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RESEARCH ARTICLE

ESTMAITION OF HEAVY METALS IN THE GROUNDWATER OF SELECTED AREAS FROM AL-DHALIA DISTRICT, AL-DHALIA GOV., YEMEN

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Abstract

In this research, the level of heavy metals Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Manganese (Mn), Lead (Pb) and Zinc (Zn) in groundwater in selected areas in the region of Al-Dhalia district, Al-Dhalia Governorate, Yemen. Sixteen groundwater samples were collected from the study area included 9 artesian wells samples and 7 of hand-dug wells, and analyzed for the presence of heavy metals using Atomic Absorption Spectrophotometer (AAS). The results of the analysis showed that the concentrations of Pb, Mn and Cu in most of the studied samples have exceeded the Yemeni and WHO standards for drinking water, while the concentrations of Fe, Cd, Cr and Zn in most of the studied samples were low and fall within the optimum specifications for local and WHO drinking water.

Keywords: Toxic metals, Groundwater, Al-Dhalia Governorate, Yemen.

1. Introduction

Today heavy metals pollution of the groundwater is one of the serious environmental problems. Groundwater pollution is one of the most important environmental problems in the present world where metal pollution has major concern due to its high toxicity even at low concentration [1,2].

Heavy metals enter in groundwater from variety of sources; it can either be natural or anthropogenic [3,4]. Usually in natural environments, the concentration of the metals is very low and is mostly derived from the minerals and the weathering of geological formations and soils of that area [5,6]. Main anthropogenic sources of heavy metal pollution are mining, disposal of untreated and partially treated effluents as well as metals from different industries such as pharmaceutical products and indiscriminate use of heavy metal containing fertilizer and pesticides in agricultural fields [7-10].

In Yemen, which is witnessing remarkable development in various development fields, most of the newly industrial, agricultural and commercial projects of origin did not take into account the circumstances and specificity of the local environments in which they are established, so these activities became an environmental burden resulting in pollution of water, soil and air (due to the lack of application of laws, and regulations related to environmental protection). As well as, the increase in the population also constitutes an environmental pressure resulting in the exacerbation of the phenomenon of environmental pollution.

In the Al-Dhalia district, Al-Dhalia governorate, wastewater is collected from different parts of the city to its center through a layer that is characterized by its penetration of these collected waters. When the rains fall, a large part of this waste is moved with the flow of torrents to different places, where there are many water wells beside the stream, "these wells are used by residents for drinking or human use". Due to the lack of sewage stations and the result of the discharge of waste to the places where the torrents run, which leads to the transfer and leakage of pollutants to the surface and ground water. As well as, this districts from the agricultural areas, where it uses a lot of pesticides and fertilizers agricultural indiscriminately. These pollutants a will be transferred to the groundwater with the flow of rain or it may leak through the soil to reach the groundwater that feeds the water of the wells, some of which are used for drinking in the study area. According to Al-Amry*et al.*, [11] about 71% of the water used for the drinking purpose.

The importance of this study comes as a result of the lack of periodic chemical analyzes. Therefore, through this study, we are trying to contribute to knowing the extent of pollution with some heavy elements in the water of some wells, finding conclusions and suggesting appropriate solutions for that.

1.1 *Spatial and temporal limits of the study area*

From the administrative point of view, the study area is located in Al-Dhalia district, Al-Dhalia governorate which determines the spatial location of Al-Dhalia governorate in the southern part of the central region of the Republic of Yemen. Where (astronomically) geography is confined between the latitudes 13 °, 30 ° - 14 °, 15 °, north of the equator, and longitudes 44 °, 10 ° - 44 °, 48 ° east of Greenwich (Fig. 1). The spatial limits of the study area from which well water was sampled are in the range of the southern area of Al-Dhalia dist. The pelvic area of the study area is estimated according to the sources of runoff of surface and ground water at about 86 square kilometers, which represents 24.9% of the total area of Al-Dhalia governorate, which amounts to about 345 square kilometers [12,13].

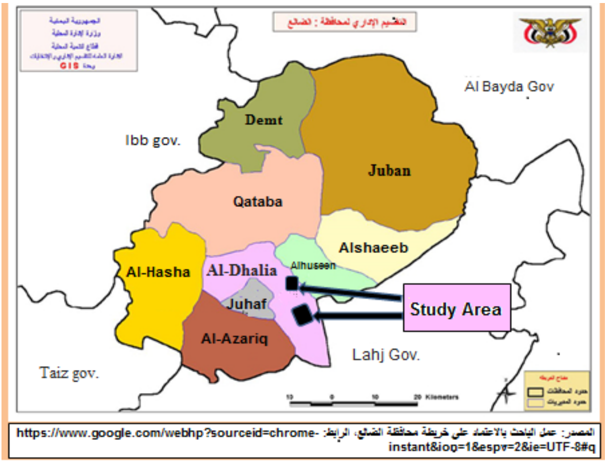

Figure 1: showing the location of the groundwater wells from which the study samples were taken in Al-Dhalia dist., Al-Dhalia governorate

Al-Dhalia governorate is bordered to the north by Al-Bayda governorate, to the east by parts of Al-Bayda and Lahj governorates, to the south by parts of Lahj and Taiz governorate, to the west by Ibb governorate, and the capital of Al- Dhalia governorate is Al- Dhalia city [12,13].

2. Experimental Section

2.1 *Positioning*

Initially, the purpose of going to the study area (Al-Dhalia Directorate) was in September (2014), for determining the location of the wells to be studied, and how close is it to the sewage? It was only a cluster of rural villages or the city of Al-Dhalia. Sixteen sites were identified for the wells to be studied. 5 located in the city of Al-Dhalia "characterized by its proximity to sewage water", while the other wells (eleven wells) are located in rural villages and far from the city of Al-Dhalia and there is no gathering of any wastewater, but it is located on the course of torrents Coming from the city. At each Location the coordinates were taken using a GPS (Tables 1 and 2).

2.2 *Sampling and analysis*

Water samples were collected using 0.75-liter polyethylene bottles and acidified with nitric acid to a pH below 2 to minimize precipitation and adsorption on container walls, and kept at a temperature of 4 °C to stop the precipitation of important metals before the commencement of the analysis [14]. To ensure the collection of representative water samples from the borehole and dug-wells, large quantity of water from were pumped out or bailout for at least thirty minutes to remove water from bore storage in the case of the borehole and the dug wells before sampling. This was done to obtain water coming directly from the aquifer. All chemicals used were of analytical reagent grade. All the plastic and glass-ware used were soaked overnight in 10% nitric acid, rinsed with distilled water, and finally with Millipore water before use. pH meter and the electrode of conductivity meter (Model: EUTECH INSTRUMENTS PC510).

2.3 *Statistical processing of data*

Statistical analysis was done for all samples by SPSS Program and origin 7.5.

3. Results and Discussion

In the present study, metals such as Cd, Cr, Cu, Fe, Mn, Pb and Zn were considered. Heavy metal concentrations of groundwater samples, the guideline values for drinking water as specified by the WHO (2011) [15] and Yemen's Ministry of Water and Environment (YMWE, 1999) [16] are summarized in (Tables 3&4).

3.1 *Cadmium (Cd)*

Cadmium level varies from 0.0014 to 0.0049 mg/L in four locations (25% of the samples analyzed), which are above the WHO maximum admissible limit of Cd in drinking water (0.003 mg/L) [15], but all the samples analyzed were found to comply the maximum admissible limits (0.005 mg/L) for Yemeni specifications [16] (Tables 3&4).

Cadmium is a natural element in the earth's crust. An acute exposure to significantly higher cadmium levels can lead to a variety of negative health effects including Diarrhea, Vomiting, fever, lungs damage, muscle pain [17,18].

Cadmium is highly toxic and responsible for several cases of poisoning through food. Small quantities of cadmium cause adverse changes in the arteries of human kidney. It replaces zinc biochemically and causes high blood pressures, kidney damage etc. [19]. It interferes with enzymes and causes a painful disease called Itai-itai[20].

The main sources of cadmium are industrial activities; the metal is widely used in electroplating, pigments, plastics, stabilizers and battery industries [21]. Another important

Table 1: Location of sampling sites with their latitude and longitude

Sample No.	Name of wells	Latitude	Longitude	Location
1	A. Algadi′s well*	13 42 14.54	44 44 3.31	Al-Dhalia city
2	M. Hamood′s well*	13 42 21.97	44 44 1.12	"
3	Ghassan′s well*	13 42 17.08	44 43 57.40	"
4	A. Ther′s well*	13 42 16.93	44 44 1.04	"
5	M. Ahmed′s well*	13 42 30.18	44 44 0.68	"
6	Urban project*	13 37 53.33	44 49 0.31	Al-Sailah (rural villages)
7	S. Saleh′s well**	13 37 20.52	44 48 55.68	"
8	A. Mohamed′s well**	13 37 15.95	44 48 57.33	"
9	F. Mahmod′s well**	13 37 21.13	44 48 48.26	"
10	A. AlhaJ′s well**	13 36 29.97	44 49 8.40	"
11	A. Al-Somali′s well**	13 36 23.85	44 49 8.02	"
12	H. Abdullah′s well**	13 36 22.66	44 49 15.22	"
13	S. Aobl′s well*	13 35 55.90	44 49 11.14	"
14	Alhamora project**	13 37 10.04	44 49 34.64	"
15	Almagbah project**	13 37 3.62	44 48 3.62	"
16	Al-Tafwah project**	13 37 17.99	44 48 50.22	"

*refer to hand dug-wells; ** refer to artesian wells

Table 2: Detailed data on the locations of the studied wells sample.

S. No.	Name of wells	Depth (meter)	Distance to the sewage site (meter)	Types of wastewater adjacent	Water Uses
1	A. Algadi′s well*	31	20	Sewerage network collected from the Al-Dhalia city	Household & Irrigation
2	M. Hamood′s well*	18	24		"
3	Ghassan′s well*	21	36	"	"
4	A. Ther′s well*	24	13	"	"
5	M. Ahmed′s well*	18	40	"	"
6	Urban project*	25	--	Absorptive holes of houses	Drinking and irrigation
7	S. Saleh′s well**	500	--	None	Household & irrigation
8	A. Mohamed′s well**	280	--	None	Household & irrigation
9	F. Mahmod′s well**	54	--	None	Household & irrigation
10	A. AlhaJ′s well**	8	150	Agricultural and rural wastes	Drinking and irrigation
11	A. Al-Somali′s well**	90	--	Agricultural and rural wastes	Household & irrigation
12	H. Abdullah′s well**	50	--	Agricultural and rural wastes	Household & irrigation
13	S. Aobl′s well*	0	--	None	Drinking and irrigation
14	Alhamora project**	40	--	None	Household
15	Almagbah project**	80	164	Rural waste	Household
16	Al-Tafwah project**	20	--	Rural waste	Household

source of Cd emission is the production of artificial phosphate fertilizers [22]. The presence of cadmium is likely due to human activities (sometime-unrequired chemicals are used in agriculture process, municipal waste, runoff from waste batteries and paints).

3.2 *Chromium (Cr)*

The amount of chromium present in water samples have been illustrated in (Table 3). In this study, the concentration of chromium of most studied water samples were found to be within the permitted limits sets (0.05 mg/L) by WHO [15] and Yemeni Standards [16], with the exception of two samples which are above the WHO [15] and Yemeni standards [16], this constituted 12.5 % of the samples analyzed (Table 4). Chromium level in the well samples was low and close to each other with the exception of three samples which were of high level, the reason may be due to the temperature of exposed pipes exposed to sunlight daily in addition to most of the studied water wells have a high temperature and therefore it could be another reason for corrosion of pipes and a change in the concentrations of heavy metals, including chromium in the water of distribution networks [23], Discharge from steel and pulp mills; erosion of natural deposits [24].

Generally, the natural content of chromium in drinking water is very low ranging from 10 to 50 µg/L, except for the regions with substantial chromium deposits [25]. Chromium in excess amounts can be toxic especially in the hexavalent form. Sub chronic and chronic exposure to chromic acid can cause dermatitis and ulceration of the skin. Long-term exposure can cause kidney, liver, circulatory and nerve tissue damages. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high level of chromium [26,27].

3.3 *Copper (Cu)*

The total concentrations of copper in the studied samples in ground water are listed in (Table 3). The concentrations of copper in the studied samples were ranged between 0.04 to 9.09 (mg/L). Of all the samples analyzed, 37.5% and 68.75% contain copper level above WHO [15] (2 mg/L) and Yemeni Standards (1 mg/L) [16], respectively (Table 4). Copper compounds are used as or in fungicides, algaecides, insecticides and wood preservatives and in electroplating, azo dye manufacture, engraving, lithography, petroleum refining and pyrotechnics. Copper compounds can be added to fertilizers and animal feeds as a nutrient to support plant and animal growth [28-30]. Copper compounds are also used as food additives (e.g., nutrient and/or coloring agent) [28,31]. Recent studies have delineated the threshold for the effects of copper in drinking-water on the gastrointestinal tract, but there is still some uncertainty regarding the long-term effects of copper on sensitive populations, such as carriers of the gene for Wilson disease and other metabolic disorders of copper homeostasis [15].

3.4 *Iron (Fe)*

Table (3) shows that the iron element concentrations of the studied samples. The range of concentration of iron in all the studied samples is 0.01 to 2.40 mg/L. the highest concentration of 2.40 mg/L was found in sample 16. The second, third and fourth highest concentrations of 0.43, 0.40 and 0.38 mg/L was found in samples 14, 1 and 15, respectively. However, the Fe values (It was found in four samples (1, 14, 15 and 16) were higher than the maximum admissible limit for WHO (0.3 mg/L) [14], and sample 16 were above the maximum admissible limit by Yemeni Standards (1 mg/L) [16].

In general, of all the samples analyzed, 25% and 6.25% contain iron level were higher than the maximum admissible limit by WHO (0.3 mg/L) [15] and Yemeni standards (1 mg/L) [16], respectively (Table 4).

3.5 *Manganese (Mn)*

Table (3) shows that manganese level in the studied samples ranged between (0.10 mg/L) as a minimum in the samples 14 and 15, and (1.40 mg/L) as a maximum in sample 4. Most of the studied samples were of highest level of manganese, and this increase is likely to be contaminated with wastewater for wells near the city. As for the wells water in Al-Sailah, the reason may be due to the temperature of exposed pipes exposed to sunlight daily in addition to most of the studied water wells have a high temperature and therefore it could be another reason for corrosion of pipes and a change in the concentrations of heavy metals, including manganese in the water of distribution networks [23]. Manganese is naturally occurring in many surface water and groundwater sources, particularly in anaerobic or low oxidation conditions and this is the most important source for drinking-water. Manganese occurs naturally in many food sources, and the greatest exposure to manganese is usually from food [15]. Manganese is a mineral that naturally occurs in rocks and soil, but human activities are much responsible for underground water pollution by this element [17].There are some places in study area where the concentration of manganese found higher than the WHO allowed limit (0.4mg/L) [15].

From figure (3.3) we can see that manganese level in samples 9, 12, 14, 15, 16 were within the MAL of WHO (0.4 mg/L) [15] and Yemeni specifications (0.2 mg/L) [16] except for the sample12, while the rest of the samples were found to be higher than the permissible limits of Yemeni [16] and WHO specifications [15].

In general, of all the samples analyzed, 68.75% and 62.5% contain manganese level were higher than the maximum admissible limit by Yemeni Standards (0.2 mg/L) [16] and WHO (0.4 mg/L) [15], respectively (Table 4).

3.6 *Lead (Pb)*

The results of lead (Pb) analysis of 16 samples of well water ground are shown in Table 3. The range of concentration of lead in all the studied samples is 0.16 to0.89 mg/L. The highest concentration of 0.89 mg/L was found in sample 10, while the lowest concentration of 0.16 mg/L in sample 13. The concentrations of Pb in all studied samples were higher than the maximum admissible limit (0.01mg/L) for WHO [15] and Yemeni standards [16] (Table 4). A lead level in all studied samples was high, and some samples recorded results of ten times the limit allowed in drinking water. Anthropogenic activities (urban, industrial and agricultural activities) play an influential role in the presence of lead, as wastewater is the main reason of increasing lead level in wells located in the Al-Dhalia city. While the water well, located at Al-Sailah, the increase in lead may be due to the quality of the rocks through which this water passes, as well as due to the temperature of exposed pipes exposed to sunlight daily in addition to the high temperature of some wells, which can be Cause corrosion of pipes [23]. The amount of lead dissolved from the plumbing system depends on several factors, including pH, temperature, water hardness and standing time of the water, with soft, acidic water being the most plumb solvent [15]. According to Gowd and Govil[32] mostly used in the manufacture of lead acid storage batteries. Lead is also released from smelting, motor vehicle exhaust fumes and from corrosion of lead pipe work. There are too many source that introduce lead in atmosphere such as industrial waste, household paint, and vehicle exhausts [33].

Table 3: Results of Heavy Metals Analysis (mean ± SD; mg/L) in the Studied Well Water

S. No.	Cd	Cr	Cu	Fe	Mn	Pb	Zn
1	0.0018±0.0007	**0.060±0.0040**	**9.09±0.36**	0.40±0.040	**1.20±0.08**	**0.37±0.01**	0.05±0.006
2	0.0029±0.0007	**0.051±0.0031**	**7.06±0.27**	0.10±0.010	**0.70±0.06**	**0.29±0.012**	0.01±0.002
3	0.0014±0.0004	0.014±0.0035	**6.05±0.18**	0.06±0.002	**0.59±0.05**	**0.18±0.026**	0.04±0.005
4	**0.0049±0.0009**	0.008±0.0007	**7.57±0.31**	0.04±0.003	**1.40±0.09**	**0.28±0.021**	BDL
5	0.0029±0.0008	0.041±0.0030	**3.52±0.12**	0.01±0.002	**0.59±0.05**	**0.22±0.017**	0.01±0.002
6	0.0020±0.0005	0.001±0.0003	**1.37±0.04**	0.18±0.025	**0.70±0.07**	**0.19±0.021**	**0.07±0.007**
7	0.0014±0.0003	BDL*	0.06±0.02	0.08±0.005	**0.49±0.04**	**0.52±0.029**	0.01±0.004
8	0.0021±0.0004	0.001±0.0002	0.04±0.02	0.08±0.005	**0.90±0.07**	**0.88±0.02**	0.02±0.003
9	0.0020±0.0005	0.003±0.0003	**1.46±0.05**	0.21±0.035	0.19±0.02	**0.30±0.006**	BDL
10	0.0020±0.0005	0.006±0.0005	**3.07±0.09**	0.01±0.001	**1.00±0.08**	**0.89±0.085**	0.01±0.002
11	**0.0039±0.0008**	BDL	0.07±0.03	0.09±0.006	**0.71±0.06**	**0.81±0.051**	0.02±0.005
12	0.0029±0.0008	0.019±0.0025	0.06±0.03	0.21±0.031	**0.39±0.03**	**0.72±0.040**	0.02±0.005
13	**0.0039±0.0007**	0.003±0.0003	0.21±0.04	0.02±0.002	**1.20±0.07**	**0.16±0.006**	BDL
14	**0.0039±0.0007**	0.001±0.0002	**1.20±0.04**	0.43±0.035	0.10±0.01	**0.17±0.017**	0.01±0.002
15	0.0029±0.0009	0.002±0.0003	**1.80±0.06**	0.38±0.030	0.10±0.01	**0.18±0.006**	BDL
16	0.0020±0.0006	BDL	**1.70±0.05**	**2.40±0.10**	0.19±0.02	**0.18±0.01**	BDL
L.S.D	0.00004	0.000127	0.01031	0.00226	0.00389	0.0021	0.00024
Ranges	0.0014-**0.0049**	BDL-**0.06**	0.04-**9.09**	0.01-**2.40**	0.10-**1.40**	**0.16-0.89**	BDL-**0.07**
WHO [15]	**0.003**	**0.05**	**2**	**0.3**	**0.4**	**0.01**	**3**
YMWE[16]	**0.005**	**0.05**	**1**	**1**	**0.2**	**0.01**	**5**

BDL*: below detection limit of the method

Table 4: Percentage of samples, which comply with WHO [15] and Yemeni Standards [16], maximum admissible limit (MAL) of different drinking water parameters.

Metal	Percent of samples more than WHO [15]		Percent of samples more than YS (YMWE) [16]	
	No. of samples	%	No. of samples	%
Cd	4	25%	Nil	Nil
Cr	2	12.5%	2	12.5%
Cu	6	37.5%	**11**	**68.75%**
Fe	4	25%	1	6.25%
Mn	**11**	**68.75%**	**12**	**75%**
Pb	**16**	**100%**	**16**	**100%**
Zn	Nil	Nil	Nil	Nil

The maximum acceptable concentration results are of concern as lead is a poisonous metal that can damage nervous connections (especially in young children's) and cause blood and brain disorders. One of the most important and serious biochemical effects of lead is its interference with haemo synthesis, which leads to hematological damage [34,35].

3.7 *Zinc (Zn)*

Results show a range between non-detected and 0.07 mg/L of zinc (Table 3). All the samples were noted to be lower than the maximum permissible limit of drinking water for WHO [15] and Yemeni standards [16] (Tables 3&4). Zinc level is low in groundwater due to its weak solubility in water with moderate acidity. Zinc is an essential trace element found in virtually all food and potable water in the form of salts or organic complexes. The diet is normally the principal source of zinc. Although levels of zinc in surface water and groundwater normally do not exceed 0.01 and 0.05 mg/l, respectively, concentrations in tap water can be much higher as a result of dissolution of zinc from pipes [15].

4. Conclusions

According to the maximum admissible limit (MAL) of drinking water by WHO and Yemeni Standards:

- The concentration of Pb was more than the MAL in the all wells water.
- More than 60 % contain Mn level were higher than the admissible limit.

- 37.5% and 68.75% contain copper level above WHO and YS, respectively.
- Cd and Fe levels were exceeded WHO value (25% of samples analyzed).
- 12.5 % of samples analyzed contain Cr level were higher than the MAL by WHO and Yemeni standards.
- Levels of zinc in all of the studied samples were low the optimal specifications of local and WHO.

Recommendations

- The study recommends accelerating the study of the sewage networks project for the major city of Al-Dhalia, which is expected to be connected to the neighboring cities during the coming years, and to develop engineering designs in line with modern methods of wastewater treatment.
- Performing chemical analyzes of heavy elements periodically to identify the level of their accumulation in water, especially for drinking.
- Water is of great importance; therefore, continuous guidelines and instructions must be put in place to reduce its consumption, pay attention to the purity of drinking water and keep its sources away from the places of pollution.
- The municipality shall set up modern technical specifications for cesspits, preventing household wastewater from seeping into aquifers, and requiring cesspits to siphere the water of those pits into basins that are prepared to receive them at the new station site.
- The study recommends the concerned authorities (official and private) to avoid using excessive fertilizers and pesticides, especially in the areas near the wells.

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مقالة بحثية

تقدير الفلزات الثقيلة في المياه الجوفية لمناطق مختارة من مديرية الضالع، محافظة الضالع، الجمهورية اليمنية

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الملخص

في هذ البحث تم دراسة مستوى تراكيز بعض الفلزات الثقيلة الكادميوم (Cd)، الكروم (Cr)، النحاس (Cu)، الحديد (Fe)، المنجنيز (Mn)، الرصاص (Pb) والزنك (Zn) في المياه الجوفية من مناطق مختارة في مديرية الضالع، محافظة الضالع. وذلك بجمع العينات من 16 بئرا شملت 9 من الابار الارتوازية و 7 من الابار المحفورة يدويا، ومن ثم التحليل باستخدام جهاز طيف الامتصاص الذري. بينت نتائج التحاليل ارتفاع تراكيز عناصر الرصاص (Pb)، المنجنيز(Mn) والنحاس(Cu) في أغلب العينات المدروسة متجاوزاً المواصفات اليمنية ومنظمة الصحة العالمية (WHO) لمياه الشرب، بينما تراكيز عناصر الحديد (Fe) والكادميوم (Cd) والكروم (Cr) والزنك (Zn) في معظم العينات المدروسة كانت منخفضة وتقع ضمن الحد الأمثل للمواصفات المحلية ومنظمة الصحة العالمية لمياه الشرب.

الكلمات الرئيسية: الفلزات السامة، المياه الجوفية، محافظة الضالع، اليمن.