



Estimating Nitrate and Manganese Levels in Drinking Water: A Case Study from Al-Jamil, Riqdalin and Zellten in Western Libya

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تقدير مستويات النترات والمنجنيز في مياه الشرب: دراسة حالة من الجميل ورقدالين وزلطن في غرب ليبيا

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Abstract:

This study examines the quality of drinking water in the regions of Al-Jamil, Ragdalin, and Zalten through an assessment of nitrate and manganese concentrations in both desalinated and groundwater sources. A total of ten desalinated water samples and eight well water samples were collected and analyzed. The obtained results were evaluated in comparison with the drinking water quality standards specified by both Libyan regulations and the World Health Organization (WHO). Nitrate concentrations in the desalinated water samples ranged from 23.6 to 62 mg/L. Two samples (A5 and A9), with recorded values of 62 mg/L and 55 mg/L, respectively, exceeded the permissible limits established by national and international standards. Similarly, several well water samples (B2, B4, and B5), showing concentrations of 58, 52, and 55 mg/L, surpassed the maximum allowable levels set by Libyan and WHO guidelines. Additionally, samples B3, B6, and B7 exhibited nitrate concentrations of 47, 46, and 50 mg/L, exceeding the limit according to Libyan specifications alone. Manganese concentrations in desalinated water were consistently within acceptable limits, maintaining a concentration of 0.2 mg/L. In contrast, manganese levels in well water samples varied between 0.2 and 2.78 mg/L, with samples B4 and B6 exceeding permissible thresholds, recording 1.11 mg/L and 2.78 mg/L, respectively. These findings highlight the need for continuous monitoring and potential intervention measures to ensure safe drinking water quality in the studied regions.

Keywords: Drinking Water, Nitrate, Manganese, Spectrophotolab 7100VIS, Hydrotest HT1000.

المخلص

تتناول هذه الدراسة تقييم جودة مياه الشرب في مناطق الجميل ورقدالين وزلطن من خلال تحليل تراكيز النترات والمنجنيز في كلٍّ من المياه المحلاة والمياه الجوفية. حيث تم جمع عشرة عينات من المياه المحلاة وثمانية عينات من مياه الآبار، ثم تحليلها مخبرياً. وقد تمت مقارنة النتائج مع المعايير المعتمدة في المواصفات القياسية الليبية ومعايير منظمة الصحة العالمية (WHO) الخاصة بمياه الشرب. تراوحت تراكيز النترات في عينات المياه المحلاة ما بين 23.6 و 62 ملغم/لتر. وقد

أظهرت العينتان (A5 و A9) قيمًا مقدارها 62 ملغم/لتر و 55 ملغم/لتر على التوالي، متجاوزة الحدود المسموح بها وفق المعايير الليبية والدولية. كما أظهرت بعض عينات مياه الآبار (B2 و B4 و B5) تراكيز بلغت 58 و 52 و 55 ملغم/لتر، متجاوزة أيضًا الحدود القصوى الموصى بها حسب المعايير الليبية والدولية. بينما سجلت العينات (B3 و B6 و B7) تراكيز 47 و 46 و 50 ملغم/لتر، وهي تتجاوز الحد المسموح به وفق المواصفات الليبية فقط. أما بالنسبة لتراكيز المنغنيز في المياه المحلاة، فقد كانت ضمن الحدود المسموح بها، مسجلة تركيزًا ثابتًا بلغ 0.2 ملغم/لتر. في حين تراوحت تراكيز المنغنيز في عينات مياه الآبار بين 0.2 و 2.78 ملغم/لتر، وقد تجاوزت العينتان (B4 و B6) الحدود المسموح بها، مسجلة 1.11 ملغم/لتر و 2.78 ملغم/لتر على التوالي. تشير هذه النتائج إلى ضرورة تعزيز برامج المراقبة الدورية واتخاذ التدابير التصحيحية الملائمة لضمان سلامة جودة مياه الشرب في المناطق المدروسة.

الكلمات المفتاحية: مياه الشرب، النترات، المنغنيز، جهاز المطياف الضوئي، هيدروتيست.

Introduction:

Water is essential for the life of all organisms. It is the medium in which all vital processes occur inside and outside living cells. The total volume of water on the Earth's surface is approximately 1,357 million km³ (Abu Bakr *et al.*, 2024). Natural water usually contains varying amounts of mineral elements, including manganese (Mn) and nitrates, which may reach drinking water as a result of natural processes or industrial and agricultural pollution (Ali, 2010). Their presence in small quantities is necessary for the body to function normally, but concentrations of these elements exceeding the permissible limits can lead to serious health problems and negative effects on water quality, such as taste, odor, and sediment formation in water networks (Abdel Fattah Ahmed Hussein, 2015). Therefore, monitoring the levels of these elements and analyzing them in drinking water is considered essential to ensure compliance with health and environmental standards (Mustafa, 2007).

Water pollution has many forms, such as poisoning by organic waste, pesticides, detergents, pollution resulting from food, thermal pollution, pollution by petroleum materials, or other countless different industries. Recently, the increasing local, agricultural, and industrial activities around the world have led to the release of various pollutants, most notably heavy metals such as iron, copper, and manganese. Pollution by these metals in the environment is one of the biggest problems facing humans due to their toxicity and disease-causing effects on living organisms (Najat, *et al.*, 2022, Hokkanen, *et al.*, 2016).

High nitrate levels in groundwater are increasingly becoming a major challenge for water supplies across the globe. Nitrate nitrogen naturally exists in both groundwater and rainwater, but only in small amounts. The issue arises particularly in regions with intensive farming activities. Farmers often rely on chemical fertilizers to boost plant growth, but these fertilizers dissolve quickly and can easily be washed away. As a result, a significant portion of these nutrients ends up leaching into the groundwater rather than staying with the plants. This leaching process contributes to elevated nitrate levels in groundwater (Hajjar *et al.*, 2008, Ahmed, 2021). In addition, urban areas face rising nitrate concentrations due to rapid urban growth and inadequate infrastructure.

Research from France has found that farmers use around 1 million tons of nitrate each year to boost soil fertility. However, not all of it gets absorbed by plants; in fact, about 2 million tons linger in the soil, with some seeping into groundwater (Ahmed, 2021). In a different study from Khan Yunis, Palestine, it was discovered that sandy soils allow more nitrates to leak into the groundwater compared to clayey soils, which can hold onto more nitrates within their structure (Kamal, 2012, Ahmed, 2021). Although there are a number of studies and researches that address water quality, the extent of pollution, and the chemical and biological properties of drinking water in Libya, this has not been extensively addressed in the study areas. Therefore, monitoring water quality is essential in managing and preserving these resources, especially in arid regions such as Libya.

This study set out to determine the levels of manganese and nitrate found in drinking water, both from desalinated sources and wells. Using precise analytical techniques, it compared these findings with the allowable limits established by Libyan standards and the World Health Organization. This study comes to meet the need for a comprehensive and updated assessment of drinking water quality.

Nitrate and manganese chemistry:

Nitrates are important chemical compounds and polyatomic ions. Manganese (Mn) is a transition element essential to chemistry and is involved in many biological and industrial processes.

Properties and presence of nitrates and manganese:

Nitrate is a naturally occurring substance found in many vegetables, such as lettuce, spinach, kale, and others. Nitrate is a negatively charged polyatomic ion. After being added to food, nitrate is converted by enzymes in the food or by bacteria into nitrite, a substance harmful to the body. Nitrates are found in agricultural fertilizers, which are considered one of the most prominent anthropogenic sources. Nitrogen fertilizers are used to increase soil fertility and often seep into groundwater and surface water.

The presence of nitrate in wastewater through the leakage of organic waste from treatment plants or household systems contributes to increased nitrate concentrations.

Nitrates are also found in animal waste, especially in intensive farms (Al-Bashir, *et al.*, 2012, Smith, *et al.*, 2007). Nitrates are still used in the curing process of meat and fish and today are added to canned meats mainly to prevent the growth of bacteria.

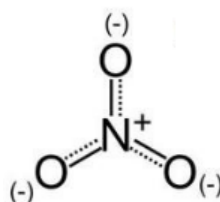


Figure (1): Structural formula of nitrate anion.

Manganese is a transition element with a silvery-grey color, brittle in nature. Manganese is considered less magnetic than iron, and it is an average conductor of heat and electricity (Mahmoud, 2005). Manganese is an element necessary in small quantities for humans, as it enters into the formation of some enzymes and in metabolic processes such as the manufacture of proteins and carbohydrates in nature. In water, manganese can cause problems at high concentrations, such as the appearance of black spots on clothes and plates, in addition to an undesirable taste in water (Ahmed, 2015). It is known that exposure of humans to high concentrations of it causes poisoning.



Figure (2): Manganese mineral.

Uses of Nitrates and Manganese:

Nitrates are primarily used in the production of agricultural fertilizers due to their easy solubility in water and biodegradability. The main nitrates are ammonia, sodium nitrate, potassium nitrate, and calcium nitrate, and several million kilograms of them are produced annually for the purpose of fertilizing crops. Nitrates are also used as oxidizing agents, particularly in explosives, where the rapid oxidation of carbon compounds results in the release of large quantities of hot gases. Sodium nitrate is also used to remove air bubbles from molten glass during glassmaking and in some types of ceramics (Fadhel, *et al.*, 2020).

Manganese is used in the steel industry by adding it to iron and many types of steel that contain manganese. Manganese steel is characterized by its extremely high strength and resistance to corrosion and shocks. Manganese is also used with copper and nickel in the manufacture of electrical wires, as this type is characterized by its unchanged resistance to heat. Manganese is also used in removing oxygen and sulfur, in whitening glass, and in the manufacture of dry batteries (Misbah, 2008). Manganese is very important for human health, as it is involved in the composition and metabolism of bones. Manganese improves the performance of the thyroid gland and is important in the functions of the brain and nerves (Abd Al-Rahman, 2009).

Nitrate and Manganese Toxicity:

High levels of nitrate in drinking water can lead to blue baby syndrome. Nitrate is converted to nitrite, which reacts with hemoglobin in the blood, making hemoglobin unable to carry oxygen due to iron oxidation (Al-Bashir, 2019). The lethal dose of nitrate for adults ranges from 15 to 70 milligrams of nitrate per kilogram of body weight. The reduction from nitrate to nitrite may be caused by microbes present in water, plants, or food during storage, or by microbial contamination of food in open containers. There is no doubt that the study of nitrate in food constitutes a large part of the study of human exposure to

this substance. Therefore, it is necessary to issue a statement on the various sources of risk (Fadhel, *et al.*, 2020).

When the body absorbs manganese, it is transferred through the blood to the liver, kidneys, pancreas, and endocrine glands. Increased concentration of manganese primarily affects the respiratory system, as it causes inflammation of the bronchi. Likewise, prolonged exposure to this element causes infertility (Akasha, 2018).

Nitrate and Manganese Removal in Drinking Water:

Both nitrate and manganese are considered undesirable elements in drinking water and can affect human health if they exceed the recommended values set by the World Health Organization and the Libyan government.

Nitrate can be removed using negatively charged ion-exchange resins that replace nitrate ions with chloride ions. This method is effective even at high concentrations but requires periodic maintenance and resin replacement (Abd El-Lateef, 2022). Alternatively, semi-permeable membranes can be used to separate pure water from nitrate and other contaminants by passing the water under high pressure. This method removes more than 90% of the contaminants, which is relatively expensive (El-Lateef, 2022). Anaerobic bacteria can also be used to convert nitrate to nitrogen gas. This method is suitable for large treatment plants and is environmentally friendly, but requires special conditions (Ebrahimi, *et al.*, 2020). Nitrates can also be removed by distillation, by heating water to evaporate it and then condensing it, thus separating nitrates and other pollutants. This is a very effective method for removing nitrates and many pollutants, and this method consumes a lot of energy (Ebrahimi, *et al.*, 2020).

Organic manganese (emulsion) can be removed in dark-colored waters by coagulation, clarification, and filtration. These processes are usually preceded by aeration. Most groundwater contains manganese bicarbonate, as well as iron bicarbonate. Manganese can also be removed by the sodium cation exchange method (Ismail, 2018). Manganese can be removed by the zeolite method. Organic manganese (emulsion) may be found in some surface waters and sometimes in well water. Manganese in this form cannot be removed by normal oxidation with filtration. It often does not respond even to the strong oxidizing action caused by chlorine, and usually responds to coagulation with alum, at which point it can be removed by filtration (Ismail, 2018).

Sources of Nitrate and Manganese Pollution:

The spread of nitrates in surface and groundwater is primarily linked to agricultural activities due to the intensive use of nitrogen fertilizers, which increase crop growth. However, a large portion of nitrates is washed from the soil into groundwater and surface water due to irrigation or rain, causing contamination of water sources. Sewage containing human waste, the washing away of industrial and agricultural waste, and the decomposition of organic nitrogen in animal waste also contribute to the formation of nitrates (Nolan, *et al.*, 2002).

Manganese is present in rocks and soil in different proportions and is transferred to groundwater and surface water through erosion and dissolution processes. Manganese is also released from manganese mines and the steel and heavy metal industries. The use of fertilizers and agricultural chemicals contributes to increasing the concentration of manganese in groundwater (Lloyd, *et al.*, 2001).

Description of the study areas:

The study addresses on three main areas: Al-Jamil, Raqdalín, and Zelten. Let's start with Al-Jamil, situated about 110 km west of Tripoli. This place is pretty flat, with clay and sandy soil dominating the landscape. Agriculture here thrives thanks to groundwater, with numerous wells supporting both farming and drinking needs. Moving to Raqdalín, it's just west of Al-Jamil and about 115 km from Tripoli. Known for its charming rural and pastoral vibe, this area relies heavily on reservoirs and wells, groundwater is crucial, meeting most of the residents' drinking water requirements. Situated 125 km west of Tripoli, the Zelten area is known for its similar landscape features. Agricultural activities here are somewhat limited, and the region depends on groundwater sources found at medium depths.



Figure (3): Study areas

Water sample collection:

In the study, researchers collected drinking water samples from various locations in Al-Jamil, Ragdalin, and Zelten to analyze and evaluate their chemical content. We focused on measuring levels of nitrates (NO_3^-) and manganese (Mn) to get a clear picture of the water quality. You can check Table (1) to see exactly where these water samples were taken.

We chose these areas because they rely on different water sources, such as well water and water from desalination plants. Our goal was to assess the water quality in these areas and see how it measures up against Libyan and international standards. We gathered a total of eighteen samples: ten from desalinated water and nine from wells. Specifically, we took six samples from the Al-Jamil area, four from desalinated sources and two from wells. In Ragdalin, we collected eight samples, five from desalinated water and three from wells. Lastly, in Zelten, we gathered four samples, with one from desalinated water and three from wells.

We gathered the study samples using clean 1-liter polyethylene plastic bottles. Each bottle had its sample number labeled clearly. To ensure accuracy, we collected three samples for each test. Before collecting the water, we rinsed each bottle with the same water to remove any impurities that could compromise our analysis. Finally, we transported the samples to the laboratory for the necessary testing.

Table (1): The locations for taking drinking water samples (desalination and wells).

Sample code	Sample type	The area	the site
A1	dessert	Al-Jamil	Al-Makman near the Al-Makman Mosque
A2	dessert	Al-Jamil	Al-Makman near Omar Ibn Al-Khattab School
A3	dessert	Al-Jamil	Al Nabaa Market near Al Shamoukh School
A4	dessert	Al-Jamil	Abu Qur'a
A5	dessert	Ragdalin	Electricity Company Road
A6	dessert	Ragdalin	Hoba near the mosque
A7	dessert	Ragdalin	The Shabshoubi, Al-Assa Road
A8	dessert	Ragdalin	Sea road near the power station
A9	dessert	Ragdalin	Near Zamzam Mosque
A10	dessert	Zelten	Malit Road
B1	well	Al-Jamil	Near Al-Jamil High School
B2	well	Al-Jamil	Al-Huda Street
B3	well	Ragdalin	Al-Sabikha Road near the cemetery
B4	well	Ragdalin	Malit Road near Al-Fida School
B5	well	Ragdalin	Ras Atiya Road near Balao Mosque
B6	well	Zelten	Al-Awtad Mosque
B7	well	Zelten	Malit
B8	well	Zelten	Near Hamza bin Jarrah Mosque

Methods and tools used in analysis and measurement:

Different devices were used to analyze and measure the concentration of nitrate and manganese in drinking water samples. These devices are:

SpectrophotoLab 7100VIS:

A spectrophotometer, manufactured by the German company WTW, was used to estimate the concentration of nitrate ions in drinking water collected from different sources. This device is used in chemical and environmental laboratories to analyze and measure the concentration of chemicals in liquids by absorbing visible light. It works by passing light of a specific wavelength through the sample,

then measuring the amount of absorption, which enables the concentration of a particular substance to be determined.

The measurement was performed using a wavelength of 220 nm to measure the absorbance resulting from the presence of nitrate in the sample, with a reference wavelength of 275 nm used to correct for interference resulting from organic matter. This spectral range is commonly used in nitrate analysis because it represents the maximum absorption of the nitrate ion in the visible spectrum.

The spectrometer was chosen to measure nitrate concentration in drinking water for scientific and technical reasons, the most important of which are high accuracy and speed, in addition to its compatibility with international standards for measuring inorganic elements in water. It is also distinguished by its ability to conduct spectral analysis in the visible range using precise wavelengths, ease of use, the possibility of storing and documenting results, in addition to its small size and ease of calibration.

To operate the device, press the start button and wait until the self-test is complete. The method was selected from the list, and we chose the nitrate method. The blank sample was calibrated by inserting a test tube containing distilled water. We wiped the tube well with a soft cloth. Then we placed the tube in the designated chamber and closed the cover. We chose "Zero" to calibrate the device.

To measure the sample, we prepared the sample using the appropriate reagents (nitrate). We wiped the tube well and placed it in the device. The device ran automatically at a wavelength of 220 nanometers with correction at 275 nanometers. We left the specified time for the reaction (nitrate takes 30 minutes in each sample). Then the reading appeared in (mg/L). The measurement was repeated three times for each sample.



Figure (4): SpectrophotoLab 7100VIS

HydroTest HT1000 device:

Hydrotest is a portable, multi-calibration photometer used for field water quality analysis. It is ideal for engineers and researchers in the fields of environment and public health. This device, from the British company Trace20, was used to estimate manganese concentration in drinking water samples.

This device relies on photometric technology, where specific chemical reagents are added to the sample to create a specific color corresponding to the concentration of the element to be measured. The device accurately measures the color intensity and then calculates the concentration based on the pre-programmed calibration in the system. This method allows for reliable and fast results.

To operate the device, we pressed the start button and waited for it to initialize. 5 ml of the sample was placed in the designated tube, then the reagent (a special tablet) was added to each sample. The tablet was ground thoroughly until dissolved, and the sample was left for five minutes to complete the chemical reaction. The tube was inserted into the device and the measurement button was pressed. The results appeared on the screen within seconds. We repeated the measurement three times for each sample.



Figure (5): HydroTest HT1000

Results and Disussion:

The study involved the analysis of eighteen samples gathered from desalinated water and wells in the regions of Al-Jamil, Raqdalín, and Zelten. Chemical tests were performed on all samples.

Nitrate concentration estimation results:

Nitrate concentration was estimated for drinking water samples (desalinated and wells). Table (2) shows the results of this analysis.

Table (2): The results of nitrate concentration for the studied drinking water samples.

Sample code	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	B1	B2	B3	B4	B5	B6	B7	B8
(NO ₃ ⁻) mg/L	25.3	27.2	39	43	62	38	23.6	42	55	24.9	26.5	58	47	52	55	46	50	40

In examining the nitrate (NO₃⁻) concentrations in desalination water samples, as depicted in Figure (6), a notable variation among the recorded values becomes evident. This variation suggests differences in nitrate levels across the samples. Notably, sample A7 showed the lowest concentration at 23.6 mg/L, while sample A5 reached the highest at 62 mg/L. Among the results, samples A5 and A9 displayed concentrations of 62 mg/L and 55 mg/L, respectively, both of which surpass the limits set by Libyan and international standards.

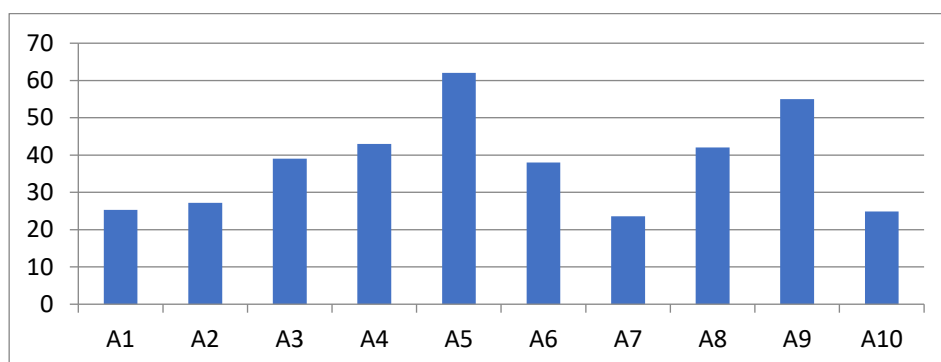


Figure (6): illustrates the nitrate concentration outcomes observed in the desalinated water samples analyzed in this study.

The results of nitrate concentration (NO₃⁻) in well water samples, as shown in Figure (7), showed a clear difference in the recorded values, indicating a difference in nitrate concentration between well water samples. The highest nitrate concentration was in sample B2 (58 mg/L), and the lowest nitrate concentration was in sample B1 (26.5 mg/L). The results showed that samples (B2, B4, B5) that recorded values (58, 52, 55) exceeded the permissible limits according to international specifications, and samples (B3, B6, B7) that recorded values (47, 46, 50) exceeded the permissible limits according to Libyan standard specifications.

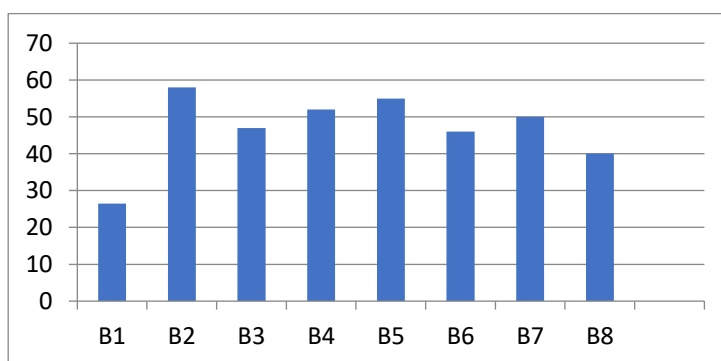


Figure (7): The nitrate concentrations observed in the well water samples under study are presented.

When comparing the results of estimating nitrate concentration in desalinated water and well water, it was found that well water contains a higher average nitrate concentration than desalinated water. The proportion of samples that exceeded the permissible limit was also greater in well water, which indicates a relative deterioration in the quality of groundwater.

Estimation Results of Manganese Concentration:

The estimated concentrations of manganese found in both desalinated water and well samples are presented in Table (3).

Table (3): The data on manganese levels found in various drinking water samples.

Sample code	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	B1	B2	B3	B4	B5	B6	B7	B8
Mn (mg/L)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.47	0.2	1.11	0.26	2.78	0.2	0.2

The concentration of manganese was estimated in the drinking water samples shown in Table (3). The results of the analysis of the desalination water samples shown in Figure (8) showed that all desalination water samples were within the permissible limits according to Libyan and international specifications (0.4 mg/L), which indicates the efficiency of the desalination process in removing the manganese element.

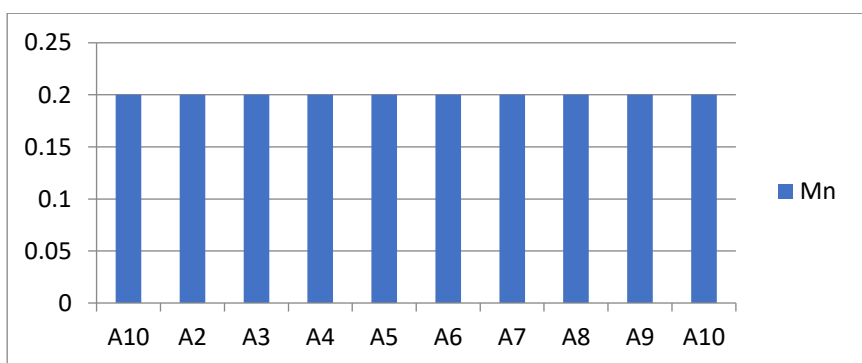


Figure (8): The results detailing the manganese concentration observed in the desalinated water samples analyzed during our study.

The results of manganese concentration in the well water samples shown in Figure (9) showed that some samples, especially the sample that reached 2.78 mg/L, significantly exceeded the permissible limits according to Libyan and international standard specifications (0.4 mg/L). This indicates the possibility of contamination or natural concentration of manganese in some groundwater sources. This increase in some samples may pose a health risk if the water is consumed without treatment. Therefore, periodic monitoring of well water must be carried out and it must be treated when necessary.

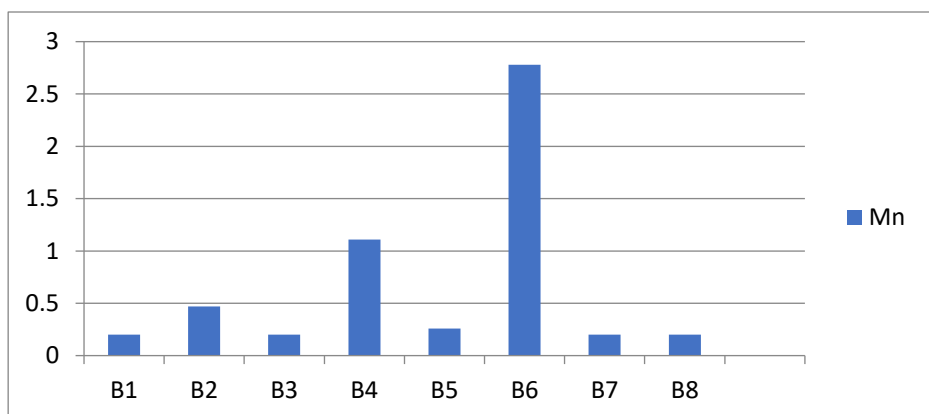


Figure (9): The results of manganese concentration analysis for the well water samples examined in this study.

Conclusions:

Through this research, the quality of drinking water was evaluated for ten samples of desalinated water (A1-A10) and eight samples of well water (B1-B8) by estimating the concentration of nitrates and manganese and comparing them with the Libyan standard specifications and the World Health Organization, as they are considered basic indicators of the safety of water and its suitability for human consumption. Water samples were collected from different sources and analyzed using approved chemical analysis methods. The results of nitrate concentration in well water samples for some samples showed that it exceeded the permissible limits, especially in samples (B2, B4, B5), which recorded values (58, 52, 55), which may pose a health risk, especially to children and pregnant women. The results of well water samples also showed high concentrations of manganese that exceeded the permissible health limit (0.4 mg/L), especially in samples (B4, B6), whose concentrations were (1.11 and 2.78 mg/L), which indicates clear metal contamination. The results suggest that, in the study areas, desalinated water is perceived as safer and superior in quality compared to well water. However, it's important to note that this conclusion comes with certain observations that necessitate ongoing monitoring. On the other hand, well water demands further treatment and regular surveillance to maintain its safety.

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