceutical or medical wastes, sanitizers in food processing or commercial cleaning facilities [10]. COD in ground water the most common reason of COD is in quantifying the amount of pollutants found in groundwater [11].

Turbidity is closely related to total suspended solids (TSS) and especially the groundwater due to the presence of soil particle that are tangled with water in aquifer [12].

Twenty heavy metals elements which are Fe, Mn, Zn, Cd, Cu, Co, Pb, Ni, Cr, As, Mo, Hg, B, Al, Li, Be, Se, V, U, Sr. and then being compared with Iraqi standards [3], WHO[4]and MCL of EPA[5].

The presence of heavy metals in water is caused by either natural anthropogenic sources that's available in the city of Samarra which is (industrial , agriculture and military activities).

Industrial causes and uses of chemical compounds (chromium, molybdenum, magnesium, cobalt, manganese, lead and nickel)[13]. Agricultural causes and use of fertilizers (arsenic, vanadium, mercury, lithium, bromide)[13]. Causes of military activities (Uranium).Non-polluting elements are strontium, selenium and copper.

Anthropogenic activity are represented forming and using fertilizer and pesticides, this kind of activity responsible for most of increasing levels of heavy metals as long as Samarra City well known in its agriculture activity and spreading of farms in all suburb area of the City, besides agriculture activity the industrial activity represented in industrial area which include car repairmen and painting and amendment of furniture beside the most important on the pharmacological factory.

The equations are applied on the results of the surface and groundwater analysis. The water quality index values are all higher than 100. According to water quality index results the polluted stations are arrange from higher to lower for ground water as (GW1>GW5>GW4>GW3>GW6>GW2),the water quality index of surface water (SW3>SW2>SW1).

7. Conclusions

1-Analysis results of Samarra City water for turbidity, TSS, TDS, EC, BOD, COD, DO are considered as unacceptable according to maximum recommended limit by the US Federal Ministry of Environment is10 mg/l (9), of all ground water samples. Water analyses reveal unacceptable values for physical and chemical parameters according to WHO standard and IQS2009 limits for drinking water, BOD, EC have shown high values in all surface and groundwater samples. Whereas, high values of TDS, COD and turbidity only in ground water samples.

2-The heavy metal concentrations in surface water samples are in the order of (Fe> Zn> Pb> Mn> Cu> Cr> Al> Mo> Ni> As> Cd> Be> V> Hg> U> Co>Sr> Li> Se).

3-The heavy metal concentrations in ground water samples are in the order of(Fe> Zn>Mn>Pb> Cu> Al> Cr> Li> Hg> Ni> Cd> Mo> Co> Be> V> As> U>Sr> Se).

4-The main sources of mercury in Samarra City are combustion facilities, including municipal solid waste incineration and hospital incineration and pharmacological factory. Other sources of mercury contamination in the study areas are hazardous waste and sewage sludge, most anthropogenic mercury emissions are released to water.

5- Sources of the most contaminants for surface water are from nonpoint source (Agriculture) as well as for ground water especially under agricultural areas its runoff loaded with fertilizer and pesticides, herbicides. Beside point source from leakage from landfill sites, sewage and septic tank systems at sites of poor services in the study area, the general direction of ground water is SW and groundwater recharging the Tigris River.

6- According to water quality index of surface and groundwater in Samarra City have shown high values that exceeding 100, which mean that the groundwater and surface water in Samarra is unsuitable for drinking , and need urgent treatment to become suitable for drinking .

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