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Contamination of groundwater with heavy metals under various land use regimes and health risks in Sharada Industrial Area of Kano, Nigeria

Hadiza Ado Suleiman[1], Marlia Mohd Hanafiah[1,2*], Rab Nawaz[2], Siti Norliyana Harun[2], and Ricky Anak Kemarau[3]
[1]Department of Earth Sciences and Environment, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi UKM, Selangor, Malaysia
[2]Centre for Tropical Climate Change System, Institute of Climate Change, Universiti Kebangsaan Malaysia, 43600 Bangi UKM, Selangor, Malaysia.
[3]Earth Observation Centre, Institute of Climate Change, Universiti Kebangsaan Malaysia, 43600 Bangi UKM, Selangor, Malaysia.
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Abstract

Groundwater, a vital source of drinking water, faces growing threats from heavy metal (HM) contamination due to human activities and natural processes. This is addressed by assessing HMs' contamination levels in groundwater in the Sharada Industrial Area, Kano, Nigeria, where 138 samples were collected near various industrial sites and analysed using atomic absorption spectroscopy (AAS) to determine the concentrations of six heavy metals: Zn, Fe, Cd, Cu, As, and Cr. However, the health risk assessments were conducted for both ingestion and dermal exposure routes. The result showed that Cd (0.031 mg L^{-1}), Cr (0.1544 mg L^{-1}), and As (0.1454 mg L^{-1}) levels exceeded WHO limits across multiple sites, with significant variation by season and proximity to specific industries. The dermal exposure near pharmaceutical (HQ_{dermal} = 2.1505) and plastic (HQ_{dermal} =1.0160) industries posed the highest risk, with Fe (1.9475 mg L^{-1}) and Cd (0.3830 mg L^{-1}) contributing to the abundance of HMs in such locations. Conversely, sites near textile industries posed a minimal risk. This study offers valuable insights into the complex relationships between industrial activities, environmental quality, and human health, thereby enabling policymakers to make informed decisions about the most effective strategies for reducing health risks and promoting sustainable development in these regions.

Keywords: Groundwater contamination; Heavy metals assessment; Health risks assessment; Land use patterns; Hazard quotient

Introduction

Globally, groundwater is the most common source of drinking water, particularly in developing nations where surface water is often unreliable due to factors such as seasonal fluctuations, contamination, or insufficient infrastructure (UNESCO, 2022). The safety and dependability of groundwater are being increasingly compromised by contamination from both natural and human resources, particularly in urban and industrial areas. Heavy metals are especially hazardous due to their ability to persist, bioaccumulate, and bio-magnify, posing serious health risks to humans and the environment even at relatively low concentrations (Tchounwou *et al*., 2012; Jaishankar *et al*., 2014). The planetary boundaries framework, which aims to establish a safe operating space for humanity, highlights freshwater use and novel entities like synthetic chemicals and heavy metals as critical environmental thresholds. Alarmingly, both these boundaries are nearing or have surpassed their tipping points, posing significant risks to the stability of the global environment and human health (Rockström *et al*., 2009; Persson *et al*., 2022; Kemarau *et al*., 2025;). Since the industrial revolution, the world's freshwater resources, particularly clean groundwater, have drastically decreased due to human activities like urbanization and industrial growth. This transformation has resulted in increased pollutant discharge, including heavy metals, into freshwater systems, severely impacting groundwater quality and threatening the world's primary drinking water source (Kemarau *et al*., 2024; Harun *et al*., 2025).

In Nigeria's rapidly industrializing cities, like Kano, poor environmental regulation and ineffective industrial waste management have heightened the risk of groundwater contamination. This study is crucial as it examines the levels, distribution, and seasonal fluctuations of six key

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heavy metals (Zn, Fe, Cd, Cu, As, and Cr) in Kano's Sharada industrial area's groundwater, a vital resource supporting agriculture, ecosystems, biodiversity, and human needs (Sophocleous, 2002). The worldwide decline in groundwater levels has led to substantial losses in aquifer storage, affecting many of the world's largest aquifers. This depletion has triggered significant environmental and agricultural consequences, including reduced spring flows, diminished groundwater supply to wetlands, and increased land subsidence, ultimately threatening crop production sustainability and exacerbating marine intrusion (Mace, 2022). Human activities exacerbate the issue by releasing

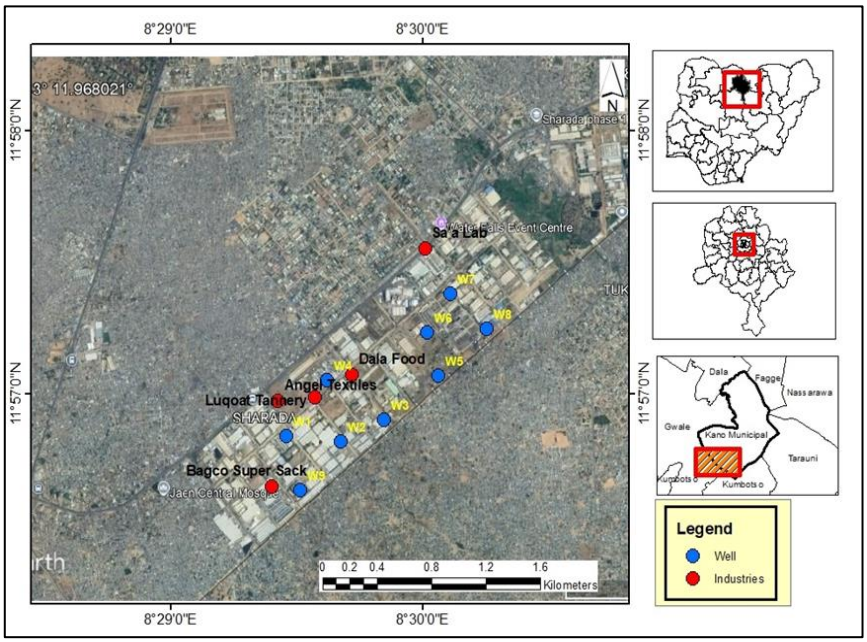


Figure 1: Map showing location of the study area and sampling point within the study area of Kano Metropolis. Source: Modified from: Google Earth, 2024; and Field Work, 2024

Table 1: Description of the groundwater samples and their respective locations

Land use type	Samples label		
	Latitude | longitude		
Plastic Industry	PS A (11.9442 | 8.4905)	PS B (11.9434 | 8.4899)	PS C (11.9449 | 8.4907)
Food Industry	FD A (11.9512 | 8.4956)	FD B (11.9510 | 8.4957	FD C (11.9492 | 8.4967)
Pharmaceutical Industry	PM A (11.9337 | 8.4908)	PM B (11.9488 | 8.4978)	PM C (11.9519 | 8.4995)
Tannery Industry	TN A (11.9498 | 8.4920)	TN B (11.9495 | 8.4922)	TN C (11.9489 | 8.4917)
Textile Industry	TX A (11.9463 | 8.4881)	TX B (11.9466 | 8.4884)	TX C (11.9443 | 8.4895)



Figure 2: A sequence of laboratory equipment used in groundwater sampling, preparation, and analysis: (a) sieve mesh, (b) weighing balance, (c) oven, (d) muffle furnace, (e) grinder, (f) incubator shaker, (g) pH analysis setup, (h) Atomic Absorption Spectrophotometer (AAS)

wastewater containing high levels of dissolved chemicals, which can contaminate groundwater and pose significant public health risks (Adeyemi and Ojekunle, 2021). Groundwater polluted with heavy metals (HMs) poses a major risk to human health because of the world's high-intensity of land use (Khurshid *et al*., 2025; Liu *et al*., 2021). These metals can significantly disrupt ecosystems, reduce agricultural productivity, and, most importantly, pose chronic health risks to human populations (Laidlaw *et al*., 2017; Geier *et al*., 2018; Hanafiah *et al*., 2019; Hu *et al*., 2020; Mendes *et al*., 2023; Wyszkowska *et al*., 2024; Good *et al*., 2024).

The use of groundwater for drinking purposes makes arsenic contamination a significant health risk, potentially leading to skin lesions, diabetes, gastrointestinal disorders, and increased incidence of cancers affecting organs like the bladder, kidneys, liver, and lungs (Monteiro De Oliveira *et al*., 2021). Arsenic poisoning can elevate cancer risk by interfering with DNA repair processes through binding to DNA-related proteins. Additionally, arsenic-contaminated drinking water can have multiple negative impacts on metabolism, potentially leading to a range of health problems (Fu and Xi, 2020). The risk of heavy metal contamination in groundwater is influenced by different land use patterns. Yet, the connection between land cover extent and groundwater pollution levels is intricate and can vary greatly depending on land type and other variables. To better understand this relationship, mathematical models have been applied to correlate land use with groundwater pollutant concentrations within a specific area, typically a 500 m radius (Bawa and Dwivedi, 2019). These studies often only show a positive or negative connection between one or two types of land usage. The relationship between the levels of groundwater pollutants and their proximity to various land uses and industries, however, still lacks a quantitative explanation (Wu and Sun, 2016). To inform effective groundwater conservation strategies, research is needed to assess the impact of different land uses, including various industries, on shallow groundwater quality, with a specific focus on heavy metal pollution.

The current study aims to evaluate the level of contamination of groundwater with HMs in Nigeria's Sharada Industrial Area, which is situated in the Kano metropolis, while investigating how it relates to the various land use types. Groundwater from various locations near six distinct industries-plastic, food, textile, pharmaceutical, and tannery-was collected during the dry (Jan-March) and wet (July-Sept) seasons. In addition, the study analyses the impact of land use patterns on shallow groundwater heavy metal fluctuations, providing insights into preserving groundwater resources and mitigating health hazards. The findings can inform sustainable water management, land use planning, and environmental sustainability, on ultimately protecting public health and promoting sustainable development in communities reliant on groundwater.

Methodology

Study area

The study was conducted in the Sharada Industrial Area of Kano city, situated between latitudes 10º and 12ºN of the equator and longitudes 8º and 9ºE of the Greenwich Meridian, as shown in Figure 1. This industrial hub is part of Kano Metropolis, covering over 600 km² and encompassing Kano Municipal and Kumbotso Local Government areas. Sharada Industrial Area is known for housing various industries, including tanneries, textiles, and manufacturing facilities, making it a significant economic zone in Kano State, Nigeria (Suleiman and Hanafiah, 2023). The area experiences a tropical dry and wet climate, with two distinct seasons (May through September is a wet season, while the other months are dry) influenced by the intertropical discontinuity

Groundwater sampling

A field survey was carried out to determine the land use pattern and to identify various industries within the research area. Groundwater samples were gathered from multiple sites from various industries that were labelled as A, B, and C. The samples were labelled PS (A, B, and C), which stands for the groundwater samples that were gathered from the three different sites near the plastics industry.

Table 1 provides an overview of the sample labels, coordinates, and industry types associated with the sampling locations. Groundwater samples were collected from shallow dug wells and boreholes near industrial sites. A total of 15 groundwater sampling sites were selected, and samples were collected over three months in 2021, covering both the wet season (July–September) and the dry season (January–March). In total, 138 water samples were obtained, consisting of 2 seasons × 23 sites × replicates (N = 3). Sampling locations were chosen within 500 meters of industrial areas, based on previous research suggesting that leaching of heavy metals typically does not extend beyond this distance in the direction of groundwater flow (Christensen *et al*., 1994). The equipment used for sampling, preparation, and analysis is shown in Figure 2.

Quality control and quality assurance

To ensure sample integrity, all equipment, sampling tools, and containers were rigorously cleaned. The process involved washing with hot water and deionised water, followed by a rinse with laboratory detergent and a 10% nitric acid solution. Glassware and containers were then dried, wrapped in aluminum foil, and stored to prevent contamination. Groundwater samples were collected using plastic containers attached to long coir ropes and transferred to labelled and sterilized 1.5 L containers. After collection, samples were transported to the laboratory in a cooler box maintained at a temperature below 5 °C. Upon arrival, they were stored in a refrigerator at a temperature below 4 °C until further analysis. This meticulous handling process aimed to minimize contamination and preserve sample quality.

Groundwater samples preparation

Ten mL of the groundwater sample and 20 mL of regia; 3:1 (v/v) concentrated hydrochloric and nitric acid mixture were combined in a 100 mL beaker and strongly stirred with a glass rod (Christensen *et al*., 1994). After that, the beaker was put on a hotplate, covered with a watch glass, and left to heat for half an hour with the addition of distilled water, and the solution was concentrated to 20 mL. Following the removal of the beaker from the hotplate and cooling, it was transported to a 100 mL volumetric flask and filtered using Whatman filter paper number 1. To ensure complete mixing, distilled water was added to make up for the mark. Finally, the samples were transferred to glass vials, labelled, and analysed using AAS.

Analysis of heavy metals in groundwater

HMs such as Cd, Ni, and Cu concentrations in the wastewater before and after the treatment were determined using atomic absorption spectroscopy (AAS) analysis. Standard operating parameters were set at wavelengths of 279.4, 232.0, and 324.7 nm for Cd, Ni, and Cu, respectively, with a fixed slit width of 0.7 for each HM (Wu and Sun, 2016).

Statistical analysis of data

The descriptive statistical characteristics, including mean, median, standard deviation, and range, were calculated for the concentration of HMs in groundwater samples taken from boreholes and wells dug near various industries using Microsoft Excel (version 2021). The null hypothesis that there is no significant variation in the content of certain HMs across industrial sites and seasons was tested using the Mann-Whitney U test. The normalcy assumption was verified using the Shapiro-Wilk test. The tests were conducted using α=0.05 and a 95% confidence interval. For each HM, an ANOVA was conducted to shed light on the differences seen across various land uses throughout the dry and wet seasons. The mean and standard deviation were then contrasted with the acceptable thresholds specified by the Federal Ministry of Environment of Nigeria or the World Health Organisation.

Data visualization

The data was visualised using box plots in Microsoft Excel (version 2021) to show the distribution of different heavy metals (HMs) throughout groundwater samples from various locations close to the various industries. The concentration of HMs for various industries at various times of the year was also shown using box plots.

Health risks assessment

The population may be exposed to a range of health issues as a result of consuming HMs-contaminated groundwater because of the higher overall content of HMs present in the water. The risks of heavy metal contamination of groundwater to human health were assessed following four stages: hazard identification, exposure assessment, dosage response assessment, and risk characterization (Liu *et al*., 2021). Oral and dermatological intakes are the two exposure routes that are accessible (Wu and Sun, 2016).

Oral exposure

The primary route to HMs' exposure is through mouth, which increases the risk of health problems for children who perform hand-to-mouth activities (Mielke and Reagan, 1998). It is essential to assess oral exposure to human health to protect children from the potential of HMs poisoning. The following formula (Eq. 1) was used to determine the risks associated with the oral route for adults.

$$\text{Oral intake} = \frac{\text{C} \times \text{WI} \times \text{DY} \times \text{EF}}{\text{BW} \times \text{AT}} \quad (1)$$

Where C stands for the concentration of HM ($mg\ L^{-1}$), WI for the rate of contaminated water ingestion (1.5 L/day), DY for exposure duration (365 days/year), EF for exposure frequency (30 years), BW = 60 for the average body weight, and AT = average toxic effect of the pollutants (10,950 days).

Dermal exposure

The health risk assessment of exposure to HMs through the route was carried out using the following formulae (Eq. 2-5).

Table 2: Mean ± standard deviation of the HMs concentration in groundwater at different industries in different seasons

Plastic		Food		Textile		Pharmacy		Tannery	
Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Mean ± SD		Mean ± SD		Mean ± SD		Mean ± SD		Mean ± SD	
Zn concentration									
0.3963± 0.39	0.1981± 0.63	0.2092± 0.15	0.3917± 0.72	0.1271± 0.11	0.0344± 0.07	0.9144± 0.71	0.2081± 0.35	0.0370± 0.02	0.4758± 1.34
Fe concentration									
6.3674± 4.68	0.5541± 0.52	4.1364± 3.24	5.7428± 6.29	0.2592± 0.53	0.5222± 0.39	20.2393± 13.49	14.9519± 22.21	0.2181± 0.28	2.4496± 1.77
Cd concentration									
0.1481± 0.22	0.0000± 0.00	0.0140± 0.03	0.0017± 0.00	0.1167± 0.31	0.0000± 0.00	0.0489± 0.13	0.0011± 0.00	0.0000± 0.00	0.0000± 0.00
Cu concentration									
0.1215± 0.08	0.0433± 0.02	0.1052± 0.17	0.1056± 0.10	0.0713± 0.04	0.0774± 0.10	0.1315± 0.12	0.0626± 0.027	0.0285± 0.02	0.0615± 0.02
As concentration									
0.6711± 0.29	1.3911± 2.39	1.1616± 0.42	0.9189± 1.66	0.2904± 0.23	0.1811± 0.65	0.5315± 0.32	0.1800± 0.46	0.5156± 0.54	0.0104± 0.04
Cr concentration									
0.1193± 0.18	1.5744± 4.69	0.0572± 0.03	0.0267± 0.02	0.0792± 0.10	0.9263± 4.00	0.4656± 0.19	1.8293± 9.13	1.9100± 0.76	0.8531± 3.2

$$\text{Dermal intake} = \frac{\text{DA} \times \text{EV} \times \text{SA} \times \text{DY} \times \text{EF}}{\text{BW} \times \text{AT}} \quad (2)$$

$$\text{DA} = \text{K} \times \text{C} \times \text{t} \times \text{CF} \quad (3)$$

$$\text{SA} = 239 \times \text{H}^{0.416} \times \text{BW}^{0.517} \quad (4)$$

$$\text{Hazard index (HI)} = \text{HQ}_{\text{oral}} + \text{HQ}_{\text{dermal}} \quad (5)$$

Where the coefficient of skin permeability is K = 1 cm h^{-1}, the contact time for a single shower is t = 0.4 h (hour day^{-1}), the conversion factor is CF = 0.001, the skin surface area is represented by SA, the height of an individual is indicated by H = 165 cm (average for adults), the daily exposure frequency of the dermal contact event (1 day^{-1}) is indicated by EV = 1 (adult), and the exposure dosage of each event is indicated by DA (mg cm^{-2}) (Wu and Sun, 2016).

Results

Spatial variation in heavy metals concentrations

Table 2 provides a summary of the descriptive data of the HMs concentration in groundwater samples near various industries. Figure 3(a) displays the Zn distribution in groundwater close to different industries. The mean Zn concentration in groundwater from the area around the textile and pharmaceutical industries was 0.562±0.665 and 0.516±0.663 *mg* L^{-1}, respectively. As shown in Table 3, the Zn concentration in groundwater varied significantly even when the samples were taken from the same industrial area at different locations. For the dry season, the average Zn content in groundwater from the plastic industrial area at site A was 0.367±0.241 *mg* L^{-1}, while at site C, it was 0.480±0.571 *mg* L^{-1}.

Temporal or seasonal variation in HMs concentration

The seasonal variation in HMs concentration in groundwater at various industrial locations is summarised in Table 4. The variation in Zn concentration in groundwater across various sites is depicted in Figure 4. The distribution of Zn concentration in groundwater across various industrial sites during the dry and wet seasons is displayed in Figure 5(a). With a high of 1.3 *mg* $L^{-1}$and a low of 0.02 *mg* L^{-1}, the mean Zn concentration at the plastic industrial site during the drying season was 03963±0.3858 *mg* L^{-1}, whereas, during the wet season, it was 0.1981±0.6304 *mg* L^{-1}, with a maximum of 2.93 *mg* $L^{-1}$and a minimum of 0.0 *mg* L^{-1}. At different locations, no clear trends in concentration during the dry and wet seasons have been noticed.

Health risks analysis

Table 5 displays the findings of the health hazards assessment. It should be noted that non-carcinogenic health risks were evaluated for the adult population. The risk associated with dermal exposure (HQ_{dermal}) is significantly higher than that associated with ingesting (HQ_{oral}) MHs-contaminated groundwater. However, the distribution of HMs across groundwater in the vicinity of different industries at two different seasons is presented in Figure 6.

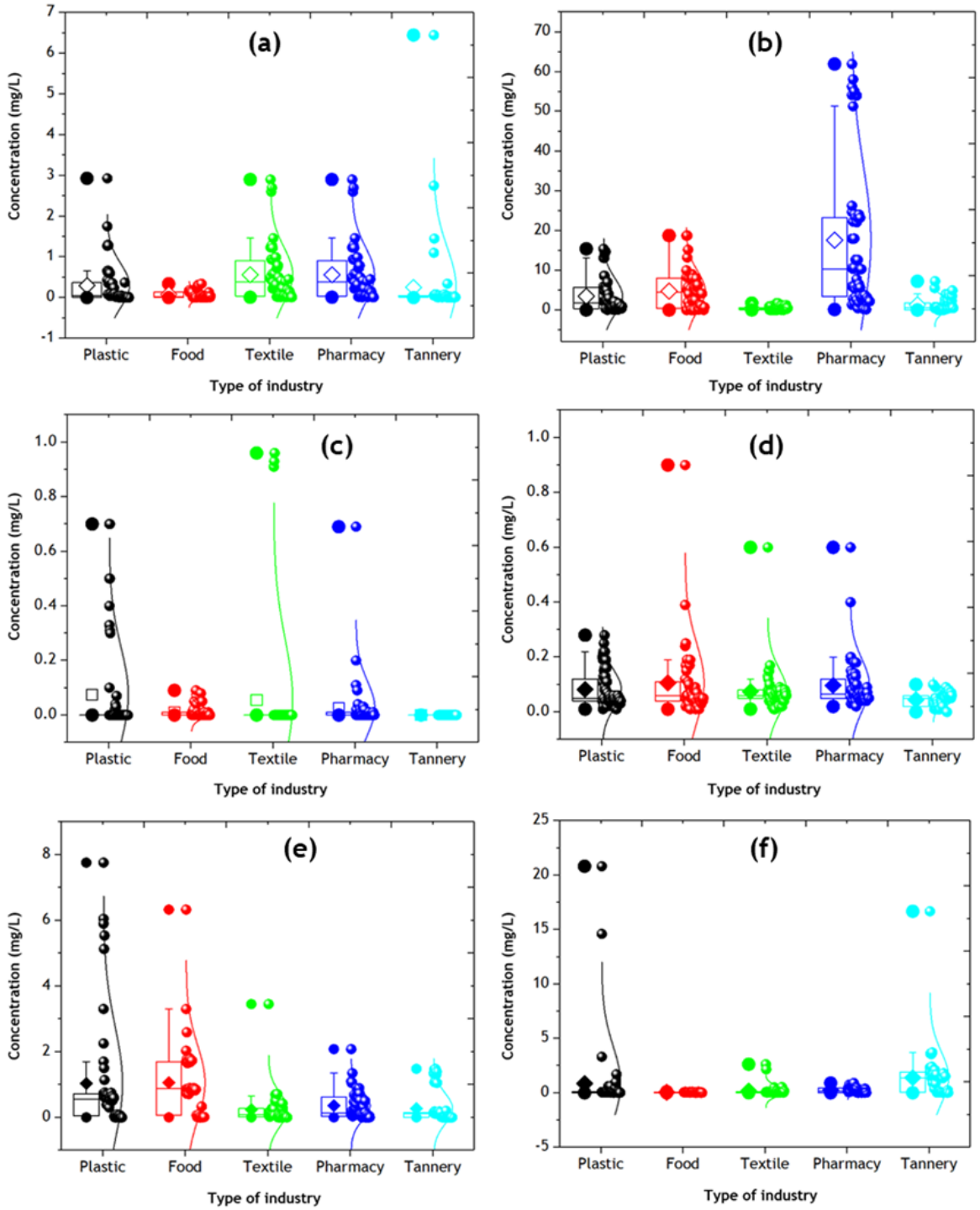


Figure 3: Distribution of HMs across groundwater in the vicinity of different industries (a) Zn, (b) Fe, (c) Cd, (d) Cu, (e) As, and (f) Cr

Table 3: Mean ± standard deviation of the HMs concentration in groundwater at different industrial sites in different seasons

HM	Site A		Site B		Site C	
	Dry	Wet	Dry	Wet	Dry	Wet
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
			Plastic			
Zn	0.367±0.240	0.336±0.910	0.342±0.225	0.208±0.545	0.480±0.571	0.051±0.113
Fe	4.544±2.777	0.386±0.182	7.274±4.618	0.689±0.741	7.283±5.644	0.588±0.442
Cd	0.416±0.206	0.000±0.000	0.011±0.031	0.000±0.000	0.018±0.023	0.000±0.000
Cu	0.112±0.068	0.043±0.012	0.139±0.057	0.038±0.016	0.113±0.099	0.049±0.023
As	0.903±0.377	1.058±2.039	0.514±0.129	1.991±2.527	0.596±0.075	1.124±2.447
Cr	0.049±0.021	2.698±6.489	0.084±0.035	0.377±0.565	0.224±0.278	1.649±4.583
			Textile			
Zn	0.146±0.022	0.050±0.103	0.010±0.017	0.013±0.009	0.275±0.030	0.040±0.035
Fe	0.311±0.440	0.483±0.494	0.000±0.000	0.491±0.300	0.570±0.806	0.592±0.349
Cd	0.311±0.440	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000
Cu	0.068±0.016	0.056±0.016	0.031±0.017	0.057±0.020	0.137±0.023	0.120±0.170
As	0.123±0.054	0.411±1.075	0.218±0.136	0.109±0.157	0.650±0.074	0.023±0.023
Cr	0.060±0.031	0.027±0.040	0.027±0.013	0.307±0.818	0.187±0.141	2.446±6.618
			Pharmacy			
Zn	1.480±0.949	0.122±0.182	0.819±0.184	0.387±0.526	0.444±0.218	0.116±0.134
Fe	29.58018.148	3.389±2.225	19.756±5.063	20.091±24.195	11.382±4.963	21.376±26.242
Cd	0.128±0.209	0.000±0.000	0.006±0.007	0.001±0.003	0.013±0.012	0.002±0.004
Cu	0.211±0.172	0.054±0.008	0.107±0.043	0.070±0.040	0.077±0.041	0.063±0.019
As	0.424±0.459	0.177±0.416	0.447±0.160	0.118±0.167	0.723±0.133	0.246±0.649
Cr	0.329±0.201	0.042±0.053	0.631±0.156	0.018±0.017	0.437±0.037	5.428±15.190
			Tannery			
Zn	0.053±0.024	0.353±0.854	0.024±0.016	0.291±0.532	0.033±0.023	0.821±2.127
Fe	0.581±0.125	2.438±1.668	0.000±0.000	2.892±1.964	0.073±0.117	1.965±1.485
Cd	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000
Cu	0.038±0.022	0.061±0.011	0.018±0.010	0.064±0.026	0.030±0.018	0.059±0.008
As	1.273±0.156	0.002±0.004	0.140±0.022	0.024±0.062	0.133±0.022	0.004±0.007
Cr	2.629±0.728	0.042±0.029	1.827±0.322	2.217±5.154	1.274±0.434	0.231±0.493

Table 4: Significance in the variation of HMs concentration across land use

Heavy Metals	Land use/industries	Season	Land use: season
Zn	0.0312 *	0.004 **	0.14401
Fe	2×10^{-16} ***	0.225	4.99×10^{-5} ***
Cd	0.0054 **	0.0001 ***	0.031 *
Cu	2.19×10^{-7} ***	0.745	0.002 **
As	1.54×10^{-5} ***	0.1454	0.0103 *
Cr	0.0011 **	0.1544	0.0027 **

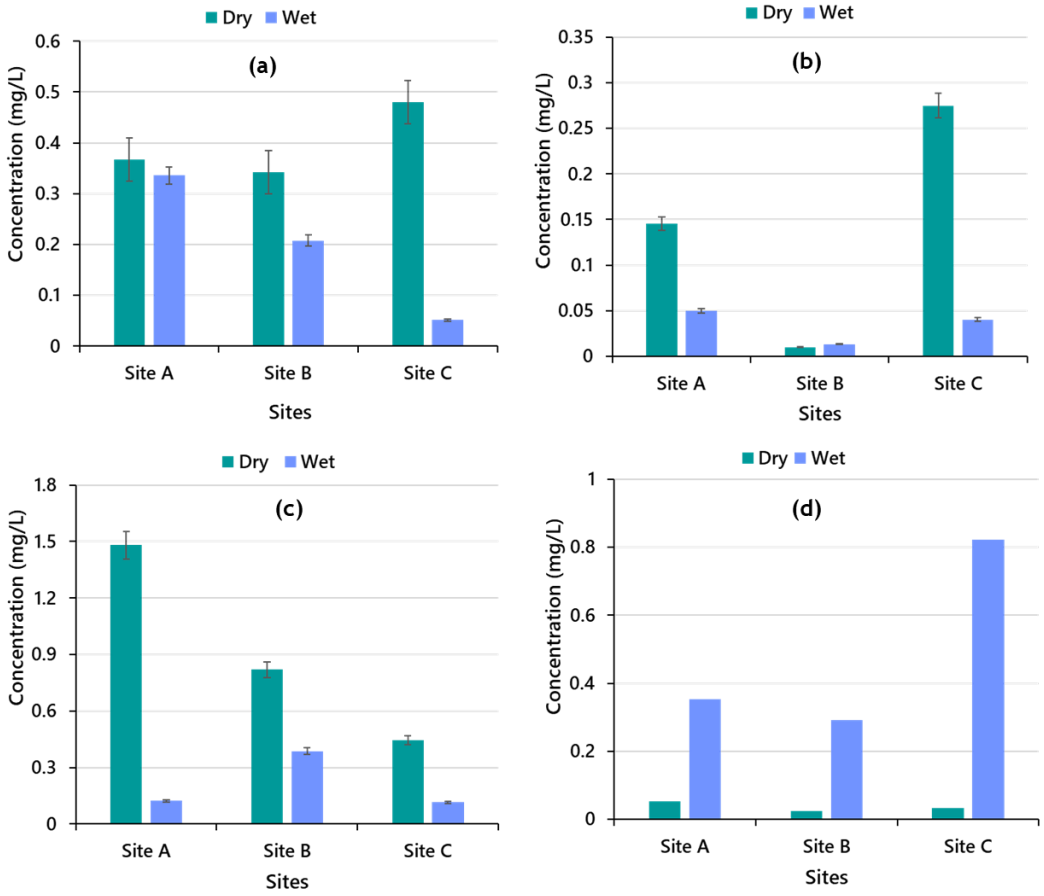


Figure 4: Variation in Zn concentration across different industrial sites (a) plastic, (b) textile, (c) pharmaceuticals, and (d) tannery

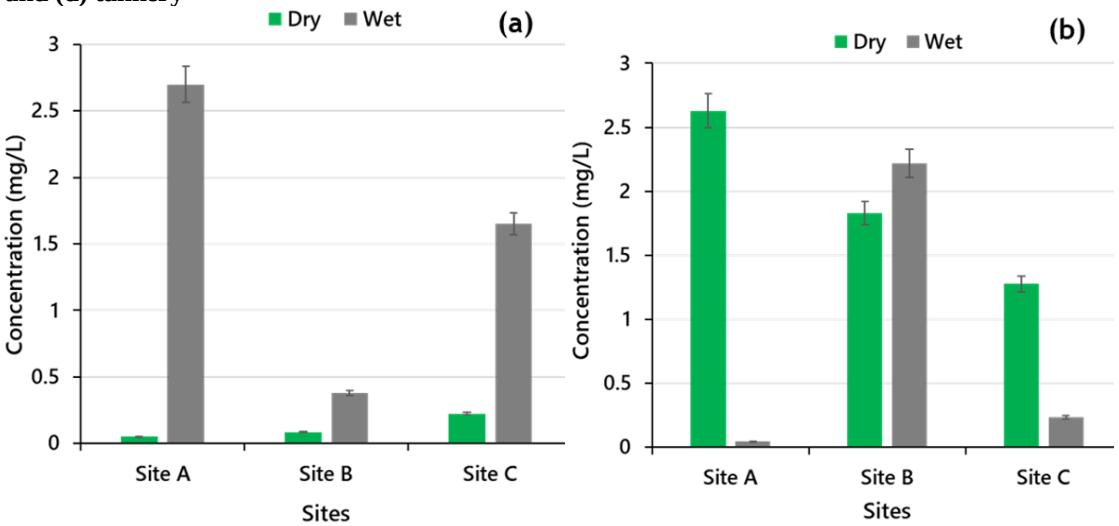


Figure 5: Variation in Cr concentration across different industrial sites (a) plastic and (b) tannery industry

Table 5: Estimated hazard quotient (HQ) for adults for different HMs in different industrial sites

Industrial sites	HQ_{oral}						
	Zn	**Fe**	**Cd**	**Cu**	**As**	**Cr**	**Total**
Plastic	0.0074	0.0865	0.0865	0.0021	0.0258	0.0212	0.2295
Food	0.0020	0.1202	0.0002	0.0026	0.0265	0.0011	0.1526
Textile	0.0140	0.0100	0.0014	0.0019	0.0058	0.0039	0.0369
Pharmaceutical	0.0140	0.4399	0.0006	0.0024	0.0089	0.0065	0.4723
Tannery	0.0062	0.0328	0.0000	0.0011	0.0067	0.0348	0.0816
Industrial sites	HQ_{dermal}						
	Zn	**Fe**	**Cd**	**Cu**	**As**	**Cr**	**Total**
Plastic	0.0329	0.3830	0.3830	0.0091	0.1141	0.0937	1.0160
Food	0.0086	0.5323	0.0086	0.0117	0.1173	0.0048	0.6833
Textile	0.0621	0.0441	0.0621	0.0082	0.0257	0.0172	0.2195
Pharmaceutical	0.0621	1.9475	0.0621	0.0107	0.0394	0.0286	2.1505
Tannery	0.0274	0.1453	0.0274	0.0049	0.0296	0.1540	0.3887

Discussion

The Zn concentration in the research area's groundwater is far below the allowable limit of 3.0 *mg* L^{-1}, even though the concentrations near the pharmaceutical and textile industries have been greater than those near other industrial sectors, including the plastic, food, and tannery industries. The higher Zn concentration in groundwater close to the pharmaceutical industry makes sense because industrial effluent from pharmaceutical industries is known to contain 0.007–2.01 *mg* L^{-1} of Zn (Rana *et al*., 2014), depending on the type of soil and other factors that may cause zinc to leach into the groundwater. The Zn concentration in groundwater close to various industries varied significantly (p=0.03122), as evidenced by the ANOVA findings displayed in Table 4. The null hypothesis revealed that there is no statistically significant difference in the Zn concentration in groundwater at various industrial sites is rejected since the Mann-Whitney test p-value is smaller than the alpha value (p=0.0537).

The type and level of exposure determine the toxicity of zinc, and long-term exposure can cause gastrointestinal irritation, renal damage, and immunosuppression (Zhang *et al*., 2012, Ahmad *et al*., 2021). Monitoring zinc intake is crucial because high levels can cause side effects like headaches, nausea, vomiting, decreased appetite, and cramping in the abdomen. Furthermore, groundwater contamination is a problem associated with water-soluble Zn. The impacts of water-soluble Zn on groundwater quality underscore the importance of proper handling and disposal practices, and careful consideration is required to avoid health problems from excessive zinc consumption (Samira *et al*., 2024).

Figure 3(b) displays the distribution of Fe in groundwater from different industrial sites. With a mean concentration of 17.59±18.56 *mg* L^{-1}, a maximum of 61.94, and a low of 0.12 *mg* L^{-1}, the Fe concentration of groundwater close to pharmaceutical industries was determined to be the greatest. It is crucial to note that the Fe concentration in groundwater from either location does not exceed the recommended threshold of 20 *mg* L^{-1}. However, compared to the textile and tannery industries, the concentration of Fe in groundwater was higher in the vicinity of the plastic, food, and pharmaceutical businesses. Fe concentrations in groundwater close to several industries were found to differ significantly ($p=2\times10^{-16}$) in Table 4. There are also notable differences in the Fe concentration across different locations in the same area. For example, site A, which is close to the textile industry, had a dry season Fe content of 0.311±0.44 *mg* L^{-1}, while sites B and C had Fe concentrations of 0.00 and 0.570±0.806 *mg* L^{-1}, respectively.

The concentration of Fe in the groundwater surrounding the pharmaceutical industry (17.59±18.56 *mg* L^{-1}) is greater than the 13 *mg* L^{-1} found in the KwaZulu-Natal area of South Africa (Demlie *et al*., 2014). Because of the anaerobic conditions, pH, and presence of pyrite and ferricrete layers, the concentration of iron in groundwater increases. According to studies, when iron-rich groundwater reaches the surface, the iron reacts with oxygen in the air to generate solid Fe-hydroxides, which gives the water a murky crimson colour and makes it unfit

for human consumption (Demlie *et al*., 2014). Research has linked exposure to Fe to Alzheimer's disease, cardiovascular illness, Huntington's disease, mitochondrial dysfunction, neurotoxicity, Parkinson's disease, and other neurological and respiratory conditions (Albretsen, 2006, Rushdi *et al*., 2023).

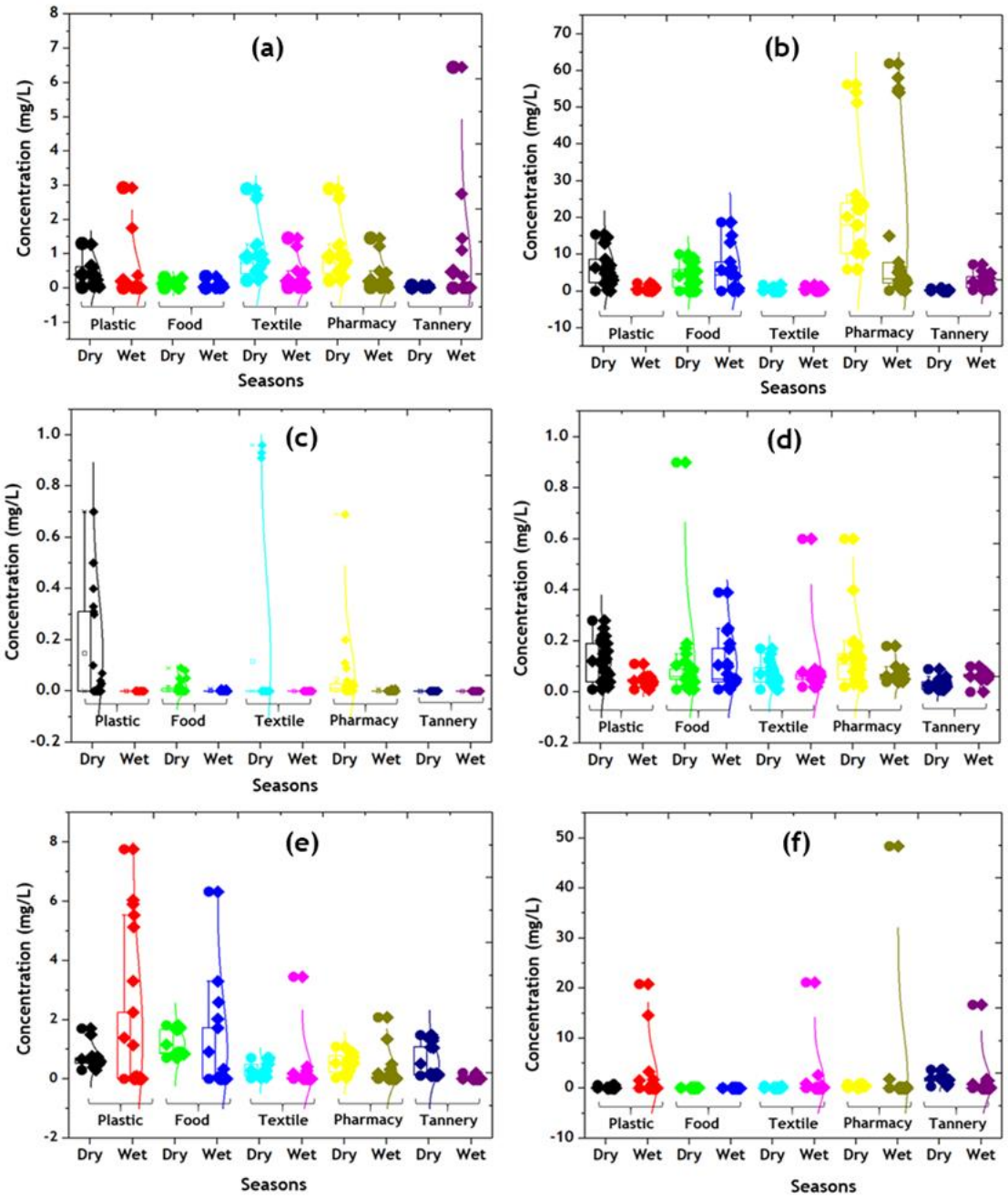


Figure 6: Distribution of HMs across Groundwater in the vicinity of different industries at two different seasons (a) Zn, (b) Fe, (c) Cd, (d) Cu, (e) As, and (f) Cr

The distribution of Cd in groundwater from several industrial sites is shown in Figure 3(c). The Cd concentration of groundwater near plastic industries was found to be the highest, with a mean concentration of 0.074±0.175 *mg* L^{-1}, a maximum of 0.7±0.7, and a minimal level of 0.00 *mg* L^{-1}. Compared to other heavy metals, the release of Cd from soil into groundwater occurs more quickly due to its higher mobilisation potential, which can be reached through competition and ligand-induced desorption (Kubier *et al*., 2019). It's interesting to note that the groundwater near the food, textile, tannery, and pharmaceutical industries either has very little or no Cd. Nonetheless, there are notable differences in Cd content amongst the industrial sites (p=0.0054). There is also a significant variation in Cd concentration in groundwater from different sites (Table 3). For example, the mean Cd concentration in groundwater at site A in the dry season near the textile industries is 0.311±0.440 *mg* L^{-1}, whereas it is 0.00 *mg* L^{-1} at sites B and C (Table 2). The Cd concentration at this site is above the maximum contaminant levels (5 µg/L) set by the USEPA, the Ministry of Health of China, and Denmark (Kubier *et al*., 2019). Groundwater with a high concentration of Cd, when used for irrigation, may release Cd into the soil, affecting soil microorganisms. It might move up the food chain and swiftly invade plants. One of the main ways that humans are exposed to Cd is through the soil-based absorption of the metal by vegetables (Huang *et al*., 2017). They are therefore quite likely to find their way up the food chain, and their impact on the species that comprise the food web is concerning. Chronic exposure to cadmium has occasionally been associated with cancer, cardiovascular illness, osteoporosis, and kidney disease (Tägt *et al*., 2022).

The distribution of Cu in groundwater from several industrial sites is shown in Figure 3(d). Cu concentrations in groundwater near the food industry are the greatest among various industries, with an average of 0.105±0.143 *mg* L^{-1}, a maximum of 0.9 *mg* L^{-1}, and a minimal value of 0.01 *mg* L^{-1}. The concentration of Cu in groundwater differed statistically significantly across different industrial areas, as demonstrated by a p-value of 2.19×10^{-7}. The Cu concentration varies from site to site, even when the groundwater is taken from the same location. For instance, site A near the plastic industry had a Cu concentration of 0.12±0.068 *mg* L^{-1} during the dry season, but sites B and C had Cu contents of 0.139±0.057 *mg* L^{-1} and 0.113±0.099 *mg* L^{-1}, respectively (Table 2). Though the Cu concentration in all Groundwater is lower than the WHO recommended maximum limit for Groundwater of 2.0 *mg* L^{-1} (Ullah *et al*., 2022), care must be taken to avoid accumulation of Cu in groundwater because a higher concentration of Cu can cause Wilson disease and significant iron deposition to hemochromatosis, liver and organ damage may occur in a small number of people with gene abnormalities. The Haber-Weiss and Fenton reactions involving reactive oxygen species produced during oxidative stress are responsible for the molecular toxicities of some HMs (Teschke, 2024).

The distribution of As in groundwater from several industrial sites is shown in Figure 3(e). In groundwater close to the food industry, the average As concentration was 1.06±1.13 *mg* L^{-1}, with a maximum of 6.33 and a minimum of 0 *mg* L^{-1}. The mean concentration of As was 1.03±1.74 *mg* L^{-1}, which is lower than the food industry, even though the groundwater near the plastics sector showed a maximum of 7.76 *mg* L^{-1}. As content in groundwater varied statistically significantly among sites (1.54×10^{-5}). The As concentration was significantly varied across different sites from the same location, as depicted in Table 3. Site A at the Tannery industrial area showed the greatest mean As concentration of 1.273±0.156 *mg* L^{-1}. On the other hand, site C showed the lowest mean of 0.133±0.022 *mg* L^{-1}.

The As concentration in groundwater at all locations was higher than the WHO-recommended level of 0.01 *mg* L^{-1}, even if it was lower in other industrial sites than in the food industry. Given that most people in the study area rely on groundwater for drinking, drinking water contaminated with As can cause health problems in people, including cancers of the bladder, intestinal disorders, skin lesions, type 2 diabetes and kidneys, liver, and lungs, among other conditions (Monteiro De Oliveira *et al*., 2021). Because arsenic adheres to proteins that bind DNA and slows down the DNA repair process, it increases the risk of cancer. Reports state that groundwater is also a major component of irrigation agriculture in the study area (Potgieter *et al*., 2020). As is more likely to enter the soil and move up the food chain when As-contaminated groundwater is used for irrigation, leading to several other diseases that impact the immune, growth-related, gastrointestinal, cardiovascular, hepatic, renal, neurological, and reproductive systems (Rai *et al*., 2019).

A thorough examination of the potential regional variances is not possible due to the current global body of literature on As-related health consequences. For instance, long-term exposure to As increases the risk of developing some forms of cancer in women compared to men in Taiwan, but not in other countries (Huang *et al*., 2015). Despite correlations being found in Argentina, Chile, Taiwan, and the United States, there was no discernible link

between skin cancer and arsenic exposure in mainland China (Huang *et al*., 2015).

The distribution of Cr in groundwater from several industrial sites is shown in Figure 3(f). The highest mean concentration of Cr (1.391±2.368 *mg* L^{-1}) with a maximum of 16.68 *mg* L^{-1} and a minimum of 0.00 *mg* L^{-1} was observed in groundwater near the tannery industry, with a maximum of 16 *mg* L^{-1} and a minimum of 0 *mg* L^{-1}. Table 4 indicates a statistically significant difference (p=0.0011) in the concentration of Cr in groundwater at various industrial locations. Furthermore, even though they were coming from the same location, the concentration of Cr in groundwater varied significantly between sites. For example, during the dry season, the mean concentration of Cr at site A in the plastic industry was 0.0489±0.021 *mg* L^{-1}, while the concentration at site B was 0.084±0.035 *mg* L^{-1}, as shown in Figure 5(a). At site A, which is close to the tannery industry, the concentration of Cr in the groundwater during the dry season was 2.629±0.728 *mg* L^{-1}, while at sites B and C, the concentrations were 1.827±0.322 *mg* L^{-1} and 1.274±0.434 *mg* L^{-1}, respectively.

These findings imply that not only does the industrial location affect the Cr concentration in groundwater, but also the various sites within the same industrial area. The Cr concentration in groundwater across all industrial areas except food industries exceeds the 0.05 *mg* L^{-1} allowable limit (Vijayakumar *et al*., 2021). Cr in groundwater poses a major risk to human health and aquatic organisms due to its ability to bioaccumulate (Egbueri *et al*., 2025). Poor haematological function, as well as digestive and dermatological problems, are associated with living in places where the groundwater contains Cr(VI). Residents in Cr(VI) impacted locations exhibited lower mean corpuscular volumes (62.8% males), fewer platelets (68% males and 72% females), and higher red blood cell counts (30.7% males and 46.1% females) than matched controls (Sharma *et al*., 2012). Moreover, Cr(VI) is frequently more dangerous than Cr(III) because of its distinct solubility and high mobility. According to Hossini et al. (2022), prolonged exposure to and bioaccumulation of Cr can damage male sperm and the reproductive system, affect other biological systems, and cause toxicity and a range of pathophysiological abnormalities, including burns, anaemia, allergic reactions, and ulcers, especially in the stomach and small intestine.

In industrial sites for plastic, textiles, and pharmaceuticals, the Zn content of groundwater was higher during the dry season than during the rainy season. However, as Table 1 illustrates, the Zn concentration in groundwater was higher in food and tannery industrial sites during the wet season than during the dry season. The p-values of 0.004 and 0.0001 in Table 3 show that the concentrations of Zn and Cd in Groundwater varied significantly by season. Since the p-value is greater than the alpha value (0.05), there was no discernible difference in the concentration of other HMs in groundwater between the dry and wet seasons.

The distribution of Fe concentration in groundwater across various industrial sites during the dry and wet seasons is displayed in Figure 5(b). With a high of 15.4 *mg* L^{-1} and a low of 0.00 *mg* L^{-1}, the mean Fe concentration at the plastic industrial site during the drying season was 6.3674±4.6860 *mg* L^{-1}, whereas, during the wet season, it was 0.5541±0.5244 *mg* L^{-1}, with a maximum of 2.17 *mg* L^{-1} and a minimum of 0.09 *mg* L^{-1} (Table 1). At different locations, no clear trends in Fe concentration during the dry and wet seasons have been noticed. In industrial sites for plastic, pharmaceuticals, and tannery, the Fe content of groundwater was higher during the dry season than during the wet season. However, as Table 1 illustrates, the Fe concentration in groundwater was higher in food and textile industrial sites during the wet season than during the dry season. The p-values of 0.225 in Table 3 show that the concentrations of Fe and Cd in groundwater do not vary significantly by season. The distribution of Cd, Cu, As, and Cr in groundwater at different industrial locations in two different seasons is presented in Figure 5(c–f). As depicted in Table 3, there was no significant difference in Fe, As, Cu, and Cr concentration during the dry and wet seasons, as indicated by a p-value higher than the alpha value.

As was previously mentioned, some of the chosen heavy metals (HMs), including Cd, As, and Cr, were discovered to have levels over the suggested limits for Groundwater, rendering it unsafe for human consumption and posing serious health hazards. The most hazardous impacts from HQ_{dermal} (2.1505) were brought on by exposure to groundwater near the pharmaceutical and plastics industries. Compared to earlier research (Wu and Sun, 2016), oral route risks are comparatively lower, whereas dermatological exposure is the greatest significant risk to human health. The HMs-contaminated groundwater near the pharmaceutical industry has the highest hazards (HQ_{oral}=0.4723) in terms of the risks through oral consumption, followed by the plastic industry (HQ_{oral}=0.2295). The greatest risks due to dermal exposure are associated with groundwater that is contaminated with HMs and situated close to the pharmaceutical industry. Distribution of HMs across Groundwater in the vicinity of

different industries at two different seasons is shown in Figure 6.

Groundwater near the pharmaceutical industries poses the biggest health concerns in both circumstances, whether by oral or dermal exposure, while the textile industry poses very little risk. The HQ values estimated for different HMs in the current study are lower than the HQ values (HQ_{oral}=0.32—3.79 and HQ_{dermal}= 8.05×10^{-6}—1.34×10^{-4}) reported in a previous study from Mansa and Muktsar districts of Punjab, districts of India (Bangotra *et al*., 2023). Similar studies have been conducted in several countries, including Nigeria (Jabbo *et al*., 2022), South Africa (Durowoju *et al*., 2020), Ghana (Opoku *et al*., 2020), Burkina Faso, Mali, Ethiopia, Namibia (Uugwanga and Kgabi, 2021), and Tanzania (Nowicki *et al*., 2023, Tomašek *et al*., 2022), due to the increased likelihood of HMs groundwater contamination and the corresponding health hazards. In the current study, a different approach was used to better understand the health risk in the research area. The contamination of groundwater HMs was evaluated based on the proximity of various industries, and the health risks were estimated and linked to the industries' groundwater contamination.

Conclusion

The assessment of groundwater heavy metal pollution near industrial sites uncovered a complex pattern of contamination, with significant differences in heavy metal concentrations among various industries. The pharmaceutical and tannery industries were identified as major sources of pollution. Furthermore, the study revealed seasonal variations in heavy metal levels, with higher concentrations during the dry season and lower levels during the wet season. The analysis further revealed that certain HMs in groundwater, such as cadmium (0.1481 *mg* L^{-1}), arsenic (1.39 *mg* L^{-1}), and chromium (1.91 *mg* L^{-1}), exceeded safe limits, posing significant health risks. The pharmaceutical and plastics industries were associated with the highest oral consumption risks, with hazard quotients (HQ_{oral}) of 0.4723 *mg* L^{-1} and 0.2295 *mg* L^{-1}, respectively, while the pharmaceutical industry posed the greatest dermal exposure risk with HQ_{dermal} of 0.4723 *mg* L^{-1}. The implications of this study are:

(i) Groundwater near industrial sites, especially pharmaceutical and tannery industries, poses significant health risks due to HM pollution, thereby making individuals vulnerable to non-carcinogenic health issues.

(ii) Seasonal fluctuations in HM concentrations suggest that groundwater quality monitoring should be conducted regularly to mitigate health risks.

(iii) Policymakers and industries must prioritise proper waste management and treatment to prevent HM pollution and protect public health.

(iv) Further research is needed to develop effective strategies for mitigating HM pollution and reducing health risks associated with groundwater contamination.

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Statements and Declarations

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contributions

All authors contributed to the study's conception and design. Material preparation, data collection, and analysis were performed by Hadiza Ado Suleiman. The first draft of the manuscript was written by Hadiza Ado Suleiman and Marlia Mohd Hanafiah, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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