Health implications of selected heavy metals around hydrocarbon impacted sites in the Niger Delta: A preliminary investigation

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GSC Advanced Research and Reviews, 2022, 11(01), 113–128

Publication history: Received on 06 March 2022; revised on 14 April 2022; accepted on 16 April 2022

Article DOI: https://doi.org/10.30574/gscarr.2022.11.1.0103

Abstract

This study appraises the levels of Heavy metals and health implications in Khana and Gokana LGAs of Rivers State, Nigeria. A random sampling approach was employed for groundwater sampling and samples were collected from a total of twenty-two (22) boreholes in the area. A total of ten (10) residential boreholes were sampled in Khana LGA and twelve (12) in Gokana LGA. Iron (Fe) in Khana area showed concentration exceeding WHO and NSDWQ regulatory limits of 0.3mg/l in BH2, BH4, BH5, BH7, BH8, BH9 and BH10 while in Gokana area, BH11, BH12, BH14, BH17, BH19 and BH20 had Fe concentration exceeding the regulatory requirements. The result shows that Fe concentration in groundwater in the study area is significantly high to render the groundwater unsuitable for oral ingestion. Manganese concentration in samples from Khana showed concentrations above WHO standard in BH3, BH6 and BH9 while only BH16 exceeded the regulatory limit in Gokana area and then all other samples concentrations were within WHO regulatory limit for potable drinking water. Copper (Cu) and Lead (Pb) concentration showed levels below permissible limits in all samples analyzed. The results of hazard index from oral ingestion of water from boreholes in the area ranged from 0.30 to 1.13, with an average of 0.69. Based on USEPA classification, apart from BH9 and BH16 where harmful effect from groundwater consumption is recognized, there is no non-carcinogenic harmful effect that may arise from oral ingestion of most of the groundwater sources in the area. The spatial map revealed that the southern central area is a hot spot that needs urgent attention. The results of hazard index from dermal contact with groundwater in the area ranged from 0.02 to 0.36, with an average of 0.18. Carcinogenic health risk from oral ingestion of groundwater in the area ranged from 1.07 to 16.69, with an average of 8.69. Similarly, cancer risk from dermal contact with groundwater in the area ranged from 0.02 to 0.25 with an average of 0.13. Based on USEPA guidelines as revealed in this study, oral ingestion or dermal contact with groundwater from any borehole cited in Gokana and Khana areas are associated with possible cancer risk. The results and of this study will serve as a baseline data in the investigation of the suitability of groundwater in oil producing areas of Khana and Gokana LGAs of Rivers State for human consumption. Thus, the study has revealed the need of an urgent remediation of oil impacted areas in the study area to mitigate further impact on human health.

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Keywords: Health Risk; Heavy Metals; Groundwater; Drinking Water; Carcinogenic; Hydrocarbon Impacted Sites

1. Introduction

Heavy metals are naturally occurring elements that have a high atomic weight and a density at least five (5) times greater than that of water [1]. Their multiple industrial, domestic, agricultural, medical and technological applications have led to their wide distribution in the environment; raising concerns over their potential effects on human health and the environment. The assumption that heaviness and toxicity are inter-related, heavy metals also includes metalloids, such as arsenic, that are able to induce toxicity at low level of exposure [2].

Metals constituting important class of the toxic substances encountered day to day life during occupational and environmental circumstances. The impact of such toxic agents on human health is presently an area of passionate interest because of ubiquity of its exposure, by increasing the use of wide verity of the metals in industry and in daily life work hood [3, 4]

Heavy metals are significant environmental pollutants and toxicity of theirs is major problem for ecological, evolutionary, nutritional and environmental balances [5]. In recent years, there has been an increasing ecological and global public health concern associated with environmental contamination by these metals. Also, human exposure has risen dramatically as a result of an exponential increase of their use in several industrial, agricultural, domestic and technological applications [6].

Reported sources of heavy metals in the environment include geogenic, industrial, agricultural, pharmaceutical, domestic effluents, and atmospheric sources (He et.al 2005). Environmental pollution is very prominent in point source areas such as mining, foundries and smelters, and other metal-based industrial operations as earlier reported by [1, 6, and 7].

Heavy metal contamination refers to the excessive deposition of toxic heavy metals in the soil caused by human activities. Heavy metals in the soil include some significant metals of biological toxicity, such as mercury (Hg), cadmium (Cd), lead (Pb), chromium (Cr) and arsenic (As). They also include other heavy metals of certain biological toxicity, such as zinc (Zn), copper (Cu), nickel (Ni), stannum (Sn), vanadium (V), and so on. In recent years, with the development of the global economy, both type and content of heavy metals in the soil caused by human activities have gradually increased, resulting in the deterioration of the environment as earlier reported by [8, 9, 10, 11, 12, and 13]. Heavy metals are highly hazardous to the environment and organisms. It can be enriched through the food chain. Once the soil suffers from heavy metal contamination, it is difficult to be remediated.

1.1. Source of Contamination of heavy metal in Water

1.1.1. Natural sources

In nature excessive levels of trace metals may occur by geological phenomena like volcanic eruptions, weathering of rocks, leaching into rivers, lakes and oceans due to action of water. Anthropogenic Sources: Small amounts of heavy metals are released while mining and uncontrolled smelting of large quantities of metal, ores in open fires. With the industrial revolution, metals were extracted from natural resources and processed in the industries from where heavy metals passed onto into the atmosphere. Similarly traces of heavy metals get into the environment through discharge of waste - both domestic, agricultural and from auto exhausts. Following list shows the various human activities through which heavy metals get into the environment; Smelting or processing of ores of metals, mining, burning of fossil fuels such as coal, petrol, kerosene oil, Discharging Agricultural waste, Discharging Industrial and Domestic waste, wastes from Auto exhaust and pesticides containing compounds (salts) of heavy metals [14].

1.2. Location and Geology of the Area

1.2.1. Description of the Study Area

The study area is the oil producing communities within Khana and Gokana LGAs in Rivers State. The area is located geographically within Latitude 4°36’36.51”N -- 4°43’42.21”N and Longitude 7°15’12.00”E -- 7°26’42.97”E. The climate of an area plays a major role in determining the vegetation of the locality. The vegetation of Niger Delta can be described by two major regions, namely the swampy forest region (coastal environment) and the rain forest region (fluvial environment). The swamp forest region can further be subdivided into the mangrove or saltwater swamp forest and the freshwater swamp forest. The saltwater swamp forest is characterized by the presence of several varieties of mangrove trees. This region forms the zone of brackish water i.e. the mixture of salt water and fresh water. The
freshwater swamp forest is formed from the influence of the tidal water. This region is characterized by raffia palms that cover the whole of the central portions of the Delta.

**Figure 1** Map showing sample points in the study locations

**Figure 2** Tectonic Map Showing the Niger Delta

**Figure 3** Stratigraphic Column of Niger Delta Formations[15]

The study area is Khana and Gokana L.G.A. of Rivers State (figure 1), located within the Niger Delta region of Nigeria, situated in the Gulf of Guinea, therefore, has same geology as the Niger Delta. The Niger Delta Basin is perhaps the most
prolific basin in Sub-Saharan Africa with respect to its petroleum resources (figure 2). The Niger Delta is composed of marine shale as the base of its stratification, (figure 3) overlying it is an intercalation of sand and shale as the intermediate layer, then the topmost layer is sandstone. The groundwater occurrence is a multi-aquifer system because of the presence of certain clayey strata in formations of various thicknesses that acts as confining layer between two distinct aquiferous rock strata. The present-day Niger Delta was formed during the Tertiary period as a result of the interplay between subsidence and deposition arising from a succession of transgression and regression of the three-tertiary subsurface litho-stratigraphic units of Akata, Agbada, and Benin Formations [16]. Further studies and evidence from deep wells drilled in the Niger Delta has also proven that the Niger Delta has a three litho-stratigraphic depositional succession (Akata, Agbada and Benin Formations) with an approximate average thickness of over 5000m of sediment body.

2. Material and methods

2.1. Groundwater Sampling

Table 1 Sampling location and geographic references for the sampled boreholes

| Location      | Borehole ID | Easting  | Northing  |
|---------------|-------------|----------|-----------|
| Khana L.G.A.  | BH1         | 318428.88| 515856.14 |
|               | BH2         | 317976.04| 516741.85 |
|               | BH3         | 320007.51| 517190.53 |
|               | BH4         | 318200.19| 517703.40 |
|               | BH5         | 319181.86| 515201.95 |
|               | BH6         | 320215.87| 516128.46 |
|               | BH7         | 317566.83| 517306.79 |
|               | BH8         | 317724.13| 518146.85 |
|               | BH9         | 317774.02| 515758.14 |
|               | BH10        | 317370.54| 518766.95 |
| Gokana L.G.A. | BH11        | 311415.80| 515607.34 |
|               | BH12        | 314641.10| 518751.29 |
|               | BH13        | 316157.97| 517409.62 |
|               | BH14        | 315540.04| 518848.68 |
|               | BH15        | 315304.79| 517898.21 |
|               | BH16        | 315401.34| 516504.62 |
|               | BH17        | 313590.93| 515734.83 |
|               | BH18        | 313148.27| 516222.46 |
|               | BH19        | 313803.46| 516453.13 |
|               | BH20        | 313094.83| 517074.10 |
|               | BH21        | 314237.74| 517104.54 |
|               | BH22        | 313385.94| 518168.20 |

A random sampling approach was adopted in groundwater sampling in Khana and Gokana local government areas of Rivers State. Groundwater samples were collected from a total of twenty-two (22) boreholes in the area (Table 1). Ten (10) residential boreholes were sampled in Khana while 12 boreholes were sampled in Gokana local government area. At each borehole where water samples were to be collected, the sterilized sample bottles were thoroughly rinsed with
the water to be sampled before actual samples were collected. The water was allowed to flow freely for about 5 minutes in order to clear all dissolved solids that may be stuck to the walls of the pipes and tap. The sample bottles were allowed to fill to the brim and corked immediately to minimize escape of dissolved oxygen. Samples were collected in duplicates for analysis of heavy metals. Samples for heavy metal analysis were collected in plastic bottles. Water samples for the determination of heavy metals were stabilized by adding few drops of diluted hydrochloric acid to them after collection. All sampling bottles were neatly labelled after sample collection and stored in an ice tight chest for onward transport to the laboratory for analysis. All sampling locations were noted with the aid of a global positioning system.

2.2. Heavy Metals

The heavy metals were determined in accordance with APHA3030B/3114B, APHA 3111B, APHA 3112B, and ASTM D3859 using an atomic absorption spectrophotometer (AAS). This method involves direct aspiration of sample into an air/acetylene flame generated by a hollow cathode lamp at a specific wavelength peculiar only to the metal under investigation. The minimum acceptable absorbance from which metal concentrations were calculated was 0.004 and values below this equipment detection limits for the various heavy metals analysed were as follows in mg/l: cadmium (Cd) = 0.002mg/L; chromium (Cr) = 0.01mg/L; copper (Cu) = 0.05mg/L; iron (Fe) = 0.05mg/L and lead (Pb) = 0.01mg/L.

Table 2 Analytical methods used for heavy metal samples

| Class         | Parameter | Symbol | Unit | Type of Test | Laboratory Standard |
|---------------|-----------|--------|------|--------------|---------------------|
| Heavy Metals  | Iron      | Fe     | mg/L | Laboratory   | APHA 3111B          |
|               | Zinc      | Zn     | mg/L | Laboratory   | APHA 3111B          |
|               | Manganese | Mn     | mg/L | Laboratory   | APHA 3111B          |
|               | Chromium  | Cr     | mg/L | Laboratory   | APHA 3111D          |
|               | Lead      | Pb     | mg/L | Laboratory   | APHA 3111B          |
|               | Nickel    | Ni     | mg/L | Laboratory   | APHA 3111B          |
|               | Cadmium   | Cd     | mg/L | Laboratory   | APHA 3111B          |
|               | Copper    | Cu     | mg/L | Laboratory   | APHA 3111B          |

2.3. Estimation of Degree of Metal Contamination

The degree of contamination (Cd) method used as reference for the estimation of the extent of metal pollution [17]. In this method, the quality of water is evaluated by computing the extent of contamination using the sum of the contamination factors of each metal component exceeding the upper permissible limit [18]. The Cd method thus, summarizes the combined effects of a number of quality parameters considered to be unsafe in drinking water [18]. [19] Proposed that, the degree of toxic heavy metal contamination (Cd) may be presented as in Eqn. 1:

\[ C_d = \sum_{i=1}^{n} C_f \]  

(1)

where, \( C_i \) is the contamination factor calculated using Eqn. 2:

\[ C_f = \frac{C_{Mi}}{C_{Si}} \]  

(2)

where, \( C_{Mi} \) and \( C_{Si} \) are the analytical value and upper permissible concentration for the ith component respectively. The degree of toxic heavy metal contamination in any water resource have been categorized as, low (Cd < 1), medium (Cd =1-3), and high (Cd > 3) [17].

2.4. Carcinogenic and Non-Carcinogenic Health Risk Assessment

The health risk from groundwater consumption was assessed in the study area. The adverse health effect due to exposure to heavy metal over a period of time is quantified in order to determine the magnitude of risk, which could be expressed in terms of carcinogenic and non-carcinogenic health effects [20]. The toxicity risk factors estimated are the reference dose (RfD) for non-carcinogenic risk and slope factor for carcinogenic risk characterizations [21]. In order to
adequately characterize these risks, the average daily dose (ADD) for the metals must be properly estimated. Average daily dose (ADD) is the estimation of the magnitude, frequency, and duration of human exposure to each heavy metal or metalloid in the environment. Exposure of human beings to the metals could occur via three main pathways including direct ingestion, inhalation and dermal absorption through skin; however, ingestion and dermal absorption are common routes for water exposure. According to the [22] as proposed in the Risk Assessment Guidance for Superfund (RAGS) methodology, the numeric expressions for risk assessment may be presented as in Eqs. 3 and 4 as follows;

$$D_{\text{ingestion}} = \frac{C_{\text{water}} \times IR \times EF \times ED}{BW \times AT} \tag{3}$$

$$D_{\text{dermal}} = \frac{C_{\text{water}} \times SA \times IR \times Kp \times EF \times CF}{BW \times AT} \tag{4}$$

where, $D_{\text{ingestion}}$: exposure dose through ingestion of water ($\mu$g/(kg day)); $D_{\text{dermal}}$: exposure dose through dermal absorption ($\mu$g/(kg day)); $C_{\text{water}}$: concentration of metals estimated in groundwater ($\mu$g/l); IR: ingestion rate (2.2 l/day); EF: exposure frequency (365 days/year); ED: exposure duration (30 years); BW: average body weight (70 kg); AT: averaging time (25,550 days); SA: exposed skin area (18,000 cm$^2$); ET: exposure time (0.58 h/day); CF: unit conversion factor (0.001 l/cm$^3$); and $K_p$(cm/h): dermal permeability coefficient. The $K_p$ for the metals utilized in this study are as follows (Cd, Fe, Cu, Mn = 0.001 cm/h; Pb = 0.004 cm/h; Zn = 0.0006 cm/h; Cr = 0.002 cm/h) [22]. Oral reference dose (RfD) of the various heavy metals from dermal absorption used for the determination of toxicity responses as proposed by [22] are presented as follows; (Fe = 140, Zn = 60, Mn = 1.84, Cr = 0.015, Pb = 0.42, Cd = 0.025, Cu = 8), and (Fe = 700, Zn = 300, Mn = 14, Cr = 3, Pb = 1.4, Cd = 0.5, Cu = 40) through oral ingestion.

Potential non-carcinogenic risks for exposure to contaminants were assessed by comparison of the calculated contaminant exposures with respect to each exposure route and the reference dose (RfD) so as to produce the hazard quotient (HQ). The HQ may be defined as in Eqn. 5 [22];

$$HQ_{\text{ingestion/dermal}} = \frac{D_{\text{ingestion/dermal}}}{RfD_{\text{ingestion/dermal}}} \tag{5}$$

Where, $HQ_{\text{ingestion/dermal}}$ is defined as the hazard quotient via ingestion or dermal contact and is unitless, and $RfD_{\text{ingestion/dermal}}$ is defined as the oral/dermal reference dose in $\mu$g/kg-day. The $RfD_{\text{ingestion}}$ and $RfD_{\text{dermal}}$ values were obtained from USEPA [23 and 24]. The hazard quotient (HQ) is a numeric estimate of the systemic toxicity potentially posed by a single element within a single route of exposure. According to [25 and 26], the toxic risk due to potentially hazardous substances in the same environmental media is presumed to be additive and the arithmetic sum of individual target hazard quotient and is equal to the hazard index (HI). To estimate the overall potential for non-carcinogenic effects posed by potentially hazardous substances, the computed HQs for each element are integrated and expressed as a hazard index (HI) as defined by Eqn. 6:

$$HI_{HQ_{\text{ingestion/dermal}}} = \sum_{i=1}^{n} HQ_{\text{ingestion/dermal}} \tag{6}$$

where, $HI_{HQ_{\text{ingestion/dermal}}}$ is defined as the hazard index via ingestion or dermal contact (unit less). According to the [22] where, HI < 1, there is no concern for potential human health risks caused by exposure to non-carcinogenic elements and where, HI > 1, there may be a concern for potential human health risks caused by exposure to non-carcinogenic elements.

Environmental Protection Agency defined carcinogenic or cancer risks (CR) as “the incremental probability of an individual to develop cancer, over a lifetime, as a result of exposure to a potential carcinogen”. Equation 3.17 was used to estimate the carcinogenic risks. The cancer slope factor (CSF) value ($\mu$g kg$^{-1}$ day$^{-1}$) is only available for Cd (6.1 $\mu$g kg$^{-1}$ day$^{-1}$), Pb (8.5 $\mu$g kg$^{-1}$ day$^{-1}$), and Cr (41 $\mu$g kg$^{-1}$ day$^{-1}$) [23], which were adopted from USEPA screening levels [23]. A risk level of $1 \times 10^{-6}$ has been considered as the point of excess cancer risk, indicating 1 per 1,000,000 chance of getting cancer via consumption of drinking water containing arsenic and toxic metals, estimated in $\mu$g L$^{-1}$ for 70 years. The safe point for carcinogenic risks must be lower than this level. The range of risks borderline by the EPA is $1 \times 10^{-4}$ to $1 \times 10^{-6}$ and unacceptable if the risks are surpassing $1 \times 10^{-4}$. A carcinogenic risk of $1 \times 10^{-4}$ poses health hazards; therefore, it is sufficiently large, poses health hazards, and need some sort of intervention and remediation [27].

$$CR = D \times CSF \tag{7}$$
3. Results and discussion

Heavy metals, Fe ranges from 0.01 mg/l to 0.70 mg/l with mean and SD of 0.37 ± 0.19 mg/l in Khana area, whereas in Gokana, Fe ranged from 0.18 to 063 mg/l with mean and SD of 0.32 ± 0.13 mg/l respectively. In Khana area, BH2, BH4, BH5, BH7, BH8, BH9 and BH10 had iron concentration exceeding WHO and NSDWQ regulatory limits of 0.30 mg/l; whereas in Gokana area, BH11, BH12, BH14, BH17, BH19 and BH20 had iron content exceeding the regulatory requirement. These results show that iron concentration in groundwater within the study area is significantly high to render the groundwater unsuitable for oral ingestion.

Zinc concentration ranges from 0.40 to 3.76 mg/l with mean and SD of 1.23 ± 1.27 mg/l in Khana, and from 0.23 to 0.95 mg/L with mean and SD of 0.59 ± 0.20 mg/l in Gokana area. Generally, WHO standard for Zn in potable drinking water is set at 5.0 mg/l. All the groundwater samples revealed Zn concentrations which are within the regulatory guideline. These results show that zinc is not a possible source of contamination of groundwater in the area.

Manganese ranged from 0.02 to 0.39 mg/l and from 0.01 to 0.43 mg/l in Khana and Gokana areas. The WHO standard for Mn in potable drinking water is set at 0.20 mg/l. In Khana area, only BH3, BH6 and BH9 exceeded this limit, while only BH16 exceeded the regulatory limit in Gokana area. All other boreholes had Mn concentrations within WHO regulatory limit for potable drinking water.

Chromium and Lead ranged from 0.0t to 0.08 mg/l and from 0.001 to 0.02 mg/L in Khana, while in Gokana, Cr and Pb ranged from <0.001 to 0.04 mg/l. The average Cr and Pb concentrations are 0.04 ± 0.03 mg/L and 0.009 ±0.008 mg/l in Khana L.G.A. and 0.04 ± 0.02 mg/l and 0.025 ± 0.01 mg/l in Gokana L.G.A. respectively. The WHO and NSDWQ regulatory limit for Cr and Pb in potable groundwater are 0.05 mg/l and 0.01 mg/l. Based on these guidelines, the average Cr and Pb concentrations in groundwater samples from Khana area are within regulatory requirements. Only Lead exceeded WHO regulatory limit at Gokana area. Nickel was below the detectable limit of the measuring instrument at all sampled boreholes.

Cadmium concentration ranges from 0.001 to 0.066 mg/l with mean and SD of 0.003 ± 0.0015 mg/L in Khana, and from 0.002 to 0.005 mg/l with mean and SD of 0.003 ± 0.001 mg/l in Gokana area. Generally, WHO standard for Cadmium in potable drinking water is set at 0.003 mg/L. Apart from BH3, BH6 and BH10 in Khana, and BH14, BH16, BH17, BH20 and BH22 in Gokana which exceeded WHO limit, all other groundwater samples revealed Cadmium concentrations which are within the regulatory guideline for potable drinking water.

Copper concentration ranges from 0.06 to 0.66 mg/L with mean and SD of 0.34 ± 0.020 mg/l in Khana, and from 0.09 to 0.62 mg/l with mean and SD of 0.38 ± 0.17 mg/l in Gokana area. Generally, WHO standard for copper in potable drinking water is set at 1.0 mg/l. Hence, all the groundwater samples revealed copper concentrations which are within the safe limit for oral ingestion.

3.1. Groundwater Contamination Degree

The groundwater contamination degree was evaluated to determine the level of groundwater contamination from heavy metals in the area. The metals utilized included Fe, Zn, Mn, Cr, Pb, Cd and Cu. The results of contamination degree ranges from 2.98 to 8.37 (Table 3), indicating moderate to high contamination degree as proposed by Rubio et al., (2000). The map showing the degree of contamination revealed that the north central part of the study area is most deteriorated with heavy metal contamination (Figure 4.). The results also show that lead and cadmium are the most significant heavy metals contributing to the high degree of contamination in the area (Table 3).

3.2. Health Risk Assessment

Health risk assessment was conducted in terms of non-carcinogenic and carcinogenic risk for adult’s resident in the area. The results of hazard index from oral ingestion of water from boreholes in the area ranged from 0.30 to 1.13, with an average of 0.69 (Table 4). Based on [22] classification, apart from BH9 and BH16 where harmful effect from groundwater consumption is recognized, there is no non-carcinogenic harmful effect that may arise from oral ingestion of most of the groundwater sources in the area. The spatial map showing the health risk areas from ingesting groundwater in the area (Fig. 6) revealed that the southern central area is a hot spot that needs urgent attention.

The results of hazard index from dermal contact with groundwater in the area ranged from 0.02 to 0.36, with an average of 0.18 (Table 5). Based on [22] classification, all the water sources have no harmful non-carcinogenic risk from dermal contact with groundwater in the area. Hence, the residents of the area can bathe and wash with these water sources without any associated health risk.
Figure 4 Histogram showing the average concentration of heavy metals in groundwater from the study area compared with WHO regulatory guidelines

Table 3 Contamination factors and degree of contamination for heavy metals in groundwater from the study area

| Symbol | Contamination Factors | Contamination Degree (CD) | CD Interpretation |
|--------|-----------------------|---------------------------|-------------------|
|        | Fe        | Zn   | Mn  | Cr   | Pb   | Cd   | Cu   |                  |
| BH1    | 0.77      | 0.09 | 0.30| 1.00 | 0.10 | 0.67 | 0.17 | 2.98 Moderate Contamination |
| BH2    | 1.47      | 0.11 | 0.40| 1.20 | 0.70 | 1.00 | 0.64 | 5.52 High Contamination |
| BH3    | 0.03      | 0.15 | 1.05| 0.80 | 0.30 | 1.33 | 0.34 | 4.00 High Contamination |
| BH4    | 1.37      | 0.08 | 0.45| 0.00 | 1.00 | 0.67 | 0.12 | 3.68 High Contamination |
| BH5    | 1.07      | 0.12 | 0.25| 1.20 | 0.90 | 1.00 | 0.06 | 4.59 High Contamination |
| BH6    | 0.73      | 0.09 | 1.10| 0.60 | 0.20 | 1.67 | 0.32 | 4.71 High Contamination |
| BH7    | 1.43      | 0.29 | 0.10| 1.60 | 2.00 | 0.67 | 0.41 | 6.50 High Contamination |
| BH8    | 1.70      | 0.75 | 0.25| 0.00 | 0.70 | 1.00 | 0.27 | 4.67 High Contamination |
| BH9    | 1.37      | 0.11 | 1.95| 0.80 | 2.00 | 0.33 | 0.66 | 7.22 High Contamination |
| BH10   | 2.33      | 0.67 | 0.15| 0.40 | 2.00 | 2.00 | 0.43 | 7.98 High Contamination |
| BH11   | 1.47      | 0.11 | 0.65| 1.20 | 3.00 | 0.67 | 0.32 | 7.41 High Contamination |
| BH12   | 2.10      | 0.11 | 0.25| 1.00 | 1.00 | 1.00 | 0.52 | 5.98 High Contamination |
| BH13   | 0.70      | 0.17 | 0.50| 0.60 | 3.00 | 0.67 | 0.11 | 5.75 High Contamination |
| BH14   | 1.07      | 0.05 | 0.30| 1.20 | 4.00 | 1.67 | 0.09 | 8.37 High Contamination |
| BH15   | 0.73      | 0.09 | 0.15| 1.40 | 2.00 | 1.00 | 0.34 | 5.71 High Contamination |
| BH16   | 0.60      | 0.13 | 2.15| 0.80 | 2.00 | 1.33 | 0.62 | 7.63 High Contamination |
| BH17   | 1.43      | 0.09 | 0.05| 0.40 | 0.00 | 1.67 | 0.48 | 4.12 High Contamination |
| BH18   | 0.93      | 0.16 | 0.15| 0.60 | 1.00 | 1.00 | 0.33 | 4.17 High Contamination |
| BH19   | 1.23      | 0.10 | 0.30| 1.00 | 3.00 | 1.00 | 0.38 | 7.02 High Contamination |
| BH20   | 1.13      | 0.12 | 0.60| 0.40 | 2.00 | 1.33 | 0.58 | 6.17 High Contamination |
| BH21   | 0.70      | 0.19 | 0.55| 0.00 | 4.00 | 0.67 | 0.46 | 6.57 High Contamination |
| BH22   | 0.63      | 0.10 | 0.25| 0.00 | 2.00 | 1.67 | 0.31 | 4.96 High Contamination |
Carcinogenic health risk from oral ingestion of groundwater in the area ranged from 1.07 to 16.69 (Table 6), with an average of 8.69. Similarly, cancer risk from dermal contact with groundwater in the area ranged from 0.02 to 0.25 with an average of 0.13 (Table 7). Based on [22] guidelines as presented in this study, oral ingestion or dermal contact with groundwater from any borehole cited in Gokana and Khana areas are associated with possible cancer risk. The maps presented in Figure 6 and 7 all show that the north central part of the area is the most significantly affected area and needs urgent remediation actions.

Table 4 Results of non-carcinogenic health risk assessment arising from ingesting groundwater in the area.

| Symbol | Fe    | Zn    | Mn    | Cr   | Pb    | Cd    | Cu    | HI Interpretation |
|--------|-------|-------|-------|------|-------|-------|-------|-------------------|
| BH1    | 0.0044 | 0.0202 | 0.0577 | 0.2245 | 0.0096 | 0.0539 | 0.0572 | 0.4276 No Harmful Effect |
| BH2    | 0.0085 | 0.0251 | 0.0770 | 0.2694 | 0.0673 | 0.0808 | 0.2155 | 0.7436 No Harmful Effect |
| BH3    | 0.0002 | 0.0328 | 0.2020 | 0.1796 | 0.0289 | 0.1078 | 0.1145 | 0.6657 No Harmful Effect |
| BH4    | 0.0079 | 0.0180 | 0.0866 | 0.0962 | 0.0539 | 0.0404 | 0.3029 | 0.5377 No Harmful Effect |
| BH5    | 0.0062 | 0.0265 | 0.0481 | 0.2694 | 0.0866 | 0.0808 | 0.0202 | 0.5377 No Harmful Effect |
| BH6    | 0.0042 | 0.0193 | 0.2117 | 0.1347 | 0.0192 | 0.1347 | 0.1078 | 0.6316 No Harmful Effect |
| BH7    | 0.0083 | 0.0651 | 0.0192 | 0.3592 | 0.1924 | 0.0539 | 0.1381 | 0.8362 No Harmful Effect |
| BH8    | 0.0098 | 0.1688 | 0.0481 | -     | 0.0673 | 0.0808 | 0.0909 | 0.4658 No Harmful Effect |
| BH9    | 0.0079 | 0.0242 | 0.3752 | 0.1796 | 0.1924 | 0.0269 | 0.2222 | 1.0285 Harmful Effect |
| BH10   | 0.0135 | 0.1504 | 0.0289 | 0.0898 | 0.1924 | 0.1616 | 0.1448 | 0.7814 No Harmful Effect |
| BH11   | 0.0085 | 0.0247 | 0.1251 | 0.2694 | 0.2886 | 0.0539 | 0.1078 | 0.8779 No Harmful Effect |
| BH12   | 0.0121 | 0.0251 | 0.0481 | 0.2245 | 0.0962 | 0.0808 | 0.1751 | 0.6620 No Harmful Effect |
| BH13   | 0.0040 | 0.0391 | 0.0962 | 0.1347 | 0.2886 | 0.0539 | 0.0370 | 0.6536 No Harmful Effect |
| BH14   | 0.0062 | 0.0103 | 0.0577 | 0.2694 | 0.3848 | 0.1347 | 0.0303 | 0.8934 No Harmful Effect |
| BH15   | 0.0042 | 0.0193 | 0.0289 | 0.3143 | 0.1924 | 0.0808 | 0.1145 | 0.7544 No Harmful Effect |
| BH16   | 0.0035 | 0.0292 | 0.4137 | 0.1796 | 0.1924 | 0.1078 | 0.2088 | 1.1349 Harmful Effect |
| BH17   | 0.0083 | 0.0198 | 0.0096 | 0.0898 | -     | 0.1347 | 0.1616 | 0.4238 No Harmful Effect |
| BH18   | 0.0054 | 0.0350 | 0.0289 | 0.1347 | 0.0962 | 0.0808 | 0.1111 | 0.4921 No Harmful Effect |
| BH19   | 0.0071 | 0.0233 | 0.0577 | 0.2245 | 0.2886 | 0.0808 | 0.1280 | 0.8101 No Harmful Effect |
| BH20   | 0.0065 | 0.0274 | 0.1155 | 0.0898 | 0.1924 | 0.1078 | 0.1953 | 0.7347 No Harmful Effect |
| BH21   | 0.0040 | 0.0427 | 0.1058 | -     | 0.3848 | 0.0539 | 0.1549 | 0.7461 No Harmful Effect |
| BH22   | 0.0037 | 0.0233 | 0.0481 | -     | 0.1924 | 0.1347 | 0.1044 | 0.5066 No Harmful Effect |
| Minimum| 0.0002 | 0.0103 | 0.0096 | 0.0898 | 0.0096 | 0.0269 | 0.0202 | 0.3029 No Harmful Effect |
| Maximum| 0.0135 | 0.1688 | 0.4137 | 0.3592 | 0.3848 | 0.1616 | 0.2222 | 1.1349 No Harmful Effect |
| Average| 0.0066 | 0.0395 | 0.1041 | 0.2020 | 0.1691 | 0.0882 | 0.1218 | 0.6868 No Harmful Effect |

Results of non-carcinogenic health risk assessment arising from ingesting groundwater in the area is presented in Table 4. Similarly, the results of non-carcinogenic health risk assessment arising from dermal contact with groundwater in the area is presented in Table 5. The spatial variation maps showing the distribution of non-carcinogenic health risk from oral ingestion of groundwater and from dermal contact with groundwater in the area is presented in Figures 6 and 7 respectively. Meanwhile, results of carcinogenic health risk assessment arising from ingesting groundwater or from dermal contact with groundwater in the area is presented in Tables 6 and 7. Figure 6 is a map showing areas likely to
be affected by carcinogenic health risk arising from ingesting groundwater in the area, while Figure 7 shows areas likely
to be affected by cancer from dermal contact with groundwater in the area.

Table 5 Results of non-carcinogenic health risk assessment arising from dermal contact with groundwater in the area

| Symbol | Hazard Quotient | Hazard Index (HI) | HI Interpretation |
|--------|-----------------|-------------------|-------------------|
|        | Fe   | Zn   | Mn   | Cr   | Pb   | Cd   | Cu   |               |
| BH1    | 0.0001 | 0.0003 | 0.0021 | 0.2131 | 0.0006 | 0.0051 | 0.0014 | 0.2226 | No Harmful Effect |
| BH2    | 0.0002 | 0.0004 | 0.0028 | 0.2557 | 0.0043 | 0.0077 | 0.0051 | 0.2761 | No Harmful Effect |
| BH3    | 0.00005 | 0.0005 | 0.0073 | 0.1704 | 0.0018 | 0.0102 | 0.0027 | 0.1930 | No Harmful Effect |
| BH4    | 0.0002 | 0.0003 | 0.0031 | -   | 0.0061 | 0.0051 | 0.0010 | 0.0157 | No Harmful Effect |
| BH5    | 0.0001 | 0.0004 | 0.0017 | 0.2557 | 0.0055 | 0.0077 | 0.0005 | 0.2716 | No Harmful Effect |
| BH6    | 0.0001 | 0.0003 | 0.0076 | 0.1278 | 0.0012 | 0.0128 | 0.0026 | 0.1524 | No Harmful Effect |
| BH7    | 0.0002 | 0.0009 | 0.0007 | 0.3409 | 0.0122 | 0.0051 | 0.0033 | 0.3633 | No Harmful Effect |
| BH8    | 0.0002 | 0.0024 | 0.0017 | -   | 0.0043 | 0.0077 | 0.0022 | 0.0185 | No Harmful Effect |
| BH9    | 0.0002 | 0.0003 | 0.0135 | 0.1704 | 0.0122 | 0.0026 | 0.0053 | 0.2045 | No Harmful Effect |
| BH10   | 0.0003 | 0.0021 | 0.0010 | 0.0852 | 0.0122 | 0.0153 | 0.0034 | 0.1197 | No Harmful Effect |
| BH11   | 0.0002 | 0.0004 | 0.0045 | 0.2557 | 0.0183 | 0.0051 | 0.0026 | 0.2867 | No Harmful Effect |
| BH12   | 0.0003 | 0.0004 | 0.0017 | 0.2131 | 0.0061 | 0.0077 | 0.0042 | 0.2334 | No Harmful Effect |
| BH13   | 0.0001 | 0.0006 | 0.0035 | 0.1278 | 0.0183 | 0.0051 | 0.0009 | 0.1562 | No Harmful Effect |
| BH14   | 0.0001 | 0.0001 | 0.0021 | 0.2557 | 0.0243 | 0.0128 | 0.0007 | 0.2959 | No Harmful Effect |
| BH15   | 0.0001 | 0.0003 | 0.0010 | 0.2983 | 0.0122 | 0.0077 | 0.0027 | 0.3223 | No Harmful Effect |
| BH16   | 0.0001 | 0.0004 | 0.0149 | 0.1704 | 0.0122 | 0.0102 | 0.0050 | 0.2132 | No Harmful Effect |
| BH17   | 0.0002 | 0.0003 | 0.0003 | 0.0852 | -   | 0.0128 | 0.0038 | 0.1027 | No Harmful Effect |
| BH18   | 0.0001 | 0.0005 | 0.0010 | 0.1278 | 0.0061 | 0.0077 | 0.0026 | 0.1459 | No Harmful Effect |
| BH19   | 0.0002 | 0.0003 | 0.0021 | 0.2131 | 0.0183 | 0.0077 | 0.0030 | 0.2446 | No Harmful Effect |
| BH20   | 0.0002 | 0.0004 | 0.0042 | 0.0852 | 0.0122 | 0.0102 | 0.0046 | 0.1170 | No Harmful Effect |
| BH21   | 0.0001 | 0.0006 | 0.0038 | -   | 0.0243 | 0.0051 | 0.0037 | 0.0377 | No Harmful Effect |
| BH22   | 0.0001 | 0.0003 | 0.0017 | -   | 0.0122 | 0.0128 | 0.0025 | 0.0296 | No Harmful Effect |
| Minimum| 0.00005 | 0.0001 | 0.0003 | 0.0852 | 0.0006 | 0.0026 | 0.0005 | 0.0157 | No Harmful Effect |
| Maximum| 0.0003 | 0.0024 | 0.0149 | 0.3409 | 0.0243 | 0.0153 | 0.0053 | 0.3633 | No Harmful Effect |
| Average| 0.0002 | 0.0006 | 0.0038 | 0.1918 | 0.0107 | 0.0084 | 0.0029 | 0.1828 | No Harmful Effect |

Figure 5 Map showing the degree of heavy metal contamination within the study area
**Table 6** Results of carcinogenic health risk assessment arising from ingesting groundwater in the area

| Symbol | Hazard Quotient | Cancer Risk (CR) | CR Interpretation |
|--------|----------------|------------------|-------------------|
|        | Cr   | Pb   | Cd   |                  |
| BH1    | 9.204082 | 0.081778 | 0.328653 | 9.61451312 | Possible Cancer Risk |
| BH2    | 11.0449  | 0.572449 | 0.49298  | 12.1103265 | Possible Cancer Risk |
| BH3    | 7.363265 | 0.245335 | 0.657306 | 8.26590671 | Possible Cancer Risk |
| BH4    | -     | 0.817784 | 0.328653 | 1.14643732 | Possible Cancer Risk |
| BH5    | 11.0449 | 0.736006 | 0.49298  | 12.2738834 | Possible Cancer Risk |
| BH6    | 5.522449 | 0.163557 | 0.821633 | 6.50763848 | Possible Cancer Risk |
| BH7    | 14.72653 | 1.635569 | 0.328653 | 16.6907522 | Possible Cancer Risk |
| BH8    | -     | 0.572449 | 0.49298  | 1.06542857 | Possible Cancer Risk |
| BH9    | 7.363265 | 1.635569 | 0.164327 | 9.16316035 | Possible Cancer Risk |
| BH10   | 3.681633 | 1.635569 | 0.985959 | 6.30316035 | Possible Cancer Risk |
| BH11   | 11.0449 | 2.453353 | 0.328653 | 13.8269038 | Possible Cancer Risk |
| BH12   | 9.204082 | 0.817784 | 0.49298  | 10.5148455 | Possible Cancer Risk |
| BH13   | 5.522449 | 2.453353 | 0.328653 | 8.30445481 | Possible Cancer Risk |
| BH14   | 11.0449 | 3.271137 | 0.821633 | 15.1376676 | Possible Cancer Risk |
| BH15   | 12.88571 | 1.635569 | 0.49298  | 15.0142624 | Possible Cancer Risk |
| BH16   | 7.363265 | 1.635569 | 0.657306 | 9.65613994 | Possible Cancer Risk |
| BH17   | 3.681633 | -     | 0.821633 | 4.50326531 | Possible Cancer Risk |
| BH18   | 5.522449 | 0.817784 | 0.49298  | 6.83321283 | Possible Cancer Risk |
| BH19   | 9.204082 | 2.453353 | 0.49298  | 12.150414  | Possible Cancer Risk |
| BH20   | 3.681633 | 1.635569 | 0.657306 | 5.97450729 | Possible Cancer Risk |
| BH21   | -     | 3.271137 | 0.328653 | 3.59979009 | Possible Cancer Risk |
| BH22   | -     | 1.635569 | 0.821633 | 2.45720117 | Possible Cancer Risk |
| Minimum| 3.6816  | 0.0818  | 0.1643  | 1.0654   |
| Maximum| 14.7265 | 3.2711  | 0.9860  | 16.6908  |
| Average| 8.2837 | 1.4370 | 0.5378 | 8.6870 | Possible Cancer Risk |

**Figure 6** Map showing areas likely to be affected by non-carcinogenic health risk arising from ingesting groundwater in the area.
Table 7 Results of carcinogenic health risk assessment arising from dermal contact with groundwater in the area

| Symbol | Hazard Quotient | Cancer Risk (CR) | CR Interpretation         |
|--------|-----------------|------------------|---------------------------|
|        | Cr   | Pb   | Cd   |                      |
| BH1    | 0.1310 | 0.0022 | 0.0008 | 0.1340 | Possible Cancer Risk |
| BH2    | 0.1572 | 0.0152 | 0.0012 | 0.1736 | Possible Cancer Risk |
| BH3    | 0.1048 | 0.0065 | 0.0016 | 0.1129 | Possible Cancer Risk |
| BH4    | -    | 0.0217 | 0.0008 | 0.0225 | Possible Cancer Risk |
| BH5    | 0.1572 | 0.0196 | 0.0012 | 0.1780 | Possible Cancer Risk |
| BH6    | 0.0786 | 0.0043 | 0.0019 | 0.0849 | Possible Cancer Risk |
| BH7    | 0.2097 | 0.0435 | 0.0008 | 0.2539 | Possible Cancer Risk |
| BH8    | -    | 0.0152 | 0.0012 | 0.0164 | Possible Cancer Risk |
| BH9    | 0.1048 | 0.0435 | 0.0004 | 0.1487 | Possible Cancer Risk |
| BH10   | 0.0524 | 0.0435 | 0.0023 | 0.0982 | Possible Cancer Risk |
| BH11   | 0.1572 | 0.0652 | 0.0008 | 0.2232 | Possible Cancer Risk |
| BH12   | 0.1310 | 0.0217 | 0.0012 | 0.1539 | Possible Cancer Risk |
| BH13   | 0.0786 | 0.0652 | 0.0008 | 0.1446 | Possible Cancer Risk |
| BH14   | 0.1572 | 0.0869 | 0.0019 | 0.2461 | Possible Cancer Risk |
| BH15   | 0.1834 | 0.0435 | 0.0012 | 0.2281 | Possible Cancer Risk |
| BH16   | 0.1048 | 0.0435 | 0.0016 | 0.1499 | Possible Cancer Risk |
| BH17   | 0.0524 | -     | 0.0019 | 0.0544 | Possible Cancer Risk |
| BH18   | 0.0786 | 0.0217 | 0.0012 | 0.1015 | Possible Cancer Risk |
| BH19   | 0.1310 | 0.0652 | 0.0012 | 0.1974 | Possible Cancer Risk |
| BH20   | 0.0524 | 0.0435 | 0.0016 | 0.0974 | Possible Cancer Risk |
| BH21   | -    | 0.0869 | 0.0008 | 0.0877 | Possible Cancer Risk |
| BH22   | -    | 0.0435 | 0.0019 | 0.0454 | Possible Cancer Risk |
| Minimum| 0.0524 | 0.0022 | 0.0004 | 0.0164 |                      |
| Maximum| 0.2097 | 0.0869 | 0.0023 | 0.2539 |                      |
| Average| 0.1179 | 0.0382 | 0.0013 | 0.1342 | Possible Cancer Risk |

Figure 7 Map showing areas likely to be affected by non-carcinogenic health risk arising from dermal contact with groundwater in the area
Figure 8 Map showing spatial variation in iron concentration across the study area

Figure 9 Map showing spatial variation in zinc concentration across the study area

Figure 10 Map showing spatial variation in copper concentration across the study area
Figure 11 Map showing spatial variation in Lead concentration across the study area

Figure 12 Map showing spatial variation in manganese concentration across the study area

Figure 13 Map showing spatial variation in chromium concentration across the study area
4. Conclusion

Iron (Fe) in Khana area showed concentration exceeding WHO and NSDWQ regulatory limits of 0.3mg/L in BH2, BH4, BH5, BH7, BH8, BH9 and BH10 while in Gokana area, BH11, BH12, BH14, BH17, BH19 and BH20 had Fe concentration exceeding the regulatory requirements. The result shows that Fe concentration in groundwater in the study area is significantly high to render the groundwater unsuitable for oral ingestion. Manganese concentration in samples from Khana showed concentrations above WHO standard in BH3, BH6 and BH9 while only BH16 exceeded the regulatory limit in Gokana area and then all other samples concentrations were within WHO regulatory limit for potable drinking water. Copper (Cu) and Lead (Pb) concentration showed levels below permissible limits in all samples analyzed.

The results and of this study will serve as a baseline data in the investigation of the suitability of groundwater in oil producing areas of Khana and Gokana LGAs of Rivers State for human consumption. Thus, the study has revealed the need of an urgent remediation of oil impacted areas in the study area to mitigate further impact on human health.

Compliance with ethical standards

Acknowledgments

The Authors are grateful to Laboratory Technologists in Geology Department, University of Port Harcourt, Nigeria.

Disclosure of conflict of interest

The Authors declares that there is no conflict of interest.

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