African Journal of Advanced Pure and Applied Sciences (AJAPAS)
Online ISSN: 2957-644X
Volume 5, Issue 4, 2026
Page No: 336-343
Website: https://aaasjournals.com/index.php/ajapas/index
ISI 2025: 1.126 SJIFactor 2024: 6.752 معامل التأثير العربي 2025: 1.65

Quantification of Total and Free Copper Concentrations in Drinking Water Sources (Desalinated and Well Water) Across Al-Jumayl, Regdalin, and Zaltan

Munera Mustafa Aonyas [1*], Ebtihal Fathy Tarish [2], Umaima Nour El-Din Ghita [3], Maha Fawzy El-Abbasi [4]
[1,2,3,4] Department of Chemistry, Faculty of Sciences, Sabratha University, Regdalin, Libya

تقدير تركيز النحاس (الكلي والحر) في عينات من مياه الشرب (تحلية وآبار) في الجميل ورقدالين وزلطن

منيرة مصطفى أونيس [1 *]، ابتهال فتحي طريش [2]، أميمة نور الدين غيطة [3]، مها فوزي العباسي [4]
[4،3،2،1] قسم الكيمياء، كلية العلوم، جامعة صبراتة ، رقدالين، ليبيا

*Corresponding author: muneramustafa020@gmail.com

Received: August 12, 2026	Accepted: October 21, 2026	Published: November 11, 2026

Abstract:
Copper is an essential trace element in human physiological processes; however, elevated concentrations in drinking water pose significant health risks, including gastrointestinal disorders and hepatic damage. This study presents a comparative analytical determination of free copper (Free Cu) and total copper (Total Cu) levels across ten desalinated water samples (A1–A10) and eight groundwater well samples (B1–B8) collected from the northwestern Libyan municipal areas of Al-Jmail, Regdalin, and Zaltan. Analytical results demonstrated that desalinated water maintained low and highly uniform copper levels, averaging 0.061 ± 0.014 mg/L for Free Cu and 0.077 ± 0.021 mg/L for Total Cu. Conversely, groundwater sources exhibited substantial spatial variation and higher mean concentrations of 0.226 ± 0.247 mg/L (Free Cu) and 0.275 ± 0.267 mg/L (Total Cu), with peak concentrations recorded in samples B2 and B5 (0.69 mg/L Total Cu). Although all tested samples remained strictly compliant with the World Health Organization (WHO) maximum allowable threshold of 2.0 mg/L, the observed spatial heterogeneity in groundwater points to localized aquifer mineral leaching and network pipe degradation. Routine hydrochemical surveillance of regional groundwater aquifers is therefore strongly advised.

Keywords: Total and free copper, HydroTest (HT1000) device, Drinking water.

الملخص:
يُعد النحاس عنصراً ضرورياً للعمليات الفسيولوجية في جسم الإنسان؛ ومع ذلك، فإن ارتفاع تركيزاته في مياه الشرب يشكل مخاطر صحية جسيمة، تشمل اضطرابات الجهاز الهضمي وتلف الكبد. تقدم هذه الدراسة تحليلاً مقارناً لمستويات النحاس الحر والنحاس الكلي في عشر عينات من مياه التحلية (A1-A10) وثماني عينات من مياه الآبار الجوفية (B1-B8) جُمعت من مناطق الجميل ورقدالين وزلطن في شمال غرب ليبيا. أظهرت النتائج التحليلية أن عينات مياه التحلية حافظت على مستويات منخفضة ومتجانسة للغاية من النحاس، بمتوسط بلغ 0.061 ± 0.014 مجم/لتر للنحاس الحر و0.077 ± 0.021 مجم/لتر للنحاس الكلي. في المقابل، أظهرت مصادر المياه الجوفية تبايناً مكانياً ملحوظاً ومتوسط تركيزات أعلى، حيث بلغت 0.226 ± 0.247 مجم/لتر للنحاس الحر، و0.275 ± 0.267 مجم/لتر للنحاس الكلي، مع تسجيل أعلى التركيزات في العينتين B2 وB5 (بواقع 0.69 مجم/لتر للنحاس الكلي). وعلى الرغم من أن جميع عينات المياه المختبرة ظلت ضمن الحدود القصوى المسموح بها وفقاً للمواصفات القياسية الليبية ومعايير منظمة الصحة العالمية البالغة 2.0 مجم/لتر، إلا أن التباين المكاني الملحوظ في المياه الجوفية يشير إلى احتمالية حدوث تسرب للمعادن من الطبقات الحاملة للمياه (المكمن المائي) أو تآكل في شبكات الأنابيب. وبناءً عليه، يُوصى بشدة بإجراء مراقبة هيدروكيميائية دورية لطبقات المياه الجوفية في مناطق الدراسة.

الكلمات المفتاحية: النحاس الكلي، النحاس الحر، جهاز الهيدروتسيت، مياه الشرب.

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Introduction

Natural water inherently contains diverse mineral elements, including copper (Cu), which typically originate from natural weathering processes or anthropogenic discharges from agricultural and industrial activities (Abdullah, 2010). Although trace concentrations of copper are essential for biological functions, excessive levels exceeding regulatory thresholds pose severe health risks and degrade water quality, often impairing organoleptic properties (taste and odor) and causing mineral deposition within distribution systems (Abd al-Fattah,2015). Therefore, continuous monitoring and quantification of trace metal concentrations in drinking water are paramount to ensuring compliance with environmental and public health standards (Salama,2007).

In certain regions, populations continue to rely on untreated groundwater directly extracted from wells for daily consumption. This practice often proceeds without prior assessment of the water's physicochemical or biological characteristics—the primary determinants of potable water safety with consumers depending solely on organoleptic evaluation (taste). In coastal regions of Libya, water scarcity is further exacerbated by climatic factors and excessive seawater intrusion into freshwater aquifers, which significantly elevates groundwater salinity and renders it unsuitable for human consumption (Najat, *et al.,* 2022, Mohammed Alwan,2017).

Distinguishing between total copper and free copper is paramount when assessing human health risks and environmental safety. Total copper accounts for all physical and chemical forms of the element within a sample, comprising particulate, colloidal, and organically or inorganically bound species (APHA, 2017). Conversely, free copper denotes uncomplexed, hydrated cupric ions (Cu^{2+}), which constitute the most toxicologically active and bioavailable fraction (Campbell, 1995; Arnold et al., 2005).

Given the escalating challenge of global water pollution, continuous monitoring of water quality remains essential to safeguard public health and ensure safe water access. Addressing this critical issue, this study evaluated the concentrations and chemical speciation of copper (Cu) across various drinking water sources using highly sensitive analytical techniques. The obtained values were systematically benchmarked against permissible thresholds established by Libyan drinking water standards and the World Health Organization (WHO) guidelines.

Properties and Occurrence of Copper

Copper is a relatively soft, lustrous, reddish metal widely recognized for its exceptional thermal and electrical conductivity, surpassed only by silver. It features a density of around 8.96 g/cm^3, a melting point of 1085^0C, and non-magnetic properties. Thanks to a protective oxide layer that forms on its surface, copper exhibits strong resistance to corrosion (Ahmed Zaki, 2017).Naturally, copper exists either in its free metallic state or within compounds such as copper sulfide (Cu_2S) and copper sulfate ($CuSO_4$). Biologically, it serves an essential role as a enzymatic cofactor with antioxidant properties. Nevertheless, elevated copper levels in drinking water exceeding safe standard thresholds can induce gastrointestinal distress, while acute toxicity poses severe risks of liver and kidney damage (Salama, 2007).



Figure (1) Copper metal

Industrial, Engineering, and Agricultural Applications of Copper

The technological utility of copper (Cu) and its chemical compounds spans diverse industrial sectors, driven by its distinct physical, chemical, and thermal properties :

Electrical Engineering: Owing to its exceptionally high electrical conductivity, copper serves as the primary standard material for power transmission wiring, microelectronics, and electrical appliances (Khalifa Misbah,2008) .

Metallurgy and Alloy Synthesis: Copper is heavily utilized as a base constituent in the fabrication of high-performance alloys (such as brass and bronze), tailored for enhanced mechanical strength and corrosion resistance.

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Chemical Stability and Fluid Dynamics: Due to its relative chemical inertness and kinetic stability upon atmospheric exposure, copper is a material of choice for plumbing, industrial piping systems, and protective coating formulations.
Thermal Management Systems: Capitalizing on its superior thermal conductivity, copper is extensively employed in the fabrication of heat exchangers, HVAC heating/cooling conduits, and thermally efficient cookware (Khalifa Misbah,2008).
Agricultural Biochemistry: Inorganic copper compounds (e.g., copper sulfates) serve vital agricultural roles as broad-spectrum fungicides and antimicrobial agents to safeguard crops against phytopathogenic fungi (Khalifa Misbah,2008).

Toxicological Effects and Clinical Pathology of Copper Overexposure

Exceeding maximum permissible exposure thresholds for copper (Cu) presents notable toxicological hazards across multiple physiological systems :
Systemic and Neurological Impairment: Chronic or excessive exposure is associated with systemic hypertension, microcytic anemia, and neurotoxicity. Elevated systemic copper levels have been linked to neurodevelopmental and behavioral disturbances in pediatric populations; however, while trace-metal dyshomeostasis (such as altered zinc/copper ratios) is frequently observed in autism spectrum disorder (ASD), a direct causal relationship between copper toxicity and ASD etiology remains an active area of investigation rather than an established primary cause (Inshirah, *et al*., 2018).
Ocular and Respiratory Irritation: Inhalation of airborne copper dust or fumes induces mucosal irritation of the upper respiratory tract and eyes, accompanied by acute cephalalgia (headaches).
Gastrointestinal and Organ Toxicity: Ingestion of elevated concentrations leads to severe gastrointestinal distress, presenting as abdominal pain, emesis, and diarrhea. In cases of acute or prolonged high-dose toxicity, unbound copper ions trigger oxidative stress and cellular necrosis, leading to severe hepatic and renal pathology (Inshirah, *et al*., 2018).

Remediation and Removal Technologies for Aqueous Copper in Potable Water

The presence of copper (Cu^{2+}) in drinking water supplies represents a critical water-quality concern when concentrations exceed the maximum contaminant levels (MCL) established by the World Health Organization (WHO) and Libyan national standards.
To mitigate potential eco-toxicological risks and achieve compliance with potable water thresholds, several chemical, physical, and electrochemical remediation technologies are utilized (Hanidi Abdul , *et al.*, 2001).
Ion-Exchange Resins: Employs functionalized synthetic or natural polymeric ion-exchange resins tailored for selective cation exchange, displacing divalent copper ions (Cu^{2+}) with non-toxic counter-ions (Hanidi Abdul , *et al.*, 2001).
Thermal Distillation and Condensation: A phase-change separation process wherein water is thermally vaporized to produce steam leaving non-volatile ionic contaminants behind—and subsequently condensed to yield high-purity liquid distillate.
Electrocoagulation (EC): An electrochemical separation technique utilizing sacrificial anodes (typically iron or aluminum) under an applied electric current. In situ anodic dissolution generates metal hydroxide coagulants, such as $Al(OH)_3$ or $Fe(OH)_3$, which facilitate the destabilization, complexation, and co-precipitation of dissolved copper ions (Ramakrishnan, *et al*., 2013).
Membrane Filtration: Leverages pressure-driven semi-permeable membranes (e.g., nanofiltration and reverse osmosis) to systematically exclude aqueous copper ions via size exclusion and charge repulsion mechanisms (Yongming, *et al*., 2023).
Adsorptive Separation: Uses high-surface-area natural or synthetic adsorbents—such as activated carbon or lignocellulosic bio-adsorbents (e.g., sawdust)—to capture Cu^{2+} ions through surface complexation, electrostatic attraction, and physisorption/chemisorption mechanisms (Zdenka, *et al*., 2019).

Mechanisms and Sources of Environmental Copper Contamination

Environmental and potable water contamination by copper (Cu) originates primarily from two major pathways: infrastructure degradation and anthropogenic industrial-agricultural discharges.
Plumbing Infrastructure Degradation: Copper tubing and piping utilized in water distribution networks represent a primary point-source of contamination. Under low-pH or acidic aqueous conditions, oxidative corrosion of internal pipe surfaces releases free divalent copper ions (Cu^{2+}) into drinking water systems.
Industrial Effluents: Diverse industrial operations—including mining/mineral processing, electroplating, printed circuit board (PCB) fabrication, and electronics manufacturing—discharge heavy-metal-bearing industrial wastewater, contributing significantly to copper accumulation in aquatic ecosystems.

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Agricultural Runoff: Agrochemical applications serve as major non-point sources. Inorganic copper compounds are extensively formulated into broad-spectrum fungicides, bactericides, and micronutrient soil amendments, which subsequently migrate into surface and groundwater bodies via agricultural runoff (Lars Järup, 2003).

Regulatory Frameworks and Standard Specifications for Copper in Potable Water

Potable water safety represents a crucial determinant of public health, necessitating strict adherence to physical, chemical, and organoleptic quality metrics defined by national and international regulatory frameworks .

World Health Organization (WHO) Guidelines: The WHO establishes a health-based Maximum Permissible Limit (MPL) of (2.0 mg/L)for dissolved copper in drinking water to mitigate chronic systemic toxicity. However, to prevent organoleptic deterioration—specifically aesthetic taste impairment and staining an upper threshold recommendation of (1.0\ mg/L) is maintained (Asmaa Abdel Hamid, *et al.*, 2019)..

Libyan National Standards: In accordance with the Libyan Standard Specifications for Drinking Water Quality, a more stringent statutory limit of less than 1.0 mg/L(< 1.0\tmg/L) is enforced to ensure both toxicological safety and consumer acceptability(Asmaa Abdel Hamid, *et al.*, 2019)..

Sample collection

To assess drinking water quality, samples were obtained from various points in Al-Jamil, Raqdalin, and Zaltan. Analytical evaluation focused on quantifying total and free copper (Cu) levels across two primary supply types: well water and desalinated water. Sampling coordinates and locations are detailed in Table (1).

Table (1) shows 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

The selected study area reflects the varied water sourcing in the region, providing a baseline to gauge compliance with Libyan and international standards.

A total of 18 water samples were obtained across the study areas, comprising 10 desalinated water samples and 8 well water samples. The distribution included six samples from Al-Jamil (4 desalinated, 2 well water), eight from Raqdalin (5 desalinated, 3 well water), and four from Zaltan (3 desalinated, 1 well water).

Water samples were collected in clean, labeled 1L polyethylene containers. To minimize potential contamination, each bottle was thoroughly rinsed three times with the sample water prior to collection. All sampling was performed in triplicate. The collected samples were subsequently transported to the laboratory for analytical determination.

HydroTest (HT1000)

A HydroTest (HT1000) device, manufactured by the British company Trace20, was used to estimate the total copper and free copper concentrations in drinking water samples collected from various sources, as shown in Figure (2).

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Figure (2) HydroTest HT1000

The instrument operates on photometric principles, wherein specific chemical reagents are added to the sample to form a colored complex proportional to the analyte concentration. The absorbance intensity is accurately measured by the photometer and converted into concentration values based on a factory-precalibrated curve, providing rapid and reliable analytical results.

To perform the measurement, a 5-mL aliquot of the water sample was transferred into a designated test tube. The corresponding reagent tablet was added and thoroughly crushed to ensure complete dissolution. The mixture was allowed to stand for five minutes for full color development. The tube was then inserted into the photometer, and the concentration reading was recorded upon measurement completion. All procedures were executed in triplicate for each sample to ensure consistency.

Results of the determination of total and fractional copper concentrations

The concentrations of both total and free copper were determined in desalinated water and well water samples; the analytical results are presented in Table (2).

Table (2) shows the total and fractional copper concentrations in drinking water samples.

Sample code	Cu (Free)	Cu (total)
A1	0.05	0.06
A2	0.05	0.06
A3	0.05	0.06
A4	0.06	0.08
A5	0.08	0.09
A6	0.09	0.11
A7	0.06	0.07
A8	0.05	0.11
A9	0.05	0.06
A10	0.07	0.08
B1	0.26	0.30
B2	0.61	0.69
B3	0.05	0.06
B4	0.06	0.08
B5	0.61	0.69
B6	0.05	0.16
B7	0.11	0.15
B8	0.06	0.07

Free and total copper (Cu) concentrations in the desalinated and well water samples were analyzed, with the results summarized in Table (2). As depicted in Figure (3) Copper Concentrations in Desalinated Water Supplies. The concentrations ofFree Cu ranged from 0.05 mg/L to 0.09mg/L, with a overall mean value of 0.061 ± 0.014 mg/L. Similarly, Total Cu concentrations varied within a narrow window of 0.05 mg/L to 0.11 mg/L, achieving a mean level of 0.077 ± 0.021 mg/L. The observed consistency and low variance in desalinated water parameters reflect effective , efficient reverse osmosis membrane filtration, and tight operational control at municipal desalination plants servicing the study region.

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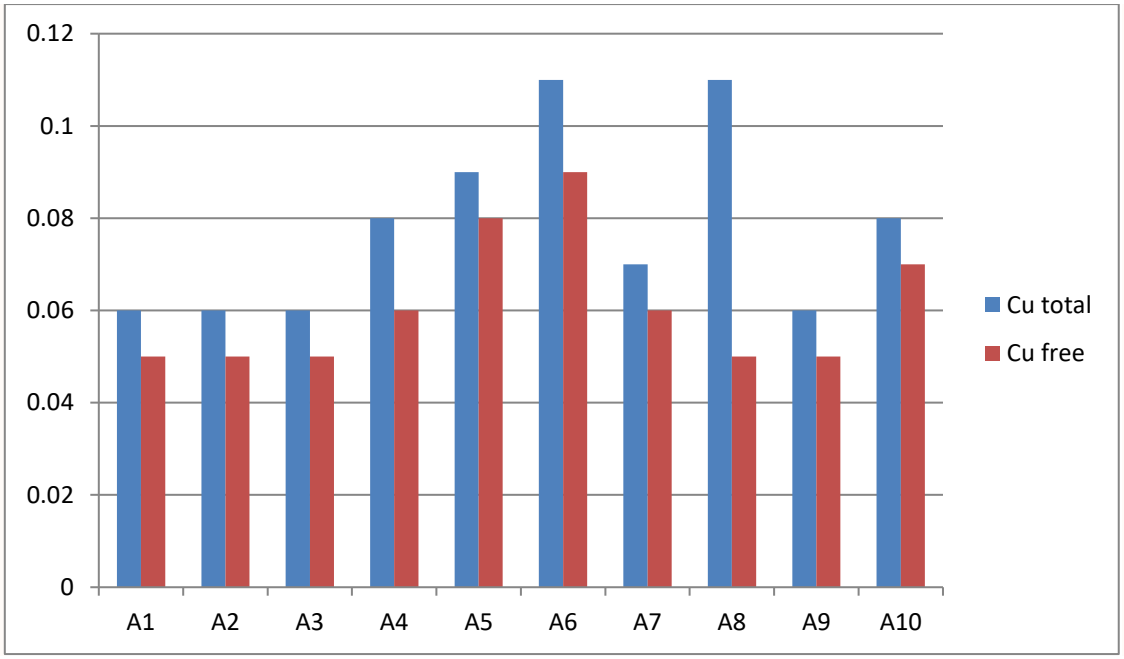


Figure (3) shows the results for total and fractional copper concentrations in the studied desalination water samples.

As depicted in Figure (4) Free Cu concentrations in groundwater ranged from 0.05 mg/L to 0.61 mg/L (0.226 ± 0.247 mg/L), while Total Cu levels varied between 0.06 mg/L and 0.69 mg/L (0.275 ± 0.267 mg/L). Notably, samples B2 and B5 recorded peak Total Cu values of 0.69 mg/L (with Free Cu = 0.61 mg/L), followed by sample B1 (Total Cu = 0.30 mg/L).

This localized enrichment can be attributed to two main factors:Hydrogeological Leaching: Natural dissolution of copper-bearing minerals within localized aquifer rock matrices and Infrastructure Degradation: Electrochemical corrosion of submersible pumps, metallic well casings, or aged distribution piping systems connected to specific extraction sites.

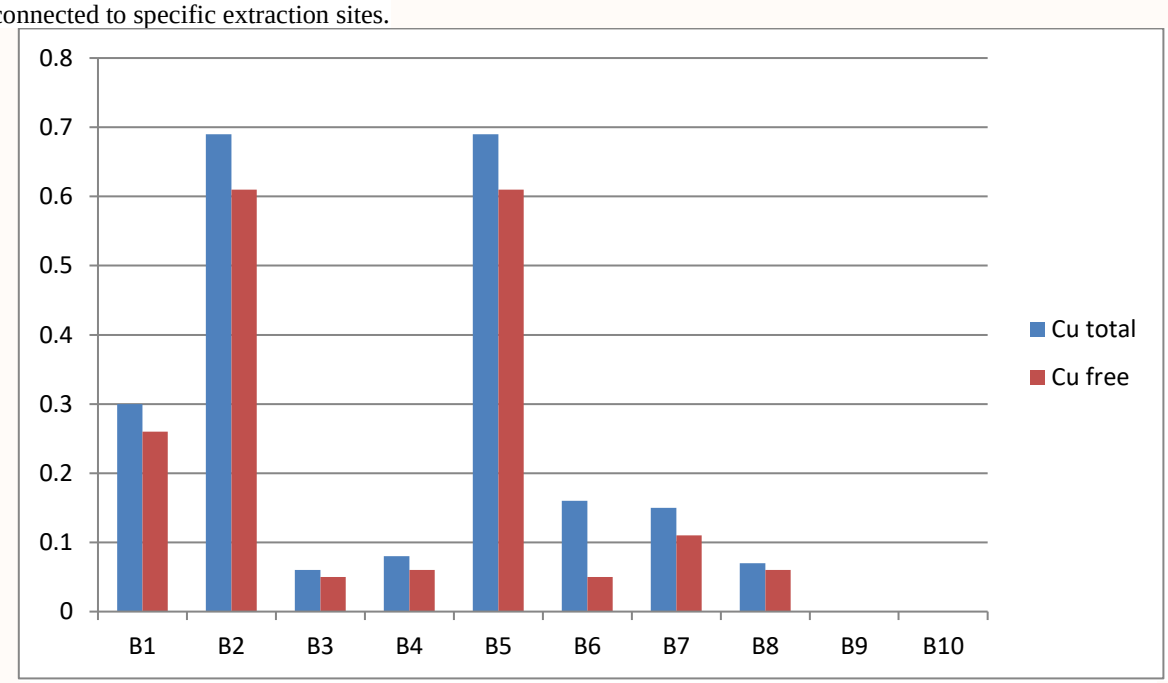


Figure (4) shows the results for total and fractional copper concentrations in the studied well-water samples.

Conclusion

In this study, drinking water quality was evaluated by measuring free and total copper (Cu) concentrations across ten desalinated water samples (A1–A10) and eight groundwater well samples (B1–B8). The obtained levels were benchmarked against Libyan national standards and World Health Organization (WHO) guidelines

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to assess compliance with human consumption safety limits. All water samples were collected from diverse regional sources and quantified using validated analytical methodologies.
The results for free and total copper concentrations were within the limits permitted by Libyan standard specifications and the World Health Organization.
In conclusion, desalinated water demonstrated superior chemical quality and a higher safety profile compared to groundwater across the studied locations. Nevertheless, periodic surveillance remains essential. Conversely, the elevated copper concentrations observed in well water highlight the necessity for targeted post-treatment strategies and continuous monitoring to ensure long-term potable safety.

Recommendations

Based on the quantitative determinations of total and free copper (Cu) concentrations in drinking water across Al-Jamil, Raqdalin, and Zaltan, the following measures are recommended:
1) Routine Chemical Surveillance: Establish systematic, periodic testing of municipal and groundwater supplies to monitor total and free copper (Cu) levels against Libyan national standards and {WHO) guidelines.
2) Targeted Environmental Monitoring: Implement continuous water quality monitoring networks, particularly in agricultural and industrial zones vulnerable to anthropogenic contamination.
3) Advanced Heavy Metal Remediation: Upgrade existing water purification infrastructure by incorporating high-efficiency technologies (e.g., membrane filtration, ion exchange, or electrocoagulation) whenever metal concentrations exceed regulatory limits.
4) Prioritization of Desalinated Water: Promote the primary utilization of desalinated water for domestic consumption, while applying supplementary treatment protocols to groundwater wells prior to distribution.
5) Expanded Water Quality Research: Support multi-element research investigating additional toxic heavy metals and emerging trace contaminants that may compromise human health and groundwater integrity.
6) Public Awareness and Emergency Response: Enhance community education regarding water resource protection and formulate strategic emergency contingency plans to manage localized contamination events, ensuring long-term water security.

Acknowledgements: We are deeply grateful to the personnel at the Chemical Analysis Laboratory, Environmental Sanitation Department in South Tripoli, for their exceptional support and assistance. Additionally, we extend our sincere thanks to the Department of Chemistry, Faculty of Science in Ragdalin, Sabratha University, for their valuable collaboration and contributions.

Compliance with ethical standards

Disclosure of conflict of interest

The authors declare that they have no conflict of interest.

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