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Research Article

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Determination of Heavy Metals in Tap and Underground Water using Atomic Absorption Spectrometry

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Abstract This study investigated the quality of drinking water supplied to the general drinking water network of Tripoli city-Libya (tap water and ground water). A total of four different sites were selected for this study. The chemical and biological parameters were carefully determined and compared to the WHO and the Libyan standard. The chemical analysis was performed mainly to estimate the level of some heavy metals (Zn, Cd, Cu, Pb, Fe) using atomic absorption spectrometry followed by biological test using the Most Probable Number (MPN) method for a possible microbial contamination. The obtained results of both chemical and biological analysis revealed that the distributed water is safe to drink except in one site. The analysis also showed that the quality of water remains mostly unchanged in terms of chemical and biological (micro-organisms) aspects. Estimation of heavy metals was below the limits. The % RSD value was less than 2.5 % based on triplicate run. Overall, investigation of both chemical and microbial aspects is an effective method of monitoring quality of drinking water. Such investigation is needed to identify possible sources of contamination which could be storage tanks and pipeline to ensure the reach of safe drinking water to the users.

Keywords Tap Water, Underground Water, Atomic Absorption Spectroscopy

Introduction

Water is an essential ingredient of living beings in the universe, without water there is no life. Most human activities involve the use of water in one way or another. The surface of our planet is nearly 71% water, only 3% of it is fresh. Of these 3% about 68.9% is in Antarctica arctic region, 30% in groundwater and 0.26% is available in the form of fresh water in rivers, lakes and ponds suitable for human consumption. Therefore, water is of major importance to all living organism since 90% of body weight in some organism are from water and up to 60% in adult human body weight is from water [1]. Each day humans must consume 2-3 liter of water to survive. Drinking water is derived from two basic sources: surface waters such as rivers and groundwater which lie beneath the surface of the earth. The major sources of drinking water supply in our country are groundwater which most of it comes from Made River Project that transports the water from south to north. It being tapped on a large scale by wells, tube wells and other come from individual house wells (private well) a household well pumps groundwater for household use. Ground water has been used for drinking for a long time due to its purity and has made it very important source for potable water widely [2]. It has been believed that ground water is pure and safer than surface water. Although the presence of more than 200 chemical constituents has been documented in it, the source of these chemicals are both naturally or anthropogenic [3]. The water we drink and use must be pure and free from harmful chemicals to ensure good health. Supply of safe drinking water to human is one of the major prerequisites for a healthy life. All water contains natural contaminants, particularly inorganic contaminants; water can also be contaminated as result from the microbial, radioactive and chemical contamination (Heavy Metals). There are numbers of chemical that cause adverse health effect on prolonged exposure through contaminated drinking water [4]. The most dangerous one which have threat to human health is the heavy metal because if there concentrations exceed safe limits it will accumulate in the human body over the years and caused serious health damage to humans. Heavy metal is defined as metal that have specific density higher than water density about five times more (5 g/cm^3) and if it's entering rate is more than its exit rate, it will accumulate in the body tissue and can be toxic. Heavy metal have been used from a thousands year in all over the world and is even increasing in some areas. Because of they harms to human, measurement should be taken to reduce human exposure in order to minimize the risk of adverse health effect. The selected heavy metals in this study are (Pb, Cd, Cu, Zn and Fe). It is well known that the effect of lead (pb) pollution in drinking water causing imbalance in brain function. In children, it causes delays in physical and mental development, whereas, it causes kidney problems like encephalopathy and proximal renal tubular damage in adults. It is rarely present in tap water as a result of its dissolution from natural source, it is usually found in water from corrosion of household plumbing systems containing lead. The overall evidence for lead as a carcinogen being only weak, the most likely one is lung and stomach cancer [4-6]. Cadmium (cd) is another heavy metal and its main source is contaminated food and water caused by impurities in the zinc of galvanized pipes, solders and some metal fittings. It has a long half-life in humans of 10–35 year and it accumulates primarily in the kidneys causing tubular damage [4, 7-9]. This damage may progress to more severe kidney damage as it was reported in some workers who had exposed to cadmium and other studies of occupational exposed workers confirm it [10, 11]. Additionally, there are other data indicated an association between cadmium exposure and kidney cancer and prostate cancer [12]. Copper (Cu) is primarily present in food and water in developed countries and in a drinking water it comes from household plumbing systems or from erosion of natural deposits. Corrosion is most often associated with acidic waters and waters with pH below 6.5. Cu has beneficial to the body in small amounts but long term exposure can cause liver and kidney damage [4]. Zinc (Zn) is another heavy metal, surface water and groundwater rarely contains zinc at high concentrations, but levels in tap water can be much high as a result of dissolution of Zn from pipes [4]. Although Zn is an essential requirement for good health, it can be harmful since it prevents absorption of iron and copper. Iron (Fe) is an essential element in human nutrition [4]. There is no guideline value In WHO for iron in drinking water. There is usually no noticeable taste at iron concentrations below 0.3 mg/L, although turbidity and color may develop [4]. Table 1 shows the recommended value of the studied heavy metals according to Libyan standard and WHO [4, 13]. Microbial contamination is also an important aspect of water. The greatest risk from microbes in water is associated with consumption of water that is contaminated with human and animal excreta. Also, some organisms grow in piped water distribution systems (e.g., *Legionella*), whereas others occur in source waters (guinea worm *Dracunculus medinensis*) and may cause human health problem [4]. There are many method to detect the bacterial in water sample including multiple tube test (Most Probable Number MPN), membrane filtration test, presence/absence test (P/A). The test used in this project is *Multiple Tube Test (MPN)* this method is used since 1914 to evaluate water quality. It is easy but time consuming and the result affected with type of media used. Thus, there are serious problems due to water contamination; therefore measures should be taken to reduce adverse health effects that occur due water contamination. There are different methods can be used to assist water quality; it can be physical, chemical or microbial tests. The physical test is usually carried out by testing parameters such as pH, temperature, electric conductivity (EC), total dissolved solids (TDS) and turbidity. Other methods as titrimetry, gravimetry, colorimetry and instrumental analysis as inductive coupled plasma (ICP), atomic absorption spectrometry (AAS) and UV\Vis spectrometry can be used. Previous studies have been carried out in other cities than Tripoli to determine some properties of water [14-16]. The aim of this study is directed toward assessment the chemical and microbial quality of drinking water from tap (Man Made River) and ground source (private wells) covering four different locations in Tripoli city including Arada, Salah Addin, Draibi and Bab Alazizia with special focus on some health concern heavy metal (Cadmium, Cupper, Iron, Zinc and Lead) using flame absorption spectrometry.

Table 1: Guideline values for the recommended level of studied heavy metals in ppm.

Metal	Concentration according to WHO	Concentration according to the Libyan standard (ppm)	
		Minimum	Maximum
Pb	0.01	0	0.05
Cd	0.003	-	0.005
Cu	2	0.01	1
Zn	-	5	15
Fe	-	0.1	0.3

Materials and Methods

Sampling

The samples were collected from Made River and private well (the depth was around 25-75 m), these source represent the drinking water in Tripoli city. The sampling was carried out in four different locations (Arada, Salah Addin, Draibi and Bab Alazizia) in Tripoli city. Three sets of the sample were collected from each location. The plan with the sampling was to test whether the city location in some way contributes to the rise of lead, zinc, copper, iron and cadmium concentration in water. Therefore, the samples were chosen to be taken from different site of the city. Each set contained three (500 mL) bottles. Before sampling, the bottles were first rinsed with sample water three times and then filled. (RD: river water Dribi, WD: wells water Dribi, RB: river water Bab Azizia, WB: wells water Bab Azizia, RA: river water Arada, WA: wells water Arada, RS: river water Salah edin, WS: wells water Salah edin).

Sample preparation

For chemical test: the collected samples were transported to laboratory, upon arrival at laboratory, 1 mL of concentrated nitric acid (HNO_3) was added to each 100 mL of sample and the samples were filtered through a filter paper. Then 10 mL was taken for AAS analysis. When not in use, the samples were kept refrigerated at + 4 °C. The standard solutions of heavy metals were prepared and used to obtain calibration curve and quantify the level of heavy metals with AAS. Thus, different concentrations ranging from 10 ppm to 0 ppm were prepared. Concentrations of 0, 0.25, 0.5, 1 ppm were prepared for Cu, Zn and Cd, whereas for Pb 0, 2.5, 5, 10 ppm and for Fe 0, 0.5, 1, 2 ppm was prepared.

For microbial test: water samples were collected in sterile bottle, the tap and bottles were sterilized by passing flame on them, then the water was allowed to run through the tap for few minutes before collect the sample to flush out any contamination within the tap. After that the water sample for microbial test was collected.

Instrumentation

Atomic absorption spectrometer (analytikjena, German, type novAA 400P, Aspect LS version 1.0.52) was used. Instrumental parameter used was as following: burner 100 mm, lamp was HCL, optical mode was single beam, the technique used was flame C_2H_2\Air, the wave length was adjusted at 217, 248.33, 324.75 and 228.8nm for Pb, Fe, Cu, Cd respectively. The pH of the water samples was firstly estimated using the inolab pH meter**.** For the Microbial test, the method used was most Probable Number, the media used was MacConkey broth which contains bromocresol purple as indicator + peptone + lactose + bile salt + NaCl + distilled water using the Durham tube. The sample to be tested was prepared in 10-fold dilution series and then the samples of each dilution were inoculated into triplicate broth culture tubes for incubation. The concentration of samples that were inoculated into triple tube was (10 ml, 1 ml, 0.1ml). Following incubation, all tubes were examined for media color change and presence of gas bubble in Durham tube, the pattern of growth in the tubes was scored against table of reference values.

Results and Discussion

The quality of the collected water samples was first tested by measuring the pH and according to the Libyan specification; pH should be within (6.5 to maximum 8.5). The obtained pH value for the all tested samples was within the recommended range as shown in Table 2.

Table 2: The obtained results of pH measurements.

Sample	pH value	Sample	pH value
RD	7.9	WD	7.9
RB	8.0	WB	8.0
RA	8.2	WA	7.8
RS	8.0	WS	7.7

The calibration curve was constructed using internal standard and the obtained calibration curve using AAS was linear. The linearity was evaluated with standard solutions at a concentration range of **0** mg/mL up to 10 mg/mL, using calibration curve. For all samples, the linearity was estimated with a correlation coefficient (R^2) of more than 0.98 as it show in Table 3 and figure 1 and the linear range was obtained at a concentration of up to 1 mg/L for Cu, up to 2 mg/L for Fe, up to 1 mg/L for Zn, up to 10 mg/L for Pb and up to 1 mg/L for Cd. The AAS was carried out by comparing the obtained concentration of the tested heavy metal with the WHO and Libyan standard (8, 13). As it can be seen in Table 4, the obtained concentrations were within the range except for Fe concentration which is less than the Libyan standard except for sample (WB).

Table 3: The regression equations and correlation coefficients (R^2) obtained for heavy metal using AAS based on triplicate runs

Analytes	**Regression equation**	**Correlation coefficient (R^2)**
Cu	y = 10.68x-0.003	0.998
Pb	y = 15.38**x**-0.483	0.985
Zn	y = 2.451**x**-0.039	0.981
Cd	y = 1.925x-0.047	0.985
Fe	y = 11.85x-0.015	0.999

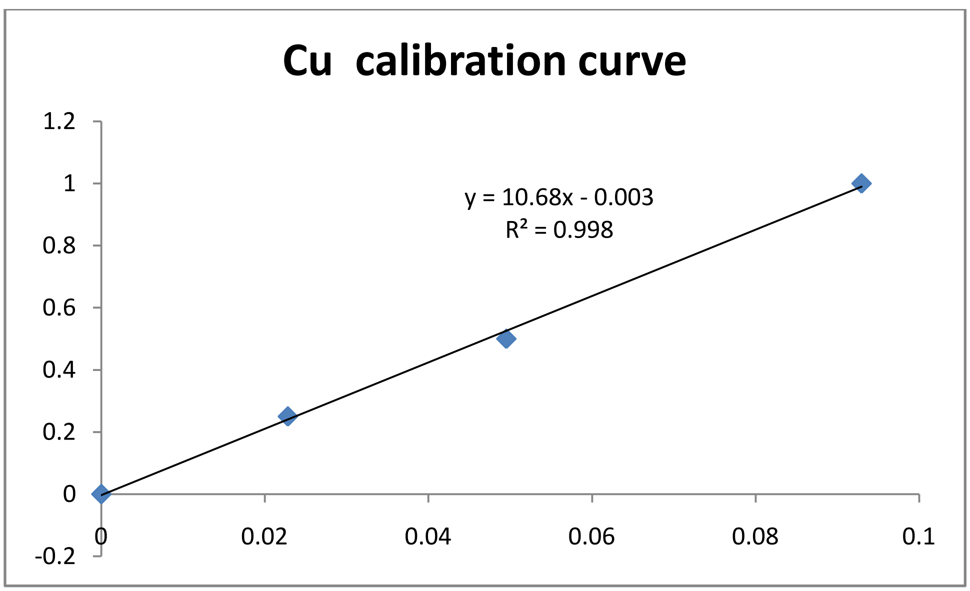

Figure 1: The obtained calibration curve for Cu using AAS

Table 4: The obtained concentration (ppm) of the tested heavy metals in water samples using AAS based on triplicate runs.

Sample	Cu	Zn	Fe	Cd	Pb
RB	<0.054	2.697	<0.015	<0.005	<0.003
WB	<0.054	2.967	0.2033	<0.005	<0.003
RD	<0.054	2.296	<0.015	<0.005	<0.003
WD	<0.054	2.732	<0.015	<0.005	<0.003
RA	<0.054	1.630	<0.015	<0.005	<0.003
WA	<0.054	2.750	<0.015	<0.005	<0.003
RS	<0.054	3.065	<0.015	<0.005	<0.003
WS	<0.054	2.601	<0.015	<0.005	<0.003

The two-way ANOVA test was carried out in the obtained concentration using AAS to clearly compare the difference between the different areas and different source of water whereas one-way ANOVA test was carried out to compare between the heavy metal levels as it can be seen in Table 5. P value of sample site is equal 0.998 (0.998 > 0.05) that mean we accept theory that there is no difference between metal concentrate from different site of collection. Moreover, P value of water type equal 0.955 (0.955 > 0.05) that mean we accept theory that there is no difference between metal concentrate from different type of water (source). P value of metal is equal 0.000 (0.000 < 0.05) that mean we reject theory of the equalization between metal concentration. Additionally, the microbial evaluation of water sample using MPN test indicated that after 24hr of incubate there is no change indicate any bacterial growth in the media. After 48hr of incubation there is also no change in media color and there is no gas bubble in Durham tube, these indicate the absence of the bacteria in all water samples from different sources and areas. Absence of bacteria may be because the water from Made River Project is treated with chlorine, may also be the good deep wall effect on absence of bacteria (as deep of wall increase, the pollution will decrease because its distance from the sewer).

Table 5A: The obtained result of Two-Way ANOVA

Source	DF	SS	MS	F	P
Sample Site	3	0.0317	0.010561	0.01	0.998
Water Type	1	0.0024	0.002387	0.00	0.955
Error	24	17.6377	0.734904		
Total	31	17.6761			

Table 5B: The obtained Results of One way ANOVA

Source	DF	SS	MS	F	P
Metal	3	17.56073	5.85358	1420.58	0.000
Error	28	0.11538	0.00412		
Total	31	17.67610			

Conclusions

The present study was performed to evaluate the quality of drinking water (both tap and underground well water) from different areas in Tripoli city and discussing some properties of drinking water that used by the public of Tripoli city, on the basis of the physical test (pH), chemical test using AAS and microbial test. According to the obtained results, all water samples are free from bacterial contamination and their pH is within the needed range. Additionally, the concentration of tested heavy metal in all samples is within the WHO and Libyan requirements based on triplicate runs and % RSD value of less than 2.5%. Thus the present investigation finding that all water samples are accepted and suitable for public health except the Fe concentration which show low concentration level than the accepted range according to Libyan standard except in the WB sample which is within the range. (This low concentration could be personal or instrumental error). Consequently, further investigation using the inductive coupled plasma with increasing the number of tested samples than three samples per each area are required and highly recommended.

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