

Spatial Distribution and Health Implications of Trace Elements in the Groundwater of Ado-Ekiti, Southwestern Nigeria

O.S Ayodele

Federal University of Technology Akure

sunday daramola (✉ sodarmola@futa.edu.ng)

Federal University of Technology Akure <https://orcid.org/0000-0003-1606-3084>

A.A Oyedele

Ekiti state university

Research Article

Keywords: Ado-Ekiti, Groundwater, Trace Elements, Contamination, Hazard Quotient, Hazard Index

Posted Date: March 9th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1399569/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

The spatial variations, potential origin and associated health risks of some trace elements in groundwater of Ado-Ekiti southwestern Nigeria were evaluated. Sixty groundwater samples were evaluated for the concentration of some selected trace elements which includes Mn, Fe, Pb, Zn, Cu and Cr. The results were presented as spatial distribution maps with respect to the world health organization and the Nigerian standards for drinking water. The result showed that the mean concentrations of some of the trace elements exceeded the threshold values stipulated by the world health organization and the Nigerian standard for drinking water in several sampling locations. However, all of the sampled wells recorded Pb concentration below both standards. The weathering of underlying bedrocks are key sources to some of the trace elements in the groundwater of the study area. A health risk assessment was undertaken using hazard quotient (HQ) and hazard index (HI). The HI values imply that the risk of contamination through oral ingestion pathway is from low through medium to high levels for both adults and children as the trace elements show mean HI values more than unity. The health risk assessment also indicates that the children are more susceptible to the non-carcinogenic risks than adults in the study area. Hence, some urgent proactive steps should be taken to avert the consequences of this health risk.

1.0 Introduction

The demand for groundwater have increased tremendously worldwide as a result of industrial and population growth in recent times. Groundwater contamination by human activities and its uncontrolled exploitation has resulted in a lot of pressure on groundwater supply (Barzegar et al (2018). Natural and anthropogenic sources of groundwater are recognized in literature (Peigei, 2021). Trace element is a major contaminant that ranks highly among the hazardous contaminants of water. This character has been attributed to their notable chemical characteristics such as chemical stability, weak degradation, wide range of sources, serious toxicity bioaccumulation and difficulty in remediation (Sun et al, 2016). Although, trace elements have been classified into essential (Copper, Chromium, Iron, Manganese, and Zinc) nonessential (Lead, Arsenic, and cadmium) groups, excessive intake of trace elements in groundwater can induce different kinds of cancer and other ailments in humans (Calderon, 2000; Dartey et al, 2017). It is on record that many countries worldwide such as Australia (Suh 2004), Hong Kong (Leung and Jiao 2006), Latvia (Levins and Gosk 2008), Canada (Shotyk et al. 2010), Bolivia (Ramos Ramos et al. 2012), USA (Toccalino et al. 2012), India (Golekar et al. 2013), Bangladesh (Muehe and Kappler 2014), Pakistan (Bhowmik et al. 2015), Nigeria (Ayedun et al. 2015); Uganda (Bakyayita et al. 2019), Tanzania (Rwiza et al. 2016). Egypt (Redwan and Abdel Moneim 2016, Emababy and Redwan 2020); South Africa (Elumalai et al. 2017), Mexico (Mora et al. 2017), China (Lu et al. 2018) and Iran (Barzega et al 2018)) are suffering from groundwater contamination by trace elements. The need to understand the sources and distribution of trace elements cannot be overemphasized as this aids the sustainable and effective management of groundwater resources (Barzega et al 2018). (Frengstad et al. (2000) and Dar et al (2017) listed a number of natural and anthropogenic sources of trace elements in

groundwater. They include urbanization, land-use changes, mining, and local industries sewage sludge to soils greywater irrigation, salt water intrusion and groundwater host lithology.

Ado Ekiti is the capital city of Ekiti state in Nigeria. It is a fast developing city which is growing sporadically both in population and urban land use (Oriye, 2016). This uncontrolled expansion has led to a sporadic increase in groundwater exploitation for both domestic and agricultural purposes in the area. A number of authors which include (Talabi and Tijani, 2013; Oyedele et al, 2019) have evaluated the chemical quality of the groundwater in the area. However, there is a dearth of publications with specific focus on the trace element characteristics of groundwater in the area. Consequent upon this, this study aims to evaluate the spatial distribution of selected trace elements in the groundwater of Ado-Ekiti and determine their sources and health implications on the populace of the area.

1.2 Description of the Study Area

The study area is located within the southern part of Nigeria and extends from longitudes 5.18°E–5.29°E and latitudes 7.57°N–7.67° N (Figure 1). The area is well drained and it is located in a tropical region with distinct wet and dry seasons. The drainage pattern is controlled by the geology of the area, where most of the streams flow in the southwestern direction is propelled by the direction of the rugged upland (Oyedele et al, 2019). The average annual temperature is 25.1 °C and average annual rainfall ranges of 1344 mm/year on the southern part of the desert.

2.0 Geology And Hydrogeology

The study area lies within the Pre-Cambrian Basement Complex of SW-Nigeria which also constitutes part of the Pan-African mobile belt lying east of the West African Craton (Oyedele and Olayinka 2012). The five prominent lithologies include migmatites, gneisses, granites, quartzites and charnockites (Figure. 1) with the migmatites dominating over half of the study area and occurring as highly denuded hills of essentially fine-medium grained textures. The low-lying exposure of migmatites is typically foliated and has been intruded by granitic and charnockitic rocks in some places. The varieties of granitic rocks occupy about 25% of the total area of Ado Ekiti (Afolagboye et al, 2015) which constitutes the fine-grained granite, medium- to coarse grained varieties and porphyritic texture types. The charnockitic rocks occur in association with coarse grained porphyritic granites (Rahaman and Malomo (1983). Xenoliths occur frequently in charnockitic and granitic bodies. The quartzites are present in the form of elongated bodies enclosed within the granites, charnockites and migmatitic rocks. Pegmatite, aplite and quartz veins occur as minor intrusions into the granitic rocks. Field studies show that the charnockites occur as dark greenish grey and greasy, medium to fine grained and weakly foliated with occasional gneissic banding. The rock outcrops are fresh with rough external appearance and little signs of weathering. The rock is in contact with migmatite and granite with the exception of the small hills and inselbergs while the bedrocks are generally covered by weathered regolith composing mainly of clay and sandy materials which are capped by lateritic soils in places depending on the bedrock types. The basement complex rocks are mechanically competent and responds to imposed strain by brittle failure. Hence, the

unweathered or fresh crystalline rocks hardly possess any potentials in terms of groundwater occurrence and flow. This low potential is also partly due to the ruggedness of the terrain which results in a high runoff and low infiltration rates. Oyedele et al (2019) classified Ado-Ekiti as a high groundwater potential region due to its high lineament density discovered from satellite imagery analysis. Hydrogeologically, like any other basement terrain, groundwater occur in the study area in weathered regoliths and fractured parent rock zones. Hence, the magnitude and characteristic of aquifer in the study area are dependent on the depth and degree of weathering and fracturing of the underlying rocks. Recharge of the aquifers are primarily achieved by rainfall while the groundwater is under influent flow conditions.

Talabi and Tijani (2013) revealed that the overall hydrogeologic setting of Ado-Ekiti is predominantly characterized by the weathered regolith or saprolite units ranging from 4.3 to 15m in thickness with characteristically low yield of 6–246 l/min. therefore, groundwater in the study area occurs at shallow depths in pockets of weathered regolith aquifers existing mainly as unconfined to semi-confined groundwater table conditions. The variable aquifers are tapped through shallow hand-dug wells that terminate mostly in the saprolite unit. It is important to state here that, Groundwater in basement aquifers has been found to be highly vulnerable to contamination due to near to the ground protective capacity and numerous anthropogenic activities

3.0 Materials And Method Of Study

Sixty groundwater samples collected for this study are from hand dug wells used for domestic and agricultural purposes (Fig. 1). The groundwater samples were collected and reserved in polyethylene bottles of 500-ml capacity equipped of closure system with double caps and filled with zero head in order to minimize the exchange with the ambient air, stored in ice box in the field, then in refrigerator at 4°C until analysis. Each bottle was rinsed 3 times with the sampled groundwater before the final groundwater sample was collected to avoid any possible contamination. In the laboratory, the samples were filtered using 0.1-µm nitrocellulose membrane Millipore filter to eliminate fine particles of solids in suspension. One aliquot of 100 ml from each sample was acidified with drops of HNO₃ to preserve the metals. The samples were analyzed for selected trace elements which includes Fe, Mn, Cr, Cu, Pb and Zn using Varian Spectra 220 Atomic Absorption Spectrometer with GTA 110 at the Water Quality Control Lab at the Federal Polytechnic Ado-Ekiti. Field blank and duplicate procedures were used for quality control assurance. Calibration of equipment was performed linearly with Merck Standard Solutions for each element. Quality assurance and control of metal analyses were acquired by using duplicates, blank reagent, and standard reference materials (USGS Geochemical Reference Materials). The spatial distribution maps of the concentrations of the samples were created using ARCGIS 10.2 and classified based on the world health organization (2011) and Nigerians standard values for drinking water (2007). The method suggested by the U.S. Environmental Protection Agency (USEPA 1999) was used to determine the non-carcinogenic (chronic) human health risk of trace elements in the groundwater. Chronic daily intake (CDI) of a single trace element through direct ingestion for children and adults was calculated by Eq. 1 (USEPA 1999; Li et al. 2016; Wu and Sun 2016; Zhang et al. 2018).

where CDI is exposure dose through intake of groundwater (mg/kg per day), C_w is contaminant concentration in groundwater (mg/L), IRW is the water ingestion rate (L/day, IRW = 2 L/day for adults and 1 L/day for children), EF is exposure frequency (days/year, EF = 365 days/year), ED is exposure duration (years, ED = 70 years for adults and 6 years for children), BW is body weight (kg, BW = 70 kg for adults and 15 kg for children) and AT is average exposure time for non-carcinogens effects (days, AT = 25,550 days for adults and 2190 days for children) (Duggal et al. 2017; Barzegar et al. 2018, 2019).

$$CDI = \frac{C_w \times IRW \times EF \times ED}{BW \times AT}$$

1

.....

The hazard quotient (HQ) is employed for assessment of non-carcinogenic risk by using Eq. (2).

where RfD is the reference dose of a specific element (mg/kg per day) and considered as Fe (0.7), Cr (1.5), Mn (0.046), Zn (0.3), Pb (0.0035) and Cu (0.04) (mg/kg/day) (Barzegar et al. 2018, 2019).

The reference dose (RfD, unit in $\mu\text{g}/\text{Kg}/\text{day}$) of As, Fe, Mn and NO₃ is 0.3, 300, 20 and 1600 respectively.

233 Hazard index (HI) that is defined as the sum of HQ is used to evaluate the overall potential non234 carcinogenic posed by measured elements. Eq. (5) of HI is expressed as follows:

$$HQ = \frac{CDI}{RfD}$$

2

.....

$$HI = HQ_1 + HQ_2 + HQ_3 \dots \dots \dots HQ_n$$

3

.....

The classification of non-carcinogenic human health risk based on USEPA (1999) is displayed in Table 1 (Su et al. 2017; Ahmed et al, 2018). HI > 1 indicates that the non-carcinogenic risk of the contaminant exceeds the acceptable limit while an HI < 1 demonstrates that the non-carcinogenic risk is within the satisfactory limits (USEPA 1999;

Table 1
Classification of non-carcinogenic risk (USEPA, 1999)

RISK LEVEL	HI	Non-carcinogenic risk
1	< 0.1	Negligible
2	$\leq 0.1 < 1$	Low
3	$\geq 1 < 4$	Medium
4	> 4	High

4.0 Results And Discussion

The statistical summary of the concentration of the selected trace elements are shown in Table 2 while a discussion on the vulnerability, spatial distribution and health risk assessment are presented in the following paragraphs.

Table 2
statistical summary of the concentration of the trace elements.

Elements	Cu(mg/l)	Fe(mg/l)	Zn(mg/l)	Pb(mg/l)	Mn(mg/l)	Cr(mg/l)
min	0.00	0.01	0.00	0.0006	0.00	0.01
max	5.10	2.00	3.70	0.0100	6.05	23.00
meab	0.69	0.79	0.65	0.0080	0.70	2.08
median	1.09	1.73	0.91	0.0086	1.18	4.44
sdev	1.04	0.74	0.78	0.0006	1.09	3.98
WHO(2011)	2.00	0.05	3.00	0.0100	0.40	0.05
NSDW(2007)	1.00	0.30	3.00	0.0100	0.20	0.05

4.1 Vulnerability and Spatial Distribution of the trace elements

4.1.1 Manganese (Mn)

Manganese is one of the most abundant metals in the Earth's crust, usually occurring with iron, oxygen, sulfur and chlorine ATSDR (2012). Just like iron, Manganese is a redox sensitive element. Although manganese is an essential metal for the body, it recently became a metal of global concern when methyl cyclopentadienyl manganese tricarbonyl (MMT), which was known to be toxic was introduced as a gasoline additive. MMT has been claimed to be an occupational manganese hazard and linked with the development of Parkinson's disease-like syndrome of tremour, gait disorder, postural instability and cognitive disorder. Exposure to elevated levels of manganese can result in neurotoxicity. Manganism is a

neurological disease due to manganese characterized by rigidity, action tremour, a mask-like expression, gait disturbances, bradykinesia, micrographia, memory and cognitive dysfunction, and mood disorder. The symptoms of manganism are very similar to that of Parkinson disease. Liao *et al* (2018) stated that mineralogical composition of rocks, redox conditions and water flow conditions are the basic factors that influences the concentration of manganese bearing minerals such as Pyrolisite, magamite, braunite and rhodochrosite found in soils and rocks. Some pyroxene bearing minerals and mica group minerals such as montdorite are notable sources of Manganese. The manganese contents in the samples range from 0 to 6.05mg/l with an average of 0.619 which is higher than the specified limit by WHO (2011). Also, about 43.3% of the samples fell short of this specification. Afolagboye *et al* (2015) identified a prominent occurrence of manganese bearing minerals in all the rocks in the study area except quartzites. This is reflected in the meagre occurrence of manganese in water samples from areas underlain by quartzite. Excessive intake of manganese can lead to intellectual impairment and decreased intelligence quotients in school-aged children (Bouchard et al 2011). High manganese concentration are observed in parts of the area (Figure 2a and 2b). However, the highest concentrations are noticed in wells located around the porphyritic granite and charnockite region which are highly enriched in hornblende, biotite and pyroxene which are recognized sources of manganese (Caretero and Kruse, 2015). Spatial maps of manganese with respect to the world health organization and Nigerian standards are shown in figures 2a and 2b, many of the samples fulfill the WHO(2011) specification than the Nigerian standard.

4.1.2 Chromium (Cr)

In most cases, Chromium (III) compounds and some other species are much less toxic and has little or no health concerns, Chromium in its hexavalent form, is the most toxic species of chromium though problems. A recent work by Madukwe *et al* (2020) reiterated that Chromium (VI) may be corrosive and also cause allergic reactions to the body. Hence, breathing high levels of chromium (VI) can cause irritation to the lining of the nose and nose ulcers. In addition, it can cause anemia, irritations, ulcer, and sperm damage and impair the male reproductive system. Severe redness and swelling of the skin are also common allergies attributed to chromium (VI). In addition, human exposure to extremely high doses of chromium (VI) compounds can result in severe cardiovascular, respiratory, hematological, gastrointestinal, renal, hepatic and neurological effects and possibly death Engwa *et al.* (2018). Jardine *et al* (1999) noted that food appears to be the major source of intake (Robson, 2003). The analyses revealed that chromium range from 0.01-23mg/l with an average of 0.5mg/l. and the main sources of chromium are chromite, chromium bearing magnetite and ilmenite. Also, Chromate found in amphiboles, pyroxenes, biotite, magnetite, olivine and feldspars (Bricker and Jones, 1995). A minimal intake of chromium has been advocated as a result of its carcinogenic nature (WHO, 2011). 61.6% of the analyzed samples recorded concentrations greater than the maximum stipulated by NSDW (2007) and WHO(2011). Figure 2a depicts the spatial distribution of chromium in the study area. It is very clear from the map that most part of the area have concentrations higher than the permissible level recommended by both WHO and the Nigerian regulating body. As such, the populace could be at risk of diseases related to high intakes of chromium as stated above. Areas with extremely high concentrations are in the southern portion and the southwestern part of the study area.

4.1.3 Zinc (Zn)

Zinc is abundant in the earth's crust. It is a chalcophile metallic element and forms several minerals, including sphalerite (ZnS), the commonest Zn mineral, smithsonite (ZnCO₃) and zincite (ZnO), but is also widely dispersed as a trace element in pyroxene, amphibole, mica, garnet and magnetite. Andrews and Sutherland (2004). It is released to the environment from both natural and anthropogenic sources; however, releases from anthropogenic sources are greater than those from natural sources Barbera et al. (1991). Apart from the dissolution of zinc in water, which increases with acidity, zinc is immobile in water Gundersen and Steinnes (2003). Toxicity in human may occur if zinc concentration approaches 400 mg/kg and 3 mg/L in soil and water, respectively. This is characterized by symptoms of irritability, muscular stiffness and pain, loss of appetite and nausea. Zinc appears to have a protective effect against the toxicities of both cadmium and lead Fergusson (1990). Zn has been shown to exert adverse reproductive biochemical, physiological and behavioral effects on a variety of aquatic organisms as concentrations exceed 20 mg/kg. Toxicity is, however, influenced by many factors such as the temperature, hardness and pH of the water WHO (2011). WHO (2011) expects drinking water to contain a maximum zinc concentration of 3mg/l. it has the ability to form soluble compounds at neutral and acidic pH. Therefore it is among the most mobile heavy metals in groundwater (Malecki et al, 2017). It is used as an agent to protect iron pipelines against corrosion which may contaminate groundwater due to oxidation. Zinc naturally occurs in sphalerite, smithsonite, hemimporphite, wurtzite and hydrozincite (Emsley, 2001). Biotite is a notable carrier of zinc in granite (Ure and Berrow, (1982). It is important to state that zinc may be linked to an organic precursor derived from limestone or coral reefs. Khatri and Tyagi (2015) stressed that zinc is not related to a particular bedrock type due to its adsorption to iron hydroxides and anthropogenic sources from agrochemicals and residential areas. The groundwater samples recorded zinc content as ranging from 0.001-3.7 and a mean value of 0.603. The average value is lower than the maximum value specified by WHO (2011) and the NSDW (2007) with only on sample exceeding both standards. Zinc does not show critical variations within the study area as value notably fell below the total limiting value specified by NSDW(2007) and WHO(2011) except one of the samples from the well locations. This well is underlain by a biotite granite. Biotite which has been recognized as a main zinc carrier (Embaby and Redwan, 2019). Therefore the enrichment at this particular location can be attributed to the weathering of this rock.

4.1.4 Lead (Pb)

The general population is exposed to lead from air and food in roughly equal proportions. Its occurrence and concentrations in drinking water is generally below 5 mg/L, although much higher concentrations (above 100 mg/L) have been measured where lead fittings are present Howard and Bartram (2003). Owing to the decreasing use of lead-containing additives in petrol and of lead-containing solder in the food processing industry, concentrations in air and food are declining, and intake from drinking water constitutes a greater proportion of total intake of lead Sawyer et al. (1998). Lead is a highly toxic metal whose widespread use has caused extensive environmental contamination and health problems in many parts of the world. The common symptom of contamination of lead is lead poisoning which displays as

anemia because lead interferes with the formation of hemoglobin. It prevents iron uptake. Higher levels of lead may produce permanent brain damage and kidney dysfunction. Engwa et al. (2018) noted that among others acute exposure of lead can cause loss of appetite, fatigue, sleeplessness, hallucinations, vertigo, renal dysfunction, hypertension and arthritis, while chronic exposure can result in birth defects, mental retardation, autism, psychosis, allergies, paralysis, weight loss, dyslexia, hyperactivity, muscular weakness, kidney damage, brain damage, coma and may even cause death. The presence of the lead in natural water is largely linked to lead bearing minerals such as galena, and Cerussite (Liao et al 2018; Lu et al, 2018). Lead values range between 0.008 and 0.01, none of the water samples have concentrations higher than the limit specified by (NSDW, 2007) and WHO (2011). On the average, wells located within areas underlain by porphyritic granite have the highest lead concentration while those within the charnokites and quartzites recorded least mean values. The intake of lead results in tiredness, anemia, irritability behavior changes and impairment of intellectual functions (Tebbubt, 1983). It is also interesting that the lead concentration falls within the limiting values of the NSDW (2007) and WHO (2011).

4.1.5 Iron (Fe)

Iron is a redox sensitive element which exhibit a high solubility at low pH. The main sources of iron in natural water are iron oxide and hydroxide minerals such as hematite, limonite, magnetite, pyrite, siderite and iron silicate. They are prominent in amphiboles, pyroxenes and micas. Iron values range between 0.006 and 2µg/l with a mean of 0.7841 and based on the mean the order of abundance with respect to the bedrock is as follows: porphyritic granite>Charnokite>Migmatite > Quartzite. This is a reflection of the influence of the mineralogy of the host rock of the wells on the chemistry of the groundwater as the rocks with higher average values are very rich in iron bearing minerals such as pyroxene, mica and amphibole (Afolagboye et al, 2015). Excessive ingestion of iron can lead to life threatening conditions such as liver disease, heart problems and diabetes. Also, high occurrence of iron concentration produces rusty hydroxides in the wells and may cause staining in laundry and undesirable taste in beverages (Daramola, 2013). It is important to note that iron concentrations in areas underlain by basement rocks are usually less than 1mg/l and rarely exceeds 2mg/l (Daramola, 2013), the results of this study is consistent as the iron concentration in the samples are well below these values. The concentrations of iron is higher than the global limit in majority of the study area (figure...). Hence, the inhabitants are at the risk of the ailments related to excessive intake of iron. Also, some unpleasant metallic taste, rust colored stains in laundry and rough and scaly skins. The spatial maps based on the Nigerian specification indicates that areas that exceed the limits stipulated are slightly higher than that of the world health organization. The WHO (2011) specified a maximum concentration of 2mg/l for copper in drinking water. Copper occurrence in groundwater are usually attributed to copper sulphides such as chalcopyrite, chalcocite, copper carbonates, malachites etc (Mapoma et al , 2017). The concentration of copper in the water samples range between 0.002 and 5.1mg/l. only 8.3% exceed the WHO(2011) standard while 30% of the samples exceed the NSDW (2007) specification. Embaby and Redwan (2019) stated that higher copper concentration in water samples from wells in a granitic terrain reflects an alteration of copper bearing minerals. Although, despite the benefits of copper to human health, a higher concentration may cause

neurological disorder, hypertension, liver and kidney dysfunction (Ahmed, et al , 2018, Obasi and Akudinobi, 2020). The spatial distribution maps for copper indicates that the concentrations are higher only in few pockets of places running from south to the northern parts of the area. However, most of the sampled wells recorded concentrations lower than the maximum permissible value recommended the Nigerian regulating body as compared with the WHO(2011) standards as shown in the spatial distribution maps (figure 2c and d).

5.0 Health Risk Assessment

The results of the non-carcinogenic risk for the selected elements (Mn, Fe, Pb, Zn, Cu, Cr) are displayed in Fig. 3. The hazard quotient and the consequent non- carcinogenic risk are presented in Table 3. The hazard quotient ranges from 0.0015 to 4.007, 0.000269 to 0.089796, 0.000105 to 0.387619, 0.71837 to 0.689796, 0 to 4.13354, 0.0002 to 0.481905 for Cu, Fe, Zn, Pb, Mn and Cr respectively and corresponding averages of 0.487, 0.035, 0.063, 0.073, 0.423, 0.036 respectively. However, in the case of adults, the maximum hazards quotients for adults are 4.007, 0.089, 0.388, 0.090, 0.388, 0.090, 4.1335, 0.482 respectively followed by averages of 0.487, 0.035, 0.063, 0.074, 0.423, 0.036 in the same order. Also, based on the mean values the hazard quotient show an order of $Cu > Mn > Pb > Zn > Cr > Fe$. The mean HI value of the groundwater contaminants are much higher than unity for the children as about 53% of the samples recorded values higher than one while only 38% of the HI for adults recorded values higher than unity. For the HI values with respect to the children, 43.3% of the samples classify as low risk, 38.3% as medium risk and 18.3% classify as high risk. On the other hand, 63.3% of the samples classify as low risk while 36.7% and 1.6% of the samples classify as medium and high risk according to the HI values for the adults. This indicates that there is a considerable significant non-carcinogenic risk as the average HI for both adults and children is greater than 1. The average values also indicates that a greater non-carcinogenic effect of groundwater pollutants on children in the study area. A slight positive correlation (Fig. 4) exists between the depths of the wells and the HI for adults ($R^2 = 0.3$) and children ($R^2 = 0.2$). Spatial distribution of non-carcinogenic risk values for adults and children classified based on the USEPA (2009) classification are shown in Fig. 6. On this basis, the area was classified into low, medium and high risk regions. High risk areas for children are found in the mid-central part, central northern corner and the southwestern end of the area. It has been shown by Reham and Cheema (2017) and Ahmed et al (2018) that children shows four fold higher HI for non-cariogenic risk than the adults. However, in this study the risk level ranges from low, medium and high, through oral exposure pathways for both children and adults. Also, the mean HI of non-carcinogenic risk from this study is 2.12 times higher for children that adults.

Table 3

The non-carcinogenic risk of groundwater contaminants for both adults and children through drinking water ingestion in the study area

PARAMETERS		Cu	Fe	Zn	Pb	Mn	Cr
HQ for children	MINIMUM	0.0001	0.0004	0.0001	0.0005	0.0000	0.0007
	MAXIMUM	0.3400	0.1333	0.2467	0.0007	0.4033	1.5333
	MEDIAN	0.0037	0.0667	0.0090	0.0005	0.0067	0.0333
	MEAN	0.0413	0.0523	0.0402	0.0005	0.0413	0.1159
	STANDARD DEVIATION	0.0695	0.0493	0.0521	0.0000	0.0725	0.2651
HQ for Adult	MINIMUM	0.0001	0.0002	0.0000	0.0003	0.0000	0.0003
	MAXIMUM	0.1603	0.0629	0.1163	0.0003	0.1901	0.7229
	MEDIAN	0.0017	0.0314	0.0042	0.0003	0.0031	0.0157
	MEAN	0.0195	0.0246	0.0190	0.0003	0.0195	0.0547
	STANDARD DEVIATION	0.0328	0.0233	0.0246	0.0000	0.0342	0.1250
HI for Adult	MINIMUM	0.0827					
	MAXIMUM	4.7483					
	MEDIAN	0.5873					
	MEAN	1.1185					
	STANDARD DEVIATION	1.1700					
HI for children	MINIMUM	0.1754					
	MAXIMUM	10.0721					
	MEDIAN	1.2459					
	MEAN	2.3725					
	STANDARD DEVIATION	2.4819					

5.1 Conclusion

This research attempts to appraise the spatial distribution of Mn, Fe, Pb, Zn, Cu, Cr and associated health risks of drinking water from dug wells from Ado-Ekiti, southwestern Nigeria based on sixty water samples.

The results revealed that the concentrations of Mn, Fe, Zn, Cu, Cr exceeds the threshold values specified by the world health organization (2011) and the Nigerian standard for drinking water (2007) in several sampling locations. Also, none of the sampled wells recorded lead values greater than the specified limits by both world health organization and the Nigerian standard for drinking water. Areas with elevated concentrations were also clearly depicted by the spatial variation maps. The concentration of some of these elements in the groundwater also correlate with the mineralogical compositions of the underlying rocks in some of the sampling sites. The non-carcinogenic risk indicates that children are more susceptible to potential health risks than adults, therefore this requires an urgent attention to avert the consequences.

References

1. Afolagboye, L.O., A. O. Talabi and Akinola, O.O. (2015): Evaluation of selected basement complex rocks from Ado-Ekiti, SW Nigeria, as source of road construction aggregates. *Bull Eng Geol Environ.* 75:853–865 DOI 10.1007/s10064-015-0766-1
2. Ahmed, N., Bodrud-Doza, M., Towfiqul Islam, A.R.M., Hossain, S., Moniruzzaman, M., Deb, N., Bhuiyan, M.A.Q. (2018),, Appraising spatial variations of As, Fe, Mn and NO₃ contaminations associated health risks of drinking water from Surma basin, Bangladesh, *Chemosphere* doi: <https://doi.org/10.1016/j.chemosphere.2018.11.104>.
3. Andrews S, Sutherland RA (2004) Cu, Pb and Zn contamination in Nuuanu watershed, Oahu, Hawaii. *Sci Total Environ* 324(1–3):173–182
4. Ayedun, H., Gbadebo, A. M., Idowu, O. A., & Arowolo, T. A. (2015). Toxic elements in groundwater of Lagos and Ogun States, Southwest, Nigeria and their human health risk assessment. *Environmental Monitoring and Assessment*, 187, 351.
5. Barzegar, R ., Moghaddam A.A. Adamowski, J. and Nazemi, A.H. (2018): Assessing the potential origins and human health risks of trace elements in groundwater: A case study in the Khoy plain, Iran. *Environ Geochem Health*, [https://doi.org/10.1007/s10653-018-0194-9\(0123456789\).-volV\(0123456789\).](https://doi.org/10.1007/s10653-018-0194-9(0123456789).-volV(0123456789).)
6. Bakyayita, G. K., Norrström, A. C., & Kulabako, R. N. (2019). Assessment of levels, speciation, and toxicity of trace metal contaminants in selected shallow groundwater sources, surface runoff, wastewater, and surface water from designated streams in Lake Victoria Basin, Uganda. *J Environ Public Health*, 2019, 18p. <https://doi.org/10.1155/2019/6734017>.
7. Barbera R, Farre R, Mesado D (1991) Determination of cadmium, cobalt, copper, iron, lead, manganese, nickel and zinc in diets: development of a method. *Nahrung* 35(7):683–687
8. Bhowmik, A. K., Alamdar, A., Katsoyiannis, I., Shen, H., Ali, N., Ali, S. M., Bokhari, H., Schäfer, R. B., Musstjab, S. A., & Eqani, A. S. (2015). Mapping human health risks from exposure to trace metal contamination of drinking water sources in Pakistan. *Science of the Total Environment*, 538, 306–316. <https://doi.org/10.1016/j.scitotenv.2015.08.069>.

9. Bouchard, M. F., Sauvé, S., Barbeau, B., Legrand, M., Brodeur, M. E., Bouffard, T., Limoges, E., Bellinger, D. C., & Mergler, D. (2011). Intellectual impairment in schoolage children exposed to manganese from drinking water. *Environmental Health Perspectives*, 119, 138–143.
10. Bricker, O. P., & Jones, B. F. (1995). *Main factors affecting the composition of natural waters* (pp. 1–5). Boca Raton: CRC Press.
11. Calderon, R. L. (2000). The epidemiology of chemical contaminants of drinking water. *Food and Chemical Toxicology*, 38, S13–S20.
12. Carretero, S., & Kruse, E. (2015). Iron and manganese content in groundwater on the northeastern coast of the Buenos Aires Province, Argentina. *Environment and Earth Science*, 73, 1983–1995. <https://doi.org/10.1007/s12665-014-3546-5>.
13. Dar, F. A., Ganai, J. A., Ahmed, S., & Satyanarayanan, M. (2017). Groundwater trace element chemistry of the karstified limestone of Andhra Pradesh, India. *Environment and Earth Science*, 76, 673–619. <https://doi.org/10.1007/s12665-017-6972-3>.
14. Daramola, S. O. (2013). Groundwater quality assessment of some boreholes from Odo-Oro Ekiti, Southwestern Nigeria. *IOSR Journal Of Environmental Science, Toxicology And Food Technology*, 7(2), 58-62.
15. Elumalai, V., Brindha, K., & Lakshmanan, E. (2017). Human exposure risk assessment due to heavymetals in groundwaterby pollution index and multivariate statistical methods: a case study from South Africa. *Water*, 9, 234. <https://doi.org/10.3390/w9040234>.
16. Embaby, A. and Redwan, M. (2019): Sources and behavior of trace elements in groundwater in the South Eastern Desert, Egypt. *Environ Monit Assess* 191:686 <https://doi.org/10.1007/s10661-019-7868-3>
17. Emsley, J. (2001). *Nature's building blocks: an "A-Z guide to the elements"*. Oxford: Oxford University Press ISBN 0-19- 850340-5, 7 and 8, 1–529.
18. Engwa GA, Ferdinand PU, Nwalo FN, Unachukwu MN (2018) Mechanism and effects of heavy metal toxicity in humans, poisoning in the modern world—new tricks for an old dog? Ozgur Karcioglu and Banu Arslan, IntechOpen. <https://doi.org/10.5772/intechopen.82511>
19. Fergusson IE (1990) *The heavy elements chemistry, environmental impact and health effects*. Pergamon press, New York
20. Frengstad, B., Skrede, A. K. M., Banks, D., Krog, J. R., & Siewers, U. (2000). The chemistry of Norwegian groundwaters: III. The distribution of trace elements in 476 crystalline bedrock groundwaters, as analysed by ICP-MS techniques. *Science of the Total Environment*, 246(1), 21–40.
21. Golekar, R. B., Patil, S. N., & Baride, M. V. (2013). Human health risk due to trace element contamination in groundwater from the Anjani and Jhiri river catchment area in northern Maharashtra, India. *Earth Sciences Research Journal*, 17(1), 17–23.
22. Gundersen P, Steinnes E (2003) Influence of pH and TOC concentration on Cu, Zn, Cd, and Al speciation in rivers. *Water Res* 37:307–318

23. Howard KWF, Beck PJ (1993) Hydrogeochemical implications of groundwater contamination by road deicing chemicals. *J ContamHydrol* 12:245–268
24. Khatri, N., & Tyagi, S. (2015). Influences of natural and anthropogenic factors on surface and groundwater quality in rural and urban areas. *Front Life Sci*, 1, 23–39.
25. Jardine PM, Fendorf SE, Mayes MA (1999) Fate and transport of hexavalent chromium in undisturbed heterogeneous soil. *Environ Sci Technol* 33(17):2939–2944
26. Leung, C., & Jiao, J. J. (2006). Heavy metal and trace element distributions in groundwater in natural slopes and highly urbanized spaces in mid-levels area, Hong Kong. *Water Research*, 40, 753–767.
27. Levins, I., & Gosk, E. (2008). Trace elements in groundwater as indicators of anthropogenic Impact. *Environmental Geology*, 55, 285–290.
28. Li, P., Li, X., Meng, X., Li, M., & Zhang, Y. (2016). Appraising groundwater quality and health risks from contamination in a semiarid region of northwest China. *Exposure and Health*, 8(3), 361–379. <https://doi.org/10.1007/s12403-016-0205-y>.
29. Li, P., Karunanidhi, D., Subramani, T. and Srinivasamoorthy, K (2021). Sources and Consequences of Groundwater Contamination. *Arch Environ Contam Toxicol* **80**, 1–10 <https://doi.org/10.1007/s00244-020-00805-z>.
30. Liao, F., Wang, G., Shi, Z., Huang, X., Xu, F., Xu, Q., & Guo, L. (2018). Distributions, sources, and species of heavy metals/trace elements in shallow groundwater around the Poyang Lake, East China. *Expo Health*, 10, 211–227. <https://doi.org/10.1007/s12403-017-0256-8>.
31. Lu, Y., Zang, X., Yao, H., Zhang, S., Sun, S., & Liu, F. (2018). Assessment of trace metal contamination in groundwater in a highly urbanizing area of Shenfu New District, Northeast China. *Frontiers in Earth Science*, 12, 569–582. <https://doi.org/10.1007/s11707-018-0677-0>.
32. Madukwe, H.Y. Ibigbami, O.A. and Obasi, R.A.(2020): Assessment of Trace and Rare Earth Element Levels in Stream Sediments in Ijero-Ekiti Area, Southwest Nigeria. *Nature Environment and Pollution Technology*. Vol. 19, No. 2 pp. 421-439
33. Małeckki, J. J., Kadzikiewicz-Schoeneich, M., Eckstein, Y., Szostakiewicz-Hołownia, M., & Gruszczyński, T. (2017). Mobility of copper and zinc in near-surface groundwater as a function of the hypergenic zone lithology at the Kampinos National Park (Central Poland). *Environment and Earth Science*, 76, 276–216. <https://doi.org/10.1007/s12665-017-6527-7>.
34. Mapoma, H.W. T., Xie, X., Nyirenda, M. T., Zhang, L., Kaonga, C. C., & Mbewe, R. (2017). Trace elements geochemistry of fractured basement aquifer in southern Malawi: a case of Blantyre rural. *Journal of African Earth Sciences*, 131, 43–52.
35. Mora, A., Mahlknecht, J., Rosales-Lagarde, L., & Hernández- Antonio, A. (2017). Assessment of major ions and trace elements in groundwater supplied to the Monterrey metropolitan area, Nuevo León, Mexico. *Environmental Monitoring and Assessment*, 189, 394.
37. Muehe, E.M., & Kappler, A. (2014). Arsenic mobility and toxicity in South and South-east Asia—a review on biogeochemistry, health and socio-economic effects, remediation and risk predictions.

- Environmental Chemistry, 11, 483–495.
38. NSDW (2007): Nigeria Standard for drinking water NIGERIAN INDUSTRIAL STANDARD NIS 554: 2007 ICS 13.060.20
 39. Obasi, P.N. and Akudinobi, B.B. (2020) Potential health risk and levels of heavy metals in water resources of lead–zinc mining communities of Abakaliki, southeast Nigeria
 40. Oriye, O (2012): URBAN EXPANSION AND URBAN LAND USE IN ADO EKITI, NIGERIA. American Journal of Research Communication Vol 1 (2)
 41. Oyedele EAA, Olayinka AI (2012) Statistical Evaluation of Groundwater potential of Ado-Ekiti, Southwest Nigeria. Transnatl J Sci Technol 2(6):110–127
 42. Oyedele, A. A., Ayodele, O. S. and Olabode O. F. (2019): Groundwater quality assessment and characterization of shallow basement aquifers in parts of ado ekiti metropolis, Southwestern Nigeria. SN Applied Sciences 1:669 | <https://doi.org/10.1007/s42452-019-0683-1>
 43. Rahaman MA, Malomo S (1983) Sedimentary and crystalline rocks of Nigeria. In: Ola SA (ed) Tropical soils of Nigeria in engineering practice, A.A. Balkema Netherlands, pp 17–38
 44. Ramos Ramos, O. E., Cáceres, L. F., Ormachea Muñoz, M. R., Bhattacharya, P., Israel Quino, I., Quintanilla, J., Sracek, O., Thunvik, R., Bundschuh, J., & García, M. E. (2012). Sources and behavior of arsenic and trace elements in groundwater and surface water in the Poopó Lake Basin, Bolivian Altiplano. Environment and Earth Science, 66, 793–807. <https://doi.org/10.1007/s12665-011-1288-1>.
 45. Redwan, M., & Abdel Moneim, A. A. (2016). Using Na/K ratios to identify the potential impacts of sewage effluent on groundwater quality in Sohag, Egypt. Groundwater Monitoring & Remediation, 36(4), 62–70.
 46. Rehman, F., & Cheema, T. (2017). Boron contamination in groundwater at a sewage waste disposal facility near Jeddah, Saudi Arabia. Environment and Earth Science, 76, 218–219. <https://doi.org/10.1007/s12665-017-6528-6>.
 47. Robson M (2003) Methodologies for assessing exposures to metals: human host factors. Ecotoxicol Environ Saf 56:104–109
 48. Rwiza, M. J., Kim, K.-W., & S-d, K. (2016). Geochemical distribution of trace elements in groundwater from the North Mara large-scale gold mining area of Tanzania. Groundwater Monit Remed, 36(2), 83–93.
 49. Sawyer R, Simpson-Hébert M, Wood S (1998) PHAST step-by-step guide: a participatory approach for the control of diarrhoeal disease.
 50. World Health Organization, Geneva (WHO/EOS/98.3)
 51. Shotyk, W., Krachler, M., Aeschbach-Hertig, W., Hillier, S., & Zheng, J. (2010). Trace elements in recent groundwater of an artesian flow system and comparison with snow: enrichments, depletions, and chemical evolution of the water. Journal of Environmental Monitoring, 12, 208–217
 52. Su, H., Kang, W., Xu, Y., & Wang, J. (2017). Assessing groundwater quality and health risks of nitrogen pollution in the Shenfu mining area of Shaanxi Province, Northwest China. Exposure and Health.

<https://doi.org/10.1007/s12403-017-0247-9>.

53. Suh, J. Y. (2004). Hydrogeochemical studies of groundwater from reclaimed land adjacent to Rozelle Bay, Sydney, Australia. *Geosciences Journal*, 8, 301–312. <https://doi.org/10.1007 /BF02910249>.
54. Sun, L., Peng, W., & Cheng, C. (2016). Source estimating of heavy metals in shallow groundwater based on UNMIX.Model: A case study. *Indian Journal of Geo-Marine Sciences*, 45(6), 756–762.
55. Talabi, A.O. and Tijani, M.N. (2013): Hydrochemical and stable isotopic characterization of shallow groundwater system in the crystalline basement terrain of Ekiti area, southwestern Nigeria. *Appl Water Sci* 3:229–245. DOI 10.1007/s13201-013-0076-3
56. Tebbubtt, T. H. Y. (1983). Relationship between natural water quality and health. Paris: UNESCO.
57. Toccalino, P. L., Norman, J. E., & Scott, J. C. (2012). Chemical mixtures in untreated water from public-supply wells in the U.S.—occurrence, composition, and potential toxicity. *Science of the Total Environment*, 431, 262–270.
58. Ure, A. M., & Berrow, M. L. (1982). The chemical constituents of soils. In H. J.M. Bowen (Ed.), *Environmental Chemistry* (pp. 94–202). London: R Soc Chem Burlington House.
60. United States Environmental Protection Agency (USEPA) (2004) edition of the drinking water standards and health advisories. Washington DC, USA: US Environmental Protection Agency. EPA822-R-04-005. www.epa.gov/waterscience/criteria/drinking/standards/dwstandards. Accessed 29th December, 2020
61. World Health Organization (WHO). (2011). Guidelines for drinking water quality, fourth edition. ISBN: 9789241548151. 564p
62. Wu, J., & Sun, Z. (2016). Evaluation of shallow groundwater contamination and associated human health risk in an alluvial plain impacted by agricultural and industrial activities, mid-west China. *Expo Health*, 8(3), 311–329. <https://doi.org/10.1007/s12403-015-0170-x>.
63. Dartey, E, Berlinger, Bb, Weinbruch,S ,Thomassen, Y, Odland,J, Brox,J, Nartey, V.K., Yeboah, F.A.,Ellingsen D.G.,(2017) :Essential and non-essential trace elements among working populations in Ghana. *Journal of Trace Elements in Medicine and Biology* 44 : 279–298

Figures

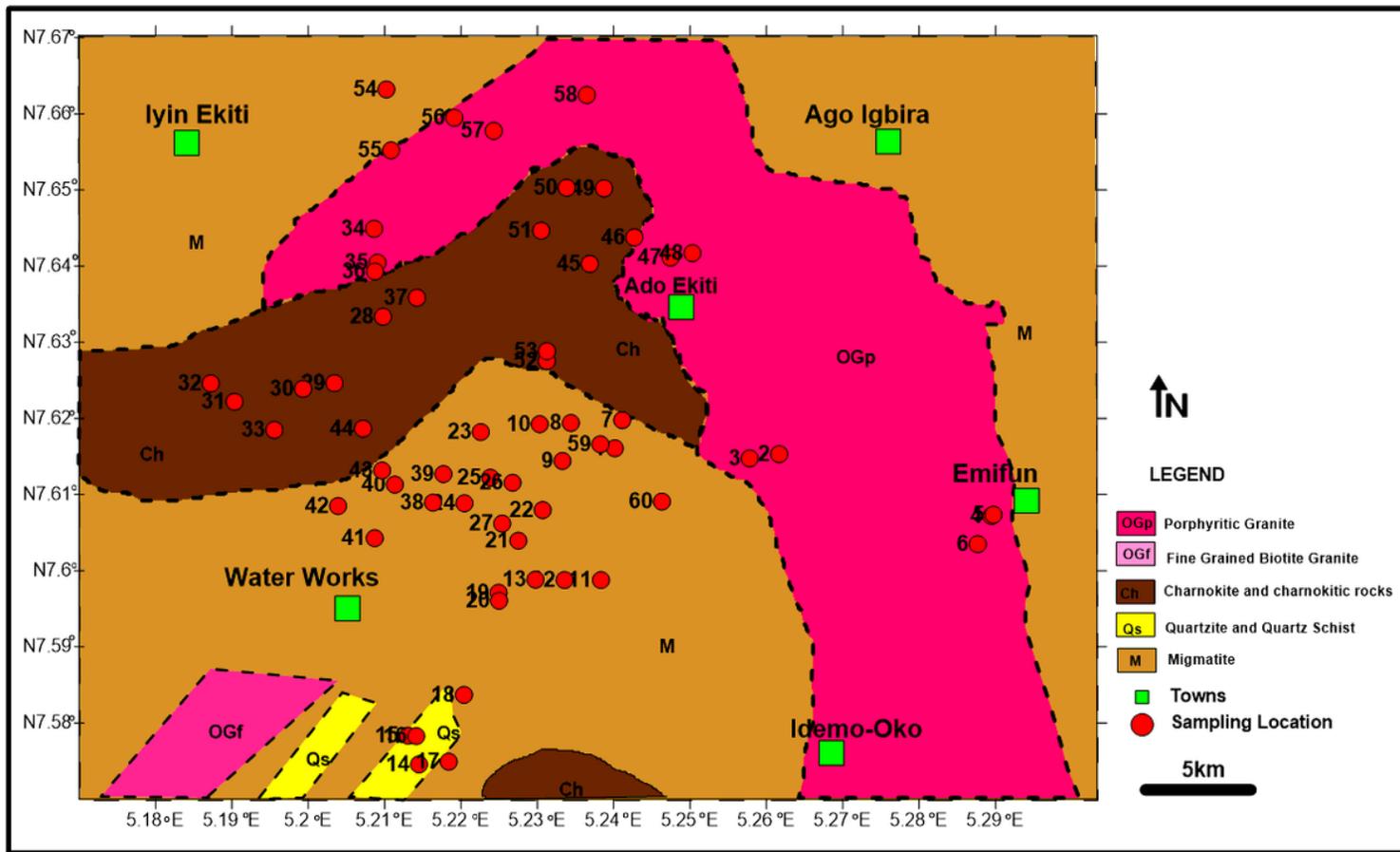


Figure 1

Geological map of the study area showing the sampling points

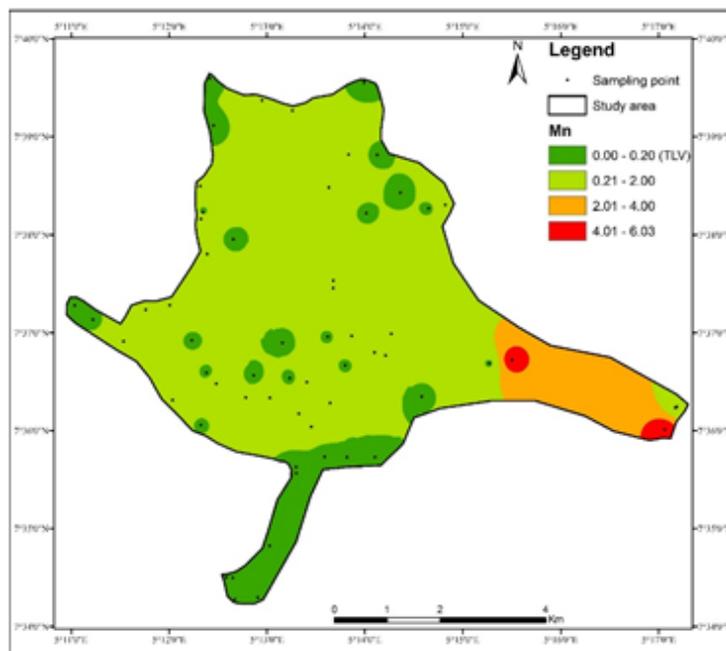
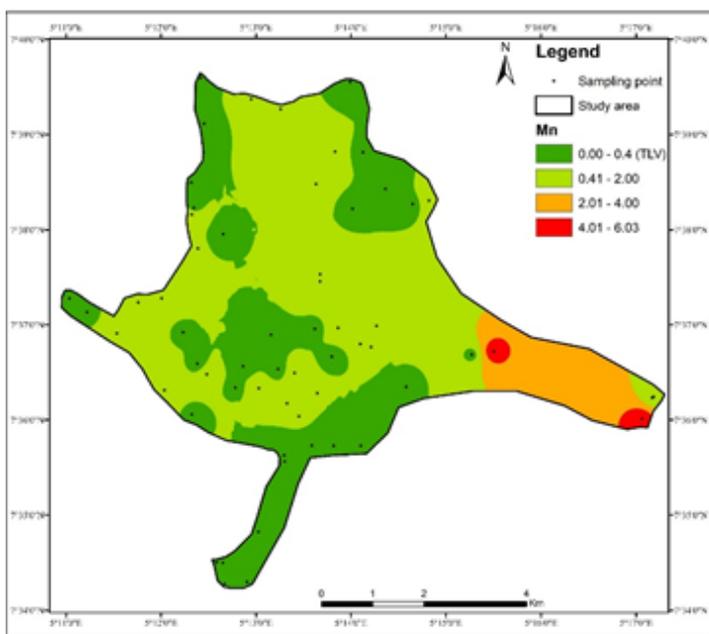


Figure 2

a; Spatial distribution of Mn classified based on the WHO(2011) specification

b: Spatial distribution of Mn classified based on the NSDW(2007) specification

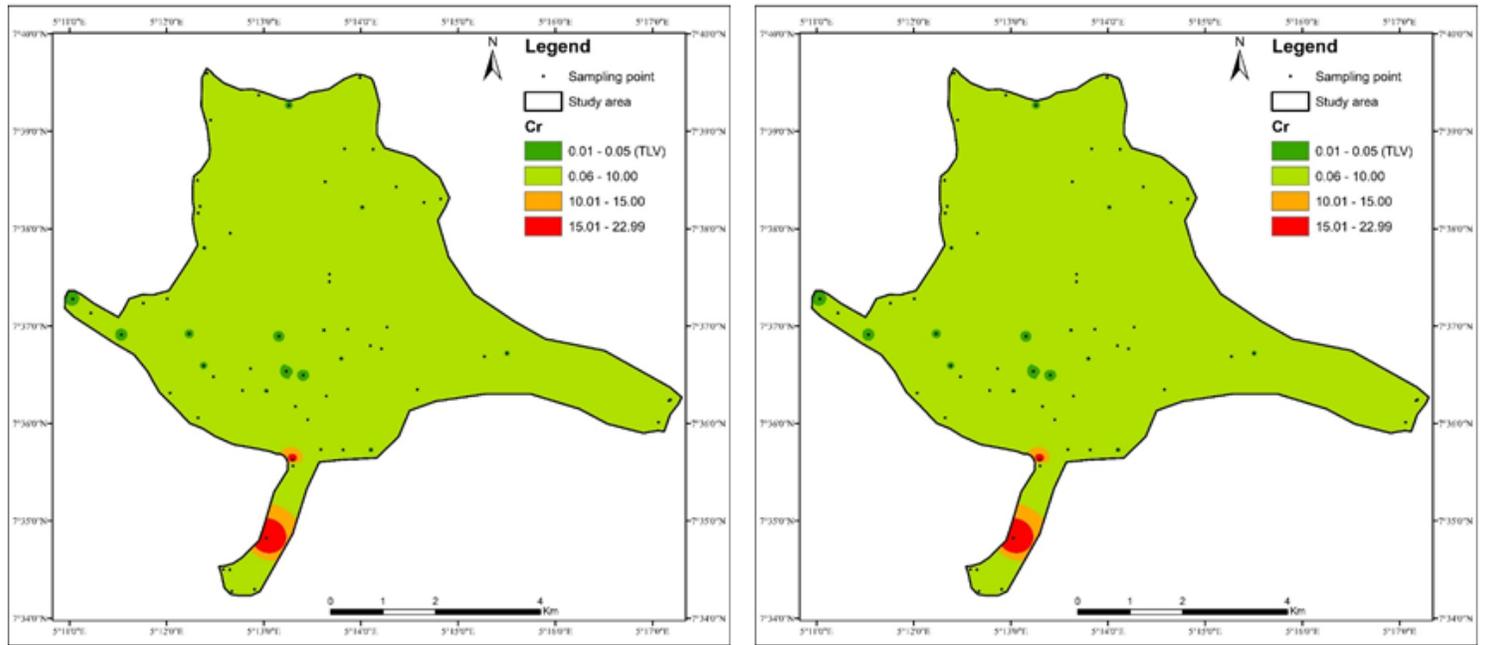


Figure 3

a; Spatial distribution of Cr classified based on the WHO(2011) specification

b: Spatial distribution of Cr classified based on the NSDW(2007) specification

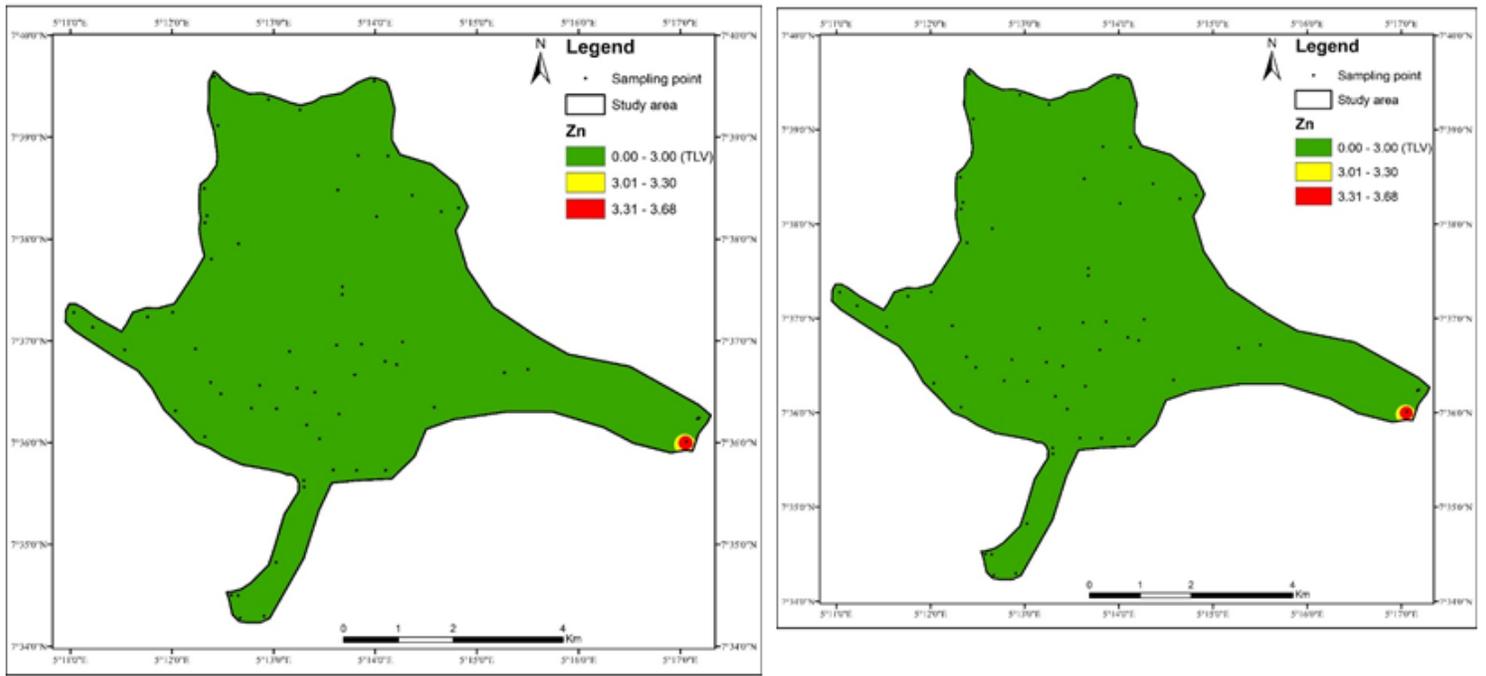


Figure 4

a: Spatial distribution of Zn classified based on the WHO(2011) specification

b: Spatial distribution of Zn classified based on the NSDW(2007) specification

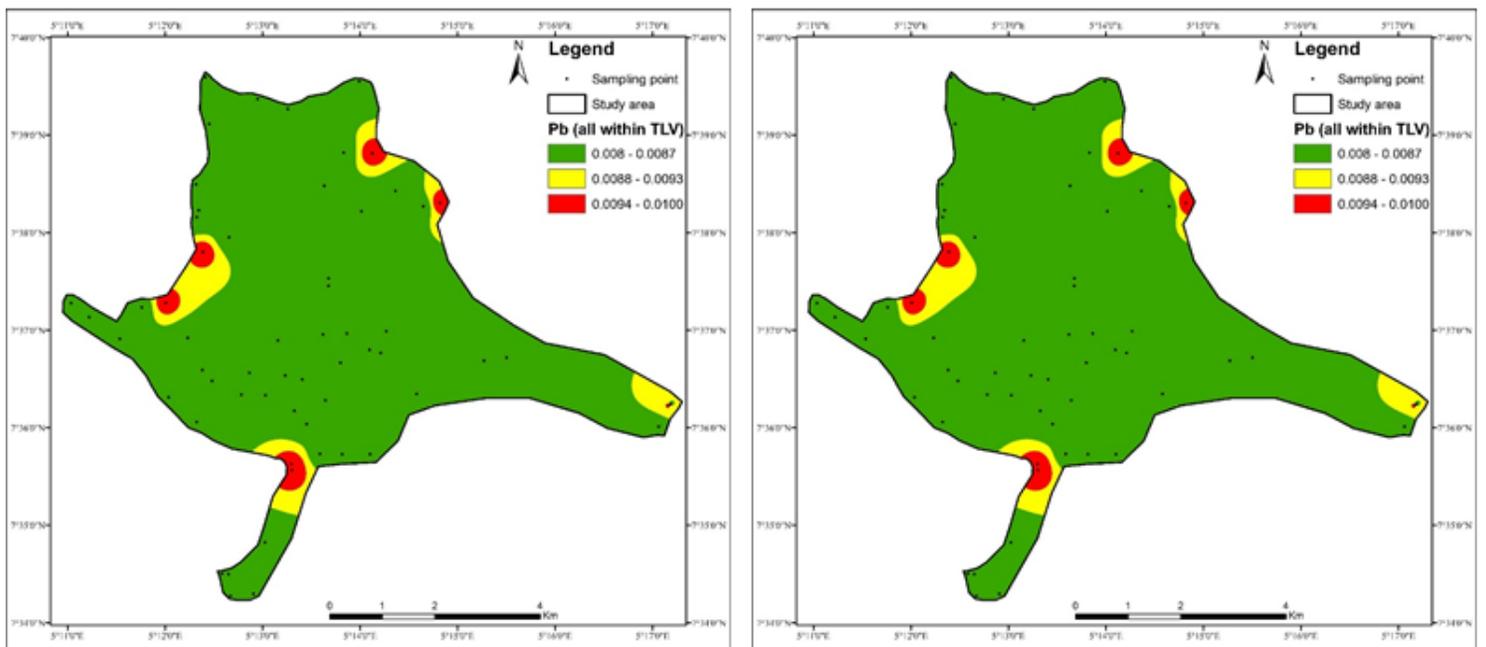


Figure 5

a: Spatial distribution of Pb classified based on the WHO(2011) specification

b: Spatial distribution of Pb classified based on the NSDW(2007) specification

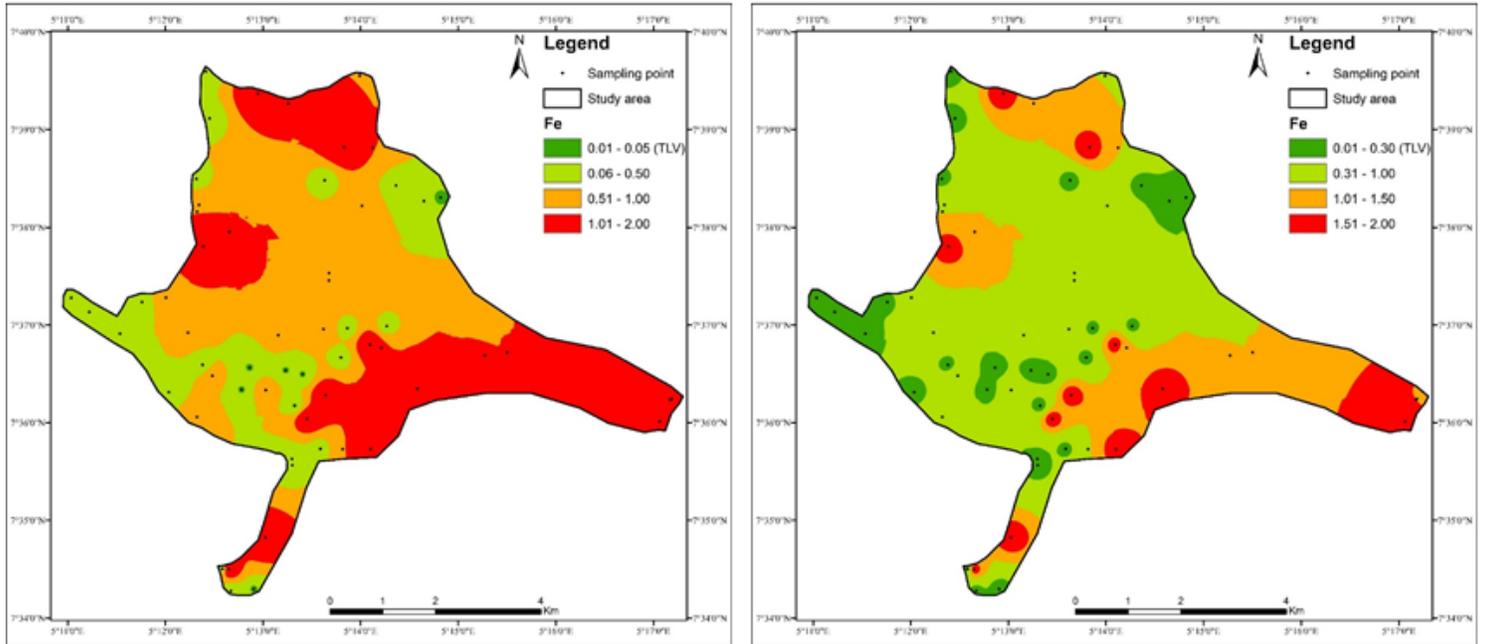


Figure 6

a: Spatial distribution of Fe classified based on the WHO(2011) specification

b: Spatial distribution of Pb classified based on the NSDW(2007) specification

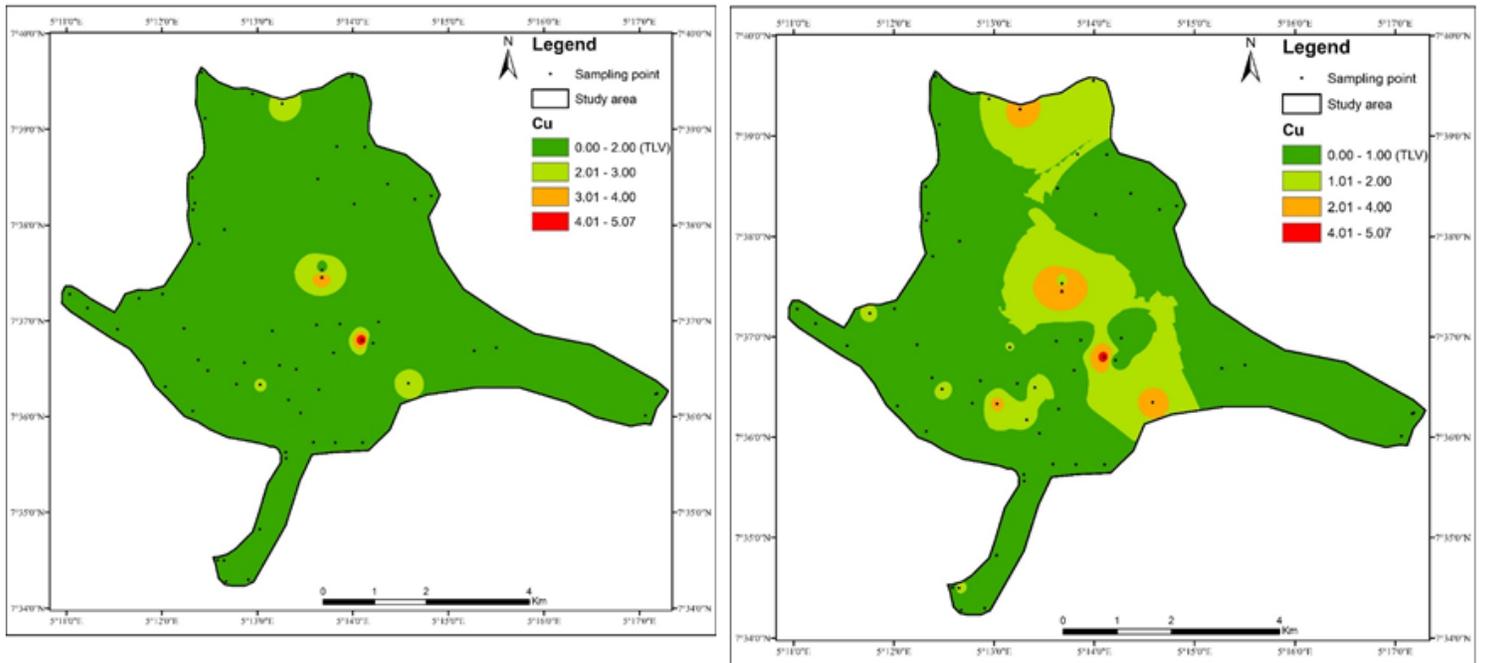


Figure 7

a: Spatial distribution of Fe classified based on the WHO(2011) specification

b: Spatial distribution of Pb classified based on the NSDW(2007) specification

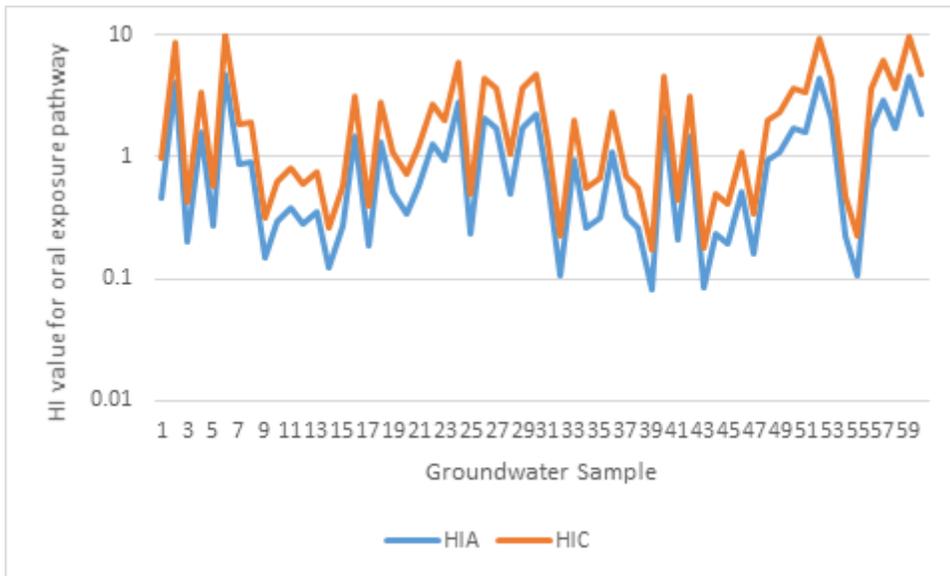


Figure 8

Hazard index (HI) for drinking water intake for adult (HIA) and children (HIC)

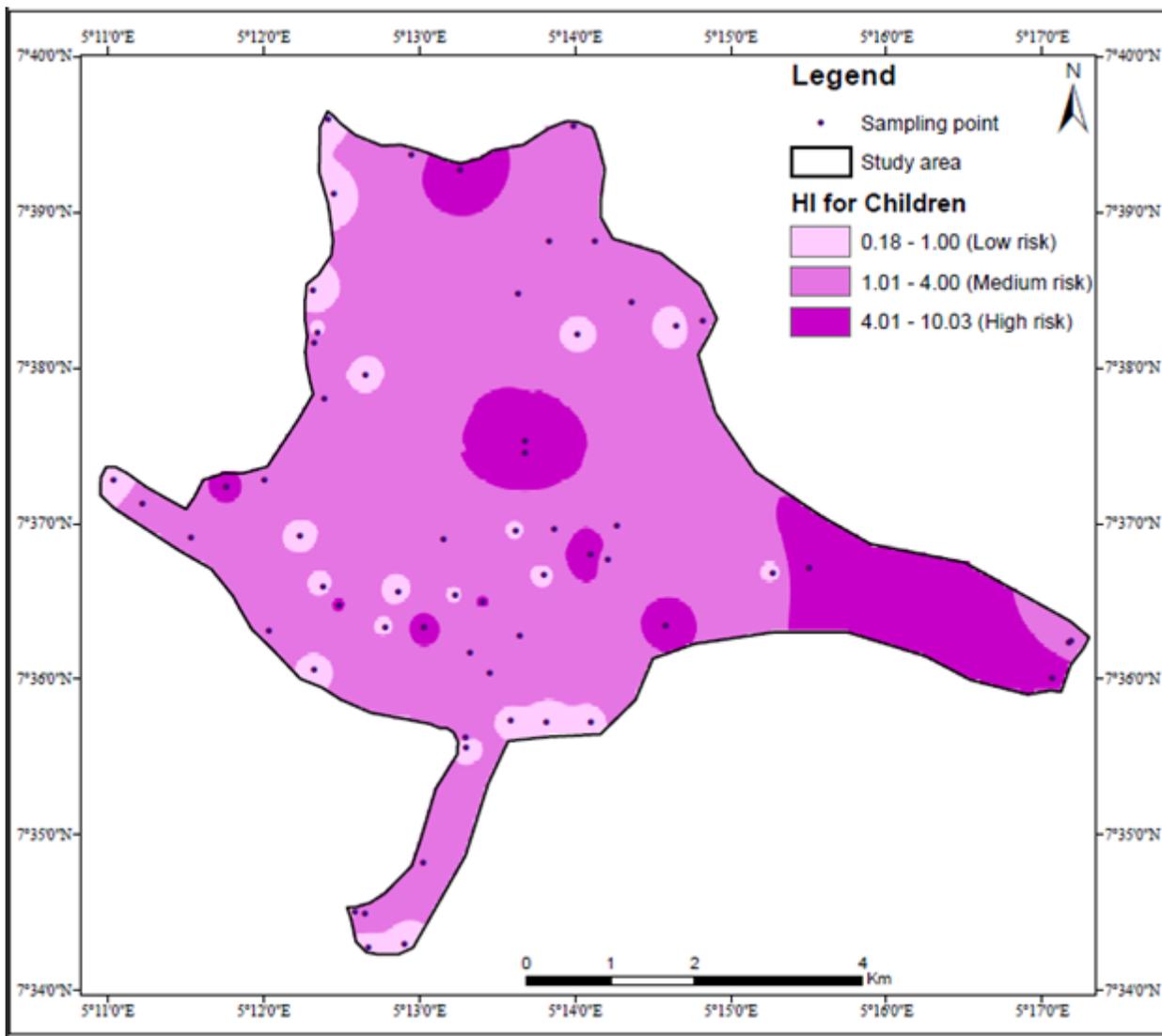


Figure 9

Spatial variations of non-carcinogenic health risk for children

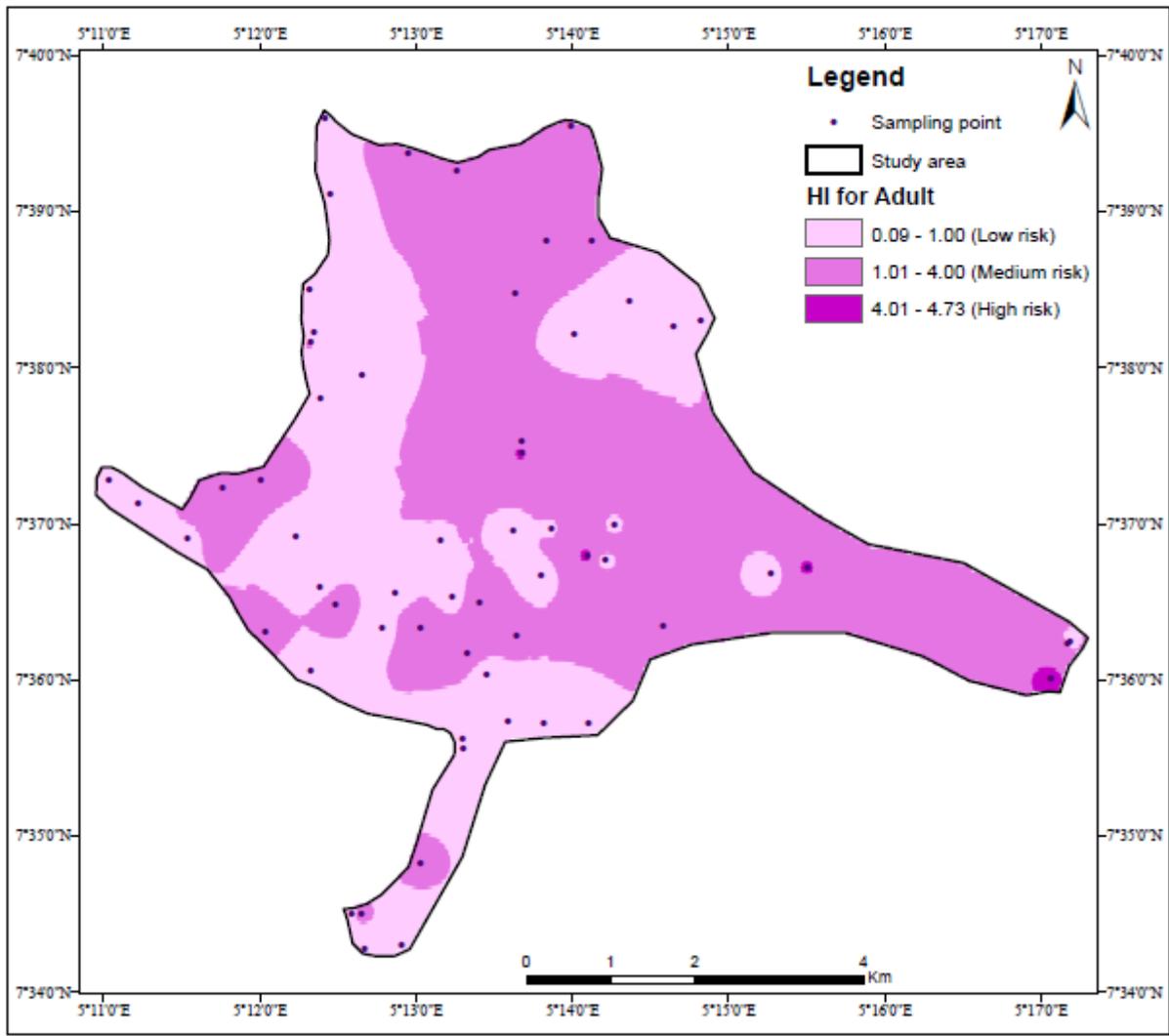


Figure 10

Spatial variations of non-carcinogenic health risk for adults