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ORIGINAL RESEARCH ARTICLE

Pollution Status of Groundwater Resource by Some Heavy Metals Using Index Approach in Some Parts of Nasarawa Area, Kano State, Nigeria

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ABSTRACT
Groundwater is the world's most significant natural resource, providing water for different purposes, including drinking, domestic, industrial and irrigational. However, polluted groundwater may endanger human survival. This research evaluated the status of groundwater resource pollution caused by some heavy metals in some parts of the the Nasarawa local government area of Kano State. Fifteen groundwater samples were collected from functional boreholes in the area. Heavy metals concentrations evaluated include Zn, Mn, Cr, Mg, Cd, Fe, Cu, and Pb and were compared with the World Health Organization and Nigerian Standard for Drinking Water Quality to establish their suitability for human consumption. Descriptive statistics was employed to summarize the analyzed data. Metal index was used to determine the pollution status of the groundwater. The result revealed that Zn, Fe, Cu, and Mn with the mean value of (0.090, 0.160, 0.191 and 0.11) were found within the stipulated limit set by WHO (3.0, 0.3, 2.0 and 0.5) and NSDWQ (3.0, 0.5-50, 1.0 and 0.2), while Pb, Cd, Cr, and Mg (0.105, 0.127, 0.206 and 0.82) exceeded the permissible limits recommended by WHO (0.01, 0.003, 0.05 and 0.5). A high concentration of Pb, Cd, Cr, and Mg may be attributed to anthropogenic influences possibly deriving from improper municipal and Bampai industrial waste disposal. The values of the metal index (MI) revealed that the water is seriously affected by Pb, Cd and Cr, which can pose serious health damage to consumers. It is recommended to constantly monitor Pb, Cd and Cr in groundwater in the study area due to its proximity to Bampai and Sharadda industrial sites.

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Heavy Metals, Groundwater, Metal Index, Pollution status, Nasarawa, Kano state

INTRODUCTION

The most significant natural water resource on the planet is groundwater. In times of drought and when surface water sources are limited and precipitation patterns are uncertain, groundwater has shown to be an important source of water supply for a range of uses, including household, industrial, and irrigation (Saha and Ray, 2019; Rahmot *et al*., 2022). Around a third of people worldwide consider groundwater their main water source for various uses (FAO, 2017; Tsor *et al.,* 2022). Some essential conditions for maintaining human life and civilization include a sufficient amount and quality of freshwater (Agrawal *et al.,* 2021). Indeed, during the past few decades, groundwater use for irrigation, industry, and home reasons has multiplied globally due to the enormous population rise and astonishing advances in science and technology (Agrawal *et al.,* 2021).

Both natural and artificial sources contribute to water contamination in wells, but the latter seems to do so to a greater extent (Narsimha & Rajitha, 2018; Khalid, 2019). Pollutants in domestic, industrial and agricultural water constitute high environmental and health risks (Billing *et al.,* 2023). Improper treatment of these pollutants may increase heavy metal concentrations in groundwater (Folorunsho *et al.,* 2022). In addition to the wide variety of contaminants that harmed water resources, heavy metals drew special attention due to their high hazardous level, even at low concentrations. Heavy metal poisoning of the groundwater ecosystem is a global environmental problem (Yahaya *et al.,* 2019; Tsor *et al.,* 2022). Trace element concentrations in water can differ due to physiologic, environmental, and other factors.

Heavy metals can accumulate in the human body system and cause major harm to the nervous system, including cardiovascular illnesses, reproductive problems, and cancer. Heavy metals are not biodegradable (Li *et al.,* 2022; Umar *et al.,* 2023). Heavy metals, for example, Fe, Cu, Zn, and Ni, are essential micronutrients for animal life and vegetation but are dangerous at excess levels, whereas Cr,

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Cd, Pb, and Co have no known physiological functions but are harmful at a certain level (Aktar *et al.,* 2010; Nasiru *et al.,* 2021). Furthermore, Cr, Cd, and Ni are carcinogenic, while Pb may cause damage to human health (Okegye & Gajere, 2015; Rezaei and Hassani, 2018; Kamalu & Habibu, 2023). The damages include gastrointestinal, liver, renal, lung, intestinal, neurological, and reproductive disorders. Infants, the elderly, and pregnant women are especially vulnerable to the consequences (WHO, 2007; Tsor *et al.,* 2022). As the World Health Organization (WHO, 2007) indicated, inappropriate or polluted water causes around 80% of all diseases in human beings.

Groundwater can harm humans through consumption and skin contact (Wu and Sun, 2016; Zhang *et al.,* 2022). Nasarawa local government is situated within the Kano metropolis. As a result of rapid urbanization and population growth, the demand for potable water has increased. Most inhabitants rely on groundwater as a major source. Several private and public boreholes are operating to meet the water demand of the people in the area. In metropolitan regions where industrial and occupational activity is primarily concentrated, there is a specific increase in the pollution of heavy metals. Unfortunately, trustworthy information about the concentration of heavy metal pollutants in a given area like Nasarawa local government of Kano state Nigeria is lacking. Therefore, this study aims to evaluate groundwater pollution status by some heavy metals and compare the parameters with the Nigerian Drinking Water Quality Standard (NDWQS, 2007) World Health Organization (WHO, 2006) to ascertain its portability.

MATERIALS AND METHODS

Study area

This study is conducted in some parts of Nasarawa's local government area of Kano state. The area is located within the Kano metropolis, approximately at 11°57'37"N 8°33'0"E to 12°1'30"N 8°37'00"E (Figure 1). It covers a total landmass of about 34km² with a population of 596,411 according to 2006 population census. Climatologically, the area is strongly influenced by the tropical continental and maritime air masses. The two air masses control the climate, making it dry and wet. The area experiences high temperatures ranging from 32^{0}C to 38^{0}C. In the study area, irregularities in time and space characterize rainfall and do not exceed 650 mm/year, and the highest rainfall period was recorded in August and September (Olofin, 2014). The relative humidity is higher during the wet season by about 80% and lowers during the dry season by about 20% (Mustapha and Aris 2012a).

The geology of the area under study is underlain by a Crystalline Basement Complex of Pre-Cambrian origin, which loses its identity by disappearing into the Chad Formation. The basement complex consists of granite rocks, generally gneiss and commonly developed in a mixture of pegmatite of schist granite, gneiss, and irregular masses of pegmatite. Aeolian sand from wind deposits covers most of the area (Tasi'u, 2019). Sudan's savannah vegetation type covers the area. The natural vegetation in this area has been modified due to several human activities, such as urban construction.

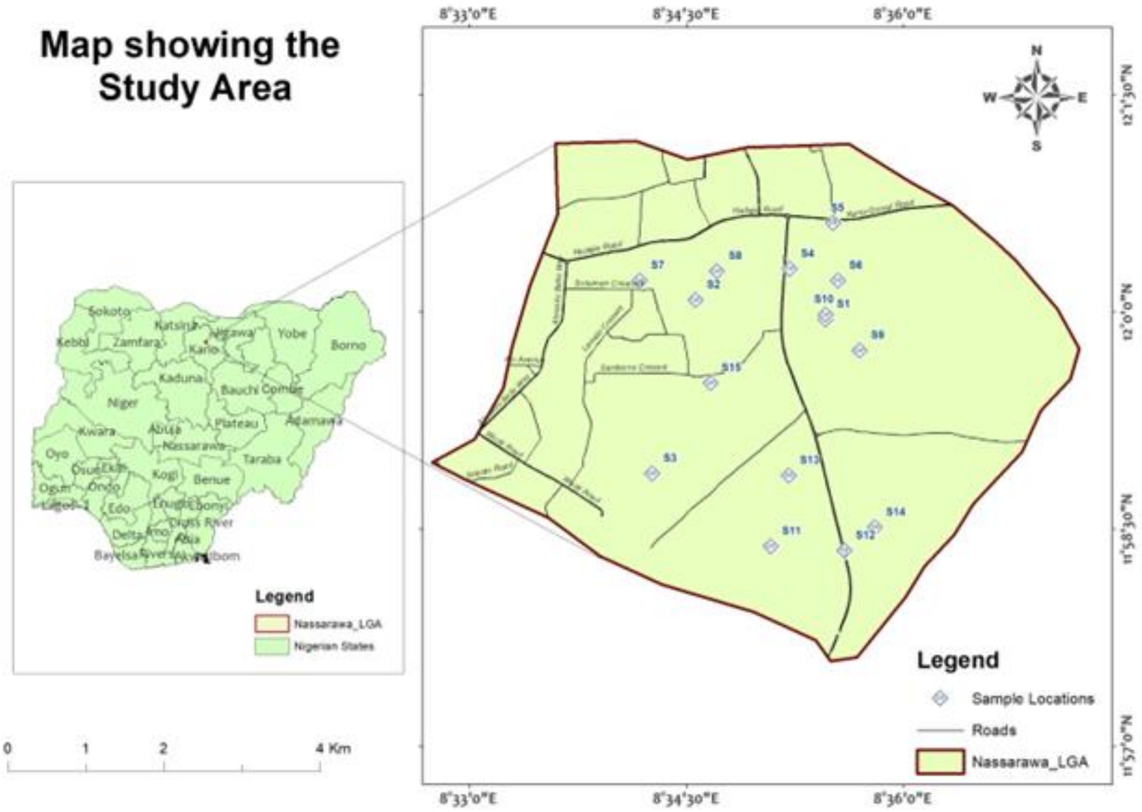

Figure. 1. Map of Nasarawa local government showing the study area

Groundwater sampling and analysis

Groundwater samples were collected randomly from fifteen functional boreholes during the rainy season of 2019 (May to September). Standard procedure for water sample collection using APHA, 2012 methods were adopted. All water samples were collected in pre-washed polythene sample bottles of 1-litre capacity. The sample bottles were washed several times with the water to be sampled and acidified with HNO_3 at the collection site. After labelling, the samples were transported to the laboratory (Department of Geography, Bayero University Kano) and stored at room temperature before laboratory analysis. The sample water was filtered in the laboratory, and 50cm^3 of the sample water was measured into the beakers.

5 cm3 of concentrated HNO3 was added to the measured samples. Hot plates were used to heat the sampled water in a fume cupboard to near dryness with a characteristic color indicating complete digestion. After which, the samples were allowed to cool, then transferred to a 50cm3 acid-washed volumetric flasks and volume filled to 50 marks with deionized water. All filtered samples were in sample bottles ready for the laboratory's atomic absorption spectrophotometer (AAS) (Greenberg *et al.,* 1992).

Metal index (MI)

The metal index (MI) of groundwater samples under study was calculated to determine the level of heavy metal contamination to assess the water quality's suitability for drinking (Caerio *et al.,* 2005).

$$MI = \sum_{n}^{i} Ci/MACi \text{ ....(1)}$$

MPI = is the metal index, Ci is the metal concentration (mg/l) in the water sample, and MACi is the maximum allowable concentration (WHO, 2004). The higher the value of MPI, the greater the risk of water to human health (Ogunkunle *et al.,* 2016).

Table 1: Classification of metal index (Caerio *et al.,* 2005).

S/No.	Categories	Degree of pollution
Class I	< 0.3	Very pure
Class II	0.3-1.0	Pure
Class III	1.0-2.0	Slightly affected
Class IV	2.0-4.0	Moderately affected
Class V	4.0-6.0	Strongly affected
Class VI	> 6.0	Seriously affected

Statistical analyses

Data were subjected to descriptive statistical analysis (minimum, maximum, mean and standard deviation) and are presented in Table 2. Furthermore, results were compared with the World Health Organization (WHO, 2006) and Nigeria Standard for Drinking Water Quality (NSDWQ, 2007) to understand the suitability for human consumption in the area under study.

RESULTS AND DISCUSSION

Heavy metals concentration

The analysis of heavy metals concentration of groundwater samples along with (NSDWQ and WHO) for human consumption are presented in Table 2.

Table 2: Heavy metals concentration in groundwater samples

Sample location	Parameters (ppm)							
	Pb	Zn	Cd	Cr	Mg	Fe	Cu	Mn
BHI	0.043	0.129	0.1	0.375	1.0	0.185	0.272	0.1
BH2	0.174	0.065	0.1	0.25	0.6	0.111	0.181	0.05
BH3	0.174	0.097	0.2	0.125	1.2	0.148	0.363	0.15
BH4	0.043	0.055	ND	0.125	0.8	0.370	0.090	0.1
BH5	0.130	0.194	0.1	0.50	1.6	0.259	0.363	0.2
BH6	0.033	0.042	0.1	0.421	0.5	0.121	0.218	0.18
BH7	0.123	0.074	ND	0.165	0.7	0.146	0.067	0.03
BH8	0.165	0.186	0.2	0.230	1.3	0.171	0.221	0.16
BH9	0.120	0.073	0.1	0.312	0.8	0.108	0.193	0.09
BH10	0.133	0.107	0.1	0.173	1.4	0.127	0.204	0.12
BH11	0.027	0.028	ND	0.097	0.3	0.106	0.196	0.04
BH12	0.056	0.013	ND	0.042	0.8	0.103	0.117	0.07
BH13	0.127	0.095	0.1	0.067	0.7	0.112	0.103	0.15
BH14	0.163	0.146	0.2	0.121	0.4	0.111	0.115	0.13
BH15	0.057	0.041	0.1	0.083	0.2	0.216	0.167	0.08
Min	0.027	0.013	0.1	0.042	0.2	0.103	0.067	0.03
Max	0.174	0.194	0.2	0.5	1.6	0.37	0.363	0.2
Mean	0.105	0.090	0.127	0.206	0.82	0.160	0.191	0.11
St. Dev	0.055	0.054	0.045	0.141	0.400	0.072	0.089	0.050
NSDWQ	0.01	3.0	0.03	0.05	0.2	0.5-50	1.0	0.2
WHO	0.01	3.0	0.003	0.05	0.5	0.3	2.0	0.5

BH = Borehole, St. Dev = Standard deviation, ND = Not detected, NSDWQ = Nigerian Standard for Drinking Water Quality, WHO = World Health Organization.

Lead: lead concentration varied from 0.027 to 0.174 with a mean value of 0.105mg/l, which exceeded the permissible limit (0.01) recommended by WHO for drinking water. This follows the findings of Hassan *et al.* (2021) in their comparative analysis of heavy metals in groundwater around Bampai and Sharadda industrial sites Kano metropolis. This high lead concentration may be due to several anthropogenic activities within the study sites, such as toxic waste disposal. Research has indicated that prolonged exposure to lead (Pb) might result in anaemia and hypertension, particularly in middle-aged and older adults. Males who are exposed to high concentrations may have kidney and brain damage, while toddlers and fetuses whose brain tissues are still growing may experience behavioural changes and possible neurological impairment from water containing less than 0.05 mg/L of lead (Jaishankar *et al.,* 2014; Fisseha *et al.,* (2016; Edokpayi *et al.,* 2018).

Zinc: The analyzed value of zinc concentration in the groundwater sample revealed the range of 0.013 to 0.194 with a mean value of 0.090 mg/l, found within the WHO and NSDWQ permissible limit for drinking water. This concentration in the borehole water samples could be traced to the leaching of chemicals and other particulate matter deposited in the area. The low concentration of Zn in the area suggests that fewer fluorescent lamps and batteries were leaked into the ground. The low concentration of zinc value is similar to the findings of Gutti *et al.* (2014). Hence, all borehole water has little to no health effects because Zn is known to have antioxidant properties that protect humans against accelerated ageing of muscles and skin. It also helps heal after an injury if a moderate and recommended dosage is ingested (Asare-Donkor *et al.,* 2016; Edokpayi *et al.,* 2018).

Cadmium: The level of Cadmium in the groundwater samples ranged from 0.1 to 0.2, and the average mean value of 0.127 mg/l. The mean value of dissolved cadmium is higher than the permissible level. It may be due to the proximity of Bampai industrial areas of urban Kano, which may influence high levels of reported cadmium concentration. However, this study suggests that the main possible source of heavy metals in groundwater can be attributed to leachate percolation. This result is similar to Hassa et al.'s (2021); Boateng et al., 2019 findings). A high concentration of cadmium may cause several damages, such as kidney damage and obstructive lung diseases. Experimental studies conducted on humans and animals show that cadmium may cause cancer in humans (Nordberg *et al.,* 2002). In comparison with other studies from developing nations, studies revealed that blood levels of this metal (Cd) in children showed increased levels, and one causative factor among many is the consumption of polluted groundwater due to industrial effluents (Horton *et al.,* 2013; Mohankumar *et al.,* 2016)

Chromium: In the present study, chromium concentration in groundwater samples gave the range values between 0.042 and 0.5 with a mean of 0.206 mg/l, which is higher than the recommended limit by WHO and the NSDWQ guidelines for drinking water. The high concentration of chromium was more pronounced than the other trace metals, as shown in Figure. 2. This result is in accord with the study of Agrawal *et al.* (2021). The maximum value obtained from this study could be sourced through septic systems or industrial discharge, possibly Bampai and Sharadda industrial sites. The disposal of metal products around this area could have led to a high concentration of Cr in the boreholes. High Cr content in the water has a possible risk of inducting gastrointestinal cancer following long-term exposure, undesirable taste and slight nausea in humans. Furthermore, an in vitro study has shown that high Cr(III) concentration in the cell could cause DNA damage in humans (Edokpayi *et al.,* 2018)

Magnesium: Magnesium is another essential mineral required to maintain the proper functioning of human health (Agagaw *et al.,* 2021). It helps to maintain the stable equilibrium of water; excess amounts of magnesium, however, slowly react with other minerals (Zhu *et al.,* 2022; Muthusamy, *et al.,* 2023). The consumption of magnesium through water helps regulate the human body's cardiovascular and immune systems. Magnesium concentration ranges between 0.2 and 1.6, with an average value of 0.82 mg/l. The value is above the acceptable limit recommended by WHO and the NSDWQ guidelines for human consumption. Natural sources such as the weathering of parent rock and ion exchange are significant sources of magnesium in groundwater. Long-term exposure to manganese may lead to serious human health effects such as muscular dystrophy, renal failure and multiple sclerosis.

Iron: The concentration of iron in this study varied from 0.103 to 0.37, with a mean value of 0.160 mg/l. The observed average value falls within the allowable range recommended by WHO and NSDWQ. These findings slightly coincide with Abdulsalam *et al.* (2019). Although iron in water has less effect on human health, higher iron concentration may cause Diabetes, hemochromatosis, stomach problems, nausea, and vomiting, as reported by Agrawal *et al.* (2021). Water with a Fe concentration of less than 0.3 mg/L slightly affects taste and other marginal aesthetic effects, such as slightly stained white clothes if used for laundry (Edokpayi *et al.,* 2018).

Copper is also characterized as unwanted heavy metals in drinking water and can infiltrate the water system. The concentration of copper in the groundwater sample ranged from 0.067 to 0.363, and a mean value of 0.191 was observed. This value is within the acceptable limit set by WHO and NSDWQ for human consumption. The lower value of copper obtained in this study is in concurrence with the values reported by Abdulsalam *et al.* (2019). The concentrations of copper in the studied groundwater samples were also comparable with earlier studies. Boateng *et al.* (2019) reported a similar to this study. Mahapatra, *et al.* (2020) in North Chennai recorded Cu concentration higher than in this study. Thus, copper might have been removed by precipitation and complexation processes before getting to the groundwater (Folorunsho *et al.,* 2022). The other reason for the low copper concentration in groundwater could be that a few discharged solid wastes at the nearest sample sites do not contain bioavailable copper forms (Ferrara *et al.,* 2013) to be released into the groundwater.

Manganese: Observed manganese concentration ranges from 0.03 to 0.2, with a mean value of 0.11 mg/l. This value falls within WHO and NSDWQ stipulated limit for drinking water. The low concentration of Mn may be attributed to the less dissolution of Mn from the surface onto the groundwater. It may also be attributed to nonbiodegradable wastes, which might have inhibited solid waste biodegradation, as Folorunsho et al. (2022) reported. Musa *et al.* (2013) reported similar to these findings. Mahapatra *et al.* (2020) in the North Chennai region also reported Mn concentration higher than in this study.

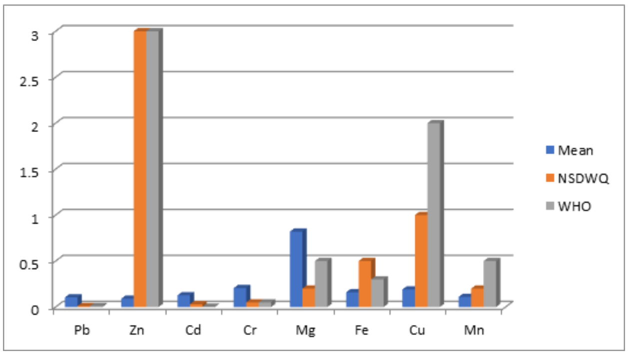

Figure. 2: The mean value of heavy metals concentration in groundwater samples collected from fifteen boreholes in some of the Nasarawa local government, Kano state.

Pollution Status using Metal Index (MI)

It can be seen from Table 3 that the majority of the groundwater samples in the study were unsafe. The metal index (MI) of groundwater samples shows great contamination by Cd and Pb in the study area. MI_{Cd} is in order BH3, 8, 14 (66.7) > BH1, 2, 5, 6, 9, 10, 13 & 15 (33.3), and MPI_{Pb} BH2, & 3 (17.4) > BH8 (16.5) > BH14 (16.3)BH10 (13.3) > BH5 (13) > BH13 (12.7) > BH7 (12.3) > BH9 (12) > BH15 (5.7) > BH12 (5.6) > BH1&4 (4.3) > BH6 (3.3) > BH11 (2.7). MI_{Cr} BH5 (10) > BH6 (8.2) > BH1 (7.5) > BH9 (6.2) > BH2 (5.0) > BH8 (4.6) BH14 (4.2) > BH10 (3.5) > BH7 (3.3) > BH3 & 4 (2.5) > BH11 (1.9) > BH15 (1.7) > BH13 (1.3) > BH12 (0.8). These MI values indicated that Pb (Class V & VI) strongly and seriously affected the studied groundwater. Furthermore, it was seriously affected by Cd (Class VI). Cr falls in Class IV, V & VI, and Mg were slightly and moderately affected, Zn and Mn falls in (Class I & II), and Fe and Cu in (Class II). The overall MPI of all studied boreholes were found above class VI, indicating seriously affected. Table 4 revealed the classification of groundwater based on the metal index. It can be observed that only station 11 was strongly affected concerning heavy metal contamination. The remaining 14 stations were seriously affected. These findings demonstrate the need for quick action to lower the heavy metal concentration in groundwater. Anthropogenic activities were the primary cause of the heavy metals found in groundwater; industrial and e-waste activities contribute more to the accumulation of heavy metals.

Table 3: Calculation of metal index

Sample ID	Parameters (ppm)								$\sum_{n}^{i} MPI$
	Pb	Zn	Cd	Cr	Mg	Fe	Cu	Mn	
BHI	4.3	0.04	33.3	7.5	2	0.62	0.14	0.2	48.1
BH2	17.4	0.02	33.3	5.0	1.2	0.37	0.09	0.1	57.48
BH3	17.4	0.03	66.7	2.5	2.4	0.49	0.18	0.3	90
BH4	4.3	0.02	ND	2.5	1.6	1.23	0.05	0.2	32.4
BH5	13	0.06	33.3	10	3.2	0.86	0.18	0.4	52.26
BH6	3.3	0.01	33.3	8.2	1.0	0.40	0.11	0.36	46.68
BH7	12.3	0.02	ND	3.3	1.4	0.49	0.03	0.06	17.6
BH8	16.5	0.06	66.7	4.6	2.6	0.57	0.11	0.32	91.46
BH9	12	0.02	33.3	6.2	1.6	0.36	0.10	0.18	53.76
BH10	13.3	0.05	33.3	3.5	2.8	0.42	0.10	0.24	53.71
BH11	2.7	0.01	ND	1.9	0.6	0.35	0.10	0.08	5.74
BH12	5.6	0.00	ND	0.8	1.6	0.34	0.06	0.14	8.54
BH13	12.7	0.03	33.3	1.3	1.4	0.37	0.05	0.3	49.45
BH14	16.3	0.05	66.7	4.2	0.8	0.37	0.06	0.26	88.74
BH15	5.7	0.01	33.3	1.7	0.4	0.72	0.08	0.16	42.07

BH = Borehole, ND = Not detected, MI = Metal Index

Table 4: Classification of groundwater based on metal index (Caerio *et al.,* 2005).

Classes	MI	Degree of pollution	Sampling Sites
Class I	< 0.3	Very pure	
Class II	0.3-1.0	Pure	
Class III	1.0-2.0	Slightly affected	
Class IV	2.0-4.0	Moderately affected	
Class V	4.0-6.0	Strongly affected	BH11
Class VI	> 6.0	Seriously affected	BH1 - 10, BH12 - 15

LIMITATION

There was a minimal sample size used (15 samples). A comprehensive investigation should be conducted to determine the levels of heavy metals pollution in Nasarawa local government area, Kano state.

CONCLUSION

The results revealed that Zn, Fe, Cu, and Mn fall within the acceptable limit set by WHO and NSDWQ, while Pb, Cd, Cr, and Mg exceeded the permissible limits recommended by WHO. The MPI reveals the groundwater resource is seriously affected since the obtained values are greater than 6.0. It is concluded that immediate measures to be taken to control the pollution as the water can pose a serious health effect to consumers. This study gives an idea of the status of heavy metal contamination in the study area and can be utilized by governmental organizations and other organizations to create a thorough plan to lower the amount of heavy metals in this location. It was also recommended that continuous monitoring of groundwater need to be made in the studied area. Domestic and industrial waste should be disposed of properly to safeguard public health from water-borne diseases.

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