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ORIGINAL RESEARCH ARTICLE

Groundwater contamination with heavy metals: A case study in Hebron, Palestine

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Abstract: The study aims to identify seasonal fluctuations in groundwater quality concerning heavy metal contamination. Specifically, it assesses heavy metal concentrations in groundwater in Wadi Al-Samen, evaluates its suitability for drinking purposes, and compares these levels with the World Health Organization standards. Groundwater samples were collected from 20 wells over two seasons and analyzed for 16 trace elements using atomic absorption spectrometry. The metals analyzed include barium, molybdenum, iron, cobalt, cadmium, chromium, boron, lithium, aluminum, arsenic, manganese, nickel, copper, zinc, lead, and selenium. Results showed that four samples exceeded the permissible limits for barium and lithium in both seasons, three samples exceeded the recommended zinc limits in both seasons, 17 samples exceeded the permissible selenium limit in the dry season, and 15 in the wet season, while one sample exceeded the recommended copper limit in both seasons. The heavy metal pollution index (HPI) and metal index (MI) were used to assess contamination levels. HPI values exhibited significant spatial variations, with recorded values of 17.2 in the dry season and 11.99 in the wet season, both below the critical threshold of 100. Groundwater quality was classified as poor in the Al-Hejreh well and very poor in the Al-Fawwar1 well, rendering it unsuitable for drinking. MI results indicated moderate heavy metal contamination, with mean MI values of 2.3 in the dry season and 2.2 in the wet season. The heavy metals detected in the study area were categorized into toxic elements, alkaline earth metals, alkali metals, transition metals, other metallic elements, and non-metallic elements. This research highlights groundwater contamination in Wadi Al-Samen and underscores the need for mitigation measures to reduce health risks for local residents.

Keywords: Heavy metals; Heavy metal pollution index; Metal index; Wadi Al-Samen

1. Introduction

Environmentally friendly wastewater management is a major challenge for developing countries, including the West Bank in Palestine. Heavy metal contamination from untreated sewage discharges is an escalating concern due to its possible risks to human health.[1] Assessing groundwater quality is crucial for water management, as both agricultural and industrial activities can negatively affect groundwater resources.[2] Heavy metals in groundwater, even in small amounts, are undesirable due to their toxicity to both human health and ecosystems.[3,4] Heavy metals tend to bioaccumulate, leading to progressively higher concentrations in organisms over time.[5] In recent years, the use of heavy metals in agriculture and industry has increased.[6] When consumed through contaminated drinking water, these substances can have detrimental effects on human health.[4] Industrial expansion has further increased human exposure to heavy metals.[7] Among the most common heavy metals associated with human poisoning are lead (Pb), arsenic (As), manganese (Mn), cadmium (Cd), nickel (Ni), chromium (Cr), and copper (Cu). Bioaccumulation of heavy metals in the human body leads to toxic effects on various tissues and cells.[8] Acute and chronic toxic effects can result in serious complications, including nervous system disorders, gastrointestinal and renal dysfunction, blood vessel damage, skin lesions, immune system dysfunction, birth defects, and cancer.[9,10]

Lead toxicity has significant adverse effects on the human body, particularly on the neurological, renal, and reproductive systems.[11,12] The kidneys are the primary organs affected, with lead exposure leading to nephropathy and renal failure.[13] As the primary route of lead excretion, the kidneys play a crucial role in detoxification.[12] Lead exposure can also result in developmental abnormalities, including intellectual impairments in children and behavioral disturbances.[14] Children are particularly vulnerable to lead poisoning due to their increased exposure to lead-laden dust and a higher susceptibility to permanent neurological damage compared to adults.[15] Chronic lead toxicity is associated with encephalopathy, peripheral neuropathy, central nervous disorders, and anemia.[16]

Arsenic exposure poses significant health risks, affecting many parts of the human body.[17] It has been linked to gastrointestinal and hepatic disorders, vascular diseases, and cardiovascular and respiratory complications. Chronic arsenic poisoning is closely linked to skin, lung, and bladder cancer. Long-term exposure to arsenic through drinking water can cause cancer in these organs in a dose-dependent manner.[12] High levels of arsenic exposure can also lead to neurological disorders, including peripheral neuropathy.[18] In addition, cognitive impairment in both children and adults has been associated with arsenic toxicity. Clinical manifestations of chronic arsenic toxicity include perforation of the nasal septum, respiratory cancer, and peripheral neuropathy, as well as dermatological conditions and increased cancer risk.[16]

Chronic exposure to increased manganese levels has been associated with Central and Peripheral Neuropathies while Nickel toxicity has been linked to an increased risk of cancer and dermatological conditions.[16]

Cadmium toxicity primarily affects the respiratory system, with inhalation leading to flu-like symptoms. Prolonged exposure through smoke inhalation has been associated with chronic obstructive pulmonary disease and chronic bronchitis. Lung cancer is one of the most likely diseases if we consider that cadmium causes cancer. Cadmium is also a known carcinogen, with lung cancer being a significant health risk.[12] Ingesting cadmium-contaminated food or drinking water can adversely impact the gastrointestinal tract, leading to renal toxicity and kidney damage. Chronic cadmium exposure is also associated with itai-itai disease[13] and an increased risk of cardiovascular disease.[12] Clinical manifestations of chronic cadmium toxicity include proteinuria, glucosuria, osteomalacia, aminoaciduria, and emphysema while those of chromium toxicity include ulcers, perforation of nasal septum, and respiratory cancer.

Some heavy metals, such as chromium and nickel, have been linked to cancer in exposed human populations. Long-term inhalation of chromium can irritate the respiratory system, increasing lung sensitivity and the risk of lung cancer. The health effects of chromium poisoning extend to respiratory, skin, gastrointestinal, cardiovascular, and reproductive toxicity, as well as an elevated risk of cancer. Dermal contact with toxic chromium compounds can result in skin ulcers and dermatitis.[12] High levels of copper exposure can destroy red blood cells, which in turn leads to anemia. Excessive copper accumulation may also cause liver toxicity, which, at extreme doses, can be fatal.[16]

The presence of these metals in water represents a significant environmental concern, threatening both aquatic ecosystems and public health.[19] Elevated levels of heavy metals, including arsenic, cadmium, manganese, iron (Fe), copper, mercury (Hg), zinc (Zn), chromium, and selenium (Se), pose significant risks to human health, especially to children.[20] Industrial discharges, especially from tanneries, have caused a substantial rise in heavy metal concentrations in water and soil worldwide.[21-23] The presence of heavy metals in groundwater is controlled by both natural and human-made factors.[24] Natural factors include soil leaching, mineral weathering, aquifer type, water infiltration quality, and residence time. Anthropogenic sources primarily stem from industrial and household wastewater, soil contamination, urban stormwater, surface runoff, landfill leachate, agricultural fertilizers and pesticides, as well as mining activities.[24,25]

In Hebron, major sources of water pollution include nearby disposal sites, wastewater from settlements, exposed sewage, runoff from wastewater and leachate pits, landfill sites, industrial activities, livestock waste, and the continuous burning of plastic and other waste.[26] While two-thirds of Hebron City is connected to a sewage network, the remaining communities use household cesspools (percolation pits) for sewage disposal, posing significant environmental risks to groundwater and surrounding ecosystems.[27]

Monitoring and evaluating water contamination has become an essential field of research due to the significant impact of water pollution on aquatic life and humans. Some metals, such as iron, copper, zinc, and manganese, are vital nutrients for the physiological and biochemical functioning of plants, animals, and humans. However, these metals can be harmful at higher concentrations. On the other hand, non-essential elements, such as lead, cadmium, and arsenic are harmful even at low concentrations when present in groundwater. These metals do not biodegrade and tend to build up in the environment, bioaccumulating through the food chain and posing serious risks to human health and ecosystems.[28-30]

The heavy metal pollution index (HPI) serves as an important tool for evaluating the overall contamination of both groundwater and surface water.[24,30] It provides a quantitative measure of water quality concerning heavy metal pollution.[31-33] Factors, such as excessive pesticide use, improper waste disposal, and the release of untreated industrial wastewater into streams contribute to the decline in groundwater quality.[34] Ensuring access to safe drinking water is a key challenge in many developing regions, including the West Bank in Palestine.[35] Over recent decades, the demand for clean drinking water has increased, yet supply and water quality remain inadequate. Consequently, many Palestinian families rely on groundwater wells and hand-dug wells as their primary water sources for both drinking and household purposes. Those living near untreated sewage sites may be unaware of the health risks posed by contaminated groundwater.

This study aims to detect seasonal changes in groundwater quality concerning heavy metal contamination. It specifically examines heavy metal concentrations in groundwater from Wadi Al-Samen, evaluates their suitability for drinking, and compares the findings with World Health Organization (WHO) standards.

2. Materials and methods

2.1. Study area

The Wadi Al-Samen area is situated in Hebron, in the southern part of the West Bank, approximately 36 km south of Jerusalem (Figure 1). The climate of Hebron is influenced by the Mediterranean Sea, resulting in a semi-arid climate classification. Winters are the primary rainy season, with precipitation varying from heavy to light. The annual average rainfall in Hebron Governorate is around 540 mm, with roughly 75% occurring between November and March. The estimated annual average rainfall in Wadi al-Samen is 492 mm.[26]

Hebron's topography is characterized by mountainous terrain with elevations exceeding 1,000 m above sea level, leading to frequent freezing temperatures during winter. The average minimum monthly temperature is approximately 3°C. Relative humidity in the western part of Hebron Governorate ranges from 55% to 60%, with a similar range observed in the mountainous areas of Hebron. Household and industrial waste is discharged directly into wadis without treatment, including into Wadi al-Samen.

In 2021, the average flow of wastewater through the Hebron Municipality network was approximately

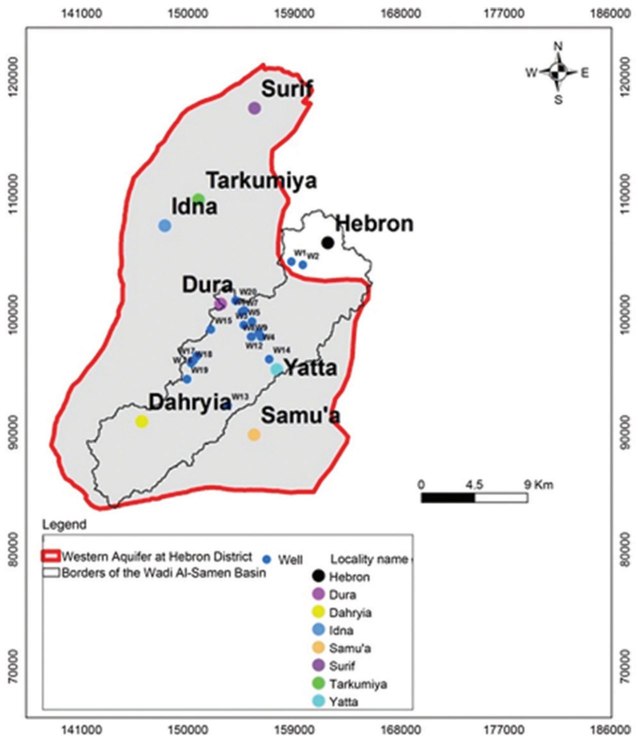

Figure 1. Geographical location of sample wells in the Hebron Governorate, Wadi Al-Saman Basin. The numbers at the borders represent the Palestinian coordinate system in West Bank.

444 m³/h (10,660 m³/day). This flow is projected to increase to 15,200 m³/day by 2027. In other parts of the Wadi al-Samen Basin, cesspits are commonly used for sanitation. The contents of the cesspits are often discharged indiscriminately into the environment, leading to potential contamination.

The area lacks comprehensive geological studies, which presents challenges in identifying geological features, comprehending tectonic processes, and defining the structural framework of the aquifer system. According to Zaarir[36] and Al-Tamimi,[37] the Hebron study area (Figure 2) is primarily composed of sedimentary carbonate rocks dating from the Albian to the Eocene periods, with quaternary alluvial deposits covering much of the surface. The primary aquifers in Hebron and the surrounding area consist of the following formations:

1. Aptian to Albian (Kobar Formation). Found in northern Hebron, west of Halhoul town, this formation primarily consists of limestone, marl, and marly limestone, with occasional marl-limestone intercalations. Thickness ranges from 30 m to 50 m.
2. Albian (Lower Beit Khail Formation). Composed of well-bedded, fine-crystalline, and highly karstic limestone, this formation also includes intermediate marl layers that increase in thickness downward, reaching depths between 120 m and 280 m.
3. Lower Middle Cenomanian (Yatta Formation). Consisting of fine- to medium-crystalline dolomite and limestone, this yellowish-brown formation occasionally includes marly limestone, which is often enriched with fossilized fauna. Thickness ranges from 50 m to 130 m.
4. Upper Middle Cenomanian (Hebron Formation). This formation includes hard, massive dolomite or limestone, typical of the Hebron area. It is highly karstic, with thickness ranging between 20 m and 120 m.
5. Upper Cenomanian (Bethlehem Formation). Rich in faunal content, this formation consists of limestone, dolomite, and chalky limestone with marl, with thickness ranging between 80 m and 270 m.
6. Upper Cenomanian (Turonian-Jerusalem Formation). Comprising limestone and dolomite, this formation covers 36.4% of the study area, ranking second in spatial extent within the study basin. Its thickness ranges from 90 m to 130 m.
7. Senonian (Abu Dis Formation). This formation is made up of chalks, chert, and marl, and it extends across the southern part of the basin. The chalk is typically white, covering approximately 0.7% of the basin, with thickness ranging from 0 m to 450 m.
8. Quaternary (Modern Deposits). This layer consists of alluvial deposits and unconsolidated sediments, such as clay, silt, gravel, and conglomerate, found on the valley floors. Thickness can reach tens of meters, and the red color of the alluvium is attributed to its limestone origin.

2.2. Field sampling and laboratory methods

Groundwater samples were collected in September 2019 and May 2020 to represent both dry and wet seasons.

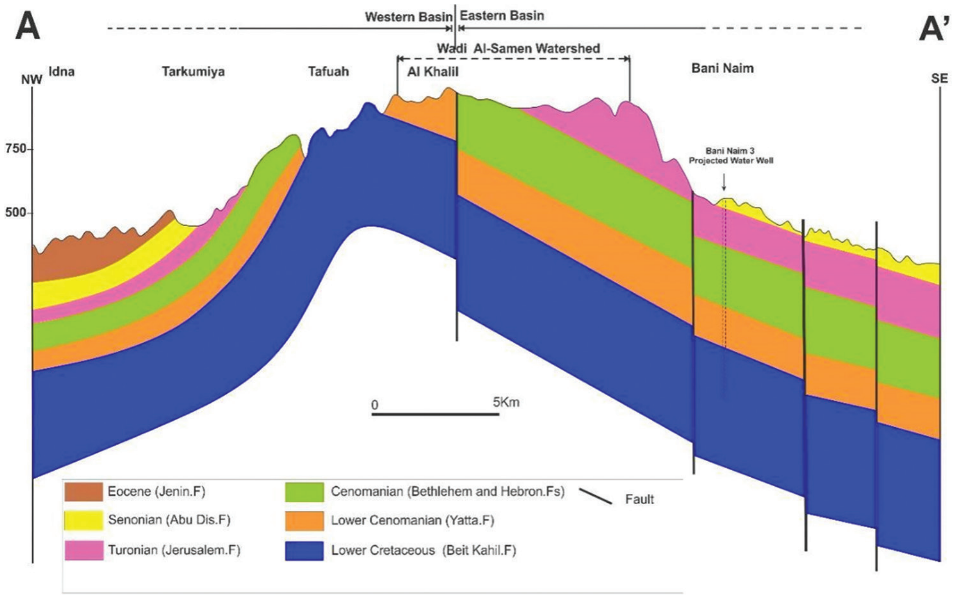

Figure 2. Geology of study area

Note: A, A' : Cross section from A(NW) to A'(SE). Abbreviations: F: Formation; NW: North West; SE: South East.

A total of 20 groundwater samples were gathered from 20 different locations. Each sample was collected in separate polypropylene bottles (Sigma, Germany) that had been pre-conditioned and acid-washed. These samples were then filtered and treated with concentrated nitric acid (Sigma, Germany) to lower the pH below 2.0, preventing precipitation and minimizing adsorption onto the walls of the container.

Before filling, each bottle was thoroughly washed three to five times with groundwater from the sampling site to ensure integrity. An atomic absorption spectrophotometer (PerkinElemer, USA) was used to measure the concentrations of heavy metals in the acidified filtrates.

2.3. HPI measurement

The HPI is a quantitative tool used to assess the combined impact of individual heavy metals on the overall quality of drinking water.[38] Ranging from 0 to 1, the HPI rating presents the relative significance of each quality parameter, and its deviation from the recommended standard (Si).[39-41]

The HPI was calculated following these steps: first, the weight of each parameter (Wi) was calculated; then the quality rating (Qi) for each heavy metal was determined; finally, the sub-indices were summed to obtain the overall index.

The Wi of each parameter (i) was determined using Equation I.

$$Wi = K/Si \tag{I}$$

Where Wi denotes the unit weight, Si is the recommended standard for the i-th parameter, and K is the proportionality constant.

The Qi for each metal was calculated using Equation II.

$$Qi = 100\ Vi/Si \tag{II}$$

Where Qi represents the sub-index for the i-th parameter, Vi is the measured value of the i-th parameter (in µg/L), and Si is the standard or permissible limit for the i-th parameter.

The HPI value, which indicates the overall quality of the drinking water in relation to heavy metals, was calculated using Equation III and Equation IV.

$$HPI = \frac{\sum_{i=1}^{n} Wi,Qi}{\sum_{i=1}^{n} Wi} \tag{III}$$

$$Qi = \sum i \frac{Mi(-)Ii}{Si - Ii} \times 100 \tag{IV}$$

Where Qi and Wi represent the sub-index and unit weight of the i-th parameter, respectively; n denotes the number of parameters considered; Mi, Ii, and Si correspond to the monitored values, the ideal value, and the standard values of the i-th parameter, respectively; − denotes the numerical difference between values, without considering the algebraic sign.

The metal quality index (MQI) serves as an early warning threshold, where a value below one is the threshold of warning. MQI was calculated using Equation V.

$$MQI = \sum_{i=1}^{n} \frac{Mi}{Si} \tag{V}$$

Where n denotes the number of parameters considered; Mi and Si correspond to the monitored values, the standard values of the i-th parameter, respectively.

The HPI categorizes water quality into three levels: low (HPI <100), threshold risk (HPI = 100), and high (HPI >100). When HPI exceeds 100, the water is deemed unsuitable for drinking. The HPI values for the dry and wet seasons are presented in Tables 1 and 2. [42-44]

In addition, the heavy metal evaluation index (HEI) was used to assess the quality of the water, specifically targeting heavy metal contamination.[31] The HEI was determined using Equation VI.

$$HEI = \sum_{i=1}^{n} \frac{Hc}{Hmac} \tag{VI}$$

Table 1. Water quality scale based on the heavy metal pollution index (HPI)[42]

HPI (%)	Water quality
0 – 24	Excellent
25 – 49	Good
50 – 74	Poor
75 – 100	Very poor
>100	Unfit for drinking

Table 2. Water quality classification using metal index (MI)[43,44]

MI	Characteristic	Class
<0.3	Very pure	I
0.3 – 1.0	Pure	II
1.0 – 2.0	Slightly affected	III
2.0 – 4.0	Moderately affected	IV
4.0 – 6.0	Strongly affected	V
>6.0	Seriously affected	VI

Where Hc and Hmac represent the monitored values and the maximum allowable concentration for the i-th parameter, respectively.

The HEI was classified into three categories: Low (HEI <10), medium (HEI = 10 – 20), and high (HEI >20). Higher HPI values correlate with increased health risks. The critical HPI threshold is typically set at 100, as shown in Table 1.[40,42]

2.4. Metal index (MI)

The MI offers a single value that encapsulates the contamination levels of the study area. An MI value exceeding one indicates a threshold warning, suggesting significant water quality degradation due to heavy metal concentrations exceeding the Maximum Allowable Concentration (MAC).[45]

The MI was calculated using Equation VII, as described by Tamasi and Cini.[46]

$$MI = \sum_{i=1}^{n} \frac{ci}{(MAC)i} \qquad \text{(VII)}$$

Where MI is the MI, Ci refers to the concentration of each element in the solution, MACi is the maximum permissible concentration for each element, and the subscript i denotes the i-th sample.

The classification of water quality based on the MI is presented in Table 2.[43,44]

3. Results and discussion

3.1. HPI

The mean concentrations of 16 heavy metals were examined for both the dry and wet seasons, showing notable variations in metal concentrations across the different sampling locations. The concentrations of molybdenum (Mo), iron, cobalt, cadmium, chromium, boron, aluminum (Al), arsenic, manganese, nickel, copper, and lead were observed to be within the maximum allowable limits set by the WHO drinking water standards (2011). Based on their concentration levels and relative abundance, the metals were ranked in the following order: Se >Ba >Li >Zn >Cu.

The HPI was calculated using the mean concentrations of the 16 heavy metals. The overall HPI for Wadi Al-Samen was 17.2 during the dry season, significantly below the critical threshold of 100, indicating that the area is not severely polluted by heavy metals.

The highest HPI values were recorded at Al-Fawwar1 (89.73), Al-Hejreh (69.55), and Al-Fawwar2 (42.39) during the dry season, and at Al-Alaqa Al-Foqa (62.60), Abdo (44.47), and Khursa (41.53) during the wet season (Figure 3). These elevated values are likely attributed to domestic sewage discharge and the interaction between rock and water.

The lowest HPI values during the dry season were recorded in Karaza (3.40), Rihia (3.76), Al-Alaqa Al-Foqa (4.05), Omran1, Omran2, Omran3 (4.3), Ein-Qashqalah (4.39), Abdo (4.43), and Bi'r al-Wad (5.12). During the wet season, low HPI values were observed at Samu'a (3.03), Rihia (3.31), Omran1 (3.83), Ein-Qashqalah (3.84), Omran2 (3.90), Al-Fawwar1 (4.05), and Omran3 (4.08) (Figure 3). These lower HPI values suggest the diluting effect of rainwater seepage and percolation.

3.2. MI value

The MI for Wadi Al-Samen was found to be 2.3 in the dry season and 2.2 in the wet season. According to the classification by Lyulko *et al.* (2001)[43] and Caerio *et al*. (2005),[44] these values indicate moderate contamination by heavy metals. The findings align with the classification scale presented in Table 2,[43,44] confirming that water in Wadi Al-Samen is moderately impacted by heavy metal pollution in both seasons.

3.3. Groundwater contamination based on different groups of heavy metals

3.3.1. Toxic elements (lead and arsenic)

Lead is a highly toxic heavy metal naturally occurring in the Earth's crust and distributed across various environmental compartments. Due to its persistence and strong adsorption to soil particles, lead contamination remains a significant concern.[47] Human activities can contribute to elevated lead levels in natural water bodies.[48,49] The WHO[50] has set the permissible limit for lead in drinking water at 0.01 mg/L. Consumption of groundwater contaminated with lead can elevate blood lead levels in humans.[49]

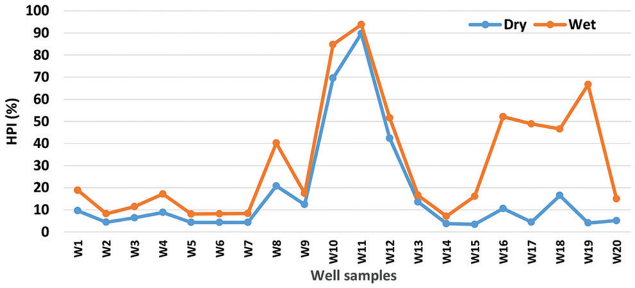

Figure 3. Seasonal variations in heavy metal pollution index (HPI). Data are presented as actual values of 20 samples.

The maximum lead concentration recorded in Wadi Al-Samen during the dry season was 0.003 mg/L, with an average of 0.00025 mg/L. In the wet season, lead concentrations ranged from 0 to 0.001 mg/L, with an average of 0.0001 mg/L. None of the 20 analyzed samples exceeded the WHO limit.

Arsenic contamination in groundwater is also a global concern, as it affects millions of people worldwide.[3,51,52] In the study area, arsenic compounds are commonly utilized in the leather tanning process, which can contribute to arsenic contamination. Prolonged exposure to arsenic in drinking water can cause severe health problems, such as cancer, skin lesions, cardiovascular diseases, and diabetes.[52] Inorganic arsenic compounds – known for their high toxicity—pose a greater risk than organic arsenic compounds typically found in seafood.[53]

The WHO (2011)[50] permissible arsenic concentration in drinking water is 0.01 mg/L. In Wadi Al-Samen, the maximum arsenic concentration during the dry season was 0.009 mg/L, with an average of 0.0009 mg/L. During the wet season, arsenic concentration ranged from 0 to 0.008 mg/L, with an average of 0.00075 mg/L. Out of twenty analyzed samples, no arsenic concentration levels higher than the allowable limit were recorded.

3.3.2. Alkaline Earth metal (barium)

Barium (Ba) contamination in surface and groundwater is primarily caused by leaching and erosion from sedimentary rocks. In addition, human activities, such as the excessive use of agricultural fertilizers contribute to elevated barium levels.

The WHO (2011)[50] permissible limit for barium in drinking water is 0.7 mg/L. In Wadi Al-Samen, the maximum barium concentration observed during the dry season was 150.7 mg/L, with an average of 21.80 mg/L. During the wet season, barium concentrations ranged from 0.014 to 148.79 mg/L, with an average of 21.32 mg/L.

Out of 20 analyzed samples, four exceeded the permissible barium limit in both seasons, (Figure 4). The elevated barium levels in these samples are primarily attributed to human activities, particularly the intensive use of agricultural fertilizers, as these samples were collected from agricultural areas.

3.3.3. Alkali metal (lithium)

Lithium (Li) is an alkali metal that occurs naturally in minerals, groundwater, and surface water as a monovalent cation.[54] It enters groundwater primarily through water-mineral interactions.[54] Lithium is widely used in energy storage (Li-ion rechargeable batteries account for approximately 70% of global lithium consumption), ceramics, glass, and lubricating grease.[55] Lithium is also used pharmaceutically to treat bipolar disorder, and studies have linked its occurrence in drinking water to human health outcomes.[54] At low levels, lithium may provide behavioral benefits and function as a nutritionally essential trace element.[56] Studies have indicated that the human and environmental toxicity of lithium is low.[57-60] Lithium exposure has also been associated with lower rates of mental health disorders.[56] However, some studies suggest possible adverse effects, such as associations with autism and thyroid hormone disruption.[61]

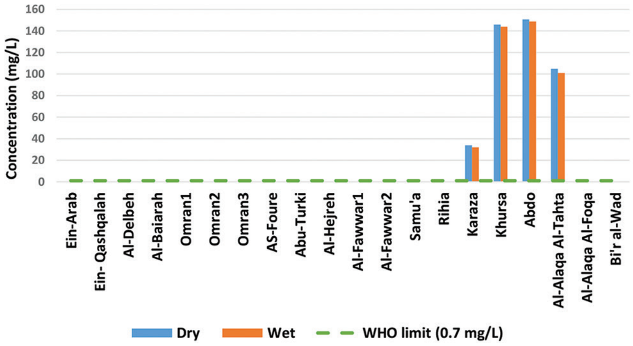

Figure 4. Barium concentrations in samples from two sampling rounds. Data are presented as actual values.

The allowable level of lithium (Li) in drinking water is 0.70 mg/L, based on the WHO (2011) standard.[50] In Wadi Al-Samen, the maximum recorded lithium concentration during the dry season was 13.55 mg/L with an average of 1.79 mg/L. In the wet season, lithium concentration ranged from 0 to 12.99 mg/L, with an average of 1.68 mg/L.

In a study by Al-Zaarir,[36] lithium concentrations in samples from Al-Alaqa Al-Foqa and Al-Alaqa Al-Tahta exceeded permissible limits during both seasons. The study also indicated that other samples, including those from Abdo, Khursa, and Karaza, surpassed the recommended lithium concentration limits, suggesting a potential long-term risk of increasing lithium contamination. Out of 20 analyzed samples, four exceeded permissible limits in both seasons (Figure 5). The elevated lithium levels in these groundwater samples are likely linked to human activities, including waste burning, accumulation of used car parts, and improper disposal of batteries. Notably, 0.2% of collected samples exceeded the maximum permissible lithium concentration in both the dry and wet seasons, suggesting a persistent low-level contamination risk.

3.3.4. Transition metals (nickel, cobalt, manganese, and molybdenum)

Nickel, cobalt, and manganese concentrations in the study area were all within the allowable limits established by the WHO[60]: 0.07 mg/L for nickel, 0.005 mg/L for cobalt, and 0.4 mg/L for manganese.

The maximum recorded cobalt concentration in Wadi Al-Samen during the dry season was 0.002 mg/L, with an average of 0.00035 mg/L. In the wet season, cobalt concentrations ranged from zero to 0.002 mg/L, with an average of 0.003 mg/L.

The maximum manganese concentration observed in the dry season was 0.053 mg/L, with an average of 0.00415 mg/L. During the wet season, manganese concentrations ranged from zero to 0.052 mg/L, with an average of 0.0039 mg/L. None of the 20 samples analyzed exceeded the permissible limits for nickel, cobalt, or manganese.

Molybdenum (Mo) typically occurs at low concentrations in groundwater, but elevated levels can be indicative of anthropogenic contamination.[62] The WHO[50] permissible level of molybdenum is 0.07 mg/L. In Wadi Al-Samen, the maximum recorded molybdenum concentration during the dry season was 0.003 mg/L, with an average of 0.0008 mg/L. During the wet season, molybdenum concentrations ranged from zero to 0.002 mg/L, with an average of 0.0006 mg/L.

3.3.5. Metallic elements (copper, cadmium, zinc, iron, and chromium)

Zinc is an essential trace element found in many foods and drinking water, typically in the form of salt or organic complexes. A zinc deficiency can lead to health issues, such as dwarfism, dermatitis, and loss of taste. However, the presence of lead, mercury, and cadmium in groundwater can pose significant health risks to humans and the environment. High chromium concentrations in groundwater are associated with health issues, such as nasal septum ulceration and dermatitis.[63,64]

Copper is an ancient metal valued for its antibacterial properties and is essential for hemoglobin production.[65] It can enter water sources through mining, the use of copper utensils, plumbing, and various industrial activities. Although beneficial in trace amounts, excessive levels of copper can be toxic. Copper from food differs chemically from the form found in water. Prolonged storage of water in copper containers can increase its concentration and pose potential health risks.[66] High copper exposure may lead to gastrointestinal issues, liver toxicity, neurological problems, Wlison's disease, Alzheimer's disease, childhood liver cirrhosis, and mental illnesses.[67-71]

The WHO (2011)[50] sets the permissible level of copper in drinking water at 2 mg/L. During the dry season in Wadi Al-Samen, the concentration of copper ranged from 0 to 7.88 mg/L, with a mean value of 0.40 mg/L. In the wet season, the concentration of copper ranged from 0 to 7.62 mg/L, with an average of 0.38 mg/L. Out of 20 samples analyzed, one exceeded the permissible limit in both seasons (Figure 6). High copper concentrations in the Karaza well are likely due to plumbing corrosion, mining, and other human activities. Copper concentrations tend to decrease in winter, possibly due to increased water flow diluting its levels. Factors influencing copper corrosion include moderate alkalinity (pH: 7.9 – 8.2), water retention time in copper pipes, and temperature.[65]

Zinc is widely used in corrosion-resistant alloys, brass, galvanized steel, iron products, rubber production, and as a white pigment in zinc oxide.[72] Excessive zinc in the environment can be harmful, potentially affecting aquatic ecosystems.[73] Drinking water with zinc levels

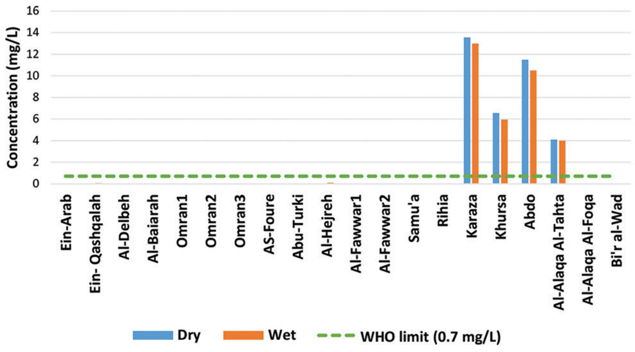

Figure 5. Lithium concentrations in samples from two sampling rounds. Data are presented as actual values of 20 samples.

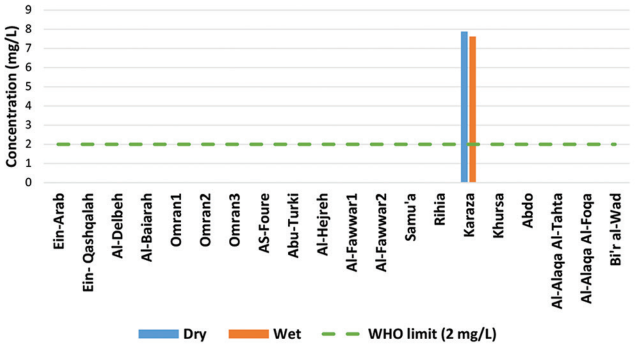

Figure 6. Copper concentrations in samples from two sampling rounds. Data are presented as actual values.

above 3 mg/L may have an undesirable astringent taste, opalescent appearance, and form a greasy film when boiled.[73] High zinc intake can cause fever, nausea, vomiting, stomach cramps, and diarrhea, along with gastric erosion and gastrointestinal disorders.[72]

A study by Al-Zaarir[36] indicated that copper, barium, or zinc levels did not exceed the permissible limits for groundwater samples. The permissible level of zinc is 3 mg/L, as established by the WHO.[50] The concentrations of zinc in the dry season ranged from zero to 7.42 mg/L, with an average of 1.04 mg/L. Out of 20 analyzed samples, 3 samples exceeded the permissible limits in both seasons (Figure 7). Elevated zinc levels in Karaza, Abdo, and Al-Alaqa Al-Tahta wells are likely due to the burning of wires and cables to retrieve copper. This highlights the need for proper waste management to protect human health and the environment.

Cadmium was not detected in significant concentrations in either season. The WHO[50] permissible level for cadmium is 0.003 mg/L.

Iron was detected in 0.1% of the groundwater sample. The WHO[50] permissible level of iron in drinking water is 2 mg/L. In Wadi Al-Samen, the maximum recorded iron concentration during the dry season was 0.143 mg/L, with an average of 0.0167 mg/L.

No samples exceeded the permissible limit for chromium concentrations. The maximum chromium concentration in the dry season was 0.001 mg/L, with an average of 0.00005 mg/L. Chromium was not detected during the wet season in any of the study locations. The WHO[50] permissible level of chromium is 0.05 mg/L.

3.3.6. Non-metallic elements (boron, selenium, and aluminum)

The WHO[50] permissible level of boron in drinking water is 2.4 mg/L. Long-term human exposure to boron compounds can cause gastrointestinal irritation. Boron typically enters water sources through industrial and domestic effluents.

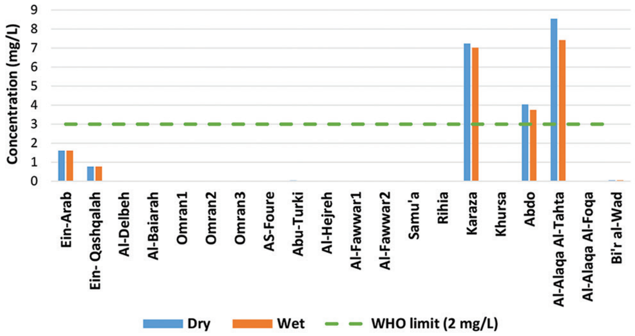

Figure 7. Zinc concentrations in samples from two sampling rounds. Data are presented as actual values.

In Wadi Al-Samen, the maximum boron (B) concentration during the dry season was 0.051 mg/L, with an average of 0.0215 mg/L. In the wet season, boron concentrations ranged from zero to 0.048 mg/L, with an average of 0.019 mg/L. No boron levels exceeded the permissible limits in either season.

Selenium (Se) is a naturally occurring element found in rocks, soil, plants, and water. Public health standards for safe selenium levels in drinking water vary widely, but the WHO[50] recommends a permissible level of 0.04 mg/L. Selenium can enter groundwater through the weathering of selenium-rich rocks and soil, often leaching into groundwater due to irrigation and rainfall.[74] While small amounts of selenium are beneficial, excessive levels can be toxic. Potential health effects associated with selenium overexposure include hair and fingernail loss, as well as numbness in the fingers and toes.[7]

In this study, selenium concentrations during the dry season ranged from 0.018 to 0.64 mg/L, with an average of 0.10 mg/L. The maximum selenium concentration in the wet season was 0.062 mg/L, with an average of 0.047 mg/L. Higher-than-permissible selenium levels were observed in 0.85% of samples in the dry season and 0.75% in the wet season.

The WHO[50] permissible level of aluminum in drinking water is 0.9 mg/L. The maximum aluminum concentration in Wadi Al-Samen during the dry season was 0.084 mg/L, with an average of 0.03 mg/L. The concentration of aluminum during the wet season ranged from 0 to 0.081 mg/L, with an average of 0.03 mg/L. None of the 20 analyzed samples exceeded the permissible limit of aluminum. Chemical processes such as carbonate/phosphate dissolution, oxidation/reduction reactions, along with agricultural practices (e.g., fertilizer application and irrigation) are likely contributors to groundwater self-pollution, as observed in Al-Zarqa Amman Basin in Jordan.[75]

Historically, these wells were considered clean; however, increasing contamination from human activities, industrial waste, sewage, and excessive groundwater pumping has degraded water quality. A study by Zaarir[36] reported no exceedance of threshold limits for copper, zinc, and barium in groundwater wells in the study area.

4. Conclusion

Wadi Al-Saman is a crucial groundwater recharge source for the Western Basin, which flows toward the

Mediterranean Sea. However, it is heavily polluted by wastewater from domestic and industrial activities in the Hebron area. This contamination is concerning, as elements such as lithium, zinc, barium, and copper originate primarily from anthropogenic sources, including industrial activities, municipal sewage, domestic wastes, and industrial discharges, all of which increase their concentrations in groundwater.

Water serves as the primary medium through which trace elements enter the environment, and the HPI effectively characterizes groundwater pollution in this region. The overall HPI for Wadi Al-Samen was found to be 17.2 in the dry season and 11.99 in the wet season, both below the critical threshold of 100. The MI was 2.3 in the dry season and 2.2 in the wet season, indicating moderate contamination. Groundwater was classified as poor in the Al-Hejreh well (W10) and very poor in the Al-Fawwar1 well (W11), rendering it unsuitable for drinking. The concentrations of barium, lithium, zinc, copper, and se exceeded permissible limits in some samples, signaling a potential threat to water resources in the Wadi Al-Samen area that necessitates immediate attention from the Palestinian local administration and the Water Authority.

This finding highlights the urgent need for wastewater treatment in major human settlements to prevent hazardous chemicals from polluting water bodies. Expanding the sampling network, increasing seasonal sampling frequency, and incorporating advanced geochemical analyses to differentiate between natural and anthropogenic contamination sources would enhance the robustness of future studies. In addition, evaluating the efficiency of existing wastewater treatment facilities and proposing targeted remediation measures would strengthen the study's practical impact on water resource management and policy development.

Our study underscores the importance of coordinated efforts by the Water Authority, Hebron Municipality, and other responsible agencies to implement biological and chemical wastewater treatment in Wadi Al-Samen. We also recommend the rapid rehabilitation and construction of a wastewater treatment plant to improve water quality in the region, safeguard public health, and protect aquatic ecosystems.

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Conflict of interest

The authors declare they have no competing interests.

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Availability of data

Data are available from the corresponding author upon reasonable request.

Further disclosure

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