



Assessment of Groundwater Wells Pollution by Some Heavy Metals in El-Beida City-Libya

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ABSTRACT

One of the most important concerns is the presence of heavy metals in water. Heavy metal pollution in groundwater is a major concern, because of their toxicity and hazard to human life and the environment. The aim of this study was to determine the quantity of five heavy metals present in groundwater wells in different sites of El-Beida city. Groundwater wells samples were collected in January 2022 from 10 randomly selected wells throughout the region and analyzed in order to determine the content of a number of heavy metals namely: Lead, Copper, Iron, Manganese, and Nickel using an Atomic Absorption Spectrophotometer (AAS), and their levels were compared to the maximum contamination limits specified by the World Health Organization (WHO) and the Libyan National Centre for Standardization and Metrology (LNCSM). The results in the current study indicate there is variation among wells. The Lead (Pb) concentrations ranged between (0.33-0.50 mg/l), whereas the Copper (Cu) value ranged (0.07-0.12 mg/l), the Iron (Fe) value ranged (1.15-1.35 mg/l), the Manganese (Mn) value ranged (0.17-0.75 mg/l), and the Nickel (Ni) value ranged (0.19-0.52 mg/l). Most of the heavy metal analyzed in this study were exceed permissible limits for international standards of drinking water by WHO or LNCSM while Copper (Cu) did not exceed permissible limits for international standards of drinking water.

تقييم تلوث آبار المياه الجوفية ببعض المعادن الثقيلة في مدينة البيضاء - ليبيا

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الكلمات المفتاحية:

المعادن الثقيلة
آبار المياه الجوفية
جهاز الامتصاص الذري
التلوث
المعايير الدولية

الملخص

يعتبر وجود المعادن الثقيلة في الماء احد أهم المخاوف والمخاطر. ويعد تلوث المياه الجوفية بالمعادن الثقيلة مصدر القلق والخطر الأكبر، بسبب سميتها وخطرها على حياة الإنسان والبيئة. الهدف من هذه الدراسة هو تقدير كمية خمسة معادن ثقيلة موجودة في آبار المياه الجوفية في مواقع مختلفة من مدينة البيضاء. تم جمع عينات آبار المياه الجوفية في يناير 2022 من 10 آبار تم اختيارها عشوائياً من جميع أنحاء المنطقة وتحليلها من أجل تقدير محتوى عدد من المعادن الثقيلة وهي: الرصاص والنحاس والحديد والمنغنيز والنيكل باستخدام جهاز الامتصاص الذري (AAS). تمت مقارنة مستوياتها مع حدود التلوث القصوى المحددة من قبل منظمة الصحة العالمية (WHO) والمركز الوطني الليبي للمواصفات والمقاييس (LNCSM). تشير نتائج الدراسة الحالية إلى وجود تباين بين الآبار. حيث تراوحت قيم تركيز الرصاص بين (0.33-0.50 مجم / لتر)، بينما تراوحت قيم تركيز النحاس بين (0.07-0.12 مجم / لتر)، قيم تركيز الحديد تراوحت بين (1.15-1.35 مجم / لتر)، اما قيم تركيز المنغنيز فقد تراوحت بين (0.17-0.75 مجم / لتر)، وتراوحت قيم تركيز النيكل بين (0.19-0.52 مجم / لتر). تجاوزت معظم المعادن الثقيلة التي تم تحليلها في هذه الدراسة الحدود المسموح بها للمعايير الدولية لمياه الشرب من قبل

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Introduction

Groundwater is a valuable resource for drinking, industrial, and agricultural purposes [1]. The quality of groundwater is gradually deteriorating in some locations due to unsustainable water resources. Groundwater is generally cleaner than surface water, although the uneven growth of urbanization and industrialization have also had an impact on groundwater quality [2]. Heavy elements are a natural component of the earth's crust (for example, eroded minerals inside sediments, ore leaching, and volcanism extruded products), and they are not biodegradable [1]. As a result, they persist in the environment and maybe filtered from rocks and soils based on their geochemical mobility or anthropogenic sources, such as disposal of solid waste, industrial or sewage effluents, and industrial pollution's aftereffects [3-4]. Heavy metals are elements with atomic weights ranging from 63.546 to 200.590 g/mol and specific gravities larger 4 or 5 times than of water. They can be found in colloidal, particle, and dissolved phases in water [5]. Heavy metals discharged by factories, transportation, city trash, and hazardous waste sites, as well as fertilizers for agricultural use and oil spills from tankers, can lead to a gradual rise in groundwater pollution [6-7]. Smelter emissions, industrial smokes, waste incinerators, lead in residential plumbing, old house paints, and industrial trash all release heavy metals into the environment [8]. Because of their toxicity and hazard to human life and the environment, heavy metal pollution in groundwater is a major concern. In small concentrations, heavy metals such as Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Hg, and Pb are potential soil and water contaminants. However, certain heavy metals are nutritionally required for a healthy life. These heavy metals are commonly present in foods, fruits and vegetables, and commercially available multivitamin supplements [1]. When heavy metals are not metabolized by the body and accumulate in the soft tissues, they become poisonous. Heavy metals can enter the human body through feeding, water, and air, or through skin absorption when they come into contact with humans in agriculture, manufacturing, pharmaceutical, and industrial settings [1]. Heavy metal can have major health dangers, with different symptoms depending on the type and amount of metal ingested [9]. High trace element concentrations are dangerous because they tend to bioaccumulation, Leading in heavy metal toxicity. Aluminum, arsenic, cadmium, lead, and mercury are the most common heavy metals to which humans are exposed [10]. As a result, it is necessary to evaluate the quality of groundwater sources.

The aim of this study was to Estimate the level of some heavy metals, which are: Lead (Pb), Coppe (Cu), Iron(Fe), Manganese (Mn), and Nickel (Ni) in groundwater wells for the study area in El-Beida City using Atomic Absorption Spectrophotometer (AAS) and determining the degree of pollution and their compliance with the guidelines of the World Health Organization (WHO) and the Libyan National Centre for Standardization and Metrology (LNCMSM). as well as providing results that are considered the first at the level of heavy metals studied in the study area. These findings are critical not only for determining the current levels of heavy metal contamination in groundwater wells but also for developing sensible pollution control management plans.

Material and Methods

1. Description of the Study Area:

The study was conducted in the Libyan city of El-Beida. The city is located in the north-eastern part of Libya and lies on the bank of the Mediterranean Sea. It covers an area of approximately 11,429 km².

The regulatory seat of El-Beida was known as Barca. El-Beida is arranged on the Cyrenaica level at the western edge of Jebel Akhdar and had an estimated population of 380,000 at the beginning 2012 with coordinates 32° 45' 59" N, 21° 44' 30" E [11]. The study area is considered one of the most valuable regions in Libya because of its location relative to the Green Mountain, as well as its agricultural

activities, including irrigated and non-irrigated cultivation and animal wealth as well as economic activities. The precise locations of the sampling points of the groundwater wells were determined in the field. The study area is influenced by the Mediterranean climate, which is characterized by hot, dry summers and mild, rainy winters. The study area has a dry climate, such as that of a semidesert, showing minimal rainfall and high evaporation rates and a clear appearance of aridity, which prevails over the entire area [11]. An assessment of 10 groundwater wells in the study area was conducted to determine the degree of water quality, as shown in figure (1). The table (1) shows the description and the coordinates of groundwater wells under study.

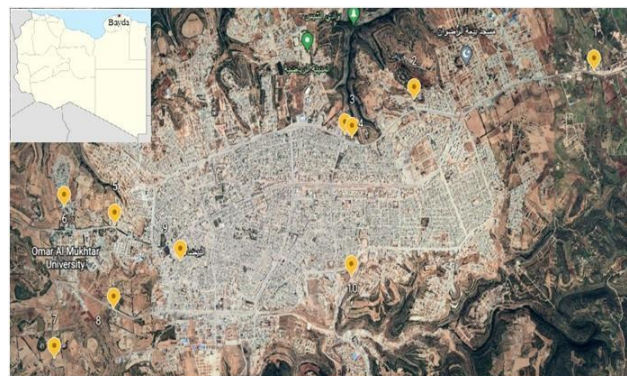


Fig. 1: Lunar image of the study area on which the study sites are located in El-Beida City.

Table 1: Description of groundwater wells.

| No. | Wells Name | Coordinates | | H |
|-----|------------------|-------------|------------|-----|
| S1 | Wardamah well | 21°48'58"N | 32°46'50"E | 678 |
| S2 | Abu Sultan well | 21°46'55"N | 32°46'37"E | 623 |
| S3 | Jawaher well | 21°46'08"N | 32°46'18"E | 596 |
| S4 | Gharbawiya well | 21°48'02"N | 32°46'19"E | 606 |
| S5 | Boughandora well | 21°43'19"N | 32°45'35"E | 605 |
| S6 | Alzawia well | 21°42'44"N | 32°45'44"E | 629 |
| S7 | Belgra well | 21°42'37"N | 32°44'30"E | 605 |
| S8 | Dream Land well | 21°43'19"N | 32°45'18"E | 601 |
| S9 | Old Alsouq well | 21°46'06"N | 32°45'10"E | 619 |
| S10 | Algarika well | 21°46'07"N | 32°45'10"E | 581 |

2. Sampling:

The samples were taken (Triplicate) by bottles (Plastic bottles of polyethylene 100 ml volume) where took the sample after pumping an amount of water equivalent to three times the volume of the casing pipes (about half an hour). After that, the samples were stored with crushed ice in a bag at 4°C and then the samples were transferred to the laboratory for preservation until preparation and analysis [12]. A total of 30 (3 x 10) samples were collected during the month of January 2022.

3. Samples Preparation:

All water samples from the sites were filtered by a 0.45-µm filter and then 100 ml of water required for analysis were taken and then transferred into acid cleaned 100 mL polypropylene bottles. About 6 ml of concentrated nitric acid (Merck, 65%) was added to each sample, then preservation at 4°C until analysis [12].

4. Samples Analysis:

The prepared samples were analyzed by Atomic Absorption Spectrophotometer (AAS) (Thermo model). The processed specimens were examined in triplicate with the average concentration of the metal present being shown in mg/L by the instrument after extrapolation from the standard curve. 1000 mg/L stock solutions of studied heavy metals were prepared. Calibration curve solutions of the focus metal ions were prepared from the standard stock solutions by serial dilution as shown in the

figures (2-6). The AAS was calibrated with relevant AAS spectroscopic grade standards [1].

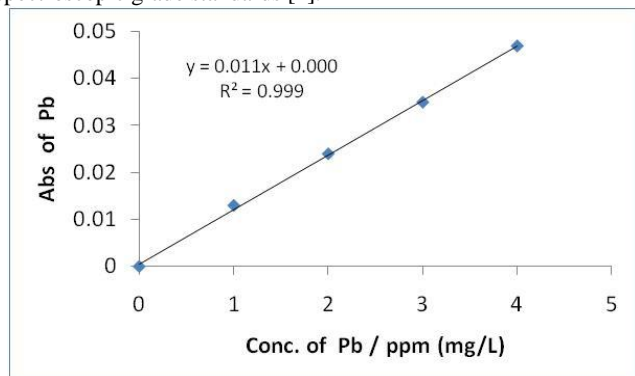


Fig. 2.: Calibration curve for standard solutions of Lead (Pb).

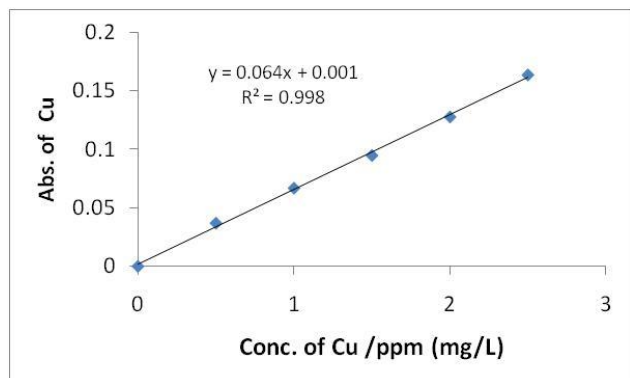


Fig. 3: Calibration curve for standard solutions of Copper (Cu).

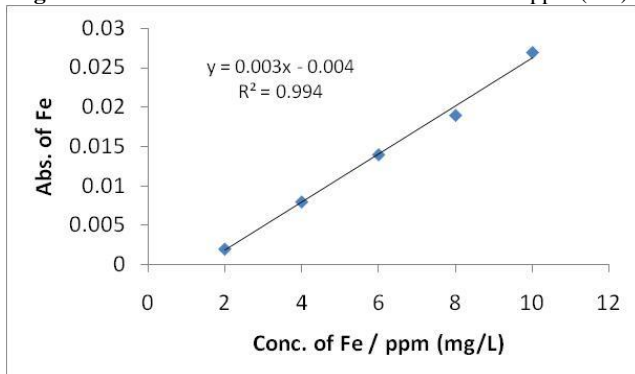


Fig. 4: Calibration curve for standard solutions of Iron (Fe).

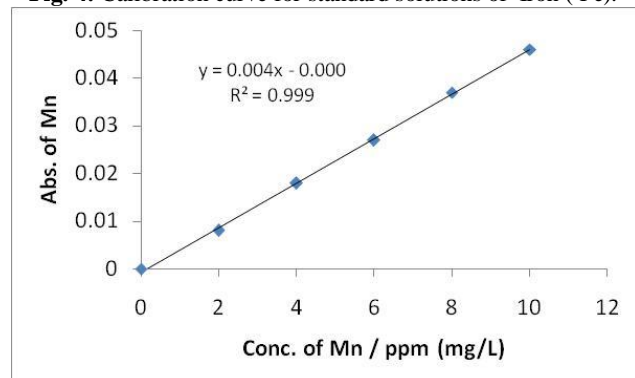


Fig. 5: Calibration curve for standard solutions of Manganese (Mn).

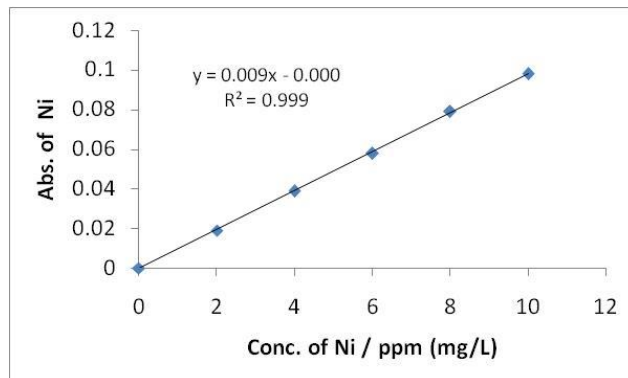


Fig. 6: Calibration curve for standard solutions of Nickel (Ni).

5.Statistical Analysis:

Statistical analysis was used through the program statistical package for social sciences (SPSS) version 24 and also Excel and Minitab version 17 to calculate some descriptive statistics such as standard error, Average, standard deviation and variance percentage. As well the indicative statistics analysis was also examined through a test of significant values (p) which results of the research were considered significant if were the calculated significant values $p \leq 0.05$ (α was chosen to be 0.05). For comparison of means, ANOVA test and Post Hoc were done.

Results and Discussion

This paragraph explains the results obtained in this study, as well as highlighting the efficiency of the methods used, together with the instrumentation.

1. Lead (Pb):

The lead element has a density of 11.3 g/cm³ and its atomic number is 82 and is obtained from ores of sulphide mineral galena, carbonate cerussite, and sulphate anglesite [13]. The ores are frequently found in combination with other recoverable metals such as Cu, Zn and Cd [14]. Lead metal has many uses. It is used in the industry of pipes and drains, battery making, plumbing, ammo industry, various paint pigments, pesticides, gasoline improver such as tetraethyl lead (TEL), were used extensively as antiknock agents in gasoline for motor vehicles in the past [15]. Lead comes second in the list 20 of heavy toxic metals which were placed from the Agency for Toxic Substances and Disease Registry (ATSDR), where Lead metal causes most cases of poisoning of heavy materials to children [16]. The results shown in figure (7) indicated that the lead (Pb) values are ranged from (0.33 – 0.50 mg/L). At the level of sites, the highest values were recorded at the site (5) and (8) with an average concentration (0.50 mg/L). This is due to contaminating this site by sewage coming from residential communities located near the studied wells 2 and 7 and corrosion of household plumbing systems as a result of the use of PVC pipes leading to increase the amount of lead in water due to the addition of lead nitrate during the process of manufacturing pipes to raise the hardness and resistance of these pipes near the study stations (5 ,8). So the lowest values were recorded at the site (6) with an average concentration (0.33 mg/L). Mean Pb concentration in water samples of Groundwater wells was found to be 0.43 mg/L (table 2). ANOVA and post hoc testing in (table 2) show that there were significant differences with a statistical significance for the Pb with the other sites ($p < 0.05$) where the value of (Sig=0.000). This indicates that there is a difference for the mean Pb between the ten sites, as a result of the difference these sites of each other in type of water source they are affected by sources of pollution. In general, the values of lead recorded in this study were ranged (0.33-0.50 mg/L) which exceeded permissible limits for international standards of drinking water (table 3) for both of the WHO and LNCMS (0.01 mg /L)[17-18].

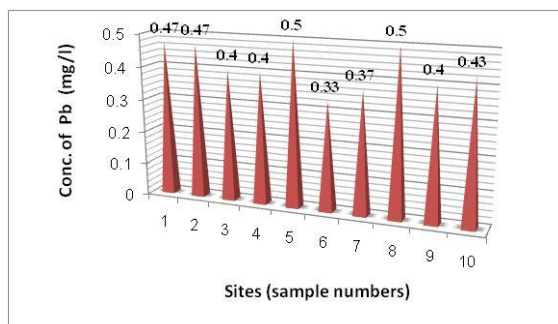


Fig. 7: The average Lead (Pb) concentration (mg/L) at different sites (samples).

2. Copper (Cu):

Copper is one of the metals that have been discovered since ancient times. Copper was used early as a result of its natural occurrence in its original form [13]. Copper is found in oxidation states (0,+1,+2) and there many copper compounds, of the most important of these compounds, are Copper carbonate (CuCO_3), which is one of the most soluble types, and they are formed in aerobic alkaline systems, as well as Copper sulfide (CuS), which is formed in anaerobic environments. Copper metal is used in many industries such as metal processing, coins, alloys, electric wires, pots and pipes electroplating, electrical industries, machine manufacturing, organic synthesis, tanning industry [19]. Copper is considered a nutrient essential for the growth of both plant and animal. But when entering high doses to the body of the organism causes many health problems such as anorexia, anaemia, gastrointestinal irritation, kidney damage, headaches, allergies, increased hyperactivity in the early stages of childhood, learning disorders [20]. The results in our study indicated in (figure 8) that the (Cu) values are ranged from (0.07 – 0.12 mg/L). The highest values recorded at the site (6) and (9) with an average concentration (0.12 mg/L). So the lowest values recorded at the site (8) with an average concentration (0.07 mg/L). Mean of Cu concentration in Groundwater wells samples was found to be 0.09 mg/L (table 2). ANOVA and post hoc testing in (table 3) show that there were significant differences with a statistical significance for the Pb with the other sites ($p < 0.05$) where the value of ($\text{Sig} = 0.000$). This indicates that there is a difference for the mean Pb between the ten sites, as a result of the difference in these sites of each other in type of water source they are affected by sources of pollution. In general, the values of copper recorded in this study were ranged (0.07-0.12 mg/L) where they did not exceed permissible limits for international standards of drinking water (table 3) for each of the WHO (2 mg/L) [17] and LNCSM (1 mg/L) [18].

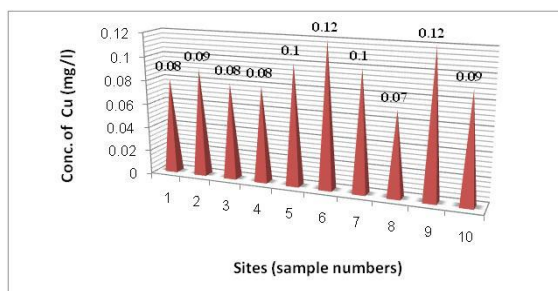


Fig. 8: The average Copper (Cu) concentration (mg/L) at different sites (samples).

3. Iron (Fe):

The results shown in figure (9) indicated that the Iron (Fe) values are ranged from (1.15 – 1.35 mg/L). At the level of sites, the highest values recorded at the site (7) and (9) with an average concentration (1.35 mg/L). Iron may also be released to water from natural deposits, industrial wastes, refining of Iron ores, and corrosion of Iron-containing metals in this site. So the lowest values recorded at the site (2) with an average concentration (1.15 mg/L). The mean Fe concentration in Groundwater wells samples was found to be 1.28 mg/L (table 2). ANOVA and post hoc testing in (table 3) show that

there were significant differences with a statistical significance for the Fe with the other sites ($p < 0.05$) where the value of ($\text{Sig} = 0.000$). This indicates that there is a difference for the mean of Pb between the ten sites, as a result of the difference in these sites of each other in type of water source they are affected by sources of pollution. In general, the values of Iron recorded in this study were ranged (1.15 - 1.35 mg/L), where they exceed permissible limits for international standards of drinking water (table 3) for both of WHO and LNCSM (0.3 mg/L) [17-18].

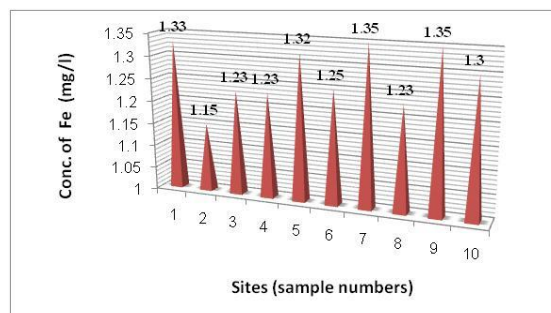


Fig. 9: The average Iron (Fe) concentration (mg/L) at different sites (samples).

4. Manganese (Mn):

Manganese is one of the heavy metals found in the earth's crust at a concentration of about 1000 ppm, thus making this element ranked 12th in the most abundant elements [21]. Manganese compounds are considered strong oxidizing agents and have different oxidation states such as the fourth oxidation state (+4) and the seventh oxidation state (+7) [21]. Among the most stable oxidation states of manganese ion is the binary state (Mn^{++}) which is used in the essential functions of the metabolic processes of living organisms however other of the states of oxidation are toxic to the human [14]. Manganese ion has several different colours depending on oxidation state. Manganese is used in several industries such as pigments manufacture and while Manganese Oxide (MnO_2) is used in the manufacture of batteries by using cathode materials in dry batteries. The free manganese element is also used in the manufacture of metal alloys, especially in the manufacture of stainless steel as well as the use of Manganese phosphating for the treatment of rust and corrosion prevention on steel [22]. Despite the importance of this metal to the living organisms, but it causes the damage to the human being's health when entering the doses of high concentration to the body of the organism and when inhaled it in large quantities causing poisoning syndrome in mammals, damage the nervous system. The results shown in figure (10) indicated that the Manganese (Mn) values are ranged from (0.17 – 0.75 mg/L). The highest values recorded at the site (9) with an average concentration (0.75 mg/L). This is attributed to the anthropogenic pollution sources by sewage coming from residential communities located on this site and may be due to dissolution of impending rocks as the rocks and soils directly exposed to ground water which is the largest natural sources [23]. So the lowest values recorded at the site (2) with an average concentration (0.17 mg/L). Mean of Mn concentration in Groundwater wells samples was found to be 0.42 mg/L (table 2). ANOVA and post hoc testing in (table 2) show that there were significant differences with a statistical significance for the Mn with the other sites ($p < 0.05$) where the value of ($\text{Sig} = 0.000$). This indicates that there is a difference for the mean of Mn between the ten sites, as a result of the difference in these sites of each other in type of water source they are affected by sources of pollution. In general, the values of Manganese (Mn) recorded in this study were ranged (0.17 – 0.75 mg/L), where they exceed permissible limits for international standards of drinking water (table 3) for each of the WHO (0.5 mg/L) [17] and LNCSM (0.05 mg/L) [18].

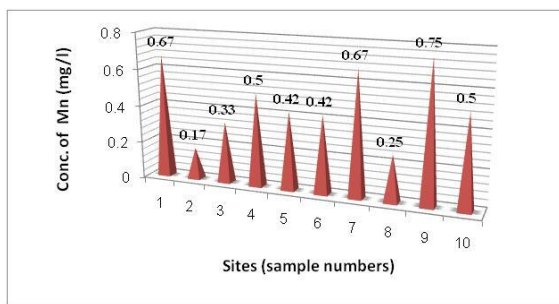


Fig. 10: The average Manganese (Mn) concentration (mg/L) at different sites (samples).

5. Nickel (Ni):

Nickel metal of within the toxic heavy metals, occupies the 24th ranking among the elements on the earth and constitute the ratio of 6% of the earth's crust [24]. Nickel has a density of 8.9 g/cm³ and it forms different alloys with metals for each of, Iron (Fe), Aluminum (Al), Zinc (Zn), Molybdenum (Mo) and Copper (Cu), which can be dissolved in dilute acids [14]. The nickel element has several compounds that have different oxidation states of +1,+3 and +4, although the most common condition is the binary oxidation state +2 [25]. Nickel ion absorption depends on its physical and chemical properties but its absorption is easier with soluble compounds in the water [13]. The results in the current study indicated that the Nickel (Ni) values are ranged from (0.19 - 0.52 mg/L) (figure 11). At the level of sites, the highest values recorded at the site (10) with an average concentration (0.52 mg/L). This is attributed to the anthropogenic pollution sources by sewage coming from residential communities located on this site and may be due to car wash position and special workshops for the replacement oils and maintenance of vehicles which is located on this site near the study station [23]. So the lowest values recorded at the site (8) with an average concentration (0.19 mg/L). The mean Nickel (Ni) concentration in groundwater wells samples was found to be 0.35 mg/L (table 2). ANOVA and post hoc testing in (table 2) show that there were significant differences with a statistical significance for the Nickel (Ni) with the other sites (p<0.05) where the value of (Sig=0.000). This indicates that there is a difference for the mean of Ni between the ten sites, as a result of the difference in these sites of each other in type of water source they are affected by sources of pollution. In general, the values of Nickel (Ni) recorded in this study were ranged (0.19 - 0.52 mg/L), where they exceed permissible limits for international standards of drinking water (table 3) for each of the WHO (0.07 mg /L) [17] and LNCSM (0.02 mg /L) [18].

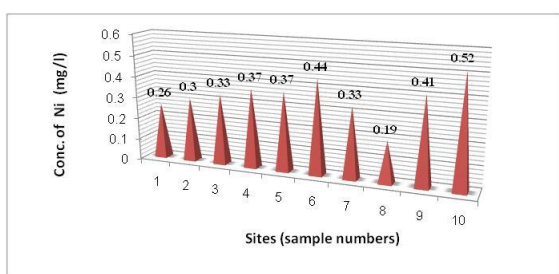


Fig. 11: The average Nickel (Ni) concentration (mg/L) at different sites (samples).

Statistical study (Validation method)

1. Linearity:

Examination of calibration curves was conducted by computing a linear least-squares regression analysis on the plot of the absorbance of each metal ion versus concentration over the specific range for each metal ion, with correlation coefficients (R²) being consistently greater than 0.994 (see table (2)). Linearity of the method was performed in a range of 1-5 ppm for Pb⁺² and the method showed good linearity regression (R² = 0.999), with y = 0.011 x + 0.000 , in the range of 0.5- 2.5 ppm for Cu⁺², with y = 0.064x + 0.001 and (R² = 0.998) , in the range of 2-10 ppm for Fe⁺³ with y= 0.003x - 0.004,

and (R² = 0.994) , in the range of 2-10 ppm for Mn⁺² with y= 0.004 x - 0.000, and (R² = 0.999) and in the range of 2-10 ppm for Ni⁺² with y= 0.009x - 0.000 and (R² = 0.999) , Which is showing good linearity, precision, accuracy and sensitivity, which could be used for determination heavy metals (see table 2).

2. Limit of detection (LOD):

Limit of detection (LOD) is defined as the concentration of analyte required to give a signal equal to three times the standard deviation of the blank. The LOD was calculated using the following equation:

$$LOD = \frac{3 \cdot s_{y/x}}{b}$$

where S is the average of the standard deviation SD_{y/x} of the Absorbance ratio (absorbance of analyte/ absorbance of external standard), and b is the average of the slope of a calibration curve. In the presented study, the limit of detection (LOD) values for each metal ion in water samples using Atomic Absorption Spectrophotometer (AAS) were recorded in table (2).

3. Limit of quantitation (LOQ):

Limit of quantitation (LOQ) is defined as the concentration of analyte required to give a signal equal to ten times the standard deviation of the blank.. The LOD was calculated using the following equation:

$$LOQ = \frac{10 \cdot s_{y/x}}{b}$$

The limit of quantitation (LOQ) values for for each metal ion in water samples using Atomic Absorption Spectrophotometer (AAS) were recorded in table (2).

Table 2: Average concentrations of heavy metals (mg/L) in water samples together with standard deviation values and some statistical parameters.

| No | Pb ²⁺ | Cu ²⁺ | Fe ²⁺ | Mn ²⁺ | Ni ²⁺ |
|----------------|------------------------------|------------------------------|------------------------------|-------------------------------|-------------------------------|
| 1 | 0.47 ^{ab} ± 0.03 | 0.08 ^{bc} ± 0.01 | 1.33 ^a ± 0.04 | 0.67 ^{ab} ± 0.18 | 0.26 ^{cd} ± 0.07 |
| 2 | 0.47 ^{ab} ± 0.03 | 0.09 ^{bc} ± 0.00 | 1.15 ^d ± 0.09 | 0.17 ^d ± 0.17 | 0.30 ^{bcd} ± 0.04 |
| 3 | 0.40 ^{abc} ± 0.02 | 0.08 ^{bc} ± 0.01 | 1.23 ^c ± 0.03 | 0.33 ^{cd} ± 0.05 | 0.33 ^{bcd} ± 0.01 |
| 4 | 0.40 ^{abc} ± 0.02 | 0.08 ^{bc} ± 0.01 | 1.23 ^c ± 0.03 | 0.50 ^{abc} ± 0.06 | 0.37 ^{abc} ± 0.01 |
| 5 | 0.50 ^a ± 0.05 | 0.10 ^{ab} ± 0.01 | 1.32 ^a ± 0.03 | 0.42 ^{bcd} ± 0.00 | 0.37 ^{abc} ± 0.01 |
| 6 | 0.33 ^c ± 0.07 | 0.12 ^a ± 0.02 | 1.25 ^{bc} ± 0.02 | 0.42 ^{bcd} ± 0.00 | 0.44 ^{ab} ± 0.07 |
| 7 | 0.37 ^{bc} ± 0.04 | 0.10 ^{ab} ± 0.01 | 1.35 ^a ± 0.05 | 0.67 ^{ab} ± 0.18 | 0.33 ^{bcd} ± 0.01 |
| 8 | 0.50 ^a ± 0.05 | 0.07 ^c ± 0.02 | 1.23 ^c ± 0.03 | 0.25 ^{cd} ± 0.11 | 0.19 ^d ± 0.12 |
| 9 | 0.40 ^{abc} ± 0.02 | 0.12 ^a ± 0.02 | 1.35 ^a ± 0.05 | 0.75 ^a ± 0.24 | 0.41 ^{abc} ± 0.04 |
| 10 | 0.43 ^{abc} ± 0.00 | 0.09 ^b ± 0.00 | 1.30 ^{ab} ± 0.02 | 0.50 ^{abc} ± 0.06 | 0.52 ^a ± 0.12 |
| Mean | 0.43 | 0.09 | 1.28 | 0.42 | 0.35 |
| Slope | 0.011 | 0.064 | 0.003 | 0.004 | 0.009 |
| R ² | 0.999 | 0.998 | 0.994 | 0.999 | 0.999 |
| LOD | 0.60 | 0.130 | 2.45 | 1.31 | 0.18 |
| LOQ | 2.01 | 0.433 | 8.18 | 0.39 | 0.58 |
| SD | 0.002 | 0.003 | 0.002 | 0.001 | 0.001 |

For a given metal, mean concentrations followed by the same letter are not significantly different (p<0.05).

Table 3: Average The safe limits of WHO and LNCSM for determining drinking water quality.

| Parameter | WHO permissible limits (mg/L) | LNCSM permissible limit (mg/L) | Current Study (mg/L) |
|-----------|-------------------------------|--------------------------------|----------------------|
| Pb | 0.01 | 0.01 | 0.33-0.50 |
| Cu | 2 | 1 | 0.07-0.12 |
| Fe | 0.3 | 0.3 | 1.15-1.35 |

| | | | |
|----|------|------|-----------|
| Mn | 0.5 | 0.05 | 0.17-0.75 |
| Ni | 0.07 | 0.02 | 0.19-0.52 |

Conclusion

The studied water samples in different groundwater well systems revealed that almost all of the chemical parameters are not in good status, expressing not their suitability for drinking purposes. Major problems in almost samples were the increasing of the concentrations in most of the heavy metals except copper metal. This may be due to the impact of pollution at these stations. Poor maintenance of the water source is the likely reason for high concentration in these parameters or may be due to the geological nature of the water source. To ensure public health, competent authorities should closely monitor the quality of drinking water supplied to consumers.

References

- [1]- Al-Paruany, K. B., Ali, A. J. A., Hussain, K. I., Khalaf, H. S., and Alias, M. F. (2018). Assessment of heavy metals in some ground water wells at Baghdad City/Iraq. *Journal of Global Pharma Technology*, 10(3), 62-70.
- [2]- Hem, J.D., (1991) Study and interpretation of chemical characteristic of natural water, US – geological survey, water supply. paper.2254. 263.
- [3]- APHA, (2005) Standard methods for examination of water and waste water. American Public Health Association 21st.edition. Wasington DC, USA.
- [4]- Tijani, M.N., Okunola, O.A., and Abimbola, A.F., (2006) Lithogenic concentrations of trace metals in soils and saprolite over crystalline basement rocks: A case study from SW Nigeria. *J. Afr. Earth Sci.* 46:427-238.
- [5]- Adepoju-Bello, A.A., Ojomolade, O.O., Ayoola, G.A., Coker, H.A.B., (2009) Quantitative analysis of some toxic metals in domestic water obtained from Lagos metropolis. *The Nig. J. Pharm.* 42(1): 57-60.
- [6]- Vodela, J.K., Renden, J.A., Lenz, S.D., Henney, W.H.M., and Kempainen, B.W., (1997). *Drinking water contaminants. Poult. Sci.*, 76: 1474-1492.
- [7]- Igwilo IO, Afonne, O.J., Maduabuchi, U.J., and Orisakwe, O.E., (2006) Toxicological study of the Anam River in Otuocha, Anambra State, Nigeria. *Arch. EnvIron. Occup. Health*, 61(5): 205-208.
- [8]- Laniyan, T.A., Bayewu OO, and Ariyo, S.O., (2012) Heavy metal characteristics of groundwater in Ibadan South Western, Nigeria. *African Journal of Environment science and technology*. Vol 7(7): 641-647.
- [9]- Adepoju-Bello A.A., and Alabi, O.M., (2005). Heavy metals:A review. *The Nig. J. Pharm.*, 37: 41-45.
- [10]- McCluggage D., (1991) Heavy Metal Poisoning, NCS Magazine, Published by The Bird Hospital, CO, U.S.A. (www.cockatiels.org/articles/Diseases/metals.html).
- [11]- URL-1, (2012). https://en.wikipedia.org/wiki/Bayda,_Libya.
- [12]- Salem, Z. B., Capelli, N., Laffray, X., Elise, G., Ayadi, H., and Aleya, L. (2014). Seasonal variation of heavy metals in water, sediment and roach tissues in a landfill draining system pond (Etueffont, France). *Ecological Engineering*, 69, 25-37.
- [13]- Chattopadhyaya, M. C., Soares, M. G., Waters, M., Campos, M. T. d. J. S., Marrs, T., Wilks, M., and Barakat, M. (2014). *Heavy Metals in Water: Presence, Removal and Safety: Royal Society of Chemistry*.
- [14]- Muiruri, M. J. (2013). *Determination Of Concentration Of Selected Heavy Metals In Tilapia Fish, Sediments And Water Frommbagathi And Ruiru Athi River Tributaries, Kenya*.Kenyatta University.
- [15]- Beattie, A., Moore, M., and Goldberg, A. (1972). Tetraethyl-lead poisoning. *The Lancet*, 300(7766), 12-15.
- [16]- ATSDR (Agency for Toxic Substances and Disease Registry) (2020). *Toxicological profile for Lead*. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.
- [17]- WHO, (Word Health Organization),(2017). *Guidelines for drinking-water quality: Incorporating first addendum*.
- [18]- LNCSM (Libyan National Center for Standardization and Metrology), (2015). *Drinking Water*. LNS 82, Second edition.Tripoli-Libya.
- [19]- Mudhoo, A., Garg, V. K., and Wang, S., (2012). Removal of heavy metals by biosorption. *Environmental chemistry letters*, 10(2), 109-117.
- [20]- Udayakumar,P., (2012). *Assessmentof Heavy metals In The Environmental compartments Of Thecentral And Northern Coastof Kerala, India*. Citeseer.
- [21]- Emsley, J., (2011). *Nature's building blocks: an AZ guide to the elements: Oxford University Press*.
- [22]- Zhang, W., and Cheng, C. Y., (2007). Manganese metallurgy review. Part I: Leaching of ores/secondary materials and recovery of electrolytic/chemical manganese dioxide. *Hydrometallurgy*, 89(3), 137-159.
- [23]- Osman, A. G., and Kloas, W., (2010b). Water quality and heavy metal monitoring in water, sediments, and tissues of the African catfish *Clarias gariepinus* (Burchell, 1822) from the river Nile, Egypt. *Journal of Environmental Protection*, 1(4), 389-400.
- [24]- Pane, E., Richards, J., and Wood, C., (2003). Acute waterborne nickel toxicity in the rainbow trout (*Oncorhynchus mykiss*) occurs by a respiratory rather than ionoregulatory mechanism. *Aquatic toxicology*, 63(1), 65-82.
- [25]- Cempel, M., and Nikel, G., (2006). Nickel: A Review of Its Sources and Environmental Toxicology. *Polish Journal of Environmental Studies*, 15(3).