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DETERMINATION OF Pb, Cd AND Cr LEVELS IN THE DRINKING GROUNDWATER FROM UBARI AND WADI ETBAH AREAS, FEZZAN, LIBYA

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ABSTRACT

This Studyconducted to measure the concentrations of lead (Pb), cadmium (Cd) and chromium (Cr) in drinking water wells. 17 sampleswerecollectedfrom one well in Tekerkiba village in Ubari area, and the samenumber of sampleswerecollectedfrom the Hamandywell in Tasawa village thatlocated in WadiUtbah area in June 2021. Metals concentration in water sampleswereanalyzedusing Flame Atomic Spectroscopy (FASS). The resultsshowedthat the mean concentration of Pb (0.15 mg/L) in the samplesfromUbariwaslowerthan Pb levels (0.22 mg/L) in the samplescollectedfrom Wadi Etbah area while the mean concentration of Cd in the samples of Wadi Etbahwasexactlysimilar to that in Ubari area with a value of 0.13 mg/L although, Cd was not detectedin 14 water samples of bothwells. The concentration of Cr in all sampleswashigherthan the threshold of Cr levels in drinking water. Therefore, mean concentrations of all studiedmetals in the samples of bothwellsweregreaterthan the standard values mentioned by world HealthOrganization (WHO) and LibyanHealth Organization (LHO).

Key words : Drinking water, Ubari, Heavy metals, Wadi Etbah, Pollution

الملخص

أجريت هذه الدراسة لقياس تركيز الرصاص والكادميوم والكروم في عينات مياه جمعت من ابار مياه الشرب. فتم جمع 17 عينة من احدى الابار بقرية تكركيبة بمنطقة أوباري ونفس العدد من العينات جمعت من بئر همندي من قرية تساوة بمنطقة وادي عتبة في شهر يونيو 2021. تم استخدام جهاز مطياف الانبعاث الذري اللهبي (**FAS**) لتقدير تركيز المعادن قيد الدراسة في عينات المياه. أظهرت النتائج ان متوسط تركيز الرصاص بلغ 0.15 **mg/L** في العينات التي جمعت من منطقة أوباري وأقل من تركيزه في العينات التي جمعت من بئر وادي عتبة 0.22 **mg/L** بينما متوسط تركيز الكادميوم ببئر وادي عتبة كام مساويا لتركيزه ببئر أوباري بالرغم من أن الكادميوم لم يتم اكتشافه في 14 عينة في كلا البئرين. تركيز الكروم في كل العينات أعلى من التركيز المسموح به في مياه الشرب ما عدا عينة واحدة ببئر أوباري. متوسط تركيز كل المعادن في المياه التي شملتها الدراسة في كلا البئرين كانت أعلى من تلك الموصى بها من قبل منظمة الصحة العالمية والمواصفات القياسية الليبية لمياه الشرب وبذلك نوصي بعدم استخدام هذه المياه للشرب.

الكلمات المفتاحية:: مياه الشرب، أوباري، المعادن الثقيلة. وادي عتبة، التلوث.

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1. INTRODUCTION

The water covers about 70% of the earth's surface. The quality and the quantity of the water are equally important to the life. Drinking water issourcedfromground sources such as groundwater and aquifers. It can alsobeobtainedfrom surface water such as rivers, glaciers and streams and fromother sources includingrain, hail, snow and seathroughdesalination. The major sources of surface water pollution include effluent discharges by industries, atmosphericdeposition of pollutants and occasionalaccidentalspills of toxicchemicals (Lafabric*et al*., 2008). One specialconcern for humanhealthis the pretence of heavymetals in drinking water.

Heavy metals are defined as metallicelementsthat have a relatively high densitycompared to water and high atomic mass rangingfrom 60 to 200 atomic mass unit such as or Heavy metals like Lead (Pb), Cadmium (Cd) and Chromium (Cr). Surface water contaminations occur, when water travels over the surface of the land or through the ground. While for the ground water, the contaminants mayleachatedfromlandfills and septicsystems, hazarddisposal of agricultural chemicals and householdcleaningproducts, through the ground(Markert, 2007) reported ,thereiscurrently a greatinterest in the use of living organisms as in aquaticecosystem. however, hedid not providesufficient information on the bioavailability of the metals in the underground water of the South Libya. Though, todayitisknownthatonly certain oxidation states of biologicallyavailablemetal ions such as Pb^{2+} can pose the greatestrisk to humanhealth and the environment(Jaishankar *al*., 2014).Various sources of heavymetalsincludesoilerosion, naturalweathering of the earth'scrust, miningactivities, industrial effluents, urbanrunoff and sewagedischarge (Morais *et al*., 2012).This results in the pollution of water withheavymetals, consequently the quality of the water deteriorates and affectingaquaticecosystems. The heavymetalsoverload has inhibitoryeffects on the development of aquaticorganisms (phytoplankton, zooplankton and fish). The metallic compounds coulddisturb the oxygenlevel and mollusksdevelopment, byssus formation, as well as reproductive processes. Pollutants can alsoseep down and affect the groundwaterdeposits. Water pollution alsooccurswhenrain water runoffthroughurban and industrial areas, agricultural land and miningoperations sites makesitsway back to receiving waters (rivers, lakes and oceans) and into the ground. (Alhibshi *al*., 2014).

Heavy metal can cause serioushealtheffectswithvariedsymptomsdepending on the nature and quantity of the metalingested (MDH, 2014). Lead is one of the mostextensivelystudiedtoxicchemicals (Archbold and Bassil, 2014). It can beabsorbedthrough the digestive tract, the lungs and the skin. It accumulates in the body and can cause lead poisoning. Even at low concentrations whenthere are no outwardsymptoms, lead can damage the brain, kidneys, nervous system and redbloodcells. Someeffects of lead poisoningmaydiminish if the source of exposureisremoved, but some damage is permanent.

"Symptoms of lead poisoningincludetiredness, a short attention span, restlessness, poorappetite, constipation, headaches, suddenbehaviour change, vomiting and hearingloss. Adultswith lead poisoningmaybe irritable and disoriented" (Dozier and McFarland, 2001).

"Exposure to lowlevel of cadmium decreasesbonedensity and disruptsbone composition. Rapidlygrowingbones are the most sensitive to theseeffects, sochildren are at an increasedrisk. Cadmium does not easilyleaveour bodies and tends to build up in the kidney. As a result, both shorter, higherexposures and lifetimelowlevelexposures to cadmium can cause kidneydisease in olderadults. Although cadmium can cause cancer wheninhaled, but thereislittleevidence to support thatit can cause cancer wheningested" (MDH, 2014).

"Chromiumtoxicity in humans varies depending on the form of the compound, itsoxidation state and the route of exposure. Studiesshowedthatthereis a little or no toxicityassociatedwith the trivalent form of chromium (Cr^{3+}), whereas hexavalent chromium compounds (Cr^{3+}) are classified as carcinogenic to humans by the inhalation route of exposure, based on sufficientevidence in bothhumans and animals. The criticalhealtheffect on which to establish a guideline for chromium in drinking water is diffuse hyperplasia of the small intestine, as itis the most sensitive endpoint and a precursor of tumor formation "(Health Canada, 2015). Therefore, the aims of thisstudywere to determine the concentration of Pb, Cd and Cr in the drinking water suppliedfromtwogroundwaterwells in Ubari and Wadi Etbah areas, Fizzan, Libya and also the relationshipsbetween the metallevels in samplescollectedfromUbari and Wadi Etbah area.

2. MATERIALS AND METHODS

2.1 Study area

The village of Tasawahis an oasis of oases of Wadi Etbahthat a part of Murzuq basin and located in southwest of Libya in the middle of Libyan Sahara(26° 05´ 37" N 13° 30´ 07" E). There are two the drinking water issupplied to citizen in this village fromtwowells, the first one calledHamandywell (thatwestudiedits water content of investigatedheavymetals) and the second one iscalledSarowell. The Hamandywellwasdugin 1973 and the depth of the wellis 350 meter, 344 meter of the wellcontains water.

Tekerkiba village is a small village located on Ubari area in southwest of Libyawith a population of 2000 person. It considers as the main gate to the lake of Gaberoun. There are severalcompaniesinterested in tourismfield and organizetourism trips to Gaberounlake. There are alsotwodrinking water wells in this village, the first is the western well (whichis the source of water sampleswereinvestigated in thiswork) withdepth about 203 meter and the otheris the northwell.

2.2Samples collection

The drinking water sampleswerecollectedfrom the wellofHamandy in Tasawah village of wadi Etbah and alsofrom a well in Tekerkiba village in Ubariarea.Tocollect water samples. The usedbottleswerepreviouslyrinsedwith double distilled water. 17 water samplesfrom the concentration of bothwellsweretaken in one dayfrom the tap water fixedinside the wells to measure lead, cadmium and chromiumlevels. 1 ml HNO_3wasadded to the samplesimmediatelyafter the collection. Thesesampleswereanalyzed to determine the levels of studiedheavymetals by using FAS type hitachi 180-30 equip No A-10 at specifiedwavelength (APHA 1992).

2.3Statistical analysis

The statistical package of social science (SPSS) wasused to analyze the data.Threereplicateswereused to do descriptive analysis and to run the independent – sample T test on SPSS.

RESULTS AND DISCUSSION

The concentrations of heavymetalsin watersamples of bothwellsweresummarized in Table 1. Among samples from Hamandy well, the results showed a high concentration of Pb in all samples except of sample H13 which was as same as the standard value recommended by Libyan Health Organization (

LHO) (0.05mg/L) (Amal and Hanai, 2018). On other hand, Tekerkiba well samples showed a low concentrations of Pb in seven samples which where T1, T2, T3, T11, T12, T13 andT14with values of (0.01, 0.04, 0.02, 0.00, 0.02, 0.01 and 0.05 mg/L) respectively. The highest value was of sample T10 (0.72mg/L). The concentration of Cadmium (Cd) in Hamandy well was not recorded in 10 samples. The highest concentration value was 0.40mg/L which belong to sample H4 While at the Tekerkiba well concentration values were not recorded in four samples, the sample T11 has given a highest concentration value at 0.53mg/L. Regarding to Chromium element (Cr), the concentrations of Cr in all samples collected from Hamandy well were in high. The highest value recorded 1.21mg/L for sample H1 however, the lowest value recorded 0.63 mg/L in sample H9. As well as, the concentration of Cr in all samples of Tekerkiba well were indicated high concentrations in all samples and the highest value recorded 1.20mg/L in the sample T6.

Table 1 The concentration values of all samplesfromHamandy and Tekerkebawells for threeelements Cd Cr and Pb (mg/L(ppm))

ofsample wellTekerkiba	**Cr**	**Cd**	**Pb**	ofsamples wellHamandy	**Cr**	**Cd**	**Pb**
T1	1.02	0.01	0.01	**H1**	1.21	0.17	0.12
T2	1.12	0.08	0.04	**H2**	1.04	0.01	0.07
T3	1.15	0.40	0.02	**H3**	0.96	0.08	0.66
T4	1.00	0.02	0.10	**H4**	1.03	0.40	0.11
T5	1.04	0.04	0.13	**H5**	1.15	0.02	0.22
T6	1.20	0.21	0.40	**H6**	1.02	0.04	0.13
T7	0.61	--	0.25	**H7**	1.06	0.21	0.11
T8	0.76	--	0.20	**H8**	1.19	--	0.22
T9	1.02	0.04	0.11	**H9**	0.63	--	0.61
T10	0.98	0.04	0.72	**H10**	0.75	--	0.61
T11	1.06	0.53	0.00	**H11**	1.05	--	0.40
T12	1.16	0.21	0.02	**H12**	0.96	--	0.13
T13	1.03	--	0.01	**H13**	1.02	--	0.05
T14	0.00	--	0.05	**H14**	1.15	--	0.13
T15	1.15	0.01	0.08	**H15**	1.00	--	0.08
T16	1.04	0.02	0.31	**H16**	1.09	--	0.07
T17	1.07	0.08	0.18	**H17**	1.15	--	0.13

According to obtained results in the drinking water samples collected from both Hamandy and Tekerkiba. Mean concentration of heavy melts in 17 samples for each element under investigation are presented inTable 2

Table 2illustrates the mean concentration of Pb, Cd and Cr (mg/L) in allinvestigateddrinking water samplescollectedfromHamandy and Tekerkebawells and recommendedlevels of theseelements in drinking water by WHO and LHO (Amal and Hanai, 2018)

elementseTh	(WT)wellSamplesofTekerkiba	SamplesofHamandywell (WH)	WHO	LHO
Pb	0.15±0.18	0.22±0.14	0.01	0.05
Cd	0.13±0.15	0.13±0.14	0.005	0.005
Cr	0.96±0.28	1.02±0.20	0.05	0.05

Mean concentrations of Pb recorded 0.15mg/L and 0.22mg/L in water samples of Tekerkiba well (WT) and Tasawah (Hamandy) well (WH) respectively,Which were too higher than that allowed value (0.05 mg/L) that recommended by LHO and WHO (Table 2). This means that the groundwater in both studied WT and WH wells is relatively highly polluted with Pb. Our results are in agreement with the study on Pb content in groundwater of northwestern Libya that states Al Jmayl (WG), Sobratah (WS) and Ajaylat (WA) with values 0.15, 0.072 and 0.056 mg/L respectively (Nour., 2015). In 2016 AbdouKh. A. et al.reported that the mean concentration of Pb in underground water samples were taken from Tripoli (WTr), Zliten (WZi) and Zawia (WZa)recorded0.03, 0.02 and 0.01 mg/L, respectively. Which were higher than standard value recommended by WHO in (WTr) and (WZi), and in the same level of WHO value in WZadistrict. The independent sample T test showed that the difference among Pb values was insignificant in the samples of both water drinking wells (*p= 0.30*).

The mean concentration of Cd is 0.13 mg/L in both WT and WH wells, which also indicated that Cd was in high level as compared with the recommended values of WHO and LHO for Cd in water which is 0.005mg/L. However, in the previous studies by (Nour, 2015) and (AbdouKh*al*., 2016), which found the mean concentrations of Cd in WG, WS, WA and WZa was 0.083, 0.029, 0.021 and 0.012 mg/L, respectively. Moreover, level of Cd in underground water of Gharian district (WGh) was below 0.02mg/L (Alhibshi*al*., 2014),which were less than the obtained data in this study as compared in Taple 3. On the other hand, the mean value of Cd was higher in WTr and WZl (0.22 and 0.24 mg/L, respectively) compared to our obtained data of both wells WT and WH(0.13mg/L). The independent sample T test showed no significant value variation between Cd levels n water samples of both wells (*p= 0.98*)

Generally, the natural content of chromium in drinking water is very low ranging from 0.01 to 0.05 mg/L except for the regions that have substantial chromium deposits (Javana*al*., 2009 and Alhibshi*al*., 2014). In this study Chromium was detected in very high level in both wells WT (0.96 mg/L) and WH (1.02 mg/L) which were higher than international and Libyan standard 0.05mg/L of Cr in drinking water. In addition, when compare this with Cr content in other places of northwestern Libya (Tripoli, Zliten and Zawia) the results were 2.10, 1.30 and 1.60 respectively, as shown in Table 3. The independent sample T test showed that there was no significant difference between what in the two sampling sites (*p= 0.44).*

Table 3 Shows the comparison of Cd Cr and Pb (mg/L) with the groundwater of northwesternLibyaregion

undergroundwaterwells	**Cr**	**Cd**	**Pb**
WT	0.96	0.13	0.15
WH	1.02	0.13	0.22
WG	--	0.083	0.15
WS	--	0.029	0.072
WA	--	0.021	0.056
WTr	2.10	0.22	0.03
WZa	1.60	0.012	0.01
WZl	1.30	0.24	0.02
WGh	<0.02	<0.02	0.03
WHO	0.05	0.005	0.01
LHO	0.05	0.005	0.05

Groundwater usually contains high levels of elements resulting from watering processes of rocks(Namaghi*al*., 2011).Trace amount of metal are common in water and sediments and normally not harmful to our health. Toxicity of metals depend on its chemical characteristics, some of them become toxic when react with organic compounds to form toxic complexes(Akbulut and Tuncer, 2011).

3. CONCLUSION

This study concludes that the concentration of all studied metals was relatively highly polluted. The mean concentrations of Pb, Cd and Cr were 0.18, 0.13, 0,54 mg/L respectively. The drinking water samples contain metal concentration more the admissible and desirable levels (WHO and LHO). Most of the water samples were at populace level, which are not possible for drinking purposes .Water from both wells is dangerous for human consumption and it needs treatment for drinking purposes. The concentration of studiedmetalswas high in the most of samples in exception of cadmium thatwas not detected in somesamples in bothwells. In general, The mean concentration of metals in samples of the Tekerkibawellwaslowerthantheir concentrations in Hamandywell in Tasawah and thatwashigherthan standard values recommended by (WHO) and (LHO). Therefore, the resultsobtainedfromthisstudysuggested a significantrisk to the consumers due to the high possible toxicity of studiedheavymetals.

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