

Oral and Dermal Risk Assessment of Some Heavy Metals and Nitrates in Groundwater of Mariri, Kano, Nigeria

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Abstract

Introduction: Globally, pollutants, such as heavy metals and nitrates, from both natural and anthropogenic sources threaten groundwater, posing significant risks to human health and the environment.

Methods: This study assessed the health risks to adults and children resulting from oral and dermal exposure to heavy metals (Pb, As, Cd, Cr, Fe, Ni, and Mn) and nitrates in the groundwater of Mariri, Nigeria, in 2024. Non-carcinogenic and carcinogenic risks were assessed using methods from the US Environmental Protection Agency.

Results: Cd is the only pollutant that poses a significant non-carcinogenic risk ($HQ > 1$) and is the major contributor to the total risk to adults (73.06%) and children (74.69%). The hazard index through the oral exposure route is greater than one ($HI > 1$), whereas that through the dermal route is less than one ($HI < 1$) for adults and children. The multi-route hazard index (MHI) is greater than one for adults (2.49) and children (2.73), suggesting a significant non-cancer risk. The oral route contributed a higher risk than the dermal route for both receptors; children are more at risk (53%) of non-cancer health effects than adults (48%). There was also a significant cancer risk ($CR > 10^{-4}$) for adults through oral exposure to Cd and Ni, and children through dermal exposure to Cr, leading to significant cumulative cancer risk (RI) for adults through the oral route and for children through the dermal route.

Conclusion: This study indicates a significant non-cancer risk, particularly due to Cd, and cancer risk due to Cd, Ni, and Cr, thus necessitating corrective measures.

Keywords: Cancer, Groundwater, Risk assessment, Environmental pollution, Heavy metals

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Introduction

Water is vital to life, and access to clean water is crucial for achieving multiple Sustainable Development Goals (SDGs). Although abundant, this essential resource is not readily available, as millions of people globally lack access to clean water. Groundwater, however, provides nearly half of the world's drinking water, 40% of the world's irrigation water, and 25% of the water used in industries, while also sustaining natural habitats and balancing ecosystems (1). It is relatively abundant (60 times more than surface water), more accessible (can be abstracted through dug wells and boreholes), more reliable, and relatively pure due to the filtration effect of the unsaturated aquifer. It is also the most cost-effective source of water for rural dwellers (2,3).

However, overexploitation and pollution threaten this world's most important natural resource. Groundwater pollution comes from both natural and anthropogenic sources. Natural sources are dependent on aquifer lithology and arise from dissolution, erosion, and weathering of soil

and rock minerals (4,5). On the other hand, human activities are increasingly impacting groundwater quality due to population growth, urbanization, and industrialization. These include pollution from industrial releases (e.g., mining, electroplating, and manufacturing), agricultural activities (e.g., fertilizers, pesticides, and herbicides), vehicular emissions, municipal waste, and landfills (6-8). Groundwater pollutants, including heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and per- and polyfluoroalkyl substances (PFASs), are a global health concern. When released into the environment, 50% of these pollutants can reach the groundwater table. Rainfall expedites the leaching of these pollutants from the topsoil (9).

Groundwater pollution affects human health, degrades natural habitats, alters biodiversity, disrupts local ecosystems, and incurs financial burdens on the local community (1). According to the World Health Organization (WHO), approximately 80% of human



diseases are water-related, with drinking water affecting approximately 500,000 people annually (10). Studies have also shown that polluted groundwater and inadequate sanitation are responsible for approximately 20% of global cancer and several thousand deaths (11,12). Humans are directly exposed to contaminants in groundwater through ingestion, dermal contact, and inhalation of aerosol or spray, and indirectly through food contaminated by irrigation water (13,14). Groundwater pollution by heavy metals is a global challenge due to their bioaccumulation, persistence, non-biodegradability, and toxicity (15,16). Although some elements (e.g., Fe, Mn, and Cu) are essential at lower concentrations in the human body, others (e.g., Pb, As, Cd, Cr (VI), and Ni) have no known function in the body. Even essential metals become toxic at higher body concentrations (17). Chronic exposure to these metals can lead to several health implications, such as kidney damage, neurological disorders, cardiovascular diseases, bone and liver damage, accelerated ageing, and infertility (18-20). They can also cause cancers and mutations, including lung, kidney, liver, and bone cancers (21,22). Every toxic metal has a specific mechanism of toxicity. However, most metals cause toxicity by generating reactive oxygen species (ROS) and suppressing antioxidant defense systems, which leads to oxidative stress, macromolecular damage, enzyme inactivation, and serious adverse effects (23,24). They also cause cancers by inhibiting tumour suppressor genes and interfering with DNA repair systems (21). The toxicity of heavy metals is also influenced by their valence state, route, duration, and quantity of exposure, as well as the bioavailable form of the metal (19,25). On the other hand, nitrate is a groundwater contaminant known to cause methemoglobinemia (blue-baby syndrome) in infants. In the body, nitrates are reduced to nitrites, which interfere with oxygen transport (26). The present research suggests that chronic exposure to low concentrations of nitrates in drinking water may be responsible for thyroid problems, adverse pregnancy outcomes, and cancers (27).

Risk assessment links environmental pollution to human health and can quantitatively estimate the risks of these pollutants (8,28). Although approximately 14.3% of Nigerian land is covered by water, most people in Nigeria lack access to clean drinking water (29). The situation worsens in suburban areas, including Mariri, the study area. Most of the population is agrarian, with groundwater as the primary source of water for drinking and other domestic applications. Due to the semi-arid nature of the area, rainfall and surface water are scarce, increasing the dependence on groundwater. There is currently a dearth of data on the pollution status and the risk of heavy metals and nitrates in the area's groundwater. Due to the risks associated with contaminated groundwater, this water resource must be evaluated and continuously monitored.

Risk assessment involves estimating the likelihood and extent of adverse effects of exposure to potential hazards (30). It is the first step in the risk analysis process, followed by risk management and communication, aimed at developing comprehensive and systematic risk

management decisions (14,31). The risk assessment proposed by the USEPA involves four steps: Hazard identification, exposure assessment, dose-response assessment, and risk characterization (32). Various researchers have conducted health risk assessments using either a deterministic approach, whereby health risk is assessed using known parameters (33-36), or a probabilistic approach, where the parameters are defined as a probability distribution (each parameter is randomly selected from a probability distribution function) (37-39). A hybrid of these approaches is also common (21,40-42).

Studies have highlighted an increasing concern about groundwater pollution in Nigeria (19,43-45). This study aimed to assess the health risk to children and adults through oral and dermal exposure to heavy metals and nitrates in the groundwater of Mariri, Nigeria. The results of this study will provide vital information to risk managers and policymakers, including a baseline value for future evaluation and monitoring.

Materials and Methods

Study area

The study area was Mariri, Kano State, Northwestern Nigeria, located approximately at latitude 11° 56'N to 11° 57'N and longitude 08° 36'E to 08° 34'E (Figure 1). The area's climate is semi-arid with two distinct seasons: Rainy and dry. The annual rainfall ranges from 800 to 1000 mm, while the temperature is between 26°C and 33°C. Groundwater in the study area occurs in the aquifer of fractured basement rocks and sandy alluvial deposits along river courses, with water tables generally less than 20 m (46). The area is about 20 km² with a population of approximately 39837. It is mainly a residential area with adjoining vast agricultural land, with residents primarily farming staple crops such as millet, sorghum, maize, and rice. Groundwater is the main water source for domestic and agricultural use for the people in the area.

Sampling and analysis

The sample locations were randomly selected in February 2024. Ten groundwater samples were collected from hand-dug wells using a clean, non-reactive bailer and placed in polyethylene bottles (previously washed with 10% nitric

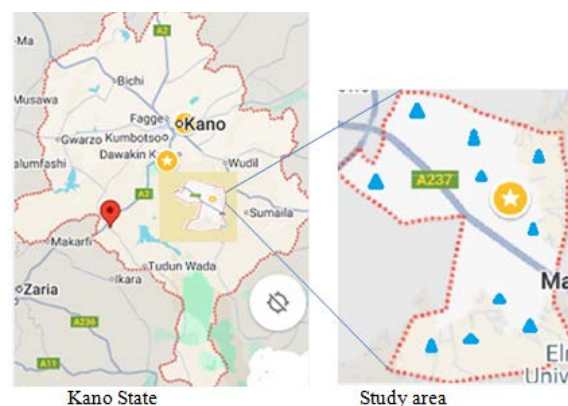


Figure 1. Map of the study area showing the sampling points

acid and rinsed with distilled water). Water samples were collected in a manner that minimized turbidity. This is to reduce the uncertainty in estimating dermal absorbed dose arising from the fact that particle-bound pollutants in aqueous media are less available for dermal absorption (47). The water samples were also filtered using 0.45 µm diameter filters to ensure the removal of suspended solids before storage in the prepared bottles. The heavy metal samples were acidified with 3 mL of 65% HNO₃ before being transported to the laboratory. The samples were labelled, sealed in airtight containers, and immediately transported to the laboratory in a cooler maintained at 4°C. The heavy metal analysis was performed in the laboratory within 2-3 weeks of the sample collection using a Buck Model 210 VGP atomic absorption spectrophotometer (AAS), while NO₃⁻ was analyzed within 48 hours using the standard method (48). Analysis of Cr was based on the total Cr content.

Quality assurance and quality control (QA/QC) procedures were strictly followed to ensure data accuracy and reliability. Each sample was measured in triplicate. The calibration graph was obtained using the blank and standard solutions of the metal ions. The limit of detection (LOD) for all metals was determined by triplicate analysis of the blanks. The LOD was calculated following the equation:

$$LOD = 3 \times \delta_{bl} \quad (1)$$

Where δ_{bl} is the standard deviation of the blank method, and the limit of quantification (LOQ) is the smallest quantity that can be reliably used to quantify an analyte. Generally, LOQ is given as 3 x LOD. Values below the LOD or LOQ are unreliable and discarded.

Human health risk assessment

Exposure assessment

Exposure assessment is the extent of human exposure to pollutants or environmental agents (49). Following a deterministic approach, the default values of exposure parameters (Table 1) from the United States Environmental

Protection Agency (USEPA) were combined to quantify the doses of pollutants ingested by the exposed populations. Chronic exposures through oral and dermal routes (showering/bathing), for adults and children, were estimated in this study.

The oral chronic daily intake (CDI) and dermal absorption dose (DAD) were calculated as follows:

$$CDI = \frac{C_p \times IR \times EF \times ED}{BW \times AT} \quad (2)$$

$$DA_d = \frac{C_p \times K_d \times SA \times EF \times ED \times ET \times CF}{BW \times AT} \quad (3)$$

Risk estimation

This quantifies how the exposure compares with health-based guidelines or reference values. Risk can be classified as non-carcinogenic or carcinogenic. Carcinogenic risk assumes no threshold for toxicity (there is no safe level for carcinogens). At the same time, the non-carcinogenic effect has a threshold dose that must be exceeded to have an adverse effect (30).

Non-carcinogenic risk assessment

Risk is the probability of adverse effects from exposure to an environmental agent or a mixture of agents (49). The non-carcinogenic risks through oral and dermal routes were estimated using the hazard quotient (HQ) and hazard index (HI), as shown in Equations 4 and 5:

$$HQ_o = \frac{CDI}{RfD_o} \quad (4)$$

$$HQ_d = \frac{DA_d}{RfD_d} \quad (5)$$

The oral dose-response factor, adjusted for absorption, can be converted to an absorbed dose basis as follows (47):

$$RfD_d = RfD_o \times ABS_{GI} \quad (6)$$

Where RfD is the reference dose (threshold), which is the daily dose of a substance that will not result in any deleterious effect in a lifetime for a given human population. ABS_{GI} is the fraction of contaminant absorbed in the gastrointestinal tract (Table 2). If HQ is less than 1 ($HQ < 1$), adverse effects due to the exposure are unlikely; HQ equal to or greater than 1 ($HQ \geq 1$) indicates a significant probability of non-cancer risk.

The HQs are summed to estimate the overall risk across all pollutants, yielding the HI for the mixture. The HI for n chemicals through the k^{th} route is the HI restricted to exposures by that route:

$$HI_k = \sum_{i=1}^n HQ_k \quad (7)$$

$HI < 1$ is below the benchmark, whereas $HI > 1$ is above the benchmark. HI is quite conservative. It should be interpreted with caution. The Multi-route hazard index (MHI) was calculated to estimate total integrated exposure

Table 1. Reference parameters used for exposure assessments (47,50,51)

Parameter	Meaning	Adult	Child
EF	Exposure frequency (d/yr.)	350	350
ED	Exposure duration (yr.)	30	6
BW	Body weight (kg)	70	15
AT	Average exposure time (d)	C = 70x365; N = EDx365	
IR	Ingestion rate (L/d)	2	0.4
SA	Body surface area (cm ²)	18000	6600
CF	Unit conversion factor (L/cm ³)	0.001	0.001
EV	Event Frequency (Event/d)	1	1
ET	Event Duration (hr)	0.58	1
K _d	Permeability coefficient (cm/h)	Chemical-specific	
C _p	Pollutant concentration (mg/L)	-	-

C = Carcinogenic; N = Non-carcinogenic

across multiple routes by summing HIs across all the exposure routes. The MHI for 'm' routes is the sum of the m route-specific HIs (52,53).

$$MHI = \sum_{k=1}^m HI_k \quad (8)$$

Assessment of carcinogenic risk

The carcinogenic risk assessment estimates the probability of an individual developing cancer over a lifetime due to exposure to a potential carcinogen. Oral carcinogenic risk (CR_o) due to oral ingestion and carcinogenic risk due to dermal absorption (CR_d) were calculated using Equations 9, 10, and 11 (48):

$$CR_o = CSF_o \times CDI \quad (9)$$

$$CR_d = DA_d \times CSF_d \quad (10)$$

$$CSF_d = \frac{CSF_o}{ABS_{GI}} \quad (11)$$

Where CSF ($mg/kg/d$)⁻¹ is the plausible upper-bound estimate of the probability of a carcinogenic response per unit of intake over a lifetime (14) (Table 2).

Results

Table 3 presents the descriptive statistics of the concentrations of heavy metals and nitrate in the groundwater samples. The mean concentrations of the pollutants followed the decreasing order: $NO_3^- > Fe > Ni > Pb > Cr > Cd > As > Mn$.

Table 4 presents the oral hazard quotient (HQ_o), dermal hazard quotient (HQ_d), and total hazard quotient (HQ_T) for

each metal, and the hazard index (HI) for all the metals (for adults and children). For adults, the oral hazard quotient is greater than unity ($HQ_o > 1$) for Cd only, whereas the dermal hazard quotients for all the metals are less than unity ($HQ_d < 1$). The total hazard quotient is also greater than unity ($HQ_T > 1$) for Cd only. Similar results were obtained for the children.

The incremental life cancer risk (CR) through oral ingestion (CR_o) and dermal absorption (CR_d) was estimated for the heavy metals classified as human carcinogens and that have available carcinogenic data (CSF). The total cancer risk (TCR) was also evaluated as the sum of the two exposure routes. The cancer risk index (RI), which is the cumulative of all the metals through all exposure routes, was also estimated (53). The results for the adults and the children are presented in Table 5.

Discussion

Concentrations of heavy metals and nitrate in the groundwater

Pb and Cd exceeded the WHO maximum permissible limits of 0.01 and 0.003 mg/l, respectively, for drinking water (10). Pb in groundwater can originate from both natural and human sources. Naturally, Pb can be leached from lead-containing bedrock or geological formations. Human activities, including industrial discharge, improper disposal of Pb-containing materials (e.g., batteries or lead pipes), and runoff from domestic or agricultural sources, also contribute to Pb contamination of groundwater (54). Similarly, Cd in groundwater has both natural and

Table 2. Reference parameters for the pollutants (47,50,51)

Pollutants	RfD _o (mg/g/day)	ABS _{GI}	Kd (cm/hr)	RfD _d (mg/g/day)	CSF _o (mg/kg/day) ⁻¹	CSF _d (mg/kg/day) ⁻¹
Pb	0.0035	1	0.0001	0.0035	0.0085	0.0085
As	0.0003	1	0.001	0.0003	1.5	1.5
Cd	0.0001	0.05	0.001	5E-06	1.5	30
Cr	0.003	0.025	0.002	7.5E-05	0.5	20
Ni	0.02	0.04	0.0002	0.0008	0.91	22.75
Fe	0.7	1	0.001	0.7	-	-
Mn	0.024	0.04	0.001	0.0008	-	-
NO ₃ ⁻	1.6	1	0.001	1.6	-	-

Table 3. Descriptive statistics of the concentrations (mg/L) of the pollutants

	Minimum	Maximum	Mean	Std. Dev.	WHO
Pb	0.009	0.015	0.012	0.002	0.01
As	0.002	0.006	0.004	0.001	0.01
Cd	0.004	0.008	0.006	0.001	0.003
Cr	0.006	0.010	0.008	0.001	0.05
Fe	0.027	0.033	0.030	0.002	0.40
Ni	0.013	0.018	0.016	0.002	0.07
Mn	0.001	0.004	0.002	0.001	0.40
NO ₃ ⁻	4.900	5.700	5.250	0.264	50.00

Table 4. Oral hazard quotient (HQ_o), dermal hazard quotient (HQ_d), and total hazard quotient (HQ_T) for adults and children

	ADULTS			CHILDREN		
	HQ_o	HQ_d	HQ_T	HQ_o	HQ_d	HQ_T
Pb	0.094	0.001	0.094	0.088	0.001	0.088
As	0.356	0.002	0.358	0.332	0.005	0.338
Cd	1.644	0.172	1.815	1.534	0.506	2.041
Cr	0.071	0.030	0.101	0.066	0.088	0.154
Fe	0.001	0.001	0.001	0.001	0.001	0.001
Ni	0.021	0.001	0.022	0.020	0.002	0.021
Mn	0.003	0.001	0.003	0.002	0.001	0.004
NO ₃ ⁻	0.090	0.001	0.090	0.084	0.001	0.085
HI	2.280	0.205	2.485	2.128	0.604	2.732

Table 5. Oral cancer risk (CR_o), dermal cancer risk (CR_d), and total cancer risk (TCR) for adults and children

	ADULTS			CHILDREN		
	CR_o	CR_d	TCR	CR_o	CR_d	TCR
Pb	1.0×10^{-6}	6.0×10^{-10}	1.0×10^{-6}	2.0×10^{-7}	4.0×10^{-9}	2.0×10^{-7}
As	7.0×10^{-5}	4.0×10^{-7}	7.0×10^{-5}	1.0×10^{-5}	2.0×10^{-6}	2.0×10^{-5}
Cd	1.0×10^{-4}	1.0×10^{-5}	1.0×10^{-4}	2.0×10^{-5}	8.0×10^{-5}	1.0×10^{-4}
Cr	5.0×10^{-5}	2.0×10^{-5}	6.0×10^{-5}	9.0×10^{-6}	1.0×10^{-4}	1.0×10^{-4}
Ni	2.0×10^{-4}	4.0×10^{-6}	2.0×10^{-4}	3.0×10^{-5}	3.0×10^{-5}	6.0×10^{-5}
RI	4.0×10^{-4}	3.0×10^{-5}	4.0×10^{-4}	7.0×10^{-5}	2.0×10^{-4}	3.0×10^{-4}

anthropogenic sources. Natural sources include erosion and weathering of Cd-bearing rocks. Anthropogenic sources include metal mining and refining, phosphate fertilizers, fossil fuel combustion, waste disposal (especially from plastics, pigments, and batteries), etc. (34,55,56). Unlike most metals, Cd is not mobilized at low pH and remains in solution at pH < 6.5 as hydrated ions or as ionic complexes with other inorganic or organic compounds (57). As, Cr, Fe, Ni, Mn, and NO_3^- were within the permissible limits for drinking water (10).

Comparing the concentration of pollutants to guideline values is insufficient, as the established safety levels often do not capture the potential adverse effects of chronic exposure. The health risk of environmental pollutants depends on factors such as pollution level, exposure level (amount of contact), and the pollutant's toxicity (49). Health risk assessment takes into account the cumulative exposure, sensitive populations, and socioeconomic factors.

Non-carcinogenic risk assessment

The results of the non-carcinogenic risk assessment (Table 4) indicate that chronic oral exposure to Cd will likely result in an adverse effect for adults and children. Hence, further actions, such as investigation or risk management, are required. Chronic exposure to other pollutants through the oral route is unlikely to pose a significant risk. Conversely, chronic exposure through dermal contact is unlikely to result in adverse effects for adults and children.

The hazard index (HI) was calculated based on the assumption that the contaminants act by the same mechanism of action and that the metals in the mixture have an additive effect. This is the default approach, as it rules out underestimation (30,57). Although interaction between contaminants is possible, according to the study by Hamm et al. (58), there is an interaction threshold, i.e., a point below which the interaction effect in a mixture may not be significant. According to the study by Yang and Dennison, interactions among environmental contaminants are not likely relevant because the interaction thresholds are likely higher than the exposure reference dose (59). In this study, the hazard index through the oral exposure route is greater than one ($\text{HI} > 1$) for adults and children, while the hazard index through the dermal route is less than one ($\text{HI} < 1$) for adults and children. An $\text{HI} > 1$ suggests that there is reason for further risk investigation, including whether the addition approach was justified or whether the risk contribution of some components is independent. It also implies that risk management actions are recommended (14). In this case, most of the HI through the oral route is attributed to Cd; hence, only Cd should be further investigated as suggested by the Oregon Department of Environmental Quality (60). This result also indicates that the cumulative risk through dermal contact for both receptors is within reasonable bounds, suggesting that a more refined risk assessment is unnecessary. Although the combined risk through oral exposure is greater for adults than children, dermal exposure is higher for

children than adults. Similar results have been reported previously (37,61). Children are at increased risk of dermal contaminants mainly because of their higher surface-to-volume ratio, immature detoxification pathways, and rapidly developing nervous system (62).

The multi-route hazard index (MHI) is greater than one for both adults (2.485) and children (2.732). This suggests that the health-based criterion for the mixture of contaminants or multiple routes has been exceeded, and corrective measures must be seriously considered. The contribution of individual pollutants and routes to the joint toxicity of the mixture should be investigated (52). Also, given that oral exposure to Cd contributed largely to the MHI, attention should be focused on Cd through the oral route. $\text{MHI} > 1$ does not automatically translate to unacceptable risk and cannot be directly related to the percentage of the population at risk (63).

Figure 2 shows the percentage contribution of each metal to the total non-carcinogenic risk for adults and children. The result for adults shows that Cd is the major contributor to the total non-carcinogenic risk and accounted for 73.06% of the total risk, whereas As, Cr, Pb, NO_3^- , Ni, Mn, and Fe contributed 14.41%, 4.06%, 3.78%, 3.64%, 0.88%, 0.12%, and 0.05%, respectively. Similarly, for children, Cd accounted for 74.69% of the total non-carcinogenic risk, whereas As, Cr, Pb, NO_3^- , Ni, Mn, and Fe contributed 12.37%, 5.65%, 3.21%, 3.12%, 0.79%, 9.13%, and 0.04%, respectively.

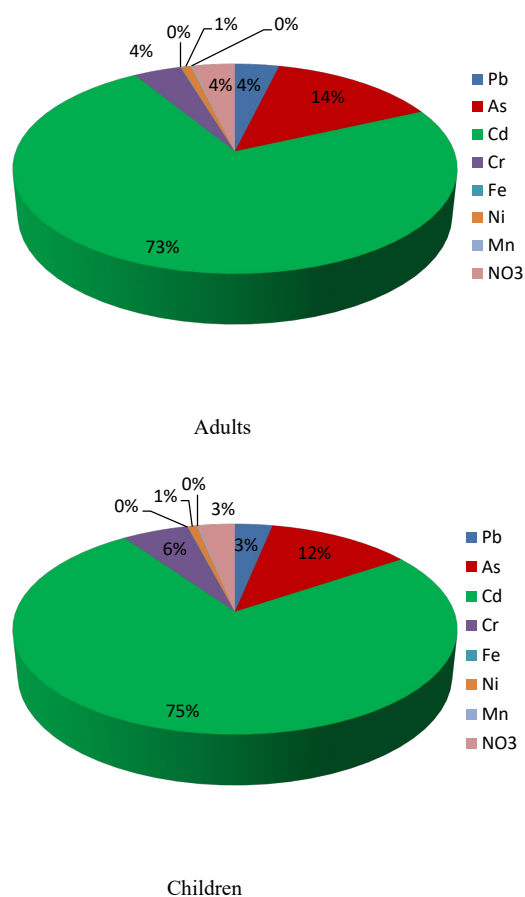


Figure 2. Percentage contributions of the pollutants to the total non-carcinogenic risk

Cd is the only pollutant that poses a significant non-carcinogenic risk ($HQ > 1$) and is the major contributor to the total non-carcinogenic risk to adults and children. It is among the 10 substances classified as a significant human health risk (39). Cd is preferentially distributed in the liver, kidneys, and bones, which are the primary targets of its toxicity. The liver and kidneys retain about 50-75% of the metal (64,65). Chronic exposure to Cd leads to renal failure, osteoporosis, liver damage, cardiovascular disease, endocrine damage, anemia, etc. (64,66-68). Its toxicity is partly related to its chemical similarity to Zn, an essential trace element. It can substitute for Zn and cause the malfunction of many metabolic processes. Cd also generates reactive oxygen species (ROS) and suppresses the antioxidant defense system, resulting in oxidative stress and macromolecular damage (64).

The results revealed that the oral route contributed 78% and the dermal route 22% of the total non-carcinogenic risk to children. Whereas the oral route contributed 92% of the total non-carcinogenic risk to adults, leaving only 8% from the dermal route (Figure 3). As widely reported, oral ingestion is the principal exposure pathway to contaminants in water. This is due to the higher absorption efficiency of the gastrointestinal tract compared to the skin, coupled with a higher ingestion rate, among other factors (43,69-71).

Figure 4 shows the comparison of the non-carcinogenic risk to adults versus children. This indicates that children are more at risk (53%) of non-cancer health effects through oral and dermal exposure to the groundwater of the area than adults (48%). Similar results have been reported previously (37,69,72). Children are more susceptible to

non-cancer risk than adults due to lower body weight (increased average daily exposure), physiological factors, contact frequency, and dietary habits (73). Children's exposure to toxic pollutants at the developmental stage can result in irreversible damage due to their immature immune, digestive, and nervous systems (74).

Assessment of carcinogenic risk

Carcinogenic Risk (CR) is the likelihood or the probability of developing cancer from exposure to certain substances (carcinogens) over a lifetime (75). CR in the range of 1×10^{-6} to 1×10^{-4} falls within the acceptable range; less than 1×10^{-6} indicates no risk, while above 1×10^{-4} indicates significant cancer risk (50). The results show a likelihood of contracting cancer through lifetime oral exposure of adults to Cd and Ni in the groundwater ($CR_o > 10^{-4}$). There is also a significant risk of cancer in children through dermal exposure to Cr ($CR_d > 10^{-4}$). The results for total cancer risk (TCR) (due to a summation of both exposure routes) give similar results for adults and children. The International Agency for Research on Cancer (IARC) classified Cd, Cr (VI), and soluble Ni compounds as group 1 carcinogens (carcinogenic to humans) and elemental Ni and Ni alloys as group 2B carcinogens (possibly carcinogenic to humans) (76,77). Environmental exposure to Cd has been linked to cancers of the breast, lung, prostate, nasopharynx, pancreas, and kidney (64,78,79). Cd carcinogenicity involves various mechanisms such as the generation of reactive oxygen species, inhibition of DNA repair and tumour suppressor proteins, epigenetic changes, and deregulation of apoptosis (64,78). Conversely, Cr (VI) causes cancer of the respiratory system, including lung, nose, and nasal sinus cancer, through oxidative stress that damages macromolecules, epigenetic modification, structural and functional impairment of nucleic acids, and mutagenesis (65,76,80). Studies on carcinogenic effects after oral exposure to Ni compounds are limited. The oral and dermal absorption of Ni compounds is low. However, human exposure to Ni causes respiratory tract, nasal, and lung cancers (21,22,55). Ni can cause cancer through mitochondrial dysfunction, leading to increased ROS production, oxidative stress, and DNA damage; interference with Fe homeostasis, leading to epigenetic alteration; generation of free radicals that impair Ca and sulfhydryl homeostasis; and interference with tumor suppressor genes (81,82).

For adults, the cancer risks through oral exposure (CR_o)

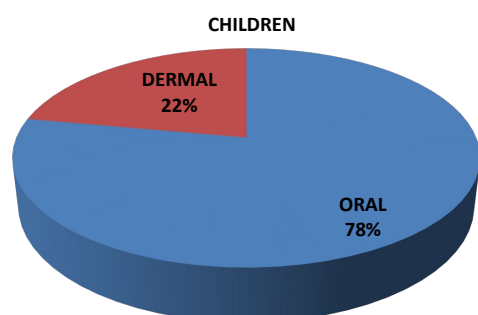
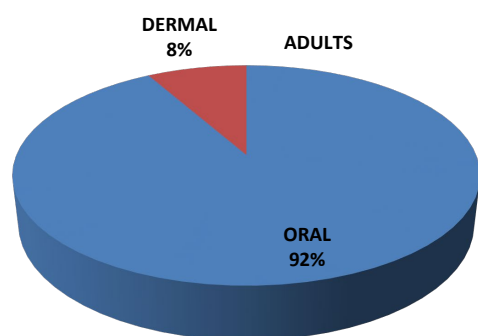


Figure 3. Non-carcinogenic risk through oral versus dermal routes

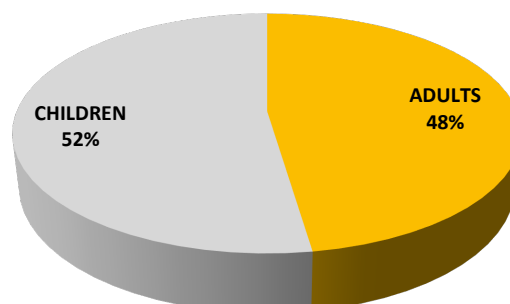


Figure 4. Ratio of non-carcinogenic risk of adults to children

to Pb, As, and Cr and dermal exposure to As and Cr fall between 10^{-4} and 10^{-6} ; while for children, the cancer risks through oral exposure to As, Cd, Cr, and Ni and through dermal exposure to As, Cd, and Ni fall between 10^{-4} and 10^{-6} . Contaminants within this range indicate a tolerable (though not recommended) level. This implies that exposure to these metals through these routes should be continuously monitored. $CR < 10^{-6}$ indicates there is no significant cancer risk. These include oral exposure to Pb by children, dermal exposure to Pb by children and adults, and dermal exposure to As by adults. Cancer risk due to combined oral and dermal exposure (TCR) indicates that for adults, Cd and Ni posed a significant risk ($TCR > 10^{-4}$), whereas Pb, As, and Cr are in the tolerable range ($10^{-4} - 10^{-6}$). For children, Cr and Cd posed a significant risk ($TCR > 10^{-4}$), As and Ni were in the tolerable range ($10^{-4} - 10^{-6}$), and Pb posed no threat ($TCR < 10^{-6}$). The cumulative risk of all the metals indicates that oral exposure poses a significant risk to adults, whereas dermal exposure poses a risk to children. However, the oral cancer risk to adults is contributed solely by Cd and Ni, while Cr contributes the entire dermal cancer risk to children.

Limitations/Uncertainties

Identifying uncertainties is crucial in the risk management process. It is not aimed at invalidating the estimated results but at acknowledging that the best outcome is not necessarily guaranteed. The exposure parameters in this study, including ingestion rate, exposure duration, and frequency, were derived from the default values of the United States Environmental Protection Agency (USEPA). This may not be entirely applicable to the local population studied, due to differences in lifestyle, dietary habits, and genetic makeup, among other factors. The study also assumed that the subgroups (adults and children) were homogeneous. Small variations that may exist can introduce some uncertainties in the risk estimate. The study was also conducted within a year; there may be temporal variation in the concentrations of the pollutants, exposure, and risk. It should be acknowledged that the pollutants assessed are not the only pollutants of concern in groundwater. Indirect exposure through ingestion of crops contaminated by irrigation water from the groundwater was also not estimated. Hence, the risk of using the groundwater may be higher than that estimated. It should also be stated that Cr concentrations were based on total Cr. Relying solely on total chromium can result in underestimating the risks associated with Cr(VI) exposure or overestimating risks if the majority of chromium present is in the less harmful Cr(III) form.

Conclusion

The assessment of oral and dermal risks associated with heavy metals and nitrates in the groundwater of Mariri, Kano, Nigeria, revealed that Pb and Cd concentrations exceeded the WHO permissible limits, whereas the concentrations of other metals and nitrates remained within acceptable ranges. Cd posed a significant non-

cancer risk via oral ingestion ($HQ > 1$) and was the major contributor to the total non-carcinogenic risk for both adults and children, emphasizing the urgency to address Cd contamination. The multi-route hazard index (MHI) for both demographics showed values exceeding one, indicating that the cumulative health risks from the mixture of these contaminants exceed safe levels. The results showed that oral ingestion accounted for a substantial portion of the non-carcinogenic risk, with children experiencing higher exposure levels than adults, underscoring their vulnerability due to physiological factors and exposure habits. Estimated lifetime risks indicate a potential for increased cancer incidence, especially for adults through oral exposure to Cd and Ni and children through dermal exposure to Cr. The study serves as a critical reminder of the need for comprehensive environmental health policies and public awareness initiatives to address the risks posed by contaminated groundwater, ensuring the safety and well-being of local populations. Continuous monitoring, risk communication, and potential remediation (e.g., source control, water treatment) are critical. Further research should focus on tailoring exposure parameters to local conditions, extending study duration, and including additional pollutants to improve risk accuracy.

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Competing Interests

The authors declare that they have no competing financial or personal interests in this research work.

Ethical Approval

The authors certify that all data used in this manuscript are original and genuine and that this research has not been published or is under consideration for publication elsewhere.

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