Modeling the impact of potentially harmful elements on the groundwater quality of a mining area (Nigeria) by integrating NSFWQI, HERisk code, and HCs

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Abstract With excess potentially harmful elements (PHEs), drinking water is marked unsuitable and could pose some health risks when ingested or absorbed by humans. Different age groups are exposed to varied risk levels of PHEs. Analyzing the health risks of PHEs for several age groups could provide detailed insights for effective water resources management. No known study in Ameka Pb–Zn mine province (Nigeria) investigated the health risks of PHEs in water resources for several age groups. Therefore, in this paper, the carcinogenic and non-carcinogenic health risks (due to ingestion and dermal contact) of PHEs in groundwater resources of this area were investigated for nine age groups. To achieve its aim, this study integrated novel HERisk code, NSFWQI (national sanitation foundation water quality index), and hierarchical clusters (HCs) in modeling the groundwater quality. Standard elemental composition analysis revealed that the groundwater is polluted with PHEs. The NSFWQI indicated that 15% of the analyzed water samples have moderate water quality whereas 85% are unsuitable for drinking. The HERisk code, which considered nine age groups (1 to < 2 years, 2 to < 3 years, 3 to < 6 years, 6 to < 11 years, 11 to < 16 years, 16 to < 18 years, 18 to < 21 years, 21 to < 65 years, and > 65 years), revealed that all the samples pose high chronic and cancer risks to all the age groups due to oral ingestion. However, it was realized that age groups 1 to < 16 and > 65 are posed with higher risks than age groups 18 to < 65. Overall, it was realized that all the age groups are far more exposed to ingest or absorb Se, Co, Cd, Se, As, Ni, and Pb than Cu, Fe, and Zn. Nevertheless, the health risks due to dermal absorption are far lower than the risks due to oral ingestion. Conclusively, children and aging people are more predisposed to the health threats than middle-aged populations. HCs and geospatial maps aided the spatiotemporal analysis of the groundwater quality.

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Introduction

Potentially harmful elements (PHEs) are usually metals and metalloids present in the food web (including water resources) that pose a number of ecological and health risks to humans when ingested or absorbed into organs (Egbueri et al., 2020a). Examples of the commonly analyzed PHEs are iron (Fe), zinc (Zn), manganese (Mn), arsenic (As), lead (Pb), cadmium (Cd), nickel (Ni), chromium (Cr), copper (Cu), cobalt (Co), mercury (Hg), and selenium (Se). The PHEs are usually noted to have a density > 4000 kg/m^3 (Rashid et al., 2021). When they occur in water, they are also known to have higher density (about five times heavier) than the water density (Birami et al., 2020; Lin et al., 2014). While Pb, As, Cd, Ni, and Cr are considered as carcinogens, the rest (Fe, Zn, Mn, Cu, Co, Hg, and Se) are considered as non-carcinogenic elements (US-EPA, 1989, 2004). Although some of the PHEs (e.g., Fe, Zn, Mn, and Cu) act as micronutrients for some human organs, their excess accumulation becomes toxic and acts as poison (Kalyoncu et al., 2012; Rashid et al., 2021; Ukah et al., 2019).

Groundwater resources are very important resources for drinking, domestic, sanitary, agricultural, industrial, and mining purposes. However, due to the rapid increase in demand of groundwater for these purposes, its contamination and pollution by PHEs have also increased. Hence, globally, there is now a steady reduction in both the quality and quantity of clean and safe groundwater resources available to satisfy the various needs of man (Egbueri & Enyigwe, 2020; Ponsadailakshmi et al., 2018; Rashid et al., 2019). There is great level of variability in the concentration of PHEs in drinking water sources in every locality. However, even at very minute concentrations, most PHEs in water resources might be very harmful and interrupt the normal functioning of human cells (Abiriga et al., 2020; Ashraf et al., 2020; Egbueri, 2020a). Thus, an outbreak of waterborne diseases (e.g., flu, sleep disorder, hearing problem, fatigue, nausea, vomiting and diarrhea, neurological anomaly, constipation, stomach cramps, loss of appetite, convulsions, coma, failure of key organs, and death in severe cases) may occur when polluted groundwater is ingested or absorbed for a certain period of time (US-EPA, 1989, 2004; Egbueri, 2020b).

Because of this fact, the evaluation and modeling of the presence and risks of PHEs in water resources, using different techniques, are of high importance (Liu & Ma, 2020; Onyemesili et al., 2020; Singh et al., 2018). For instance, in different parts of the world, various numerical (indexical) and statistical models (e.g., correlation analysis, principal component analysis, factor analysis, and hierarchical cluster analysis) have been utilized in assessing the quality of groundwater and the impact of several contaminants/pollutants on water quality and human health (Egbueri & Mgbenu, 2020; Egbueri et al., 2020b; Murasingh et al., 2018). Similarly, geographic information system (GIS) has also been utilized by several researchers (Chappells et al., 2014; Singh & Kamal, 2014; Subba Rao et al., 2021) in reporting PHE contamination and pollution in surface and groundwater resources.

However, the use of an integrated study approach has proven to present a more reliable assessment. This is partly due to the fact that different techniques provide different levels of insight regarding the water quality data. Thus, when different scientific techniques are combined, a more robust data interpretation is likely to be obtained. Several studies that utilized integrated approach have reported PHE contamination and pollution in water from different countries across the globe, including India (Aithani et al., 2020; Ravindra & Mor, 2019; Subba Rao et al., 2021), Bangladesh (Bodrud-Doza et al., 2020), Saudi Arabia (Ghrefat et al., 2014; Mohamed & Al Shehri, 2009; Zumlot et al., 2013), China (Li et al., 2014; Xu et al., 2015), Australia (Saha et al., 2017), Pakistan (Rashid et al., 2019, 2021; Shah & Tariq, 2006), and Nigeria (Egbueri & Unigwe, 2019; Ngele et al., 2015; Onyemesili et al., 2020).

These previous studies (highlighted above) proved that both geogenic and human-induced processes are responsible for the PHE contamination and pollution. The natural, geogenic sources of PHEs include rock weathering, mineral dissolution, sediment deposition, redox processes, and influx of geothermal water (Buchet & Lison, 2000; Macklin & Klimek, 1992; Maity et al., 2020). On the other hand, surface runoff in environments with poor sanitation, industrial waste-water effluents, petrochemicals, poor waste disposal in landfills, acid mine drainage, inadequate agricultural practices, emissions from plants and vehicles, and mining are some of the anthropogenic

input channels responsible for PHEs released in water (Egbueri & Enyigwe, 2020; Rashid et al., 2021; Ukah et al., 2019). In Nigeria, previous studies that applied integrated approaches also indicated that both human-induced and geogenic factors are responsible for groundwater quality deterioration (Ighalo & Adeniyi, 2020; Ighalo et al., 2020). Being influenced by both geogenic processes and anthropogenic activities (Egbueri et al., 2020b), PHEs in water resources have formed a strong basis for water quality studies, environmental impact analysis, and human health risk assessment.

Numerous studies have been conducted across the globe to assess the human health risks of PHEs in water resources. Most of these studies have been based on the conventional health risk assessment methodology proposed by US-EPA (1989). Nevertheless, several limitations have been identified to mar the effectiveness of the US-EPA approach for human health risk assessment (Neris et al., 2019, 2021). Previously, Neris et al. (2019) introduced HHRISK code for assessing human health risk. The HHRISK code broadly considers two age groups (i.e., child and adult populations) and two exposure pathways (i.e., ingestion and dermal routes) in the health risk assessment of water resources (Neris et al., 2019). Although the HHRISK code addressed some limitations of the US-EPA methodology, some important details could not be obtained from its application (Neris et al., 2021). Thus, there was need to broaden and enhance the scope of HHRISK code. In attempt to resolve the limitations of the HHRISK code, Neris et al. (2021) introduced a novel HERisk code with broader scope and functions. In HERisk coding, nine age groups are considered and evaluated for, which makes its assessment to be more precise, comprehensive, robust, and reliable.

The present study is focused on the groundwater resources of Ameka mine province in southeastern Nigeria. Previously, some studies have been conducted in this mining region to account for the PHE contamination and pollution of the water resources (Ngele et al., 2015; Nnabo, 2015; Okolo et al., 2018). Recently, other studies were conducted in this region to investigate the ecological and human health risks of PHEs in the water resources of this mine province (Egbueri & Enyigwe, 2020; Egbueri et al., 2020; Obasi & Akudinobi, 2020). Although these studies presented interesting findings on

human health risks, there seems to be some limitations regarding the number of age groups they considered. Literature review has suggested that different age groups are exposed to varied risk levels of PHEs (US-EPA, 2004, Neris et al., 2019, 2021), and the number of age groups considered in every assessment determines the amount of information available to policymakers for sustainable water resources management (Neris et al., 2021). Analyzing the health risks of PHEs for several age groups seems to provide detailed and more comprehensive insights needed for effective water resources management. No known study in the Ameka mine province investigated the health risks of PHEs in water resources for several age groups. Therefore, in this paper, the carcinogenic and non-carcinogenic health risks (due to ingestion and dermal contact) of PHEs in groundwater resources of this area were investigated for nine age groups. In order to achieve its aim, the present study integrated the novel HERisk code, NSFWQI (national sanitation foundation water quality index), hierarchical clustering (HCs), and geospatial mapping in modeling the groundwater quality of this mine province. The specific objectives are to (1) analyze the elemental compositions of the groundwater resources and the possible effects of the PHEs analyzed, (2) evaluate the drinking suitability of the groundwater using NSFWQI model, (3) assess the human health risks of the PHEs in the groundwater resources using the HERisk code, and (4) analyze the spatiotemporal water quality of the mine area using HCs and geospatial maps. More details on the selected models for this work are given in the "Materials and methods" section. It is hoped that this paper will provide deeper insights necessary for the planning, protection, pollution mitigation, and sustainable management of the groundwater resources in the study area. Additionally, the information provided in this research would be useful for public health protection and in advancing water quality research.

Materials and methods

Study area

The study area lies within latitudes 6° 8′N–6° 13′N and longitudes 8° 5′E–8° 10′E (Fig. 1). It is easily accessible through the Abakaliki-Onueke Road, and
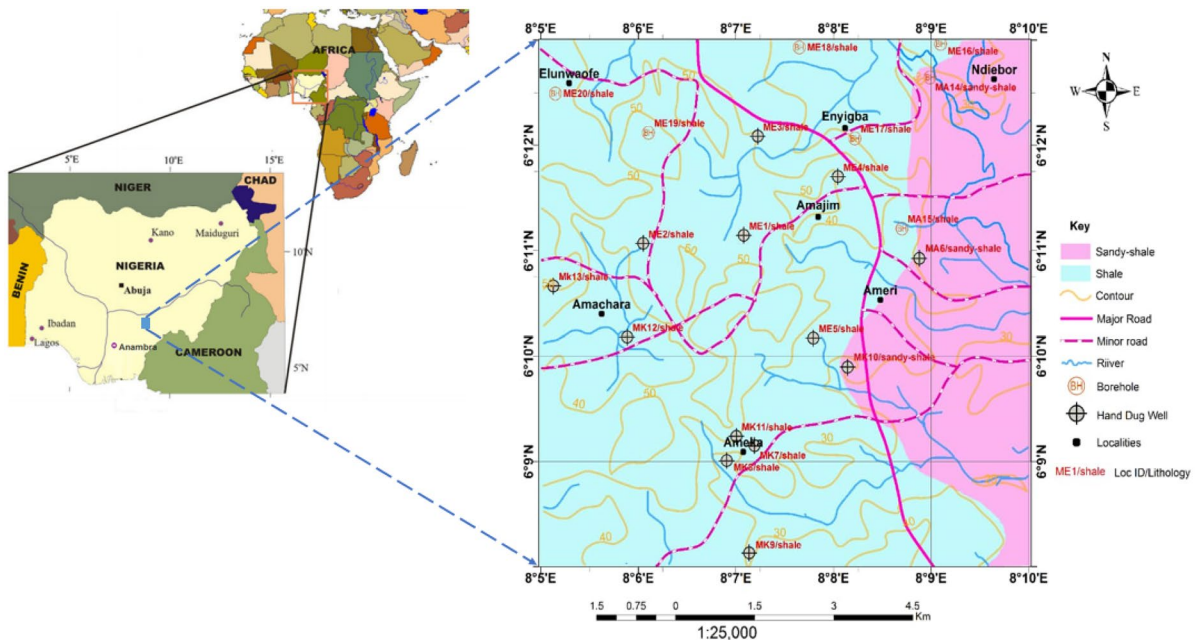
Fig. 1 Location and geologic map of the area

a diversion at Nkwegu through the Enyigba-Ikwo Road. Other minor roads include Ameri-Nwafor-Egu, Mbareke-Ameka, and Ameka-Enyigba. Footpaths also facilitate access into the interior of the area. The footpaths facilitated the collection of water samples from different settlements. Ameka metallogenic district is well blessed with economically valued minerals like galena, pyrite, quartz, sphalerite, and chalcopyrite (Egbueri & Enyigwe, 2020). Salt springs are also present in the study area. Due to the presence of economic deposits in the area, many inhabitants now practice indiscriminate and illegal mining of the available natural resources. Aside from the mining of the resources, the inhabitants of this locality rely so much on agricultural activities, which usually involve the use of different types of agrochemicals such as pesticides and herbicides. These human activities, combined, seem to pose threats to the water environment and public health.

Two seasons (i.e., rainy/wet and dry seasons) are experienced in this area annually. The rainy season, which averages between 1750 and 2250 mm, often extends from April to October while the dry season usually extends from November to March. For the dry season, the temperature range is about 25–39 °C. However, for the rainy season, the temperature range

could drop to about 20–28 °C (Egbueri & Enyigwe, 2020). In this area, most people rely on surface water resources (ponds and streams) and hand-dug wells for mining, domestic, and agricultural water supply, as deeper borehole wells are much more expensive. This rural area has an uneven, undulating topography, with most of its isolated hillocks placed at elevations ≥ 150 m. Being drained by a number of surface water networks, the rural community is mainly drained by the perennial Ebonyi River and its interlinked dendritic and rectangular tributaries. However, it is believed that the predominant drainage pattern of the area is largely influenced by its topography and geology (Egbueri & Enyigwe, 2020).

Geologically, the study area is mainly underlain by the Abakaliki Shale (Lower Cretaceous) (Fig. 1). This lithostratigraphic unit is fundamentally composed of calcareous shales with alternating sequences of sandstones, siltstones, limestones, and mudstones in some places (Agumanu, 1989; Farrington, 1952; Kogbe, 1989). Most of the shale deposits occurring in this study area have been intensely weathered and ferruginized. Some portions were either fractured (faulted or jointed) or folded (Nwajide, 2013). These deformational structures house the minerals' veins being mined for. Proximal to some veins are bands of

ironstones and baked shales. The clayey soils derived from the weathering of the mudrocks present in this area are usually waterlogged within valleys and flood plains.

Collection of groundwater samples and PHEs analysis

In order to achieve the objectives of this paper, twenty groundwater samples from Ameka and environs were collected and analyzed for PHEs. Specifically, thirteen hand-dug wells and seven boreholes were sampled across the Pb–Zn mining areas using polyethylene bottles in September 2019. The sampling period represents the rainy season. The water sources availability and distribution influenced the sample numbers, in that most of the rural inhabitants rely more on hand-dug wells than boreholes, as the former is cheaper than the latter. The sample locations are depicted in Fig. 1. It is pertinent to note that, prior to the collection of water from the various groundwater sources, the sample bottles to be used were prewashed and acidified with hydrochloric acid. This was done to maintain the integrity and quality of the samples. However, at each sampling point, the water to be sampled was first used to rinse the sample bottle before the water sample collection. The collected samples were subjected to temperature and pH measurements in situ using a portable thermometer and HANNA pH-meter, respectively. Afterwards, the samples were kept under refrigeration before laboratory analysis. The groundwater samples were analyzed for Pb, As, Cd, Ni, Co, Cu, Fe, Mn, Se, and Zn in the laboratory using atomic absorption spectroscopy standard techniques. It is also worthy to note that the sampling and analytical procedures adopted in this work are in line with the guidelines and recommendations of the American Public Health Association (APHA, 2005, 2012).

Groundwater quality modeling based on NSFWQI

The NSFWQI was utilized to examine the state of water quality in the current research. It offers a reliable approach for evaluating freshwater quality. Most previous studies that have applied NSFWQI focused on surface water quality assessment. However, in the present study, this model was applied in groundwater quality assessment of the Ameka mine area. A total

of 12 parameters (that included PHEs) were considered in this process, and the calculation is done as expressed in Eq. (1).

$$\sum_{i=1}^{n} w_i q_i \tag{1}$$

where, q_i is the sub-index for ith water quality parameter, and w_i is the weight factor for ith parameter ranging from 0 to 1, as shown in Eq. (2). The obtained weight factors for the analyzed parameters are given in Table 1. The parameter weighing factors were assigned based on the relative importance of the water quality parameters and the relevant water quality criteria (Brown et al., 1970). In the present study, twelve parameters were considered in the NSFWQI calculation, and each factor was assigned a weight (as shown in Table 1) based on its importance in water quality, which is one effective way to assess water quality index in order to give relative water quality status of different water systems (Bordalo et al., 2006; Shokuhi et al., 2012; Wills & Irvine, 1996).

$$\sum_{i=1}^{n} w_i = 1 \tag{2}$$

Since NSFWQI index is a reduction index, it decreases with increasing water pollution. This index ranges from 0 to 100 and is categorized according to Table 2 (Brown et al., 1970; Matta et al., 2020).

Table 1 Weight factor of water quality parameters for NSFWQI evaluation

Parameters	Weighting factor
pH	0.11
Temperature (^{o}C)	0.10
Arsenic (mg/L)	0.10
Lead (mg/L)	0.10
Cadmium (mg/L)	0.08
Nickel (mg/L)	0.12
Cobalt (mg/L)	0.05
Copper (mg/L)	0.08
Iron (mg/L)	0.08
Manganese (mg/L)	0.08
Selenium (mg/L)	0.05
Zinc (mg/L)	0.05

Table 2 Water quality classification based on NSFWQI model

Water quality category	Index value range
Excellent	90–100
Good	75–90
Medium	50–75
Unsuitable	25–50
Very unsuitable	0–25

Groundwater quality modeling based on novel HERisk code

The inhabitants of this mining area could be risking several health defects by ingesting contaminated or polluted groundwater resources. The higher the loads of PHEs in drinking water resource, the higher the human health risk, usually referenced as the chronic daily intake. Thus, the toxicity of the PHEs will be much dependent on the rate of ingestion or absorption of the polluted water. In the present study, HERisk (health, ecological, and radiological risk) model, which was recently developed by Neris et al. (2021), was tested and applied in this study to model the human health risks of the PHEs in the analyzed groundwater resources. The outcome of this assessment could (1) demonstrate the effectiveness of the HERisk model in pollution and health risk assessment, (2) provide essential information for environmental monitoring of the groundwater resources, and (3) provide possible insight towards the management of the water pollution challenges in time and space.

The HERisk code was first applied in assessing inorganic pollutants in soils and water resources in a mining region of Brazil (Neris et al., 2021). Neris et al. (2021) developed the HERisk software to incorporate a standardized technique for evaluating risks associated to several activities with special reference to the standard toxicological criteria stated by the United States Environmental Protection Agency (US-EPA). While allowing the overall aging effect of the human population exposed to risk to be considered, this model ensures that risk evaluations are tailored towards varying exposure routes in an area. The greater flexibility and convenience associated to the novel HERisk model (Neris et al., 2021) justifies why it can be described as the improved version of HHRISK code which was developed by Neris et al. (2019). Moreover, the HERisk is believed to provide

a more realistic and unique risk assessment than other health risk algorithms; in that the new HERisk algorithm provides insight regarding the incremental mental effects due to exposures to PHEs and the specific timeframe when the PHEs exposures would become critical (Neris et al., 2021).

The first step in HERisk modeling is the calculation of the daily intake dose (for oral route) and the daily absorbed dose (for dermal route), which depicts the actual quantity of the PHEs that goes into the human organs and systems. The daily dose intake is mathematically expressed as Eq. (3) (for water ingestion by oral route) and Eq. (4) (for water absorption by dermal contact route).

$$D_{ing\_w}^{IA}(t) = \sum_{t=\Delta t}^{ED} \frac{C_w(t) \bullet IR_w(i) \bullet FI_w \bullet EF(i) \bullet \Delta t}{BW(i) \bullet AT} \quad (3)$$

$$D_{der\_w}^{IA}(t) = \sum_{t=\Delta t}^{ED} \frac{C_w(t) \bullet CF_3 \bullet SA_w(i) \bullet PC \bullet ET_w \bullet EV_w(i) \bullet EF(i) \bullet \Delta t}{BW(i) \bullet AT} \quad (4)$$

where, IA is the initial age, $C_w(t)$ is the PHE concentration in water at time t (mg L^{-1}); ED is the number of years of exposure duration; $IR_w(i)$ is the ingestion rate of water for age group i (L day^{-1}); FI_w is the fraction ingested of water; $EF(i)$ is the exposure frequency for age group i (day year^{-1}); Δt is the time variation (y); $BW(i)$ is the body weight for age group i (kg); AT is the averaging time (day); CF_3 is the volumetric conversion factor (L cm^{-3}); $SA_w(i)$ is the skin surface area available for contact (when swimming or showering) with water for age group i (cm^2); PC is the dermal permeability of the PHEs (cm h^{-1}); ET_w is the water exposure time during swimming or showering for age group i (h event^{-1}); and $EV_w(i)$ is the swimming or showering event frequency for age group i (events day^{-1}) (Neris et al., 2021). The parameter values used for the exposure dose computations and appropriate references are outlined in Table S4 in Neris et al. (2021).

It is important to mention that the IA is for nine age groups. According to Neris et al. (2021), the HERisk code performs the evaluations of the health risks for initial ages (IA = 1, 2, 3, 6, 11, 16, 18, 21, and 65 years), separately. This model utilizes the following values for age groups (i): > 65 years (i = 9), 21 to < 65 years (i = 8), 18 to < 21 years (i = 7), 16 to < 18 years (i = 6), 11 to < 16 years (i = 5), 6 to < 11 years (i = 4), 3 to < 6 years (i = 3), 2 to < 3 years (i = 2), and 1 to < 2 years (i = 1).

After the daily intake dose has been evaluated, the hazard quotient (non-cancer risk) at time t for initial age IA (Eq. (5)), cancer risk at time t for initial age IA (Eq. (6)), aggregated hazard index (non-cancer risk) at time t for initial age IA (Eq. (7)), total or cumulative hazard index (non-cancer risk) at time t for initial age IA (Eq. (8)), aggregated cancer risk at time t for initial age IA (Eq. (9)), and total or cumulative cancer risk at time t for initial age IA (Eq. (10)) were calculated accordingly.

$$HQ_w^{IA}(t) = \frac{D(t) \bullet BAF}{RfD} \tag{5}$$

$$CR_w^{IA}(t) = D(t) \bullet SF \bullet BAF \bullet ADAF \tag{6}$$

$$HI_{agg}^{IA}(t) = \sum_{w=1}^{z} HQ_w(t) \tag{7}$$

$$HI_{tot}^{IA}(t) = \sum_{j=1}^{n} HI_{agg,j}(t) \tag{8}$$

$$CR_{agg}^{IA}(t) = \sum_{w=1}^{z} CR_w(t) \tag{9}$$

$$CR_{cum}^{IA}(t) = \sum_{j=1}^{n} CR_{agg,j}(t) \tag{10}$$

The components of Eqs. (5)–(10) are defined as thus: $D^{IA}(t)$ is the dose at time t for initial age IA (mg kg^{-1} day^{-1}); SF is the slope factor of PHEs (mg kg^{-1} day^{-1})$^{-1}$; BAF is the PHE dose fraction or simply the bioavailability factor; RfD is the reference dose of the PHEs (mg kg^{-1} day^{-1}); $ADAF$ is the age-dependent adjustments factors; and n is the number of the PHEs (Neris et al., 2021).

Spatial–temporal analysis of groundwater quality

The spatio-temporal analysis is believed to be useful in establishing the similarities and clusters within groundwater samples of any region. By this analysis, the possible contamination sources could be predicted. In this paper, the spatio-temporal distribution of groundwater quality in the study area was to introduced to strength its scope and focus. This analysis was performed using GIS technique and hierarchical clustering of the samples based on their NSFWQI

and HERisk values. Surfer GIS package (v. 9) was employed in generating the water quality spatial maps. However, for the hierarchical clustering, the Ward's linkage method with squared Euclidean distance and *z-score* transformation optimizer was utilized in generating Q-mode dendrograms for the NSFWQI and HERisk models. The hierarchical clustering was performed in SPSS (v. 22).

Results and discussion

Elemental composition of groundwater resources and potential impacts

Water pH

The obtained pH values for the groundwater samples ranged from 4.8 and 7.8 mg/L (Table 3). The groundwater samples were acidic to alkaline in nature. Alkaline water has been shown to cause hair fiber swelling and gastrointestinal irritation (Rose, 1986). On the other hand, acidic water has been identified to be unpalatable for human consumption (WHO, 2017) and causes mucous membrane cell injury, eye irritation, and skin irritation (WHO, 1984; Meinhardt, 2006). Moreover, acidic water is known to also contribute significantly to metal pipe corrosion and scaling (Egbueri, 2021; Egbueri et al., 2020c) and disinfection quality, which has an indirect impact on human health. The alkalinity of the groundwater samples could be attributed to soil bicarbonates which could have percolated into the groundwater by rainwater. In turn, soil bicarbonate could be influenced by the biological degradation of waste in the soil. The acidic nature of the groundwater samples could be due to carbonic acid deposit usually formed by carbon dioxide (CO_2) reacting with rain water (Tiwari et al., 2015). Over time, some chemical processes can transport this from the surface of the soil to form deposits in the groundwater system.

Temperature

Another critical parameter in the assessment of potentially hazardous elements is the temperature of the groundwater. The range and mean values of temperature in the groundwater area were observed to be from 27.0 to 39.0 °C and 13.02 °C, respectively (Table 3).

Table 3 Water quality data for the present assessment

Nomenclature		Physical parameters		Carcinogenic elements				Non-carcinogenic elements						
Sample ID	Source	pH	T (°C)	As	Pb	Cd	Ni	Co	Cu	Fe	Mn	Se	Zn
ME/1	HDW	6.6	29	0.23	0.12	5.1	1.17	4.21	0.17	0.45	0.31	2.46	0.2
ME/2	HDW	5.1	28	0.17	0.1	3.2	1.04	1.26	0.08	0.24	0.34	2.46	0.2
ME/3	HDW	4.8	39	0.2	0.12	6.2	1.51	1.71	0.03	0.33	0.4	2.48	0.2
ME/4	HDW	5.2	29	0.31	0.2	0	1.7	0.63	0	0.64	0.47	2.47	0.2
ME/5	HDW	6.1	29	0.24	0.13	0	1.44	3.08	0.08	0.23	0.38	2.51	0.4
MA/6	HDW	7.6	31	0.23	0.11	0.01	1.61	1.05	0.04	0.24	0.46	2.49	0.6
MK/7	HDW	7.8	36	0.24	0.13	0.11	1.9	8.21	0.01	0.3	0.55	2.52	0.5
MK/8	HDW	5.2	35	0.18	0.1	0	0.81	2.21	0.01	0.21	0.34	2.45	0.2
MK/9	HDW	4.9	31	0.14	0.31	0	0.93	8.64	0.02	0.71	0.52	2.5	0.3
MK/10	HDW	6.3	29	0.24	0.12	1.4	1.03	0.97	0.03	0.36	0.47	2.51	0.2
MK/11	HDW	4.8	28	0.19	0.09	1.3	0.94	4.67	0	0.41	0.25	2.47	0.7
MK/12	HDW	5.3	30	0.23	0.18	0	1.08	2.39	0	0.68	0.43	2.45	0.2
MK/13	HDW	5.2	31	0.3	0.25	0	0.96	5.06	0.06	0.57	0.45	2.48	0.3
MA/14	BH	6.9	27	0.18	0.11	8.3	0.81	3.92	0.02	0.25	0.47	2.47	0.2
MA/15	BH	6.6	30	0.13	0.07	5.2	0.85	1.04	0.01	0.19	0.47	2.48	0.8
ME/16	BH	6	27	0.24	0.12	0	0.88	4.48	0	0.48	0.55	2.48	0.1
ME/17	BH	6.6	29	0.16	0.08	0	0.77	3.46	0	0.3	1.01	2.45	0.2
ME/18	BH	6.7	28	0.15	0.06	0	0.89	9.13	0	0.44	1.14	2.49	0.2
ME/19	BH	6.8	28	0.15	0.06	0	0.72	1.95	0	0.28	0.47	2.45	0.2
ME/20	BH	5.6	30	0.17	0.09	0	1.44	5.21	0	0.39	0.25	2.47	0.2
Average	–	6.0	30.2	0.204	0.128	1.541	1.124	3.664	0.028	0.385	0.487	2.477	0.305
Minimum	–	4.8	27	0.13	0.06	0	0.72	0.63	0	0.19	0.25	2.45	0.1
Maximum	–	7.8	39	0.31	0.31	8.3	1.9	9.13	0.17	0.71	1.14	2.52	0.8
CV	–	0.1547	0.1028	0.2481	0.4966	1.6763	0.3104	0.7098	1.5135	0.4175	0.4527	0.0086	0.6336
SD	–	0.9288	3.1052	0.0506	0.0633	2.5832	0.3489	2.6001	0.0424	0.1607	0.2203	0.0213	0.1932
SON (2015)	–	6.5–8.5	Ambient	0.01	0.01	0.003	0.07	–	0.1	0.3	0.2	0.01	3
WHO (2017)	–	6.5–8.5	Ambient	0.01	0.01	0.003	0.07	0.004	0.05	0.3	0.4	–	3

HDW, hand-dug well; *BH*, borehole; *CV*, coefficient of variance; *SD*, standard deviation

Overall, the groundwater samples were observed to be in warm condition. Such condition makes the water unpalatable for drinking and might even lead to the growth of potentially toxic microbes (WHO, 2017; Egbueri, 2019). The groundwater sample (ME/3) had the highest temperature, while the groundwater samples (MA/14 and ME/16) had the lowest. The pH and oxygen-reduction potential levels of groundwater might have influenced the temperature of the groundwater. Furthermore, it is thought that due to the propensity of dissolved ions to stay in the aqueous form, the concentration of potentially hazardous elements in groundwater possibly increased as a result of higher temperatures (Sari & Tuzen, 2008).

Arsenic

Both geochemical processes and human activities have greatly contributed to arsenic pollution of water (US-EPA, 2005; WHO, 2017; Egbueri & Enyigwe, 2020). In the examined groundwater samples, respective minimum and maximum arsenic concentrations were 0.13 to 0.31 mg/L, respectively (Table 3). This indicates that all the groundwater samples exceeded the SON (2015) and WHO (2017) drinking water standard of 0.01 mg/L, as a result of ore degradation in the Pb–Zn mining area. According to the ATSDR (2007), arsenic is found in metal ores such as copper and lead and can also be found in volcanic rocks. It

is known that arsenic can be present in a variety of forms in the earth's crust, including occurrence as sulfides, arsenides, and arsenates. It is mainly present as arsenate in water, but it is more likely to be present as arsenite in anaerobic conditions (Almela et al., 2002). It is usually found in natural waters at concentrations of less than 12 mg/L. Moreover, it is worthy to mention that arsenic concentrations can be significantly elevated in waters, especially groundwaters, where sulfide mineral deposits and sedimentary deposits derived from volcanic rocks exist, up to 12 mg/L WHO (2011). However, it has also been reported that arsenic can be found in the diet, particularly in fish and shellfish, where it is mostly present in the less harmful organic type (Garvey et al., 2013).

Health-wise, arsenic is a protoplasmic poison since it mainly affects the sulfhydryl community of cells, disrupting cell respiration, enzymes, and mitosis (Gordon & Quastel, 1948). Arsenic is known to be highly carcinogenic and can cause cancer of lungs, liver, bladder, kidney, and skin (US-EPA, 2005). Furthermore, arsenic compounds are linked to a variety of health issues, including lymphatic cancers, gastrointestinal disturbances, and the development of neoplasms, due to their high toxicity (Shi et al., 2004). Reduced red and white blood cell output, which can cause weakness, irregular heart rhythm, blood vessel damage, which can cause bruising, and reduced nerve function, which can cause a "pins and needles" feeling in the hands and feet, are all possible side effects of excess arsenic in humans (ATSDR, 2007). Nevertheless, acute poisoning may occur as a result of deliberate ingestion of arsenic in the case of suicide attempts or accidental intake by children (Mazumder, 2008; Saha et al., 1999).

Lead

Lead (Pb) is one of the abundant natural elements on the planet. It has a wide range of industrial applications due to its physical properties, which include a low melting point and high malleability. It is ranked fifth on the list of metals in terms of use (Karrari et al., 2012). The general public is exposed to lead in nearly equal amounts by air and food. While much higher concentrations (over 100 mg/L) have been calculated where lead fittings are present, its occurrence and concentrations in drinking water are usually below 5 mg/L (Howard & Bartram,

2003). From the result analysis, lead concentrations of the groundwater samples ranged between 0.06 and 0.31 mg/L (Table 3). The result indicates that the concentration of lead in all the analyzed groundwater sources in the study area is above the standard limit of 0.01 mg/L for drinking water (SON, 2015; WHO, 2017; Table 3). This finding clearly shows that the gangues and mine wastes of lead ores (galena) have a substantial impact on the safety of the area's groundwater supplies. Aside the amount of waste and gangues in the area, low pH, salinity, and presence of CO_2 in the water sources may be responsible for the high lead accumulation in the groundwater (ATSDR, 2007). Other sources of Pb have been mentioned to include gasoline, house paint, plumbing pipes, lead bullets, storage batteries, pewter pitchers, toys, industrial processes, automotive exhaust, and faucets (Hernberg, 2000; Malekirad et al., 2011; Ukah et al., 2019).

Lead, a potent toxicant with widespread use, is a major source of concern due to massive environmental pollution, which has resulted in serious health issues in many parts of the world (WHO, 2017; Egbueri, 2020b). As a stable pollutant, its toxicity manifests itself in a variety of ways, from subclinical and subtle symptoms to life-threatening complications (Pourmand et al., 2012). Acute exposure may trigger nausea, headaches, asthma, stomach pain, renal impairment, exhaustion, insomnia, arthritis, hallucinations, and vertigo, whereas chronic exposure can cause intellectual disability, birth defects, paranoia, autism, allergies, dyslexia, weight loss, hyperactivity, paralysis, muscle weakness, brain harm, and even death (Egbueri, 2020b; Papanikolaou et al., 2005; Ukah et al., 2019). Owing to play behavior and increased hand-to-mouth movements, children are more susceptible to its toxicity than adults (CDCP et al., 2005). It has been stated in the literature that children with a rapid growth path have higher intestinal absorption of lead than adults, given the fact that this ability decreases with age (Ziegler et al., 1978).

Cadmium

According to ATSDR (2007), cadmium is the seventh most toxic heavy metal. Humans and animals can be exposed to it at work or in the ecosystem as a by-product of zinc processing. Once humans

absorb this metal, it will build up within their bodies for the rest of their lives. The levels of cadmium's occurrence in drinking water are normally less than 1 mg/L (Elinder, 1985). From the analysis, cadmium concentration of the groundwater samples ranges from 0 mg/L (in most of the samples) to 8.3 mg/L (Table 3). About 60% of the samples are below the WHO (2017) guideline value of 0.003 mg/L for drinking water. This reveals a low concentration for cadmium in these localities. Meanwhile, high values of Cd were recorded in some mine localities, represented by ME/1, ME/3, MA/14, and MA/15. This observation is typical of an acute pollution scenario. The weathering and eventual dissolution of the chalcopyrite and pyrite ores in the area can be attributed to these high levels.

Cadmium movement in water is influenced by a number of factors, including pH and the presence of organic matter. Cadmium binds tightly to organic matter in particular, and this immobilizes cadmium for the most part (Autier & White, 2004). When the pH of the water is low (acidic), cadmium is more readily available (Elinder, 1992). Cd poisoning may trigger *itaiitai*, a degenerative bone disease, by causing Cd to replace Ca in the bones. Furthermore, studies on animals and humans have shown that cadmium can cause bone mineralization, resulting in osteoporosis (i.e., skeletal damage). Short-term cadmium inhalation can cause serious lung damage and respiratory discomfort, whereas higher doses of cadmium ingestion can cause stomach irritation, resulting in vomiting and diarrhea (Egbueri, 2020b). Cadmium is extremely toxic to kidneys, and it accumulates in higher concentrations in the proximal tubular cells resulting in renal dysfunction and disease. Cadmium poisoning can also lead to calcium metabolism problems, the development of kidney stones, and hypercalciuria (Obasi & Akudinobi, 2020).

Nickel

Nickel and its compounds are common noxious agents in industry, but they have also been linked to several health problems (SON, 2015; WHO, 2017; Ukah et al., 2019). Nickel can be found in the air, food, and water, putting the general public at risk. In relation to health hazards, inhalation is a common route of occupational nickel exposure. However, the majority of nickel in the human body comes from

drinking water and food; but, due to reduced intestinal absorption, the gastrointestinal route is of lesser significance (Cempel & Nikel, 2006). According to WHO (2011), nickel occurs naturally in water at concentrations of less than 0.02 mg/L. However, in this present study, the amount of nickel concentration of the groundwater samples in this mine area was found to range from 0.72 to 1.90 mg/L, with an average concentration of 1.124 mg/L (Table 3). This result demonstrates that the groundwater samples have higher values above the SON (2015) and WHO (2017) guideline value of 0.07 mg/L for drinking water. This reveals high concentration for nickel in the water environment. It is worthy to note that the high nickel contents found in mining areas may be linked to effluent water from mining and smelting activities, drainage from tailing piles, or utility water used for mine operations (ATSDR, 2005).

This element is known to cause both carcinogenic and non-carcinogenic organ ailments when ingested or adsorbed in excess (Egbueri & Mgbenu, 2020; Egbueri, 2020b; Ukah et al., 2019). Nickel has a wide variety of carcinogenic pathways, including transcription factor, regulated gene expression, and the production of free radicals (Engwa, 2018). Nickel has been found to play a role in the regulation of the transmission of complex long non-coding ribonucleic acids, and has also been shown to produce free radicals, which leads to carcinogenic processes (Engwa, 2018). Asthma, conjunctivitis, allergic reactions to nickel-containing prostheses and implants, and systemic reactions following parenteral administration of nickel-contaminated fluids are all symptoms of nickel hypersensitivity. Because of the vulnerability to nickel, it is important to keep an eye on nickel levels in drinking water, and nickel-allergic people should be aware that drinking water on an empty stomach increases absorption (Nielson et al., 1999).

Cobalt

Cobalt can rarely be found in its original state but also exists in sulfide and arsenide form as minerals which are linnaeite (Co_3S_4), carrollite ($CuCo_2S_4$), cobaltite (CoAsS), and smaltite ($CoAs_2$) (Turekian & Scott, 1994). In the examined sample locations, the respective minimum and maximum Co concentrations were 0.63 mg/L and 9.13 mg/L (Table 3). Cobalt is highly radioactive, according to ATSDR (2004), and high

concentrations can pose a serious health risk. Cobalt concentration in drinking water above 0.004 mg/L is considered to be unacceptable (WHO, 2017). Based on the water analysis result (Table 3), all of the groundwater samples were observed to show high cobalt concentrations. This may be attributed to the area's rock weathering and mining. The action of cobalt in water is affected by acidity and redox potential. Since increasing H^+ concentration competes with metal binding sites, cobalt adsorption by particulate matter decreases as pH decreases (Andreev & Simenov, 1990). Cobalt is needed for the synthesis of vitamin B-12, which is an important nutrient for humans. However, people exposed to high levels of cobalt have been confirmed to develop lung disorders such as wheezing, asthma, and pneumonia (Chaney, 1982).

Copper

Copper is a mineral that is essential for good health. Higher doses, on the other hand, may be dangerous (WHO, 2017; Ukah et al., 2019). In other words, copper is both an essential element and a contaminant in drinking water (WHO, 2017). In developed countries, the main sources of copper toxicity are food and water. Geogenically, chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), covellite (CuS), cuprite (Cu_2O), and malachite ($CuCO_3.Cu(OH)_2$) are different types of ores that harbor copper (ATSDR, 2007). From the result presented in Table 3, the minimum and maximum copper concentrations were recorded to be 0 mg/L and 0.17 mg/L, respectively. This result further indicated that about 70% of the analyzed groundwater samples have copper values below the permissible concentration of 0.1 mg/L specified by the SON (2015) and 0.05 mg/L specified by the WHO (2017). When excess copper is present in water (i.e., above the permissible level), gastrointestinal disorder occurs after a long period of exposure. Apart from the copper concentrated in the drinking water resources, copper dust in the mining area can irritate human nose, mouth, and eyes, as well as cause headaches, dizziness, nausea, and diarrhea if one is exposed to it for an extended period of time. Furthermore, copper poisoning can result in liver and kidney damage, as well as death, if consumed in excess (ATSDR, 2004; Egbueri, 2020b). However, copper's ability to cause cancer in humans is unknown. Since there are no

sufficient human or animal cancer studies, the US-EPA does not recognize copper as a human carcinogen (ATSDR, 2004).

Iron

Iron, like manganese, is found in nature as ores (e.g., magnetite, taconite, and hematite) in rocks, soils, and minerals, accounting for around 5% of the Earth's crust (Colter & Mahler, 2006). When it is pure, it is a dark-grey color, and it is found in groundwater as ferric hydroxide. The minimum and maximum iron concentrations of 0.19 and 0.71 mg/L were recorded respectively (Table 3). From the analyzed groundwater samples, about 65% of the groundwater samples have Fe concentrations above the permissible SON (2015) and WHO (2017) standard value of 0.3 mg/L. Fe is good for blood formation, as anemia has been identified in humans as a result of Fe deficiency. However, hemosiderosis (liver damage), diabetes mellitus, arteriosclerosis, and a variety of other neurodegenerative diseases may all be caused by drinking water with high Fe concentrations (Brewer, 2009; Nagendrappa et al., 2010). The observed Fe concentrations above the acceptable amount could be attributed to (1) weathering of iron minerals and rocks in the soil (Egbueri & Mgbenu, 2020), and (2) leaching of iron natural deposits into groundwater bodies.

Manganese

Manganese (Mn) is a naturally occurring element found in ores and rocks. It is an essential component of biological systems whose chemical behavior is determined by pH, oxidation, and reduction reactions (Clewell et al., 2003; Shand et al., 2007). The water analysis shows that the concentration of manganese for the groundwater samples ranges from 0.25 to 1.14 mg/L (Table 3). This result shows that about 65% of the groundwater samples have higher values above the WHO (2017) guideline value of 0.4 mg/L. The degradation of manganese from the chalcopyrite and siderite ores that underlie the study area could be responsible for the high concentration. Moreover, the high Mn content is believed to be influenced by the solubility, pH, Eh (i.e., redox potential) and the characteristics of the available anions in the groundwater (Clewell et al., 2003). High manganese levels have negative consequences such as metallic and

unpleasant flavor in water, blackish staining of washing and plumbing due to water as well as the formation of dark-colored scales in water pipes (Takeda, 2003). Although manganese is a necessary elemental component of the human body, it has recently become a source of global concern. Excess manganese in the human body may lead to the development of Parkinson's disease–like tremor, manganese poisoning, gait disorder, rigidity, postural instability, mood disorder, bradykinesia, micrographia, and cognitive disorder (Obasi & Akudinobi, 2020).

Selenium

Result of the analysis shows that the concentration of selenium for the groundwater samples ranges from 2.45 to 2.52 mg/L (Table 3). All examined groundwater samples revealed selenium concentration above the permissible standard values of 0.01 mg/L (SON, 2015). Selenium in high doses can cause serious side effects (Obasi & Akudinobi, 2020) including nausea, vomiting, nail changes, fatigue, and irritability. Hair loss, white horizontal streaking on fingernails, nail inflammation, weakness, irritability, nausea, vomiting, garlic breath odor, and a metallic taste are all signs of long-term use poisoning, which is close to arsenic poisoning. Selenium can also be present in rocks and soils, often in conjunction with sulfur-containing minerals or silver, copper, lead, and nickel minerals (ATSDR, 2003).

Zinc

According to research, the earth crust contains around 0.05 g/kg of zinc naturally (Dohare et al., 2014). From the study areas, the minimum and maximum zinc levels were 0.1 mg/L and 0.8 mg/L, respectively (Table 3). All examined samples revealed zinc concentration below the permissible standard values of 3 mg/L (SON, 2015; WHO, 2017). This may be signifying that zinc in its natural mineral form (sphalerite) did not leach into groundwater sources in any of the samples studied (Broadly et al., 2007). Although zinc tends to defend against both cadmium and lead toxicity (Fergusson, 1990), its toxicity in humans can

occur if the zinc concentrations in the groundwater exceeded 3 mg/L. Electrolyte imbalance, vomiting, acute renal failures, and abdominal pains have been identified by medical experts as symptoms of excessive zinc exposure in humans. Other effects of excess zinc include negative reproductive biochemical, physiological, and behavioral effect on a variety of aquatic species. Nevertheless, it is worthy to mention that zinc toxicity is influenced by a number of factors, including the temperature, hardness, and pH of the water (Egbueri et al., 2020d).

NSFWQI modeling of water quality

In a scenario where several parameters are analyzed for water quality assessment, succinctly determining and defining the water quality by comparing the various parametric concentrations is often difficult. Hence, the development and application of index, numerical methods have been found useful for summarizing and clearly defining the water quality status of various analyzed samples (Mgbenu & Egbueri, 2019). In other words, the application of indexical methods helps in distinctly depicting the groundwater quality status during a study period. In this study, the drinking suitability of the groundwater resources was determined by applying the NSFWQI model. It was noticed that all the NSFWQI values presented in Table 4 varied between the medium quality and unsuitable quality ranges (Table 2). The NSFWQI spatial distribution map of the study area (produced with Surfer 9) is shown in Fig. 2. While only about 15% of the total groundwater samples showed medium water quality, the rest (85%) showed unsuitable water quality (Table 4; Fig. 2). This judgment is in accordance to the NSFWQI classification given in Table 2. With respect to the Table 4, the NSFWQI scores for all the groundwater samples range between 41 and 58, and the average NSFWQI for these sampling points is 46.6. Thus, indicating that, overall, the groundwater quality of this rural mining area is unsuitable for drinking purpose. This result further suggests that the groundwater quality of the study sites is adversely affected by anthropogenic activities such as mining and agricultural practices.

Table 4 NSFWQI result and classification of the groundwater samples

Sampling ID	NSFWQI	Water quality status
ME/1	50	Unsuitable
ME/2	42	Unsuitable
ME/3	57	Medium
ME/4	41	Unsuitable
ME/5	44	Unsuitable
MA/6	45	Unsuitable
MK/7	58	Medium
MK/8	47	Unsuitable
MK/9	50	Unsuitable
MK/10	43	Unsuitable
MK/11	44	Unsuitable
MK/12	43	Unsuitable
MK/13	47	Unsuitable
MA/14	51	Medium
MA/15	47	Unsuitable
ME/16	42	Unsuitable
ME/17	44	Unsuitable
ME/18	50	Unsuitable
ME/19	41	Unsuitable
ME/20	46	Unsuitable

HERisk modeling of human health risk

Elemental daily dose intake, hazard quotient, and cancer risk

Although the major indices utilized for the assessment of the human health risk are HI_{agg}, HI_{tot}, CR_{agg}, and CR_{tot}, the results of the elemental daily dose intake, hazard quotients, and cancer risks were reported to show the level of contribution each of the PHEs has. The daily dose intake, hazard quotient, and cancer risk values of the analyzed PHEs for oral ingestion and dermal absorption are given in Tables S1–S27 (presented herein as Supplementary Material) and summarized in Table 5.

With respect to the daily dose intake for both routes, it was realized that all the age groups who use the polluted groundwater resources seem to be far more exposed to ingest or absorb Se, Co, Cd, Se, As, Ni, and Pb (Tables S1–S27). Moreover, the PHEs seem to follow the same trend for the hazard quotients for all the age groups (Tables S1–S27). Similarly, it was observed that the contributions of the

four carcinogens (As, Pb, Ni, and Cd) in the cancer risk evaluation varied across the age groups for the oral and dermal routes (Tables S1–S27). However, As and Cd seem to have higher risk contributions than Ni and Pb.

Overall, it was realized that the PHEs pose very high risk via oral ingestion (for the daily dose intake, hazard quotients, and cancer risks) for the nine age groups considered in this study. However, lower risks were observed for the dermal absorption route (for the daily dose intake, hazard quotients, and cancer risks) for all the age groups. These observations suggest that the inhabitants are predisposed to a higher risk of drinking the polluted water resources than showering with the polluted water resources. Nevertheless, it is predicted that the children age groups would be at higher toxicity risk than the adult age groups.

Non-carcinogenic and carcinogenic health risks due to oral ingestion

The results of HERisk coding for the non-carcinogenic health risk (HI_{agg} and HI_{tot}) due to oral ingestion of the polluted groundwater resources by the nine age groups are presented in Table 6. Hazard index (HI) has been utilized in classifying the propensity of non-carcinogenic risk of PHEs as thus: $HI > 1$ signifies that the non-carcinogenic health risk of PHEs is above the acceptable benchmark while $HI < 1$ indicates PHEs are present within the acceptable threshold (US-EPA, 1989). Precisely, the chronic risk due to ingestion or absorption of PHEs may be classified based on the HI as follows: $HI < 0.1$ signifies negligible chronic risk level; $HI \geq 0.1 < 1$ indicates low chronic risk; $HI \geq 1 < 4$ signifies medium/moderate chronic risk; and $HI \geq 4$ indicates high chronic risk (US-EPA, 1989; Egbueri & Mgbenu, 2020; Egbueri et al., 2020).

With respect to the obtained HI_{agg} scores for the various age groups, it was noticed that all the age groups are posed with high chronic risk due to the oral ingestion of the polluted water resources. However, it was noticed that the age ranges 1 to < 16 and > 65 are exposed to higher risks than age ranges 18 and 21 (Table 6). The higher risk predicted for children within the ages of 1 to < 16 could be due to their lower ingestion rate and lower body weights (Neris et al., 2021). However, the lower risk observed in ages > 65 than in age ranges of 18 to < 65 could be

Fig. 2 NSFWQI spatial map showing that the sites are mostly unsuitable water sources
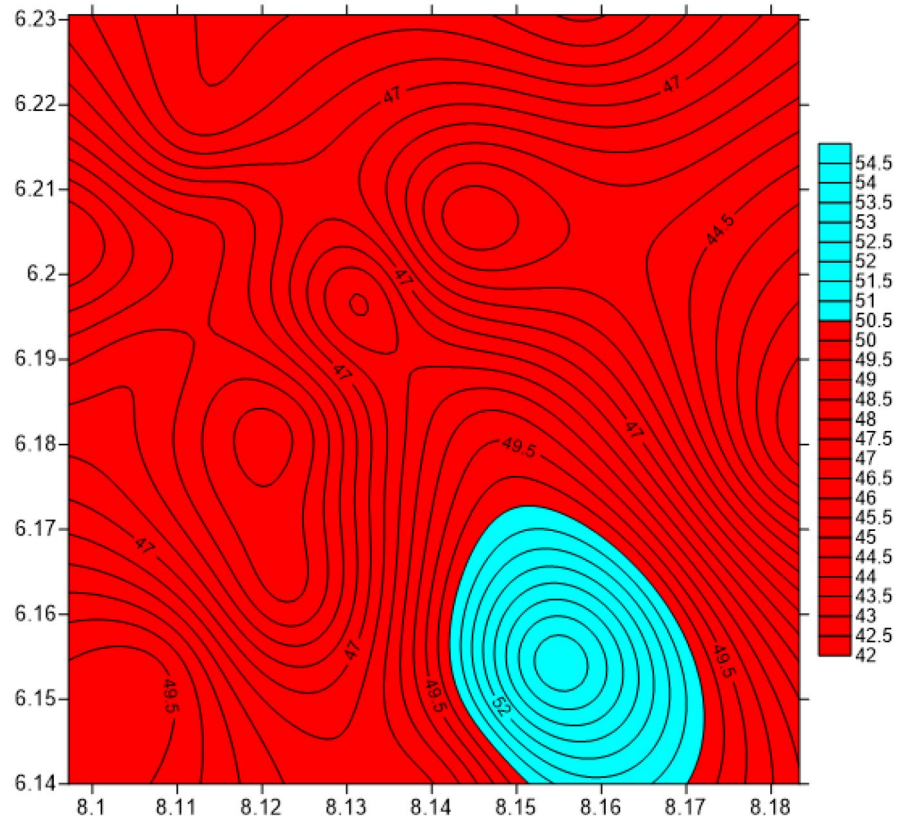
due to aging that usually slows down their immune systems. Nevertheless, Fig. 3a shows the risk trend for the different age groups for the different groundwater study sites. It was also observed from Fig. 3a that samples 1, 7, 9, 11, 13, 14, 18, and 20 pose the highest non-carcinogenic risks than the other locations, with samples 4, 6, 10, and 15 having the least risk. The HI_{tot} result is consistent with findings of the HI_{agg} (Table 6; Fig. 3a), as extreme total non-carcinogenic

risk was observed in all the groundwater locations. Additionally, the spatiotemporal map of the non-carcinogenic risk assessment for oral ingestion shows that the study area is predominated by HI_{tot} scores ranging between 50–100 and 100–145 (Fig. 4a).

The results of HERisk coding for the non-carcinogenic health risk (CR_{agg} and CR_{tot}) due to oral ingestion of the polluted groundwater resources by the nine age groups are presented in Table 7. The classification

Table 5 Results of the daily dose intake, hazard quotients, and carcinogenic risks of the PHEs for the various age groups

Initial age (age group range)	Daily dose intake	Hazard quotient	Cancer risk
1 (1 to < 2 years)	Table S1	Table S2	Table S3
2 (2 to < 3 years)	Table S4	Table S5	Table S6
3 (3 to < 6 years)	Table S7	Table S8	Table S9
6 (6 to < 11 years)	Table S10	Table S11	Table S12
11 (11 to < 16 years)	Table S13	Table S14	Table S15
16 (16 to < 18 years)	Table S16	Table S17	Table S18
18 (18 to < 21 years)	Table S19	Table S20	Table S21
21 (21 to < 65 years)	Table S22	Table S23	Table S24
65 (> 65 years)	Table S25	Table S26	Table S27

Table 6 Aggregated and cumulative/total non-carcinogenic risk due to water ingestion for the various age groups

Sample ID	Source	HI_{agg}-1	HI_{agg}-2	HI_{agg}-3	HI_{agg}-6	HI_{agg}-11	HI_{agg}-16	HI_{agg}-18	HI_{agg}-21	HI_{agg}-65	HI_{tot}
ME/1	HDW	28.8363	23.5742	18.1442	11.4935	6.8716	5.5973	5.2345	4.7635	4.9764	109.4914
ME/2	HDW	10.2384	8.3701	6.4421	4.0808	2.4398	1.9873	1.8585	1.6913	1.7669	38.8752
ME/3	HDW	14.4423	11.8069	9.0873	5.7564	3.4416	2.8034	2.6216	2.3858	2.4924	54.8375
ME/4	HDW	5.1381	4.2005	3.2330	2.0479	1.2244	0.9973	0.9327	0.8488	0.8867	19.5094
ME/5	HDW	19.6312	16.0489	12.3522	7.8245	4.6781	3.8106	3.5635	3.2429	3.3878	74.5398
MA/6	HDW	7.5255	6.1522	4.7352	2.9995	1.7933	1.4608	1.3661	1.2432	1.2987	28.5744
MK/7	HDW	50.2201	41.0559	31.5992	20.0166	11.9673	9.7481	9.1161	8.2959	8.6666	190.6859
MK/8	HDW	14.3216	11.7082	9.0113	5.7082	3.4128	2.7799	2.5997	2.3658	2.4715	54.3791
MK/9	HDW	52.5859	42.9900	33.0878	20.9595	12.5311	10.2073	9.5456	8.6868	9.0749	199.6689
MK/10	HDW	7.7465	6.3329	4.8742	3.0876	1.8460	1.5037	1.4062	1.2797	1.3368	29.4134
MK/11	HDW	29.6263	24.2200	18.6413	11.8084	7.0599	5.7507	5.3779	4.8940	5.1127	112.4912
MK/12	HDW	15.4798	12.6550	9.7401	6.1699	3.6888	3.0047	2.8100	2.5571	2.6714	58.7769
MK/13	HDW	31.5046	25.7556	19.8231	12.5570	7.5075	6.1153	5.7188	5.2043	5.4369	119.6231
MA/14	BH	28.5861	23.3697	17.9868	11.3937	6.8120	5.5488	5.1890	4.7222	4.9332	108.5414
MA/15	BH	9.8472	8.0502	6.1960	3.9249	2.3466	1.9114	1.7875	1.6267	1.6994	37.3897
ME/16	BH	27.9354	22.8377	17.5773	11.1344	6.6569	5.4225	5.0709	4.6147	4.8209	106.0706
ME/17	BH	21.7288	17.7637	13.6720	8.6606	5.1779	4.2177	3.9443	3.5894	3.7498	82.5043
ME/18	BH	55.4768	45.3533	34.9067	22.1117	13.2200	10.7685	10.0703	9.1643	9.5738	210.6455
ME/19	BH	12.7219	10.4004	8.0048	5.0707	3.0316	2.4694	2.3093	2.1016	2.1955	48.3052
ME/20	BH	32.1739	26.3028	20.2443	12.8238	7.6670	6.2452	5.8403	5.3149	5.5524	122.1644
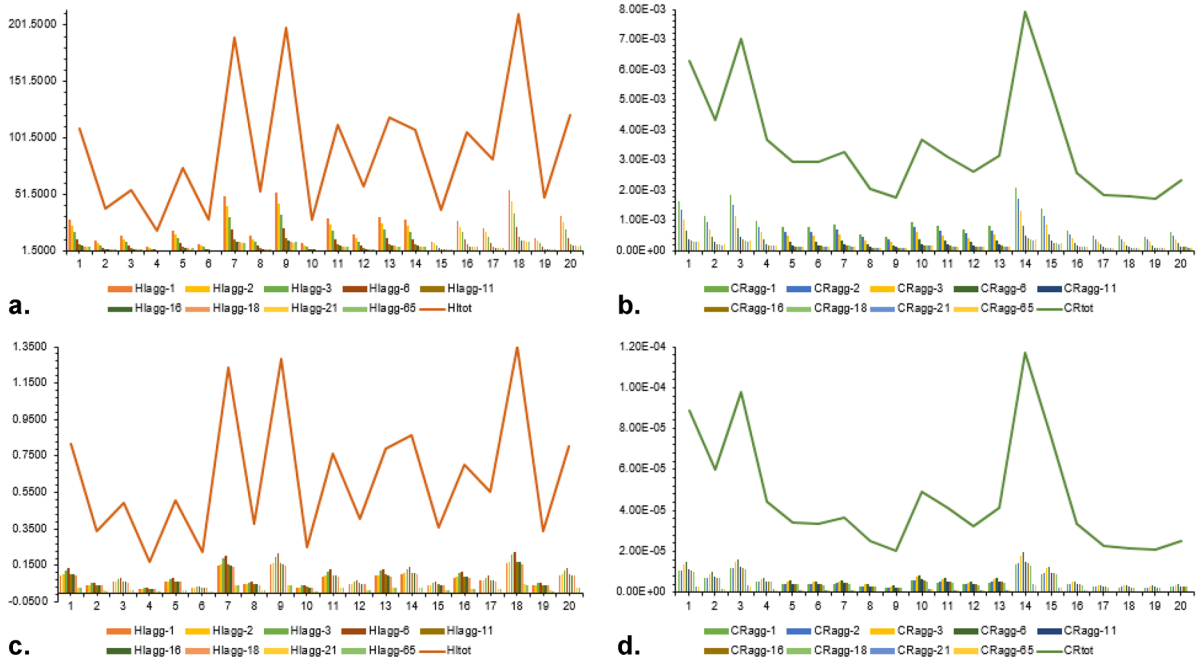
Fig. 3 Graphical distribution of the a HI_{agg} and HI_{tot} for ingestion; b CR_{agg} and CR_{tot} for ingestion; c HI_{agg} and HI_{tot} for absorption; and d CR_{agg} and CR_{tot} for absorption
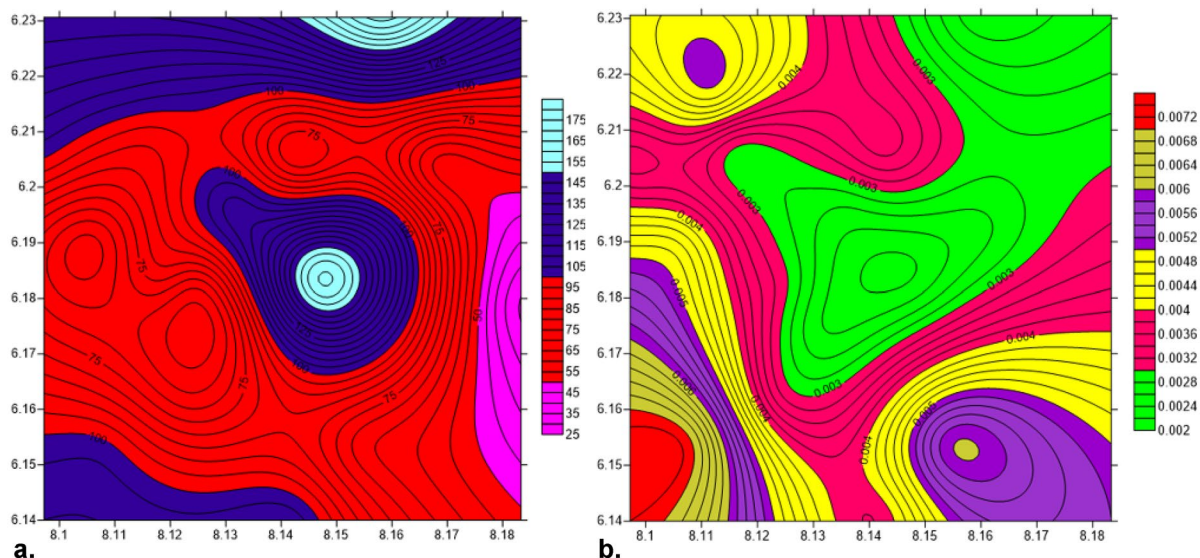
Fig. 4 Spatial map for the distribution of a HI_{tot} for oral ingestion and b CR_{tot} for oral ingestion

scheme for carcinogenic risk of PHEs suggests that the acceptable cancer risk value is $\leq 1 \times 10^{-6}$ or a range of 1×10^{-6} to 1×10^{-4} (US-EPA, 1989; Egbueri et al., 2020). With respect to these benchmark values and in relation to the CR_{agg} and CR_{tot} results for oral ingestion given Table 7, it was realized that all the age groups are posed with cancer threats due to the ingestion of the polluted waters. In this analysis, the age group > 65 years appears to be posed with the highest risk of cancer, as the group's CR_{agg} values are in the range of 10^{-3} (Table 7). This seems to be in line with the common notion that elderly people are more exposed to risk cancer than younger people (mostly children). Moreover, it was also noticed that age ranges of 16 to < 65 are at lower risks than the other age groups (Table 7). From Fig. 3b, it is seen that groundwater sites 1, 2, 3, 14, and 15 pose the highest total cancer risk to the age groups. Based on the information presented in Fig. 4b, it is sufficed to say that most part of the study area is predisposed to cancer risk in the range of 1×10^{-3} to 5×10^{-3}.

Non-carcinogenic and carcinogenic health risk dermal absorption

Not only are humans exposed to PHEs via drinking polluted water. They can also be exposed to health risks due to dermal contact (absorption) with polluted

water resources (Neris et al., 2021). Thus, in this study, the non-carcinogenic and carcinogenic human health risks due to dermal absorption were evaluated. The HI_{agg} and HI_{tot} utilized for the absorption route evaluation are presented in Table 8. For all the age groups, the aggregated hazard index (HI_{agg}) was observed to be < 1 across all the sample locations (Table 8), implying that they generally pose low chronic risk to the rural inhabitants. However, similar to the observation made in the HI_{agg} for oral ingestion, it was observed that age ranges 1 to < 16 and > 65 are exposed to higher chronic risk than age ranges 18 to < 65. Although the HI_{agg} scores indicated low chronic risk to all the age groups, it is realized that the HI_{tot} scores indicated a higher level of overall chronic risk posed to the inhabitants of the Ameka mining area (Table 8). Figure 3c graphically explains that groundwater samples 1, 7, 9, 14, 18, and 20 pose higher chronic risk due to absorption. Spatially, and with respect to the HI_{tot}, the study area is characterized mostly by negligible and low chronic risks, with few spots of medium chronic risk (Fig. 5a).

The results of CR_{agg} and CR_{tot}, for the carcinogenic risk evaluation due to dermal absorption of the PHEs in the groundwater resources for all the nine age groups, are given in Table 9. Following a similar trend with the HI_{agg} and HI_{tot}, the cancer risk due to the dermal absorption of the PHEs in the waters

Table 7 Aggregated and cumulative/total carcinogenic risk due to water ingestion for the various age groups

Sample ID	Source	CR_{agg}-1	CR_{agg}-2	CR_{agg}-3	CR_{agg}-6	CR_{agg}-11	CR_{agg}-16	CR_{agg}-18	CR_{agg}-21	CR_{agg}-65	CR_{tot}
ME/1	HDW	1.66E−03	1.35E−03	1.04E−03	6.60E−04	3.95E−04	3.21E−04	3.01E−04	2.74E−04	2.86E−04	6.29E−03
ME/2	HDW	1.15E−03	9.37E−04	7.21E−04	4.57E−04	2.73E−04	2.22E−04	2.08E−04	1.89E−04	1.98E−04	4.35E−03
ME/3	HDW	1.85E−03	1.51E−03	1.16E−03	7.37E−04	4.41E−04	3.59E−04	3.36E−04	3.05E−04	3.19E−04	7.02E−03
ME/4	HDW	9.69E−04	7.92E−04	6.10E−04	3.86E−04	2.31E−04	1.88E−04	1.76E−04	1.60E−04	1.67E−04	3.68E−03
ME/5	HDW	7.70E−04	6.30E−04	4.85E−04	3.07E−04	1.84E−04	1.50E−04	1.40E−04	1.27E−04	1.33E−04	2.92E−03
MA/6	HDW	7.77E−04	6.35E−04	4.89E−04	3.10E−04	1.85E−04	1.51E−04	1.41E−04	1.28E−04	1.34E−04	2.95E−03
MK/7	HDW	8.66E−04	7.08E−04	5.45E−04	3.45E−04	2.06E−04	1.68E−04	1.57E−04	1.43E−04	1.49E−04	3.29E−03
MK/8	HDW	5.34E−04	4.36E−04	3.36E−04	2.13E−04	1.27E−04	1.04E−04	9.69E−05	8.82E−05	9.21E−05	2.03E−03
MK/9	HDW	4.65E−04	3.80E−04	2.93E−04	1.85E−04	1.11E−04	9.02E−05	8.44E−05	7.68E−05	8.02E−05	1.77E−03
MK/10	HDW	9.65E−04	7.89E−04	6.07E−04	3.85E−04	2.30E−04	1.87E−04	1.75E−04	1.59E−04	1.67E−04	3.66E−03
MK/11	HDW	8.20E−04	6.70E−04	5.16E−04	3.27E−04	1.95E−04	1.59E−04	1.49E−04	1.35E−04	1.41E−04	3.11E−03
MK/12	HDW	6.90E−04	5.64E−04	4.34E−04	2.75E−04	1.64E−04	1.34E−04	1.25E−04	1.14E−04	1.19E−04	2.62E−03
MK/13	HDW	8.27E−04	6.76E−04	5.20E−04	3.29E−04	1.97E−04	1.60E−04	1.50E−04	1.37E−04	1.43E−04	3.14E−03
MA/14	BH	2.08E−03	1.70E−03	1.31E−03	8.30E−04	4.96E−04	4.04E−04	3.78E−04	3.44E−04	3.59E−04	7.91E−03
MA/15	BH	1.40E−03	1.14E−03	8.80E−04	5.58E−04	3.33E−04	2.72E−04	2.54E−04	2.31E−04	2.41E−04	5.31E−03
ME/16	BH	6.79E−04	5.55E−04	4.27E−04	2.71E−04	1.62E−04	1.32E−04	1.23E−04	1.12E−04	1.17E−04	2.58E−03
ME/17	BH	4.83E−04	3.95E−04	3.04E−04	1.92E−04	1.15E−04	9.37E−05	8.76E−05	7.97E−05	8.33E−05	1.83E−03
ME/18	BH	4.80E−04	3.92E−04	3.02E−04	1.91E−04	1.14E−04	9.31E−05	8.71E−05	7.92E−05	8.28E−05	1.82E−03
ME/19	BH	4.52E−04	3.70E−04	2.84E−04	1.80E−04	1.08E−04	8.78E−05	8.21E−05	7.47E−05	7.80E−05	1.72E−03
ME/20	BH	6.14E−04	5.02E−04	3.86E−04	2.45E−04	1.46E−04	1.19E−04	1.11E−04	1.01E−04	1.06E−04	2.33E−03

Table 8 Aggregated and cumulative/total non-carcinogenic risk due to water dermal absorption for the various age groups

Sample ID	Source	HI_{agg}-1	HI_{agg}-2	HI_{agg}-3	HI_{agg}-6	HI_{agg}-11	HI_{agg}-16	HI_{agg}-18	HI_{agg}-21	HI_{agg}-65	HI_{tot}
ME/1	HDW	9.80E−02	1.02E−01	1.25E−01	1.36E−01	1.04E−01	1.00E−01	9.39E−02	2.77E−02	2.69E−02	8.15E−01
ME/2	HDW	4.07E−02	4.21E−02	5.20E−02	5.66E−02	4.33E−02	4.17E−02	3.90E−02	1.15E−02	1.12E−02	3.38E−01
ME/3	HDW	5.91E−02	6.12E−02	7.56E−02	8.22E−02	6.30E−02	6.06E−02	5.67E−02	1.67E−02	1.62E−02	4.91E−01
ME/4	HDW	2.03E−02	2.10E−02	2.59E−02	2.82E−02	2.16E−02	2.08E−02	1.94E−02	5.70E−03	5.60E−03	1.69E−01
ME/5	HDW	6.12E−02	6.34E−02	7.83E−02	8.52E−02	6.52E−02	6.27E−02	5.87E−02	1.73E−02	1.68E−02	5.09E−01
MA/6	HDW	2.67E−02	2.76E−02	3.41E−02	3.71E−02	2.84E−02	2.73E−02	2.56E−02	7.50E−03	7.30E−03	2.22E−01
MK/7	HDW	1.48E−01	1.54E−01	1.90E−01	2.07E−01	1.58E−01	1.52E−01	1.42E−01	4.19E−02	4.07E−02	1.23E+00
MK/8	HDW	4.56E−02	4.72E−02	5.83E−02	6.35E−02	4.86E−02	4.67E−02	4.37E−02	1.29E−02	1.25E−02	3.79E−01
MK/9	HDW	1.54E−01	1.60E−01	1.97E−01	2.15E−01	1.64E−01	1.58E−01	1.48E−01	4.35E−02	4.23E−02	1.28E+00
MK/10	HDW	3.03E−02	3.14E−02	3.88E−02	4.22E−02	3.23E−02	3.11E−02	2.90E−02	8.50E−03	8.30E−03	2.52E−01
MK/11	HDW	9.20E−02	9.53E−02	1.18E−01	1.28E−01	9.80E−02	9.43E−02	8.81E−02	2.59E−02	2.52E−02	7.64E−01
MK/12	HDW	4.92E−02	5.10E−02	6.29E−02	6.84E−02	5.24E−02	5.04E−02	4.71E−02	1.39E−02	1.35E−02	4.09E−01
MK/13	HDW	9.53E−02	9.87E−02	1.22E−01	1.33E−01	1.02E−01	9.77E−02	9.13E−02	2.69E−02	2.61E−02	7.92E−01
MA/14	BH	1.04E−01	1.07E−01	1.33E−01	1.44E−01	1.10E−01	1.06E−01	9.93E−02	2.92E−02	2.84E−02	8.61E−01
MA/15	BH	4.35E−02	4.51E−02	5.56E−02	6.05E−02	4.64E−02	4.46E−02	4.17E−02	1.23E−02	1.19E−02	3.62E−01
ME/16	BH	8.47E−02	8.78E−02	1.08E−01	1.18E−01	9.03E−02	8.69E−02	8.12E−02	2.39E−02	2.32E−02	7.04E−01
ME/17	BH	6.65E−02	6.90E−02	8.51E−02	9.26E−02	7.09E−02	6.82E−02	6.38E−02	1.88E−02	1.82E−02	5.53E−01
ME/18	BH	1.63E−01	1.69E−01	2.08E−01	2.26E−01	1.73E−01	1.67E−01	1.56E−01	4.59E−02	4.46E−02	1.35E+00
ME/19	BH	4.09E−02	4.23E−02	5.23E−02	5.69E−02	4.35E−02	4.19E−02	3.92E−02	1.15E−02	1.12E−02	3.40E−01
ME/20	BH	9.63E−02	9.98E−02	1.23E−01	1.34E−01	1.03E−01	9.88E−02	9.23E−02	2.72E−02	2.64E−02	8.01E−01
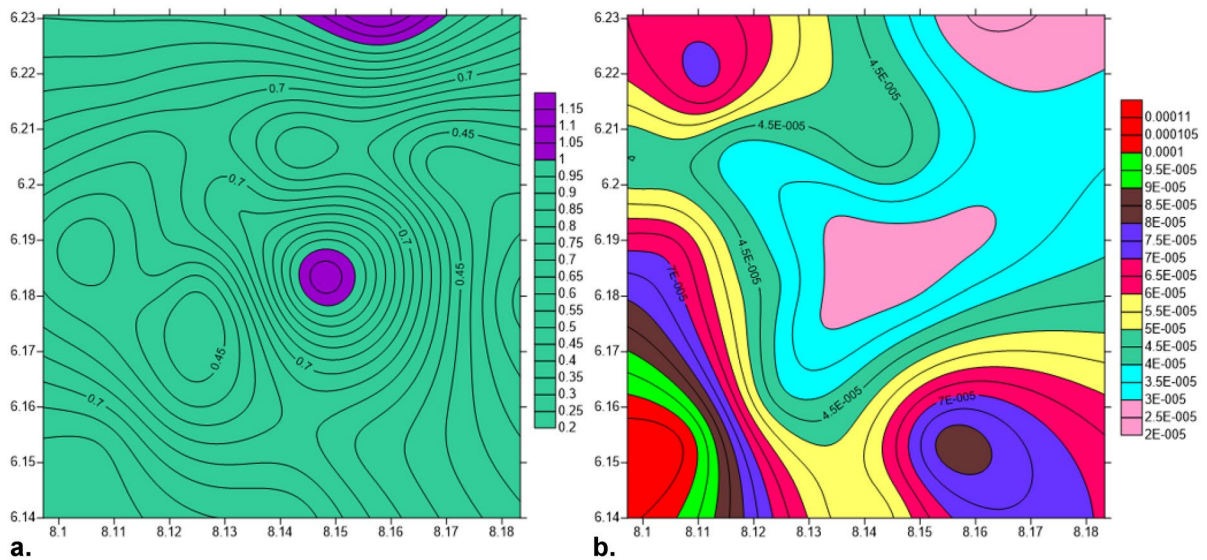
Fig. 5 Spatial map for the distribution of a HI_{tot} for dermal absorption and b CR_{tot} for dermal absorption

is estimated to be low for all the age groups, as their scores are found within the acceptable range of 1×10^{-6} to 1×10^{-4} (Table 9; US-EPA, 1989; Egbueri et al., 2020). However, it is depicted graphically that much of the cancer risk due to the dermal absorption of PHEs would likely be expected from groundwater locations 1, 3, 14, and 15 (Fig. 3d). Spatially, it was noticed that the central and northeastern portions of the study area have the least HI_{tot} scores (Fig. 5b), indicating that the inhabitants in these localities face negligible cancer risk. When compared with the risk of oral ingestion, it is sufficed to say that the chronic and cancer risks associated with the dermal absorption of the polluted groundwater are low and, thus, do not pose any serious threat. This implies that the water resources are still suitable for sanitary purposes such as bathing/showering and laundry. The incremental dermal absorption risks prevalent to age ranges 1 to < 16 could be attributed to such factors as the available skin surface area for the PHE absorption and other physiological features peculiar to these age groups (Neris et al., 2021).

Hierarchical cluster modeling of water quality and health risk

In order to provide further insights regarding the suitability of the groundwater resources for human use,

it was necessary to analyze the spatial distribution of water quality and health risks using HCs. This is owed to the fact that geostatistical methods seem to provide a more reliable prediction of spatial dataset. For this purpose, five hierarchical dendrograms were generated based on the NSFWQI, HI_{tot} (ingestion), CR_{tot} (ingestion), HI_{tot} (absorption), and CR_{tot} (absorption). By this analysis, the groundwater sites are classified based on their levels of PHE pollution and health risk information. Figure 6 shows a dendrogram with respect to the NSFWQI values for drinking water quality evaluation. Three cluster groups were identified in Fig. 6. The first cluster has samples 3 and 7 which have been noted, based on NSFWQI, to have the best drinking water quality amongst the total samples. Cluster 2 has two sub-clusters (Fig. 6). In the first sub-cluster, five water samples with their NSWQI in the range of 45–47 were grouped, indicating that these sites are unsuitable. The second sub-cluster is primarily composed of water samples with their NSFWQI ranging between moderate and unsuitable water quality (Fig. 6; Table 4). However, cluster 3 is composed of nine water locations (Fig. 6) with the worst water quality (Table 4). Thus, these nine stations should be the first to be considered in any pollution mitigation planning and execution.

Figure 7a contains the HCs for the HI_{tot} (ingestion). Two main clusters were identified, each having

Table 9 Aggregated and cumulative/total carcinogenic risk due to water dermal absorption for the various age groups

| Sample ID	Source	CR_{agg}-1	CR_{agg}-2	CR_{agg}-3	CR_{agg}-6	CR_{agg}-11	CR_{agg}-16	CR_{agg}-18	CR_{agg}-21	CR_{agg}-65	CR_{tot}
ME/1	HDW	1.07E−05	1.11E−05	1.37E−05	1.49E−05	1.14E−05	1.10E−05	1.02E−05	3.02E−06	2.93E−06	8.89E−05
ME/2	HDW	7.19E−06	7.45E−06	9.19E−06	1.00E−05	7.66E−06	7.37E−06	6.89E−06	2.03E−06	1.97E−06	5.97E−05
ME/3	HDW	1.18E−05	1.22E−05	1.50E−05	1.64E−05	1.25E−05	1.20E−05	1.13E−05	3.32E−06	3.22E−06	9.77E−05
ME/4	HDW	5.32E−06	5.51E−06	6.80E−06	7.40E−06	5.66E−06	5.45E−06	5.10E−06	1.50E−06	1.46E−06	4.42E−05
ME/5	HDW	4.14E−06	4.29E−06	5.30E−06	5.77E−06	4.42E−06	4.25E−06	3.97E−06	1.17E−06	1.14E−06	3.44E−05
MA/6	HDW	4.04E−06	4.18E−06	5.16E−06	5.62E−06	4.30E−06	4.14E−06	3.87E−06	1.14E−06	1.11E−06	3.36E−05
MK/7	HDW	4.40E−06	4.56E−06	5.62E−06	6.12E−06	4.68E−06	4.51E−06	4.21E−06	1.24E−06	1.21E−06	3.65E−05
MK/8	HDW	3.05E−06	3.16E−06	3.90E−06	4.24E−06	3.25E−06	3.12E−06	2.92E−06	8.59E−07	8.35E−07	2.53E−05
MK/9	HDW	2.44E−06	2.53E−06	3.12E−06	3.39E−06	2.60E−06	2.50E−06	2.34E−06	6.88E−07	6.69E−07	2.03E−05
MK/10	HDW	5.91E−06	6.12E−06	7.56E−06	8.22E−06	6.29E−06	6.05E−06	5.66E−06	1.67E−06	1.62E−06	4.91E−05
MK/11	HDW	4.96E−06	5.14E−06	6.34E−06	6.90E−06	5.28E−06	5.08E−06	4.75E−06	1.40E−06	1.36E−06	4.12E−05
MK/12	HDW	3.90E−06	4.04E−06	4.99E−06	5.43E−06	4.16E−06	4.00E−06	3.74E−06	1.10E−06	1.07E−06	3.24E−05
MK/13	HDW	4.99E−06	5.17E−06	6.38E−06	6.94E−06	5.31E−06	5.11E−06	4.78E−06	1.41E−06	1.37E−06	4.14E−05
MA/14	BH	1.41E−05	1.46E−05	1.80E−05	1.96E−05	1.50E−05	1.44E−05	1.35E−05	3.97E−06	3.86E−06	1.17E−04
MA/15	BH	9.16E−06	9.49E−06	1.17E−05	1.28E−05	9.76E−06	9.39E−06	8.78E−06	2.59E−06	2.51E−06	7.62E−05
ME/16	BH	4.01E−06	4.16E−06	5.13E−06	5.59E−06	4.28E−06	4.11E−06	3.85E−06	1.13E−06	1.10E−06	3.34E−05
ME/17	BH	2.72E−06	2.82E−06	3.48E−06	3.78E−06	2.90E−06	2.79E−06	2.61E−06	7.67E−07	7.45E−07	2.26E−05
ME/18	BH	2.59E−06	2.68E−06	3.31E−06	3.60E−06	2.76E−06	2.65E−06	2.48E−06	7.30E−07	7.09E−07	2.15E−05
ME/19	BH	2.55E−06	2.64E−06	3.26E−06	3.55E−06	2.72E−06	2.61E−06	2.44E−06	7.19E−07	6.99E−07	2.12E−05
ME/20	BH	3.03E−06	3.14E−06	3.88E−06	4.22E−06	3.23E−06	3.11E−06	2.91E−06	8.56E−07	8.31E−07	2.52E−05

Fig. 6 HCs of water samples based on NSFWQI
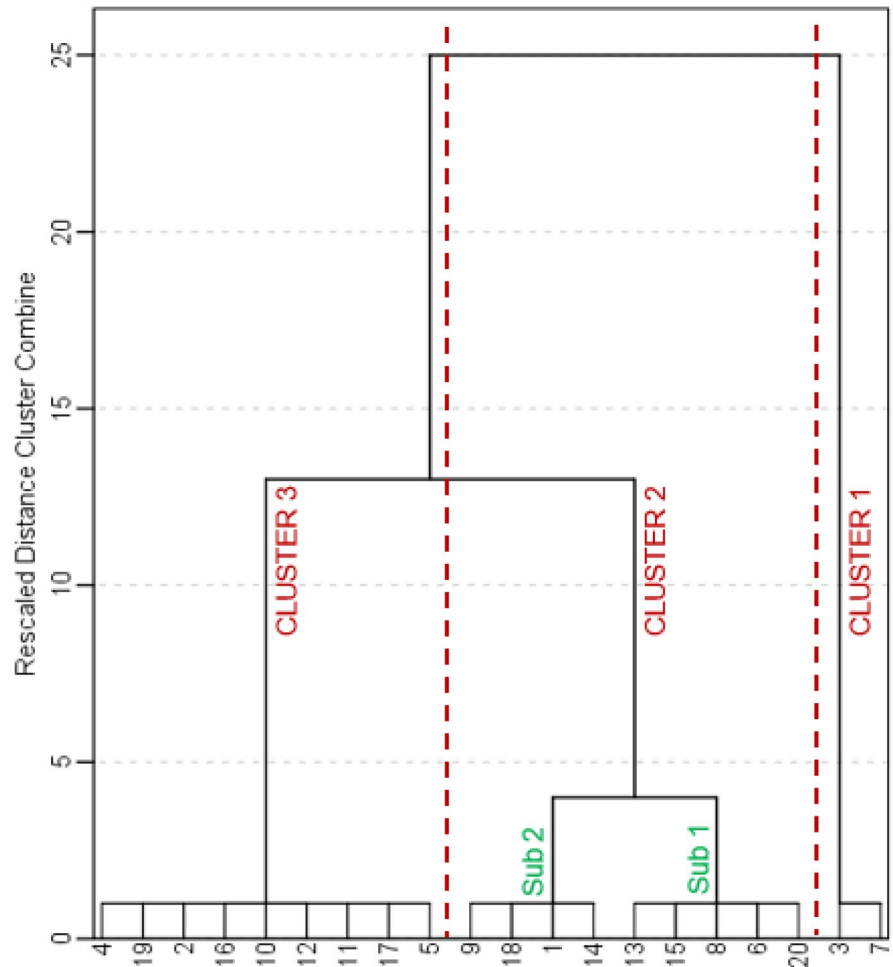
two sub-clusters. Although all the HI_{tot} (ingestion) scores showed high chronic risks, the HCs aided in adequate demarcation of the groundwaters into classes. While cluster 1 has the groundwater locations with extremely high non-carcinogenic risk to the inhabitants, cluster 2 has the samples with very high risk (Fig. 7a). The decreasing order of chronic risk posed by the groundwater resources (locations) follows the trend: sub-cluster 1 (cluster 2, HI_{tot} range = 19–38) < sub-cluster 2 (cluster 2, HI_{tot} range = 48–82) < sub-cluster 1 (cluster 1, HI_{tot} range = 106–119) < sub-cluster 2 (cluster 1, HI_{tot} range = 190–210). For the carcinogenic risk (CR_{tot} ingestion), two main clusters were identified (Fig. 7b). The first cluster has no sub-cluster groups and is composed of those water samples with the highest cancer risk in the range of 6.29E − 03 to 7.9E − 03. On the other hand, the second cluster is composed of those

samples with lesser cancer risk. Nevertheless, the second cluster has two sub-clusters. While the first sub-cluster members have their cancer risk ranging between 2.94E − 03 and 4.35E − 03, the second sub-cluster members have their cancer risk ranging from 1.72E − 03 to 2.62E − 03 (Fig. 7b; Table 7).

Figure 8 contains the dendrograms for the classification of HI_{tot} (absorption) and CR_{tot} (absorption). Figure 8a shows the HCs of the water resources with respect to HI_{tot} (absorption). Two clusters were also realized for the HI_{tot}. The first cluster showed the highest chronic risk due to absorption; with its first sub-cluster having a risk range of 7.04E − 01 to 8.61E − 01 and its second sub-cluster with a risk range of 1.23E + 00 to 1.35E + 00 (Fig. 8a; Table 8). However, the second cluster showed lesser chronic risk due to absorption: with its first sub-cluster having a risk
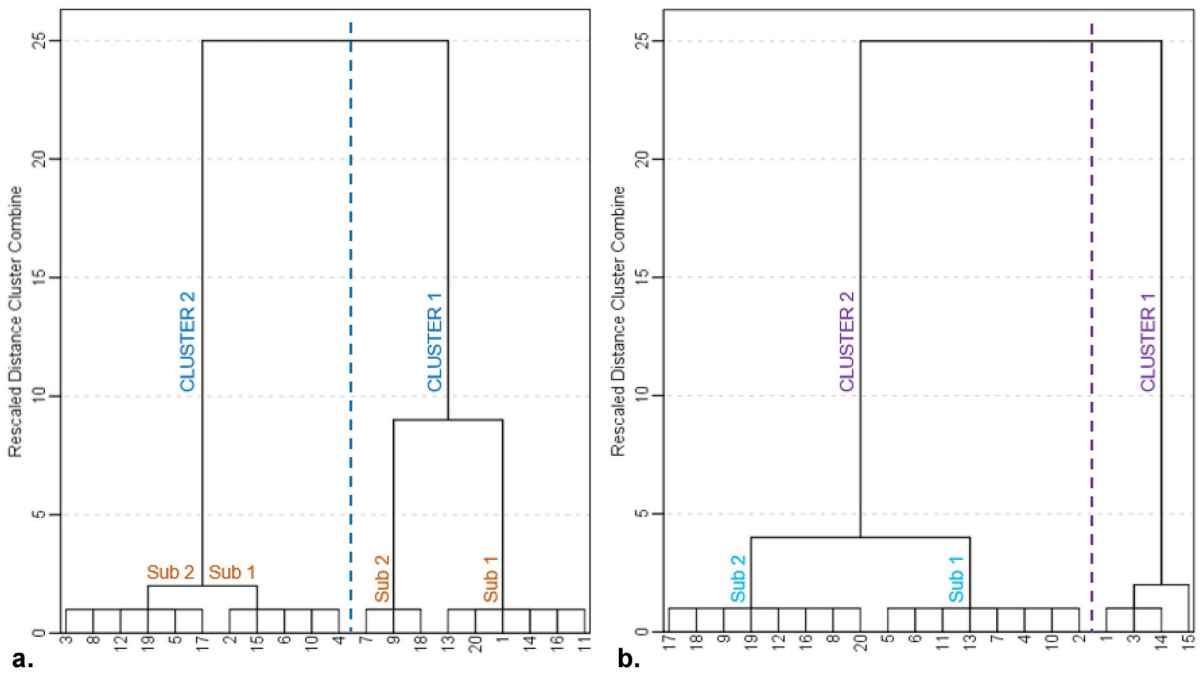
Fig. 7 HCs of water samples based on a HI_{tot} for oral ingestion and b CR_{tot} for oral ingestion
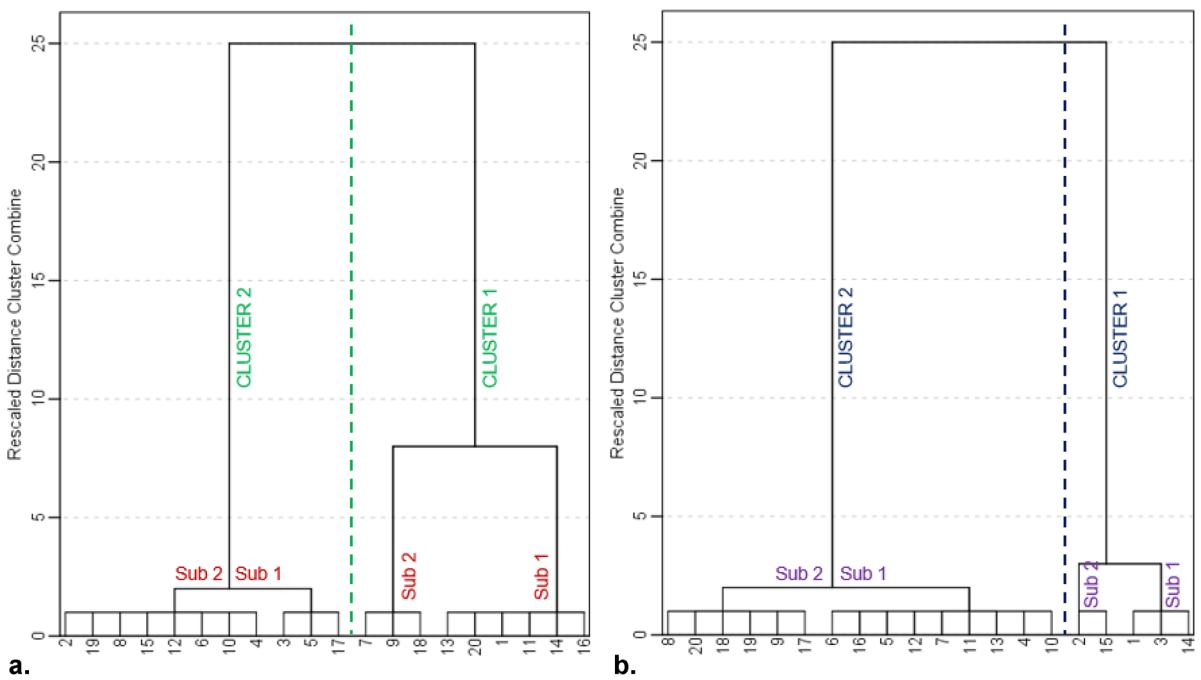
Fig. 8 HCs of water samples based on a HI_{tot} for dermal absorption and b CR_{tot} for dermal absorption

Table 10 Pearson's correlation matrix of the indices utilized for spatiotemporal analysis

	NSFWQI	HI_{tot} (ingestion)	CR_{tot} (ingestion)	HI_{tot} (absorption)	CR_{tot} (absorption)
NSFWQI	1.000	0.543[*]	0.433	0.602[**]	0.404
HI_{tot} (ingestion)		1.000	−0.215	0.992[**]	−0.214
CR_{tot} (ingestion)			1.000	−0.097	0.995[**]
HI_{tot} (absorption)				1.000	−0.094
CR_{tot} (absorption)					1.000

[*]Correlation is significant at the 0.05 level (2-tailed). [**]Correlation is significant at the 0.01 level (2-tailed)

range of 4.91E−01 to 5.53E−01 and its second sub-cluster with a risk range of 1.69E−01 to 4.09E−01 (Fig. 8a; Table 8). The cancer risk due to dermal absorption (CR_{tot}) is classified with the HCs in Fig. 8b. While the cluster 1 identified those samples with higher cancer risk level due to PHEs absorption, the cluster 2 members seem to pose lesser cancer risk due to PHE absorption (Fig. 8b; Table 9). The cluster 1 has two sub-clusters with their risk ranges between 8.89E−05 and 1.17E−04 and 5.97E−05 and 7.62E−05 (Fig. 8b; Table 9). Similarly, the cluster 2 also has two sub-clusters. While the first sub-cluster has cancer risk ranging from 3.24E−05 to 4.91E−05, the second sub-cluster has a risk range of 2.03E−05 to 2.53E−03 (Fig. 8b; Table 9).

So far, the hierarchical clustering has successfully shown the demarcations in the water quality and health risks. However, correlation analysis was performed on the indices utilized for spatiotemporal analysis of drinking water quality and human health risks to flag the level of agreement between them. The Pearson's correlation matrix is presented in Table 10. Based on the results obtained, the following assumptions seem to hold true for the present study area: (1) the NSFWQI moderately trended in a similar pattern with the HI_{tot} (ingestion) and HI_{tot} (absorption); (2) a strong correlation exists between the HI_{tot} (ingestion) and HI_{tot} (absorption), indicating high similarity in trend; (3) a strong relationship was observed between the CR_{tot} (ingestion) and CR_{tot} (absorption), which suggests a high similarity in trend between the two; and (4) CR_{tot} (ingestion and absorption) did not show any significant correlations with NSFWQI and HI_{tot} (ingestion and absorption), possibly because they did not consider the same number of parameters in their evaluations.

Conclusions

The present paper aimed to model the quality and associated human health risks of groundwater resources in Ameka mine area in southeastern Nigeria, using an integrated numerical, geostatistical, and geospatial approach. The elemental composition of the groundwater was analyzed and this showed that all of the analyzed water sources are polluted with PHEs. The associated health impacts were also descriptively discussed. The suitability of groundwater was modeled using NSFWQI, which showed that 15% of the analyzed groundwater samples have moderate water quality while 85% was marked as unsuitable water for drinking. Furthermore, the carcinogenic and non-carcinogenic human health risks of the PHEs (Pb, As, Cd, Ni, Co, Cu, Fe, Mn, Se, and Zn) in the groundwater resources, for oral ingestion and dermal absorption, were modeled using the novel HERisk code. This modeling was particularly done using the HERisk code as it provides wider scope and functions for human health risk assessment. The HIs obtained for all the water samples were found to be > 4 whereas the carcinogenic risk assessment revealed that all the samples have calculated risks > 1×10^{-4}. Overall, the HERisk model, which considered nine age groups (1 to < 2 years, 2 to < 3 years, 3 to < 6 years, 6 to < 11 years, 11 to < 16 years, 16 to < 18 years, 18 to < 21 years, 21 to < 65 years, and > 65 years) revealed that all the samples pose high chronic and cancer risks to all the age groups due to oral ingestion. However, it was realized that age ranges 1 to < 16 and > 65 are posed with higher risks than age ranges 18 to < 65. Also, it was realized that all the age groups seem to be far more exposed to ingest or absorb Se, Co, Cd, Se, As, Ni, and Pb than Cu, Fe, and Zn. Nevertheless, the HERisk evaluation of health risk due to dermal absorption is far lower than the risk due to oral ingestion. In other words, from the HERisk coding,

the oral ingestion of the PHEs was identified as the main exposure pathway that seriously threatens human health, far more than the dermal absorption pathway. Thus, the health risk linkable to the dermal absorption of the polluted groundwater resources does not appear to pose a serious threat. However, the current study established that children and aging people are more predisposed to the health threats than the middle aged populations. The spatial–temporal distribution and classification of drinking groundwater quality and health risks (with respect to the NSFWQI and HERisk models) was successfully done using geospatial maps and HCs.

Perspectives and recommendations

The present study has provided an updated information on the human health risk assessment of the Ameka mine province. Also, this paper indicated that the HERisk code is an effective approach for comprehensive health risk assessment. Based on the findings of this study, a number of recommendations and research prospects are provided.

- The polluted groundwater resources should be treated using appropriate treatment techniques before human consumption.
- There is a need to educate local residents in the study region on the health risks of drinking the polluted groundwater resources and how to prevent or minimize the associated risks.
- Future studies in the study area should consider testing the concentration levels of the analyzed PHEs in the blood samples of the residents. This approach would go a long way in strengthening public health management in the area.
- Although the HERisk code has been adjudged to be more effective than previous health risk methods, inclusion of sensitivity analysis would ensure the validation of its findings. Sensitivity analysis verifies the validity of an indexing strategy by identifying over-reliance on a parameter that could otherwise be considered insignificant.
- Artificial intelligence models should be incorporated in the simulation and predictive modeling of the health risk of the water resources in future research. This would enhance effective and sustainable groundwater resources management.

Declarations

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