Spectroscopic and Hydrogeochemical Analysis of Heavy Metal and Ion Transport in Tripoli's Suburban Aquifers

Amal Boker
Physics Department, Faculty of Education, Janzour
University of Tripoli
Libya
a.boukar1984@gmail.com

Malak Abduarrazag Alya
Physics Department, Faculty of Education, Janzour
University of Tripoli
Libya
malakalya44@gmail.com

Samar Khaled Almarghany
Student at Physics Department
, Faculty of Education, Janzour

Abstract

This study comprehensively investigates the physicochemical characteristics and contamination levels of groundwater from wells of varying depths across four suburban areas in Tripoli. Utilizing advanced atomic absorption and emission spectroscopy, we precisely quantified heavy metals (Pb, Cd, As) and major cations (Na, Ca, K) to evaluate water quality and associated health risks. Our results indicate significant element concentration variations, with a statistically supported correlation between well depth and contaminant levels, shaped by the region's unique hydrogeological features. Notably, elevated heavy metal and ion concentrations in shallower wells frequently surpassed WHO and Libyan safety standards. These findings establish a vital baseline for ongoing environmental surveillance and underscore the need for developing predictive physics-based models for contaminant transport in local aquifers. This research provides an integrated spectroscopic and hydrogeochemical perspective essential for environmental management.

Keywords:

atomic absorption and emission, groundwater, heavy elemenst, Pollutio of heavy elements, cations , Pollution

I.INTRODACTION

Groundwater is an important source of drinking water in arid regions. It is important to monitor the quality of this water, especially with the increase in pollution sources in recent years. This makes heavy metal pollution a significant environmental challenge, as increased concentrations can negatively impact human health. There are several different techniques for measuring heavy metal concentrations in groundwater, among which spectroscopy is generally used for its accuracy and ability to efficiently analyze a wide range of elements [13]. The basic principle of optical atomic absorption methods (atomic absorption spectroscopy) is that radiation is absorbed by unexcited atoms in the gaseous state. Absorption occurs at the molecular level in visible and ultraviolet spectroscopies. As a result of this energy absorption, electronic transitions occur in the atoms within the molecules. [2,14]. Absorption also occurs at the molecular level in infrared spectroscopy, causing vibrations within the molecules. The molecule transitions from the zero vibrational level to the high-energy vibrational levels, leading to expansion or contraction of the chemical bonds between the atoms or a change in the

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angles between the bonds that make up the molecules. In the case of atomic absorption spectroscopy of elements, absorption occurs only at the atomic level and not at the molecular level. There are several types of spectroscopic devices, the most important of which are the atomic absorption device and the atomic emission device. [6] These devices are an effective tool for accurately determining pollution levels, which contributes to assessing water quality and its suitability for human consumption. [9,11]

II. Research problem, hypotheses and questions

The problem of the study

it is to study the physicochemical properties of well water flows such as pH, electrical conductivity (EC), and total dissolved salts (TDS), which is essential to determine the extent of groundwater pollution and its impact on health and the environment. These measurements also help in understanding the nature of pollution and developing appropriate strategies to treat it and reduce its negative effects, as well as calculating the concentrations of toxic elements and their positive ions in different areas in Tripoli using spectroscopic methods, namely atomic absorption spectrometry and atomic emission spectrometry.

Study questions

1- What are the concentration levels of toxic elements (lead, cadmium, arsenic) in the groundwater of the four areas (Janzour, Al-Saraj, Al-Maya, Al-Ameriya) of the study community?
2- What is the effect of well depth on the concentration of lead, cadmium, and arsenic, and on the physicochemical properties?
3- Identify the concentrations of positive ions in the water of these wells, namely (sodium, calcium, potassium). 4-To what extent do the results obtained from this study match the limits permitted by the World Health Organization for determining water quality?
5- What are the differences in pollution levels between the four regions?

Study objectives

This study aims to determine the concentration of some heavy elements (lead, cadmium, arsenic) in groundwater wells using an atomic absorption spectrometer. It also aims to determine the percentage of positive ions (sodium, calcium, potassium) present in them using a flame atomic emission spectrometer in the areas (Janzour, Al-Saraj, Al-Maya, Al-Ameriya), as well as to study the effect of well depth on the concentration of toxic elements and physicochemical properties.

Study population

Groundwater sample, and the sample type in this study is a purposive sample, where specific samples were chosen from specific locations with the aim of measuring the concentration of heavy elements, positive ions and physicochemical properties in those areas where the depths of the wells varied as shown in the following table.

Table (1) : shows Well depth of area of samples.

Sample number	Area	Well depth (meters)
1	Janzour	40m
2	Al-Saraj	75m
3	Al-Maya	25 m
4	Al-Ameriya	200m

Study Methodology

This study was conducted as a descriptive and analytical study aimed at measuring the levels of groundwater pollution with heavy elements in four areas (Janzour, Al-Saraj, Al-Maya, and Al-Ameriya) using a dual-beam atomic absorption spectrometer (AAS220) equipped with a graphite furnace (GF), as well as measuring the concentrations of positive ions using a flame photometer. Water samples were collected from groundwater wells in these areas and placed in clean, sterile plastic bottles to ensure the accuracy of the results. The samples were transferred to the laboratory on the same day they were collected and analyzed using an atomic absorption spectrometer to measure the concentration of lead, cadmium, and arsenic. The physicochemical properties of the water were also measured using a multimeter, including pH, electrical conductivity (EC), and total dissolved salts (TDS). The concentration of catins for sodium, calcium, and potassium was also calculated using an atomic emission spectrometer. The resulting data were recorded and compared with the limits recommended by the World Health Organization (WHO). The results were compared between the four areas to determine the area with the highest concentration. Based on the results of the study, recommendations will be made to improve treatment techniques. Water currently used in these areas.

III. Previous studies

In a local study conducted by (Al-Barouni, 1996) [3] aimed to examine groundwater in Libya using the atomic absorption spectrometer (AAS), the results of this study showed the presence of some heavy metals (HM) in varying concentrations in water samples collected from the Tajoura tannery swamp and from a drinking water well at the Al-Nada'id factory in Tajoura. Water samples from some wells near them were also analyzed. The results of this study also showed that the concentration of the elements cadmium (Cd), cobalt (Co), chromium (Cr), nickel (Ni), lead (Pb), and zinc (Zn) depend on the proximity of these wells to the Tajoura tannery[12. (Karima Al-Suwaih, Salem Al-Fitouri, Jamal Abudia, Salem Al-Jawashi, Ezz El-Din Arafa, (2018) [5] were able, through what they published in the Libyan International Journal, to conclude that the atomic absorption spectrometry (AAS) method can be relied upon to determine cadmium concentrations with high accuracy and sensitivity. Cadmium (Cd II) concentrations were verified in drinking water samples obtained commercially from the spring factory in the town of Qasr Bin Ghashir, and they were estimated at about 0.50 ± 0.011 ppm. The atomic absorption spectrometry (GF) (AAS) can be adopted as a typical device in determining

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cadmium (Cd II) concentrations in aqueous solutions. Professor (Fawzi Al-Tumi, (2013) [1] conducted a study to estimate lead and some heavy elements of environmental importance in well water near the liquid smelting plant in Tajoura using the atomic absorption spectrometer (AAS)[15]. The aim was to estimate the levels of lead, chromium, and cadmium as heavy elements, in addition to some other groundwater properties such as pH, total dissolved salts (TDS), and electrical conductivity (EC), and compare them with the safe limits for humans in well water near the liquid smelting plants in the Tajoura region of Libya. The results showed the following: The average lead level was 0.004 ± 0.0004, and there was not a sufficient percentage of both cadmium and chromium to estimate them in all the wells under study. The average pH, total dissolved salts, and electrical conductivity were 7.28 ± 0.039, 1498.82 ± 79.631 ppm, and 2126.62 ± 109.29 µs/cm, respectively. We conclude from this that: This study showed that the levels of lead concentration and pH in the well water studied were within the permitted range locally and internationally. The levels of cadmium and chromium did not reach the standard level, while the concentration of dissolved salts and electrical conductivity were within the range not permitted locally or internationally, which means that this water is unfit for drinking and human consumption. (Halima Abdel Salam Abdullah, Judeya Gabriel Saqr, Zainab Miftah Khalifa,(2024) studied some of the physical and chemical properties of samples of water used in some bakeries in the city of Tarhuna. Six random samples of water used in bread making in the city were collected, which were taken from the city center where the population density is high. These samples were subjected to multiple tests to determine some properties. The acidity (pH), electrical conductivity (EC), and total dissolved salts (TDS) were measured using a portable device designed specifically for this purpose. The results showed that the pH values ranged between 6.91 and 7.63 with an average of 7.25, which is within the permissible limits according to Libyan specifications and the World Health Organization (WHO). The TDS values were also within the recommended limits, with the exception of sample No. 6, which exceeded the permissible limit, as the values ranged between 11 mg/L and 1429 mg/L with an average of 757.83 mg/L. As for the electrical conductivity values (EC), The values ranged between 23µS/cm and 2177µS/cm, with an average of 1305µS/cm. The samples fell within the permissible limits for drinking water. Sample No. 6 recorded the highest value, indicating that it is water with high salinity, which may affect the appearance and taste of bread when used.

Table (2): shows the limits recommended by the World Health Organization and the Environmental Protection Agency for heavy metal concentrations and cations concentrations in water. [4]

Metal	WHO (µg/L)	EPA (µg/L)
Al	100-200 µg /L	50-200 µg/L
Cd	3 µg /L	5 µg /L
Cu	2000 µg /L	1300 µg /L
Pb	10 µg /L	15 µg /L
Hg	6 µg /L	2 µg /L
As	10 µg /L	10 µg /L
K^+	20 µg /L	Less than40
Na^+	200 µg /L	Less than 200
Ca	200 µg /L	Less than 200

Table (3): shows the permissible concentrations of total dissolved salts, electrical conductivity and pH in drinking water according to the World Health Organization (WHO) and Libyan specifications.

Property	units	WHO (1984)	Libyan specifications (2008)
pH	-	6.5-8.5	6.5-8.5
Electrical conductivity	µS/cm	Less than 2300	Less than 2500
dissolved salts	mg/L	Less than 1000	Less than 1200

IV.Sources of sample and collection methods

Sample preparation: Samples were collected in clean, dry plastic bottles that were sterilized and vacuumed with 30% nitric acid. These bottles were tightly sealed with glass stoppers. Water samples were digested using 50 ml of a mixture of concentrated nitric and perchloric acid. The samples were then placed in cold digestion flasks and dried to 25 ml using distilled water. They were then filtered using Whatman filter paper. The samples were then stored refrigerated in polypropylene bottles for examination and analysis using spectroscopic methods. A beam of light with a specific wavelength was shone on the free atoms. Each element has a special light source (cathode), in which the free atoms absorb light energy at its characteristic wavelength, which leads to the excitation of their electrons to higher energy levels. The amount of light absorbed was compared to standard solutions with known concentrations of the element to be analyzed, allowing the concentration of the element in the sample to be determined with high accuracy.

V. Results

a-Physicochemical properties

1- Power of Hydrogen (pH)

The results obtained from the measurements showed that all water samples were acidic and unfit for drinking and that their pH value was less than the minimum recommended limit (6.5). The pH value of the sample taken from the Al-Maya area was 4.5, which is the lowest value obtained, and for the sample taken from the Janzour area it was 4.66. As for the sample taken from the Al-Saraj area, the pH value reached 4.9, and the highest recorded pH value was for the sample taken from the Al-Ameriya area, which reached 5.60.

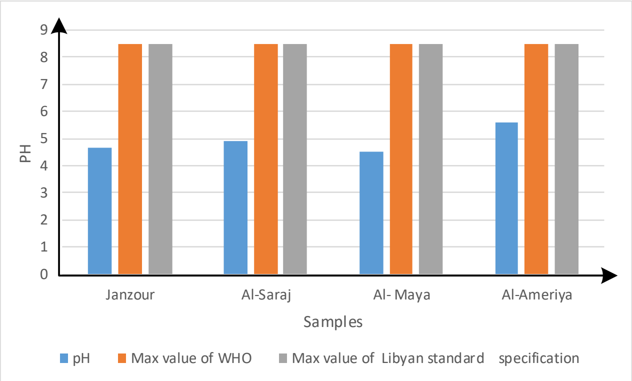

Fig1: Shows the pH values of the studied samples and the maximum allowed by WHO and libyan standard.

2-Electrical conductivity (EC)

the lowest electrical conductivity value was for the sample taken from the Al-Saraj area, which reached 1190 µS/cm, followed by the sample taken from the Al-Maya area, where the conductivity value was 1735 µS/cm, followed by the sample taken from the Janzour area, which had a conductivity value of 1878 µS/cm. As for the sample taken from the Al-Amiriya area, the electrical conductivity value was 3464 µS/cm, which is the highest value obtained. When comparing these results with WHO and libyan standard we find that the values of all samples fall within the permissible limit, except for the conductivity value of the sample taken from the Al-Ameriya area, which is much higher than the limit permitted by the World Health Organization and the Libyan specifications for drinking water. The reason for this may be that the concentration of dissolved ions in the water is very large, meaning that the water in this sample is highly saline, or it may be a result of the semi-arid climate of the region and the evaporation rates. High or as a result of the high level of pollution of the area's water.

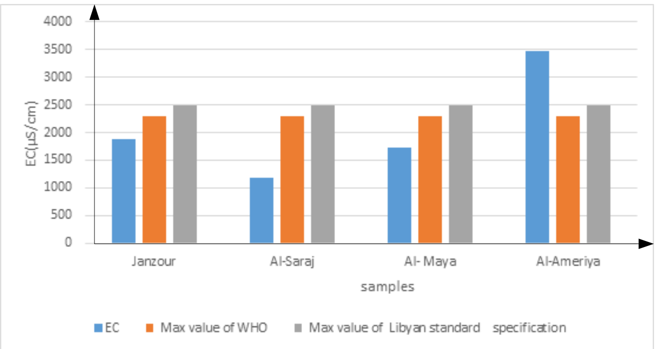

Fig2: Shows the EC values of the studied samples and the maximum allowed by WHO and libyan standard.

3- Total Dissolved Salts (TDS).

the lowest value of total dissolved salts was for the sample taken from the Al-Saraj area, which is 911 mg/L, which is within the permissible limit set by the World Health Organization and the Libyan specifications for drinking water. The remaining results were much higher than the permissible limit. The value of total dissolved salts for the sample taken from the Janzour area reached 1462 mg/L, and for the sample taken from the Al-Maya area it was 2100 mg/L. The value of TDS for the sample taken from the Al-Ameriya area was 2779 mg/L, as this result was the highest value recorded in the studied samples. Therefore, the water samples from the Janzour, Al-Maya, and Al-Ameriya areas are not suitable for drinking. The reason for the high total dissolved salts in these samples may be due to the passage of water through layers of rocks and minerals that dissolve salts, or due to the leakage of fertilizers and pesticides used in agriculture, or as a result of industrial activity and pollution with wastewater. The lack of rainfall can also affect it, as it leads to a reduction in the replenishment of groundwater. And the increase in salt concentration in it, and in coastal areas such as Janzour and Al-Maya, the reason for the increase in total salts may be due to the interaction between seawater and groundwater.

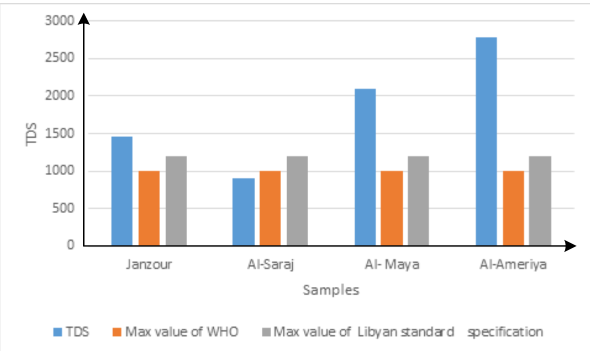

Fig3. Shows the TDS values of the studied samples and the maximum allowed by WHO and libyan standard.

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4-The relationship between TDS and EC.

There is a direct relationship between TDS and EC, as the concentration of dissolved ions, such as salts and minerals, increases, and the electrical conductivity of the water increases. This means that the relationship between them is a direct relationship.

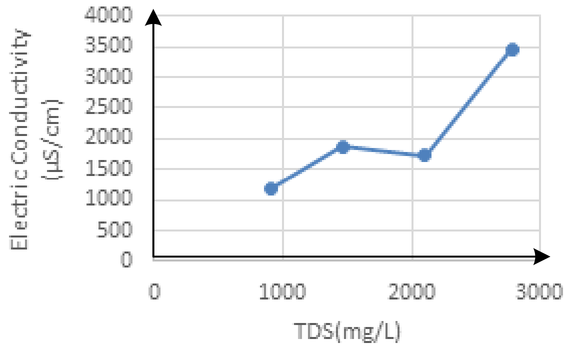

Fig4. Shows the relationship between total dissolved salts and electrical conductivity.

b-Concentration of heavy metals.

1-Lead concentration(pb).

The average lead concentration in the four wells ranged between 0.005-0.003 µg/L, where the highest value of lead was recorded in the Al-Ameriya area, reaching 0.005 µg/L. The lowest value was recorded in the Janzour and Al-Saraj areas, reaching 0.003 µg/L. The lead concentration in the Al-Maya area reached 0.004 µg/L. Based on Table (1.2), the maximum value allowed for the presence of lead is 10 µg/L. Thus, the lead concentration in the four areas falls within the limits recommended by the World Health Organization (WHO), and the lead concentration in the four areas is very low and largely safe.

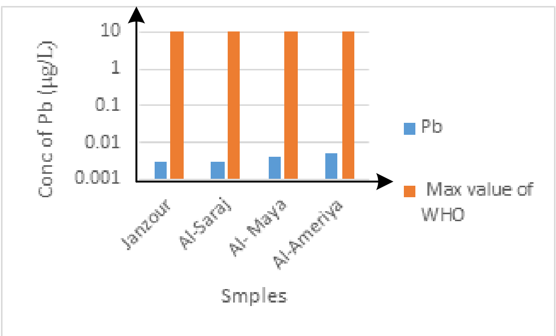

Fig5: Shows the lead concentration in the four areas.

2- Cadmium concentration(cd).

There was no any presence of cadmium in the four regions, as its concentration in all regions was 0. This may be due to the fact that the regions in which the concentration was measured do not have many factories that would cause cadmium pollution.

3-Arsenic Concentration(As).

The average concentration of arsenic in the sample taken from the Maya area was 13 µg/L. When comparing this result with the limits recommended by the World Health Organization, it became clear that there was an increase in the concentration of arsenic, as the maximum permissible limit for arsenic to be present in water is 10 µg/L. The reason for the high concentration of arsenic in this well is perhaps because it is considered a surface well, as its depth reached only 25 meters compared to other wells. It is known that surface wells are more exposed to pollution than others, as there is likely a source of external arsenic pollution near the well from which the sample was taken. As for the rest of the areas, the results showed that they were free of arsenic, as its concentration in them reached 0.

4-The relationship between the depth of the well and the concentration of lead.

Through the results obtained from the analysis of the samples, it was found that the deepest well, 200m, contains the highest concentration of lead, 0.005µg/L, while the well, 40m deep, and the other, 75m deep, contain the lowest concentration of lead, 0.003µg/L, and the shallower well, 25m, contains a higher concentration than the two wells (40, 75)m, and the value of the lead concentration in it is 0.004µg/L. The Lead concentration has been shown to increase in deeper wells but not in a clear linear manner as in deeper wells there can be less mixing of water leading to accumulation of heavy elements and there may be fluctuations in lead concentration based on chemical reactions and geological distribution of the

water.

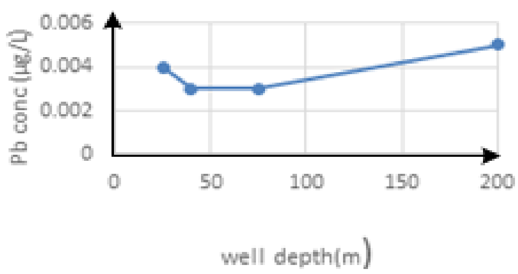

Fig6: Shows the relationship between the depth of the well and the concentration of lead.

5-The relationship between the depth of the well and the concentration of arsenic.

Through the results obtained from the analysis of the samples, it was found that the water of the shallowest well (25m) contained arsenic at a concentration of 13µg/L, and this value is considered high compared to the limit permitted for the presence of arsenic in water by the World Health Organization, while the rest of the wells did not contain any concentration of arsenic. From the figure below, it is clear that the relationship between the depth of the well and the concentration of arsenic is an inverse relationship, as the less deep the well, the higher the concentration of arsenic.

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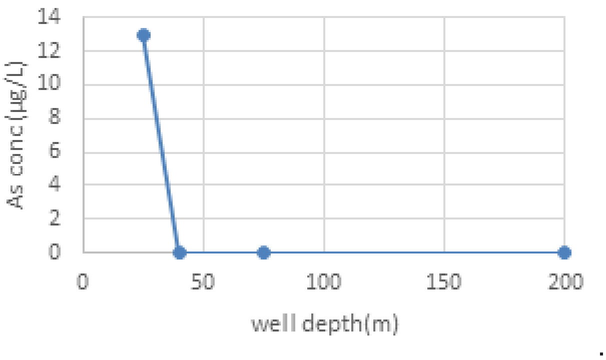

Fig7: Shows the relationship between the depth of the well and the concentration of arsenic.

c-The relationship between well depth and physicochemical properties.

1- The relationship between well depth and pH.

The results obtained showed that the pH value increases with the increase in well depth, i.e. there is a direct relationship between them, and the gradual increase in pH with increasing well depth may be the result of interaction with alkaline rocks at greater depths, which increases the pH of the water, or it may be the result of water near the surface being affected by organic materials and biological processes that produce acids leading to a decrease in the pH value.

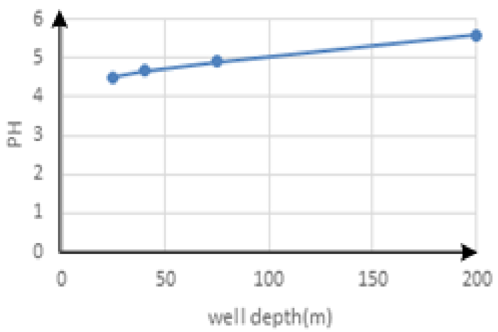

Fig8: Shows the relationship between the depth of the well and the pH.

2-The relationship between well depth and electrical conductivity (EC).

The results showed that increasing depth is not associated with a linear increase in electrical conductivity, and that water from different depths interacts with different geological materials, affecting the concentration of dissolved ions and, consequently, the electrical conductivity. The 25m deep well has moderate electrical conductivity, indicating a reasonable presence of dissolved ions. The 40m deep well has a slight increase in electrical conductivity, which may indicate that the deeper layers contain a slightly higher concentration of dissolved minerals. The 75m deep well has the lowest electrical conductivity value, which may mean that the water passes through less reactive geological layers or contains materials that are less soluble in water. The 200m deep well is very deep and has a very high conductivity, and it is likely that the water has passed through layers containing highly soluble minerals, which increases the concentration of dissolved ions.

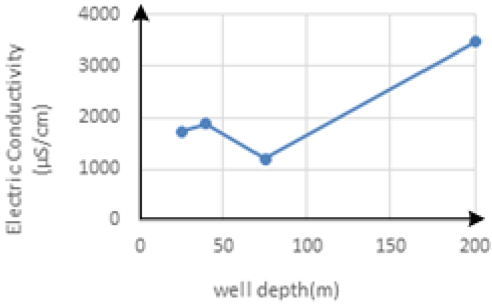

Fig9: Shows the relationship between the depth of the well and the EC**.**

3-The relationship between well depth and total dissolved salts.

The results obtained show that there is no fixed and direct relationship between well depth and TDS value, as the value of total dissolved salts is affected by a group of geological and environmental factors that may vary significantly from one region to another. The well with a depth of 25 m has a relatively high TDS value, which may be a result of pollution or the presence of large quantities of minerals in the surface layers. The well with a depth of 40 m has a lower TDS value than the first well. This may be due to the fact that the layers at this depth contain water with a lower concentration of minerals, or that the nature of the rocks and soil in the area of this well is different from the first well. The well with a depth of 75 m has the lowest TDS value, and this may be due to the fact that the soil and rocks through which the water passes act as natural filters and remove many solid materials, or that the well area is far from sources of pollution that could affect water quality. As for the well with a depth of 200 m, it has the highest TDS value. This may be because water at this depth contains high concentrations of dissolved minerals or flows through layers rich in minerals such as calcium, magnesium, and sodium, which increase the TDS value.

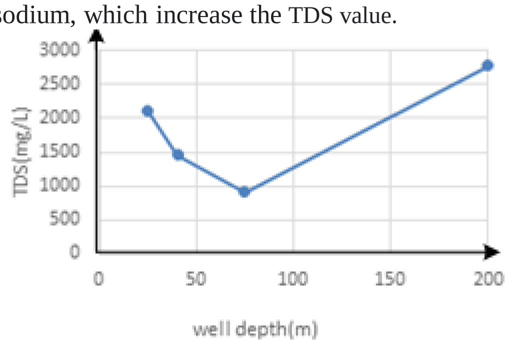

Fig10: Shows the relationship between the depth of the well and the TDS value**.**

D-Estimation of catins concentrations.

1- Potassium ion concentration: The potassium ion concentration of the studied samples was estimated using a flame atomic emission device and was between 24 and 160 mg/L. The highest concentration of this ion was recorded in the Al-Amiriya area, and this is likely due to the salt rocks present in the depths of this area.

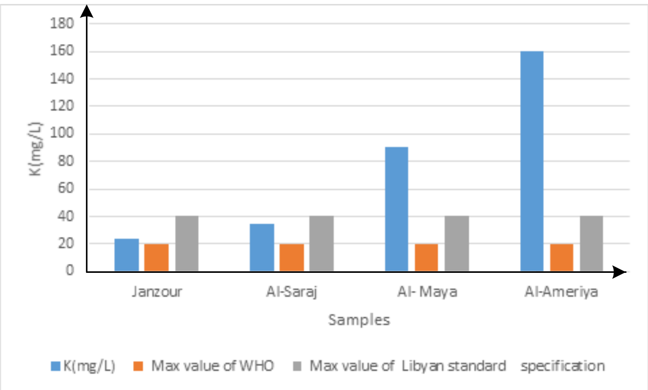

Fig11: Shows the Potassium ion concentration in the four areas.

2-Sodium ion concentration: The concentration of this ion ranged between 120 and 530, exceeding the permissible limit in the Al-Ameriya and Al-Maya areas. This is probably due to the salt rocks that produce this ion. Therefore, the water in these wells is not suitable for drinking or irrigation due to the high percentage of salts in it**.**

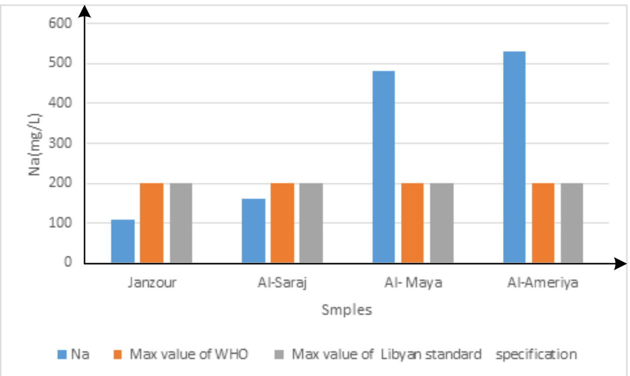

Fig12: Shows the Sodium ion concentration in the four areas.

3-Calcium ion concentration: The calcium concentration values for the studied samples ranged between 400 and 450, with the highest concentration recorded for the well water of the Al-Ameriya area.

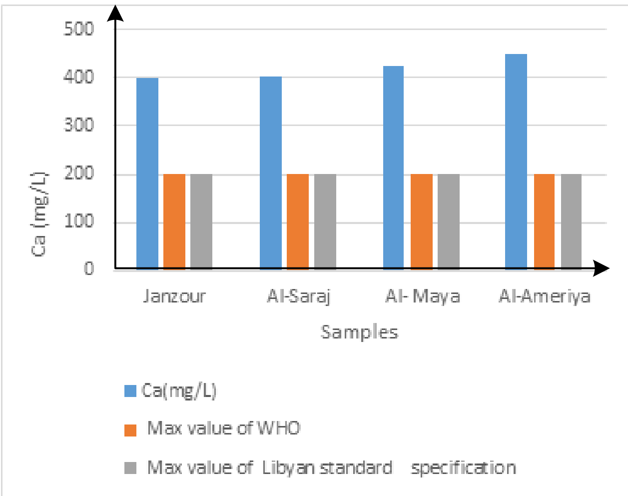

Fig13: Shows the Calcium ion concentration in the four areas.

VI. Statistical Analysis

A statistical analysis was conducted using SPSS software (Version 26) to examine the relationship between well depth and concentrations of heavy metals and physicochemical parameters. Pearson correlation coefficients were calculated alongside significance levels (p-values) to verify the strength and reliability of observed trends. The analysis revealed significant correlations, notably an inverse relationship between arsenic concentration and well depth ($p < 0.05$), supporting the study's conclusions with robust statistical evidence. This quantitative validation enhances the confidence in interpreting environmental risks associated with groundwater contamination in the study area.

VII. Discussion

This study provides important insights into the physicochemical characteristics and contamination levels of groundwater in Tripoli's suburban areas. The significant variations in heavy metal concentrations, correlated with well depth, align with findings from previous regional studies such as Al-Barouni (1996) and Al-Toumi (2013). These consistencies strengthen the understanding of hydrogeochemical dynamics affected by both natural geological formations and anthropogenic activities.

The elevated concentrations of arsenic and other heavy metals in shallow wells raise important environmental and health concerns. The statistical analysis supports these observations, confirming significant correlations between well depth and contaminant levels, emphasizing the need for targeted water quality management.

Furthermore, effective water purification methods, increased public awareness campaigns, development of safe water distribution networks, and stringent regulatory controls are strongly recommended to mitigate contamination risks and safeguard public health.

VIII. conclusion

This study examined the physicochemical properties and the estimation of the concentration of some heavy metals in

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groundwater wells using an atomic absorption spectrometer and the estimation of the concentration of some cations using an atomic emission spectrometer. This was achieved by collecting and accurately analyzing samples. Important results were obtained that reflect the current status of groundwater quality in the studied areas. The results showed variations in lead concentrations between different samples, and arsenic was present in only one sample, and its concentration was high, indicating the impact of human, industrial, and agricultural activities on groundwater pollution. This pollution may have serious health and environmental impacts, necessitating urgent measures to reduce and address it. Cadmium was not present in any of the studied samples. The study also revealed the importance of monitoring physicochemical properties such as pH, electrical conductivity, and total dissolved salts, as these factors play a major role in understanding the nature of water and the effects of pollutants on it. These measurements are essential for assessing water quality and guiding future efforts to purify and improve water resources. Based on these results, the need to implement practical recommendations that include continuous assessment of water quality and the use of effective treatment technologies is highlighted.

IX. Recommendations

1. Expand new research into quantitative estimations of heavy metals contaminating water using techniques other than those already studied 2. Use appropriate water purification techniques to remove or reduce the concentration of heavy elements in groundwater, such as filtration, ion exchange, and the use of activated carbon. 3. Increase cultural awareness among the population by holding seminars that highlight the harms and diseases caused by high concentrations of heavy elements 4. Develop water distribution networks to ensure access to clean and safe water for the population and reduce reliance on contaminated groundwater sources. 5. Establish central databases containing comprehensive information on groundwater quality and heavy element concentrations, to serve as a reference for researchers and decision-makers. 6. Tighten controls on industrial and agricultural activities that may lead to groundwater contamination with heavy elements, and strictly enforce environmental laws to prevent pollution.
7. It is recommended to expand the sample size and increase the number of sampling sites in future studies to improve the accuracy and reliability of groundwater quality assessment results.

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