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Assessment of Water Quality of Shallow Aquifer Resources of Agbabu, Ondo State, Nigeria

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ABSTRACT

Groundwater, through hand dug wells, provide drinking water to an estimated 59 % of Nigerians. There is, however, a growing concern on the deterioration of groundwater quality due to anthropogenic activities. In this study, water quality index (WQI) was used to assess the groundwater quality of Agbabu, while health risk assessment was carried out by calculating the chronic daily intake (CDI), hazard quotient (HQ), hazard index (HI) and carcinogenic risk (CR) of some heavy metals and nitrate. The WQI shows that the groundwater of the area were in the very poor water quality (76 < WQI < 100) and unsuitable for drinking class (WQI > 100). Oral ingestion is the major pathway of risk exposure, accounting for 86.54 % of total exposure to the risk, while dermal contact accounted for only 13.46%. Cd and Cr are the major contributors to non-carcinogenic risk and accounted for 51.07% and 39.51% respectively of the total risk, while Pb, Mn, Fe and NO_3^- showed no risk to the population (HQ < 1). There is also a life time probability of contracting cancer due to groundwater contaminated with Cr and Cd in the study area. The groundwater of the area were contaminated mainly by heavy metals, and therefore should be continuously monitored and proper legislation taken to avoid health risk associated with these toxic metals.

Keywords: Aquifer, Carcinogenic, Groundwater, Health risk

INTRODUCTION

Groundwater constitutes a major portion of the earth's water circulatory system and occurs in permeable geologic formations known as aquifers (i.e. formations having structure that can store and transmit water at rates fast enough to supply reasonable amounts to wells) (ARGOSS, 2001). Groundwater is tapped at shallow depths for domestic uses through the construction of hand dug wells. An estimated 2 billion people worldwide rely on aquifers for drinking water supply (WWF, 2009).

The extraction of groundwater is often the first resort of rural water users confronted by scarcity (UNEP, 2005). In Nigeria, with an estimated population of over 200 million and about 70% of its population residing in rural areas, 59% (118 million) Nigerians depend on hand dug wells for drinking water sources (estimation from 2006 census) (FGN, 2007). The use of hand dug wells for groundwater exploitation is also common in Agbabu. Large population of people living in rural and peri-urban areas of Agbabu have no access to pipe borne water, and hence resort to the use of hand dug wells for domestic use (including drinking).

While hand dug wells provide an effective alternative to the public water supply sources, there is a growing concern on the deterioration of groundwater quality due to geogenic and anthropogenic activities. Shallow aquifers are most in danger of pollution from human activities. Human health is threatened by most of the agricultural development activities particularly in relation to excessive application of fertilizers and also due to other unsanitary conditions like indiscriminate waste disposal (ARGOSS, 2001)

Hence, it is imperative to regularly monitor the quality of groundwater and to device ways and means to protect it, because once the groundwater is contaminated, its quality is difficult to be restored. However, groundwater monitoring has not been accorded much attention in Nigeria to date. Little is known about the status of groundwater in the country. Apart from the lack of monitoring, there has been little coordination of collection, collation or analysis of the data that have been collected by state water agencies and external support agencies (Joshua and Adewale, 2020). It is information obtained from water quality assessments that lead to water quality standards, legislation and regulation (Commonwealth of Australia, 2012).

One of the difficult tasks facing environmental managers is how to transfer their interpretations of complex environmental data into information that are understandable and useful to technical policy individuals as well as the general

public. Internationally there have been a number of attempts to produce a method that meaningfully integrates the data sets and converts them into information (Awachat and Salkar, 2017). Water quality index is one of the most effective tools for water quality assessment and can be used to effectively communicate information on the quality of water to the concerned citizens and policy makers. It thus becomes an important parameter for the assessment and management of groundwater. Since 1965 when Horton, (1965) proposed the first water quality index, a great deal of consideration has been given to the development of water quality index methods. The concept is based on the comparison of the water quality parameters with respective regulatory standards (Khan *et al*., 2003).
Water Quality Index has been defined as a single number that expresses water quality by integrating measurements of selected water quality parameters (UNEP GEMS, 2007). WQI can also been defined as a rating reflecting the composite influence of different water quality parameters (Ramakrishnaiah *et al*., 2009). Some of the advantages of WQIs are summarized in the UNEP GEMS (2007) workshop report as follows: WQI can be used to show water quality variations both spatially and temporally; Provide a simple, concise and valid method for expressing the significance of regularly generated laboratory data; Aid in the assessment of water quality for general use; Allow users to easily interpret data; Can identify water quality trends and problem areas; Provide screening tools for further evaluation; Improve communication with the public and increase public awareness of water quality conditions; Assist in establishing priorities for management purposes.

Human health risk assessment uses risk as an evaluation index to link environmental pollution with human health and quantitatively describe the risk of pollution to human health (Tian *et al*., 2019). The main aim is to provide useful information to policy makers and regulators (Commonwealth of Australia, 2012). Risk depends on the amount of chemical present in an environmental medium, the amount of contact (exposure) a person has with the pollutant in the medium, and the toxicity of the chemical (IPCS, 2010). The aim of the present study is to assess the groundwater quality of the area using WQI and to assess the non-carcinogenic and carcinogenic risk posed by Pb, Cr, Cd, Mn, Fe and NO_3^- through drinking and dermal contact of the groundwater.

MATERIALS AND METHODS

Study Area

Agbabu is located (6°30ˈN and 4°50ˈE) in Ondo State of Nigeria (Fig. 1). Agbabu bitumen belt is made of the main Agbabu, inhabited by about 1800 people and other smaller farm settlements such as Mulekangbo, Ilu-binrin and Mile 2 Agbabu villages made up of about 600 people. Agbabu is in the bituminous belt of Ondo State. However, due to the ground bitumen deposit, use of inorganic fertilizer and other human activities such as domestic and industrial waste disposal, the groundwater of Agbabu stands the chance of being polluted.

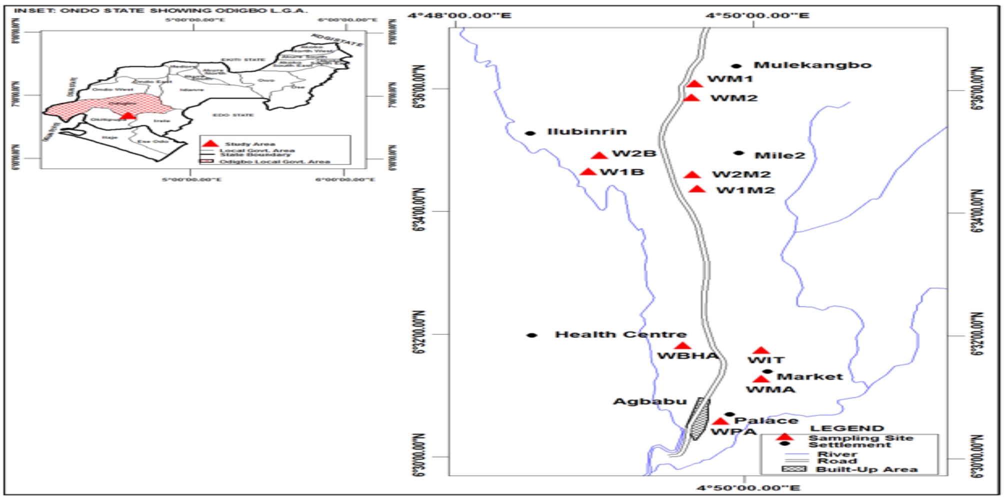

Figure 1: Map of the Study Area

Sampling Area

Water samples were collected from the following selected points, WMA: well at the market; WPA: well at the palace; WBHA: well beside health centre; WIT: well inside town; W1M2: first well at mile 2; W2M2: second well at mile 2; W1B: First well at Ilu-binrin; W1B: second Wellat ilu-binrin; WM1: First well at Mulekangbo; WM3: second well at Mulekangbo.

Preparation of Samples for Metal Analysis

Samples for the metal analysis were acidified at the time of collection with concentrated nitric acid in other to bring the pH below 2. Exactly 100 cm^3 of each water sample was then transferred into a 200 cm^3 beaker, 5cm^3 of concentrated HNO_3 was added and digested on a hot plate at 90 °C to 95 °C until the volume was reduced to 15-20 cm^3 (Ademoroti, 1996). The digested samples were transferred into a 50 cm^3 volumetric flask. Distilled water was used to make up the solution to the mark. This was used to check for the determination of the elements Fe, Cd, Mn, Cr, and Pb using Atomic Absorption Spectrophotometer (Unicom 969).

Chemical Parameters

The determination of physicochemical parameters such as pH, Sulphates, Phosphates, Nitrates, Hardness, Total Dissolved Solids, were carried out in accordance with the method described by AOAC, (1990).

Water Quality Index (WQI)

In order to evaluate the overall impact of pollution in the study area, water quality index was calculated using the weighted arithmetic index method as reported by Douglas *et al.*, (2015).

$$WQI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i} \quad (1)$$

$$W_i = \frac{w_i}{\sum_{i=1}^{n} w_i} \quad (2)$$

$$Q_i = \frac{C_n - C_i}{S_i - C_i} \times 100 \quad (3)$$

Where: w_i is the assigned weight ($w_i = \frac{1}{S_i}$), W_i is the relative weight, Q_i is the quality rating for the ith water quality parameter, n is the total number of the water quality parameters, C_n is the concentration of ith water quality parameter, S_i is the standard value of the ith water quality parameter, C_i is the ideal value of the ith water quality parameter (C_i for pH = 7, for other parameters, C_i = 0) (Alobaidy *et al.*, 2010;Otene and Nnadi, 2019). WQI ratings according to this method are shown in Table 1.

Table 1: Water Quality Index Scale (Douglas *et al.*, 2015)

WQI	Water Quality
< 25	Excellent
26 - 50	Good
51 - 75	Poor
76 - 100	Very poor
> 100	Extremely Poor

Table 2: Reference standards (SON, 2007) and relative weights of water quality parameters

Parameter	standard	relative weight
pH	6.5 - 8.5	0.0532
Nitrate	50	0.00745
Sulphate	100	0.00372
TDS	500	0.00072
Hardness	150	0.0025
chloride	250	0.00149
Fe	2	0.186
Mn	0.5	0.745

Health Risk Assessment

Risk assessment is an evaluation index that links environmental pollution with human health, and can provide useful information to policy makers whose management decisions will result in improvement in water quality. Risk assessment involves four stages: hazard identification, dose-response assessment (hazard assessment), exposure assessment, and risk characterization (Commonwealth of Australia, 2012).

Exposure Assessments

The chronic daily intake (CDI) (mg/kg/day) was used to calculate the non-carcinogenic and carcinogenic risk of the toxic pollutant in the groundwater via ingestion and dermal routes of exposure. CDI via ingestion (CDI_{ing}) and dermal contact (CDI_{dern}) in this study were calculated following the formula reported by USEPA, (1989) as in equation 4.

$$CDI_{ing} = \frac{C_w \times IR \times EF \times ED}{BW \times AT} \quad (4)$$

$$CDI_{derm} = \frac{C_w \times K_i \times SA \times EF \times ED \times BF \times CF}{BW \times AT} \quad (5)$$

The detailed meaning and reference values of each parameter used for the calculation are presented in Table 3.

Table 3: The Reference Parameters of all Pollutants (USEPA, 1989)

Parameter	Meaning	Value	Unit
EF	Exposure frequency	365	d/a
ED	Exposure duration	Non-carcinogens 30, Carcinogens 70	A
BW	Body weight	70	kg
AT	Average exposure time	Non-carcinogens 30, Carcinogens 70	A
IR	Ingestion rate	2	L/d
SA	Body surface area	16600	cm^2
BF	Bathing frequency	1	time/d
CF	unit conversion factor	0.002	L/cm^3
Ki	Dermal adsorption		cm/h
C_w	Concentration in water		mg/L

Non-carcinogenic Risk Assessment

The non-carcinogenic risk due drinking water and dermal contacts were estimated using the hazard quotient (HQ) and hazard index (HI).

$$HQ = \frac{CDI}{RfD} \quad (6)$$

Where RfD is the oral reference dose (mg/kg/day), defined as the daily oral exposure to a substance that will not result in any deleterious effect in a life time for a given human population (FAO/WHO, 2013). The RfD values for the assessed pollutants are listed in Table 4.

The scale of hazard quotient (HQ) based on average daily intake (CDI) and RfD is classified as follows: HQ$\leq$ 1 (no risk); 1 < HQ $\leq$ 5 (low risk); 5 < HQ$\leq$ 10 (medium risk); HQ > 10 (high risk) (USEPA, 1989).

The hazard index **(**HI**)** was calculated as the summation of the Hazard Quotient (HQ) arising from all the pollutants examined.

$$HI = \Sigma HQ \quad (7)$$

The value of the hazard index is proportional to the magnitude of the toxicity of the water to the population.

Carcinogenic Risk Assessment

Carcinogenic risk (CR) assessment estimates the probability of an individual developing cancer over a lifetime due to exposure to the potential carcinogen. CR was calculated using equation 8.

$$CR = CSF \times CDI \quad (8)$$

Where CDI and CSF are the chronic daily intake (mg/kg/day) and cancer slope factors $(mg/kg/day)^{-1}$ respectively. The CSF for the studied heavy pollutants are listed in Table 4.

According to US EPA, (2011) CR between 1 x 10^{-6} to 1 x 10^{-4} represent a range of permissible predicted lifetime risks for carcinogens. Chemical for which the risk factor falls below 1 x 10^{-6} may be eliminated from further consideration as a chemical of concern.

Table 4: Toxicological characteristics of the selected pollutants (US EPA, 2011)

Pollutants	Reference dose		Cancer slope factor	Permeability coefficient
	Oral route	Dermal route		
Pb	0.0014	0.0042	0.0085	0.004
Cd	0.0005	0.00005	0.38	0.001
Cr	0.003	0.0006	0.5	0.002
Mn	0.046	0.0184	-	0.001
Fe	0.3	0.045	-	0.001
NO_3^-	1.6	1.1	-	0.001

RESULTS AND DISCUSSION

Selected Water Quality Parameters

The mean values of the selected water quality parameters are displayed in Table 5. The results show that the groundwater samples are slightly acidic. The pH ranged from 4.00±0.06 to 6.50±0.47 which are below the standard permissible range of 6.5 – 8.5. Slightly acidic pH may be indicative of great deal of organic pollutants in water (Srivastava and Kumar, 2013). The mean values of nitrate, sulphate and chloride fall below the maximum permissible limit of 50 mg/L, 100 mg/L and 250 mg/L respectively in all the sampling stations, except chloride at WM1, which was exceptionally high (8029.79±119.50). While sulphate and chloride have no known health impact, nitrate is associated with cyanosis and asphyxia (blue baby syndrome) for infants under three months (SON, 2007). TDS exceeded the maximum permissible limit of 500 mg/L at WMA (516.67 mg/L), WBHA (856.70 mg/L), W2B (1803 mg/L), and WM1 (2605 mg/L), while the mean concentrations of Hardness are above the standard limit except at W1M2, W2M2, and WM2. Hardness of water is as a result of calcium and magnesium salts, while TDS include salts, some organic materials and a wide range of other things from nutrient to toxic materials (Srivastava and Kumar, 2013).

Table 5: Mean values of selected water quality parameters

Sample	pH	Nitrate (mg/L)	Sulphate (mg/L)	TDS (mg/L)	Hardness (mg/L)	Chloride mg/L
WMA	5.00±0.27	6.73±1.86	12.33±0.42	516.67±162.58	387.77±80.32	26.96±1.51
WPA	6.50±0.47	3.47±1.92	8.83±0.76	24.33±4.04	203.87±54.3	4.90±1.74
WBHA	5.50±0.21	11.83±0.38	15.33±0.83	856.70±77.67	871.37±79.77	3.20±2.50
WIT	5.00±0.20	11.63±1.23	12.83±0.43	60.00±20.00	212.07±97.11	7.56±1.06
W1M2	5.00±0.36	ND	12.33±0.42	46.61±30.55	103.83±25.01	6.99±1.38
W2M2	4.50±0.35	0.60±0.44	14.13±0.32	66.64±11.55	127.43±35.21	13.90±1.81
W1B	6.00±0.15	3.10±0.39	9.60±1.39	96.77±25.17	348.90±87.20	7.26±0.83
W2B	5.50±0.31	ND	12.53±0.50	1803.30±69.95	164.30±24.51	22.76±1.63
WM1	6.00±0.25	ND	9.77±0.15	2605.91±86.95	213.37±103.72	8029.79±119.50
WM2	4.00±0.06	2.73±1.27	10.40±0.10	41.00±10.00	117.47±25.03	12.26±1.33

Water Quality Index (WQI)

The WQI of the studied sites are presented in Figure 2. The results show that the studied stations are contaminated in the following order: W2B > WPA > WIT > WMA > WM2 > W1B > WM1 > WBHA >W2M2 >W1M2. It can be seen that the water quality of the sites fall under three categories;

1. Water unsuitable for drinking (WQI > 100) (W2B, WPA, WIT and WMA).
2. Very poor water quality (76 < WQI < 100) (W2M2, WBHA, WM1, W1B and WM2).
3. Good water quality (26 < WQI < 50) (W1M2).

The extremely poor water quality of the first category can be attributed to the low pH in the areas and high levels of metals which, mostly exceeded the standard limits. Although there was extremely high concentrations of TDS and chloride at WM2, these parameters have no known health impact, and therefore weighed low. There was no significant input from the high weighed metals and pH. This explains why this site still falls in category 2 despite the extremely high levels of TDS and chloride.

Most of the physico-chemical parameters used for calculating WQI, (including chloride, hardness, pH, sulphate and total dissolved solids), have no health impact and occur in drinking water at a concentration well below those at which toxic effects may occur (WHO, 2008), however, they are generally used as indicator of water pollution (Bharathi *et al*., 2916), which means their presence in high concentrations may indicate presence of other potentially toxic pollutants like organic pollutants and toxic metals. It has also been reported that good WQI does not necessarily translate to no hazard (Otene and Nnadi, 2019), hence there is need to investigate other toxic pollutants in water.

However, the WQI values can be used as a reference or base line for future monitoring of pollution to the groundwater aquifer of the area.

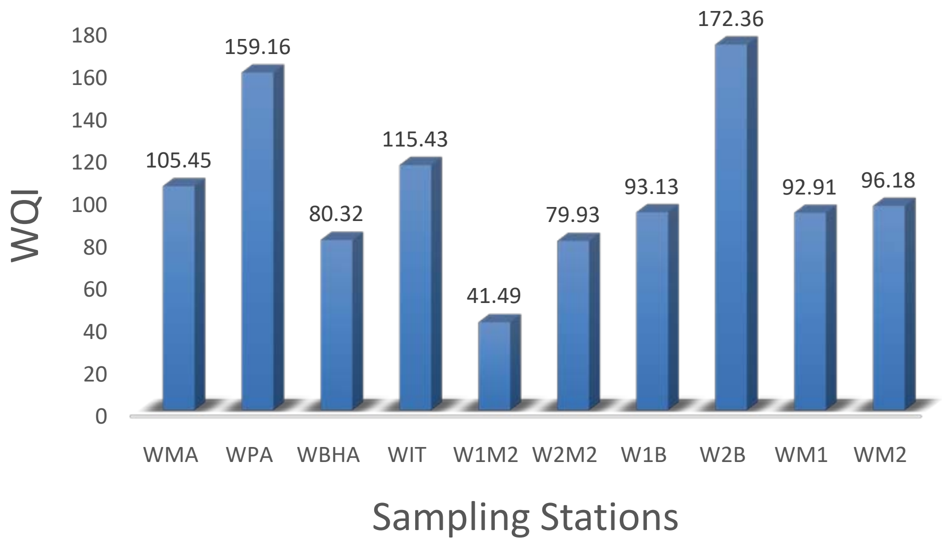

Figure 2: Water quality index values for all the sampling stations

HEALTH RISK ASSESSMENT

Exposure Assessment

Human health risk depends on the amount, the exposure and the toxicity of the chemical substance (IPCS, 2010). The present study explored the risk of Pb, Cd, Cr, Mn, Fe, and nitrate in the groundwater through oral ingestion and dermal contact exposure pathways. Exposure assessment using the chronic daily intake (CDI) shows that the human exposure to the pollutants through oral ingestions are in the following range: Pb (2.86×10^{-4} – 8.57×10^{-4}), Cd (2.86×10^{-4} – 5.14×10^{-3}), Cr (2.86×10^{-3} – 2.43×10^{-2}), Mn (5.71×10^{-3} – 2.29×10^{-2}), Fe (6.86×10^{-3} – 1.48×10^{-1}), NO_3^- (1.17×10^{-2} – 1.92×10^{-1}). This shows that average human exposure to the pollutants through oral route are in the following order: NO_3^-> Fe > Mn > Cr > Cd > Pb, while exposure through dermal contact are far less and are in the following order: NO_3^- (2.72×10^{-3}) > Fe (7.71×10^{-4}) > Cd = Cr (4.0×10^{-4}) > Mn (2.52×10^{-4})>Pb (2.76×10^{-5}).

Non-carcinogenic Risk Assessment

To assess the potential non-carcinogenic risk posed by the groundwater to the human population, hazard quotient (HQ) and hazard index (HI) were calculated. Because health risk due to potential toxic substance in the same environment is additive (Ayantobo*et al*., 2014), total HQ and total HI due to combination of oral ingestion and dermal contact pathways were estimated and the result summarized in Figure 3. The result shows that oral ingestion is the major pathway and constitutes 86.54% of the total exposure to the risk, while dermal contact accounted for only 13.46%. The total HQ for Pb, Mn, Fe and NO_3^- are all less than one (HQ < 1), showing that these pollutants constituted no non-carcinogenic risk to the population through drinking water and dermal contact. However, Cd constituted no risk (HQ < 1) at site W1M2 (0.667), low risk (1 < HQ≤ 5) at sites WPA (1.332), WPHA (1.998), WIT (4.664), W1B (1.066), and WB2 (2.666), medium risk (5 < HQ ≤ 10) at sites WMA (5.996), W2B (7.326), and high risk (HQ > 10) at sites W2M2 (10.658), WM1 (11.986). There was also low and medium non-carcinogenic risk due to Cr in the sites as follows: Low risk (WMA, W1M2, W1B, W2B, WM1), medium risk (WBHA, W2M2, WM2). The percentage contribution of each of the pollutants to the total non-carcinogenic risk (Figure 4) can be arranged in the following order: Cd (51.07%) > Cr (39.51%) > Mn (3.65%) > Pb (3.20%) > Fe (1.82%) > NO_3^- (0.78%). This shows that Cd and Cr are the major contributors to non-carcinogenic risk, accounting for 90. 58% of the total risk.

HI is the cumulative effect of all the studied pollutants. Total HI (HI_{oral}+ HI_{derm}) are shown in Figure 3. The result shows that the order of human health risk due to the studied pollutants from the groundwater of the sites are as follows: WM1 (16.98) > W2M2 (16.53) > WM2 (12.97) > W2B (11.90) > WBHA (11.04) > WMA (9.97) > WIT (5.99) > W1B (4.12) > WPA (2.83) > W1M2 (2.37). This result shows that the order of risk of sites as obtained from health risk assessment is not exactly the order of pollution of the sites as obtained from WQI, thus confirming the earlier report that good WQI does not necessary translate to no hazard (Otene and Nnadi, 2019).

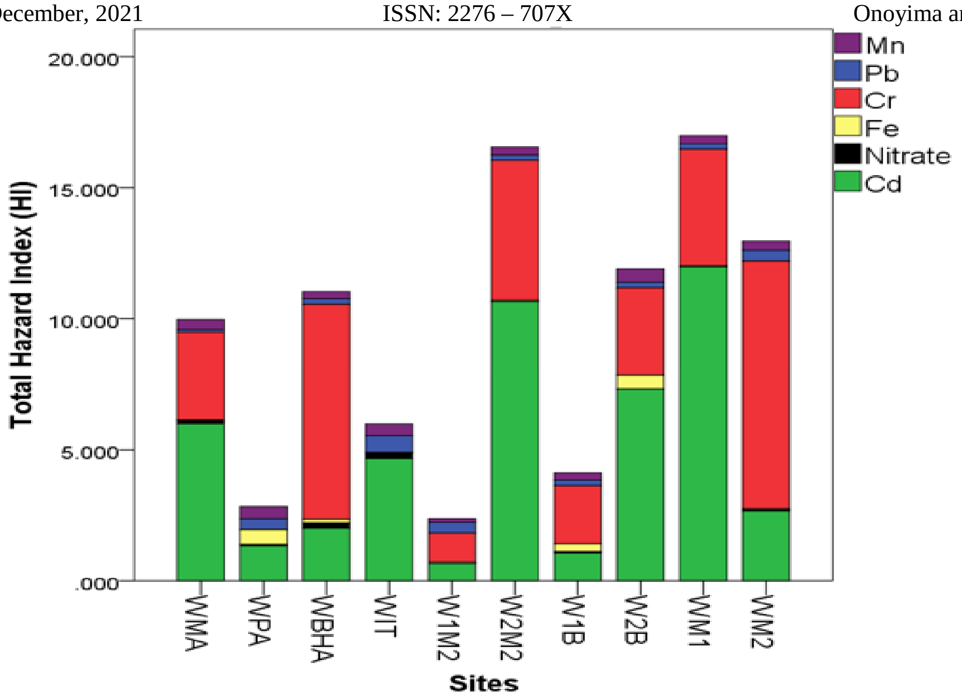

Figure 3: Total hazard quotient and total hazard index of the pollutants through oral and dermal pathways

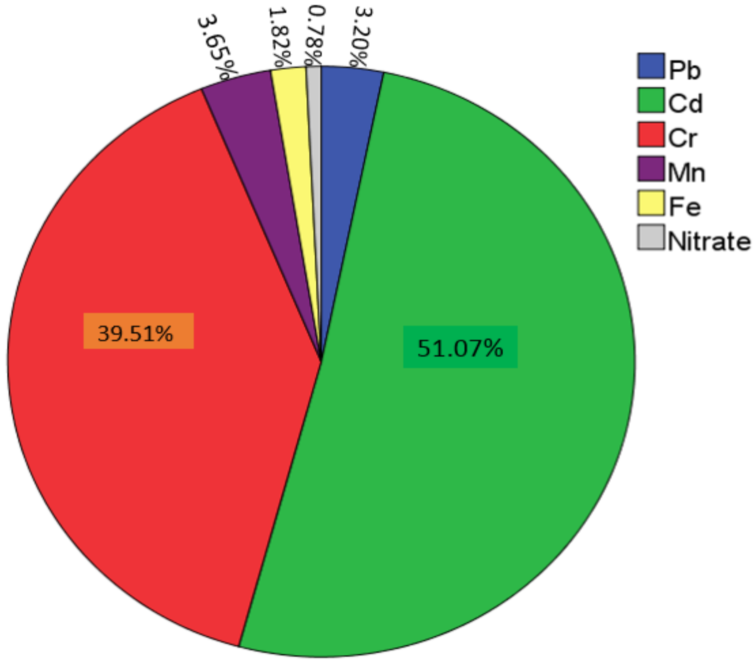

Figure 4: Percentage contributions of the pollutants to non-carcinogenic risk due to oral and dermal pathway

Carcinogenic Risk Assessment

Carcinogenic Risk is the incremental risk or the probability of an individual developing cancer over life time (Gebeyehu and Bayissa, 2020). The normal range set by USEPA is from 1.0 x 10^{-6} to 1.0 x 10^{-4} (USEPA, 2011). The results of this study are presented in Table 6. It shows that the cancer risk due to Pb ranged from 1.22 x 10^{-6} to 7.28 x 10^{-6}, showing that there is no cancer risk due to Pb from the groundwater of the area. However, the range of values for Cd and Cr are 1.09 x 10^{-4} – 9.77 x 10^{-3} and 1.43 x 10^{-3} – 1.21 x 10^{-2} respectively, showing that Cd and Cr exceeded the upper threshold of 1.0 x 10^{-4} at all the sites. There is therefore a life time probability of contracting cancer due to groundwater contaminated with Cr and Cd in the study area. Hence, Cr and Cd should be placed for further consideration as chemicals of concern with regard to the studied population.

Table 6: Carcinogenic risk of the pollutants in the groundwater of the area

Site	Pb	Cd	Cr
WMA	1.22×10^{-6}	9.77×10^{-3}	4.29×10^{-3}
WPA	4.85×10^{-6}	2.17×10^{-4}	-
WBHA	2.43×10^{-6}	3.26×10^{-4}	1.06×10^{-2}
WIT	7.28×10^{-6}	7.60×10^{-4}	-
W1M2	4.85×10^{-6}	1.09×10^{-4}	1.43×10^{-3}
W2M2	2.43×10^{-6}	1.74×10^{-3}	6.85×10^{-3}
W1B	2.43×10^{-6}	1.41×10^{-4}	2.86×10^{-3}
W2B	2.43×10^{-6}	1.19×10^{-3}	4.29×10^{-3}
WM1	2.43×10^{-6}	1.95×10^{-3}	5.74×10^{-3}
WM2	4.85×10^{-6}	4.34×10^{-4}	1.21×10^{-2}

CONCLUSION

There is indication that the groundwater of the area is contaminated and mostly not safe for drinking. The contaminants of concern are heavy metals, mostly Cd and Cr which accounted for 90.58% to the total non-carcinogenic risk in the groundwater. There is also life time probability of contacting cancer from the groundwater due to Cd and Cr contamination. The groundwater of the area should be continuously monitored to avoid the carcinogenic and non-carcinogenic risk arising from toxic pollutants from the groundwater.

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