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Imokhai Theophilus Tenebe
Texas Commission on Environmental Quality

Praisegod C. Emenike
Covenant University

E. O. Babatunde
Texas State University

J. B. Neris
Universidade Federal de São Carlos

Omowunmi H. Fred-Ahmadu
Covenant University

See next page for additional authors

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Assessing the state of rainwater for consumption in a community in dire need of clean water: Human and health risk using HERisk

Imokhai Theophilus Tenebe[a,*], PraiseGod C. Emenike[b], E.O. Babatunde[c], J. B. Neris[d], Omowunmi H. Fred-Ahmadu[e], Nathaniel Dede-Bamfo[f], Egbe-Etu Etu[g], Nkpa M. Ogarekpe[h], Joshua Emakhu[i] and Nsikak U. Benson[e]

[a] Critical Infrastructure Division, Texas Commission on Environmental Quality, 1200 Park 35 Circle, Austin, TX 78711, USA
[b] Department of Civil Engineering, Covenant University, Ota, Ogun State, Nigeria
[c] Department of Civil Engineering, Texas State University, 601 University Drive, San Marcos, Texas, USA
[d] Department of Chemistry, Federal University of São Carlos, São Carlos, São Paulo, Brazil
[e] Department of Chemistry, Covenant University, Ota, Ogun State, Nigeria
[f] Albert B. Alkek Library, Texas State University, 601 University Drive, San Marcos, Texas, USA
[g] Department of Marketing & Business Analytics, San Jose State University, One Washington Square, San Jose, CA 95192, USA
[h] Department of Civil Engineering, Cross River University of Technology, Calabar, Nigeria
[i] Department of Industrial & Systems Engineering, Wayne State University, 4815 4th Street, Detroit, MI 48202, USA
*Corresponding author. E-mail: yoshearer@gmail.com

ABSTRACT

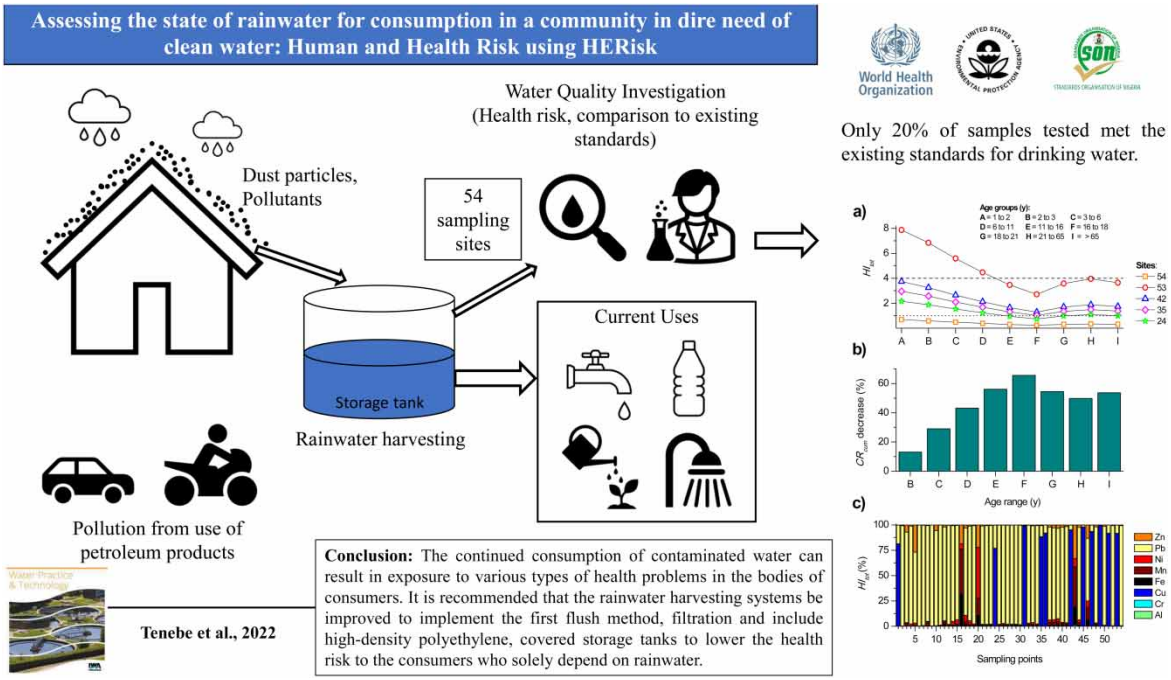
This study examines the case of Ekpoma community, Edo State, Nigeria, where roof-harvested rainwater is the primary source of water for drinking and domestic purposes. Eight potentially toxic elements (PTEs), namely aluminum, chromium, copper, iron, manganese, nickel, lead, and zinc, were detected in rainwater samples, collected and analyzed from 54 sampling locations across the community. The elemental concentrations were quantified using atomic absorption spectrophotometry and compared using the regulatory standards of the World Health Organization, United States Environmental Protection Agency, and Nigerian Drinking Water Quality Standards. The PTEs detected in the rainwater samples can be attributed to the nature of the materials used in the roof catchment systems, storage tank conditions, anthropogenic effects from industrial and agricultural processes, and fossil fuel emissions. However, only 20% of the evaluated samples contained PTE concentrations below the allowable regulatory limits. Spatio-temporal health risk analysis conducted using HERisk software showed that children in the development phase (1–18 years) are most vulnerable to health risks in the community. After age 18, the risk increased by approximately 10% and remained constant until old age. In addition, the evaluation of the studied sites showed that 33% of the evaluated sites had negligible carcinogenic risks, while the other 61% were sites with low carcinogenic risks to residents.

Key words: chemical elements, drinking water, pollution, public health, rainwater, risk assessment

HIGHLIGHTS

- The study examines the water quality and human health risk from drinking and using roof-harvested rainwater in Ekpoma community.
- Eight chemical species were detected and analyzed.
- Only 20% of the samples tested contained PTE concentrations within allowable limits.
- Samples from the studied sites presented carcinogenic risks (61%) for residents.
- Water ingestion route provided 98% risks for all resident.

GRAPHICAL ABSTRACT



1. INTRODUCTION

Water is an essential resource for humans. Since the advent of water quality testing, many private and government agencies have sought clean, safe, and readily available water. Studies have revealed that rainwater is a relatively clean source of water, presenting a slightly acidic pH of 5.0–5.6 (Charlson & Rodhe 1982), and low dissolved minerals with mean electrical conductivity of ≈ 200 μS cm^{-1} (Omokpariola & Omokpariola 2021). These qualities differ depending on variations in atmospheric conditions, ocean proximity, harvesting, storage, and usage conditions (Khayan *et al.* 2019; Zhang *et al.* 1999). The practice of harvesting rainwater has been in existence for nearly 5000 years in countries such as India, the Middle East, and Africa and has been a major source of water for agricultural purposes, particularly in semi-arid and arid regions of the world (Singh *et al.* 2022). Based on the public perception in some studies, treated rainwater is perceived as more acceptable than reclaimed water because of its safety and cleanliness. In a 2022 study, 50% of the respondents found the use of rainwater for non-domestic purposes acceptable. Some of the respondents in the study were of the opinion that rainwater poses a risk level when used for drinking and direct consumption (Mankad *et al.* 2019; Liu *et al.* 2022). However, the physiochemical qualities of rainwater make it aggressive, enabling the dissolution of potentially toxic elements (PTE) and minerals from rooftops and storage tanks (Khayan *et al.* 2019). Toxic metals are said to be absorbed faster through catabolism into the human tissues in comparison to the rate of elimination (Emenike *et al.* 2016). Chemical elements with atomic weights ranging between 63.546 and 200.590 g mol^{-1} and with a density greater than 5.0 g cm^{-3} are considered potentially toxic to human health (Anyanwu & Nwachukwu 2020). These elements occur naturally and can be found in different states – solid, colloidal, and dissolved – on Earth. Recently, advances in industrial activities have led to an increase in air pollution, which has significantly affected the quality of rainwater worldwide (Briffa *et al.* 2020; Mentese *et al.* 2021). Aerosols, PTEs, dust particles, and many others have been discovered in rainwater samples (Suvarapu & Baek 2017; Khayan *et al.* 2019; Valappil *et al.* 2020).

Rainwater has also been described as a medium for collecting and removing atmospheric pollutants (Cerqueira *et al.* 2014; Emenike *et al.* 2016). This indicates that for harvested rainwater to be considered suitable for drinking and domestic use, it should be subjected to regular testing and treatment processes to remove contaminants. However, the concentrations of PTEs in the air, soil, and water have increased owing to anthropogenic activities (Tenebe *et al.* 2018). According to studies in the literature, almost 35 chemical elements are of concern to humans. Twenty-three of these elements are PTEs, which have been shown to have no significant benefit to

human health and can cause health problems when present in the human system at low and high concentrations (Jaishankar *et al.* 2014). Some of these chemical elements, such as zinc, copper, iron, magnesium, manganese, and selenium, present benefits to human metabolism provided that they are ingested in small amounts as macronutrients (Emenike *et al.* 2016). A study investigated the quality of domestic water sources, rainwater, river water, and boreholes in the Esan area of Edo State (Nigeria) and discovered significantly high concentrations of lead (Pb), sulfate (SO_4^{2-}), and nitrate (NO_3^-) in harvested rainwater samples (Dic-Ijiewere *et al.* 2018). Other studies have also discovered chemical elements such as copper (Cu), zinc (Zn), manganese (Mn), chromium (Cr), iron (Fe), and cadmium (Cd) at concentrations higher than the regulatory guidelines in harvested rainwater samples (Malassa *et al.* 2014; Igbinosa & Aighewi 2017; Imarhiagbe & Osarenotor 2020; Mentese *et al.* 2021). Diseases linked to the presence of PTEs in the human body include cancer, kidney and liver diseases, cognitive issues, and reproductive and fertility issues (Khayan *et al.* 2019; Algül & Beyhan 2020). Zdeb *et al.* (2020) discovered that the concentrations of PTEs in harvested rainwater samples collected and tested in 2016 were lower than those analyzed in 2015 because of the higher rainfall intensity in 2016. This implies that the amount of rainfall experienced in a location per time affects the concentration of chemical pollutants in rainwater collected and stored for use.

Rainwater is commonly used to support existing drinking water supplies and reduce the demand for tap water in times of drought (Zdeb *et al.* 2020). Approximately a quarter of the world's population currently experiences water scarcity (Tenebe *et al.* 2018). Many communities in Nigeria lack access to potable water despite the abundance of source water in the country (Nnaji *et al.* 2019). This poor water supply and lack of proper sanitation practices have resulted in the prevalence of many water-related diseases (Omole *et al.* 2015). Thus, rainwater harvesting is a cheaper, environmentally viable alternative to mitigate floods (Uchechukwu *et al.* 2018; Ogarekpe *et al.* 2020), and also improves the lack of potable water supply in many Nigerian communities due to social, climatic, economic, and political shortcomings (Nnaji *et al.* 2017, 2019). Despite its abundance and benefits, rainwater is not present without contamination.

Ekpoma is a community that depends primarily on roof-harvested rainwater for drinking water and domestic use (Okeke *et al.* 2011; Turay *et al.* 2014; Tenebe *et al.* 2020). Rainwater harvesting as a primary source of drinking water in Ekpoma is unique in Nigeria because many parts of the country have access to fair quality groundwater and surface water. The geological characteristics of Ekpoma adversely affect the accessibility of groundwater in the area (Okeke *et al.* 2011). Seasonal variations also affect the quantity of water available to the community from rain and surface water sources. These variations can affect the concentration of contaminants in the water consumed by the community (Emenike *et al.* 2020a, 2020b). In the rainy season, individuals in the community harvest rainwater via rooftop catchments and store it in concrete wells or plastic storage tanks (Tenebe *et al.* 2020). Roofing materials have been reported to be major contributors to pollutants in roof-harvested rainwater (RHRW) (Angela *et al.* 2019). The components of roofing materials have been found to contribute to the pH levels of RHRW, which could result in increased acidity and could also have an effect on the leaching of roofing and storage tank materials, thus impacting water quality and increasing the concentration of PTEs (Angela *et al.* 2019; Müller *et al.* 2019). Akoto *et al.* (2011) reported relatively high concentrations of Pb and Cd in RHRW from asbestos and clay tile roof materials compared with control samples obtained directly from the sky. Several studies have been conducted to investigate the effects of roof materials on the quality of RHRWs. The results of these studies have shown that there is a relationship between the age and material composition of the roof materials and the safety of the RHRW (Charters *et al.* 2021; De Buyck *et al.* 2021; Itodo *et al.* 2021; Osayemwenre & Osibote 2021; Richards *et al.* 2021). A phenomenon known as dry deposition also leads to the accumulation of microorganisms, fecal matter from birds and animals, dust, and tree litter on roof surfaces, which in turn affects RHRW quality (Lee *et al.* 2010; Deng 2021). Particulate matter generated from automobile emissions, as well as industrial and agricultural processes, also constitutes a part of dry deposition (Emenike *et al.* 2020a, 2020b). Metals and ions, such as Fe, Pb, Zn, and Cl^-, have been reported in RHRW owing to dry deposition (Morrow *et al.* 2010; Mendez *et al.* 2011; Charters *et al.* 2021). High levels of bacteriological pollutants have been reported in RHRW compared to rainwater collected directly from the sky (Zdeb *et al.* 2020).

Thus, it is important to investigate the presence of PTEs in harvested rainwater samples from Ekpoma and determine whether the consumption of water poses a health risk to inhabitants of the community across varying age groups. Over a decade ago, the study conducted by Okeke *et al.* (2011) to investigate the hydrogeological characteristics of the Northern Ishan district which includes Ekpoma revealed that groundwater samples obtained from the district contained Fe concentrations of 1.08–1.55 mg L^{-1}, exceeding the World Health Organization (WHO) limits of 0.3 mg L^{-1} for drinking water. In addition, Ekpoma is a member of the Edo State Oil and

Gas Producing Areas Development Commission (EDSOGPADEC), making it an oil-producing community in the state. This means that exploration activities within and around the community can impact the quality of rainwater in the area (Imarhiagbe & Osarenotor 2020).

Therefore, this study aimed to investigate the concentrations of PTEs in roof-harvested rainwater samples collected from storage tanks and wells in Ekpoma, Edo State, Nigeria. An attempt was made to relate the physical characteristics of the samples collected to the composition of the storage tank materials and the rainwater collection system. The chemical results obtained were compared to existing regulatory standards, such as the United States Environmental Protection Agency (USEPA), World Health Organization (WHO), and Nigerian Drinking Water Quality Standards (NDWQS). Subsequently, the health risks associated with oral and dermal consumption of water were estimated for different age groups. Findings of this study would serve to enlighten the members of Ekpoma community on the need for water quality assessment, monitoring, and the maintenance of rainwater harvesting catchment systems. The information presented would provide insight into the health risks associated with consuming roof-harvested rainwater in the Ekpoma community, as well as create international awareness of the unique situation of Ekpoma, Nigeria.

2. RESEARCH METHODOLOGY

2.1. Study site

Ekpoma is a town located in the northern Ishan area of Edo State, South-South Nigeria. It is located in the same area as the towns of Irua, Uromi, and Ubiaja. The Northern Ishan area is positioned between Latitudes 6° 41′ – 6° 5′ and Longitudes 6° 00′ – 6° 30′ and covers an area of about 150 km^2 (Figure 1). The towns in the Northern Ishan area have elevations that range from 243.9 m (800 ft) to 426.6 m (1400 ft) above mean sea level (Okeke *et al.* 2011). Ekpoma has mostly sedimentary bedrock with a groundwater aquifer located approximately 405 m below the Earth's surface (Molindo & Alile 2007). Studies conducted during rainy periods in Ekpoma have revealed that aquifers do not allow for efficient groundwater recharge. These characteristics limit the access to

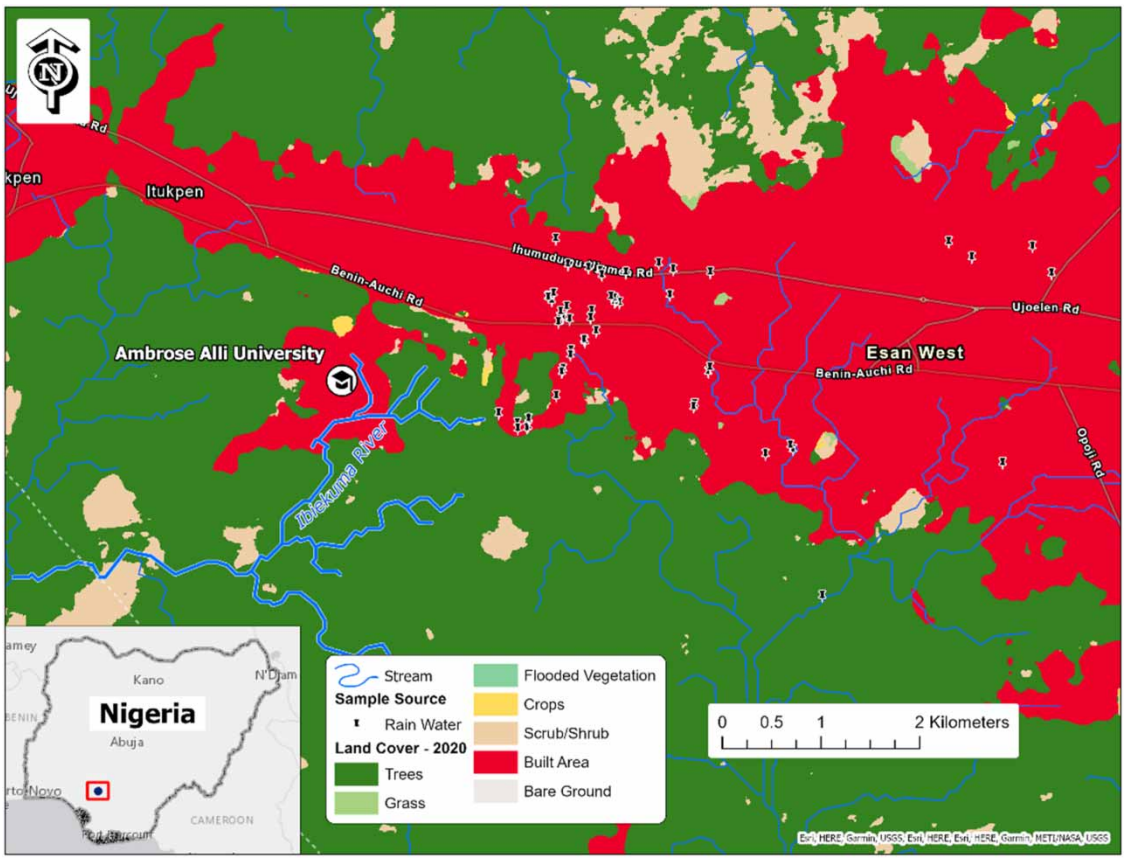


Figure 1 | Identification of PTEs in harvested rainwater samples; Rainwater sampling locations in Ekpoma, Edo State.

borehole water in the Ekpoma region. Like most parts of Nigeria (Ngene *et al.* 2015), Ekpoma has two main weather seasons: dry and rainy. The rainy season in Ekpoma occurs between March and November, with the region experiencing an average annual rainfall of 1562–1867 mm (Nigerian Meteorological Agency 2007; Emenike *et al.* 2020a, 2020b). The topography, climate, and human activities in a particular area play a role in the quality of RHRW (Chubaka *et al.* 2018; Norman *et al.* 2019; Jia *et al.* 2021). As of 2005, Ekpoma was estimated to have a growing population of 834,750, with an estimated annual population growth rate of 3% (Okeke *et al.* 2011). Ekpoma is classified as a rural community, with a majority of the occupants living in small-to medium-scale agricultural practices (Tenebe *et al.* 2020). The population of Ekpoma has a low average daily income of <1 USD daily (United Nations 2013), and must contend with the ever-increasing prices of rainwater being sold in the community. As of 2020, 25 liters of rainwater was sold between 50 and 60 naira (~ 20 cents) during periods of low rainfall. The rainwater sold to members of the community comes through the roof-top system and into storage tanks with water containing potentially harmful bacteria (Tenebe *et al.* 2020) and possibly toxic chemical elements.

The rainwater harvesting systems in this study comprised corrugated iron roofing sheets, metal pipes, plastic polyvinyl chloride (PVC) pipes, concrete, and plastic storage tanks (Figure 2). No first-flush system was observed in place to control the inflow of pollutants into the storage tanks. However, during an interview with residents, the majority of them mentioned that during a very light storm event, the roof water pipeline is disconnected and prevented from collecting water into storage tanks. This prevents accumulated debris gathered during the dry season from entering the storage tanks. Generally, water flows directly from the roof surface into the storage tanks via folded corrugated iron sheets or PVC pipes. The site investigation revealed that some of the storage tanks were improperly covered with corrugated iron and asbestos sheets, which provided an opportunity for further contamination with PTEs from the environment. In some cases, storage tanks were left uncovered. It was also observed that there were no proper channels in place for water collection from the storage tanks to some homes, and residents had to manually withdraw water from the storage wells using buckets and long ropes, which are again likely to introduce contaminants.

Figure 2 | Rainwater harvesting system in Ekpoma.

2.2 Sampling procedure

Fifty-four sampling locations (Table SR of the Supplementary Material) were assessed, and three representative samples were obtained from each sampling location. The samples were retrieved from rainwater storage tanks in Ekpoma and stored at 4 °C in high-density polyethylene (HDPE) bottles. The physical characteristics of the samples, including pH, electrical conductivity (EC), salinity, temperature (°C), and total dissolved solids (TDS),

were measured on-site using a Hanna H198130 probe attached to a waterproof Hanna Edge® Multiparameter EC/TDS/Salinity Meter-HI2030. The samples were collected during the rainy season, specifically in September, immediately after the August break, which is a short dry break in August lasting 2–3 weeks following the peak rainfall in June and July.

2.2.1. Physical characteristics

It is important to measure the physical characteristics of harvested rainwater samples, as this provides insights into the potential reasons for contamination of the rainwater samples tested. A total of 162 rainwater samples (triplicate samples) collected from 54 sampling locations were analyzed *in situ* for pH, electrical conductivity (EC), salinity, temperature (°C), and total dissolved solids (TDS) with the aid of a Hanna H198130 probe attached to a waterproof Hanna edge® Multiparameter EC/TDS/Salinity Meter-HI2030. These tests were conducted according to the standard methods for the examination of water and wastewater. The multiparameter instrument used was standardized and calibrated with buffer solutions of 4.0 and 7.01 (pH) and potassium chloride (EC) (Baird *et al.* 2012).

2.3 Quantification of potentially toxic elements (PTE)

Ten chemical species (Al, Ca, Cr, Cu, Fe, Mg, Mn, Ni, Pb, and Zn) were quantified by analyzing a representative 10 mL aliquot of each sample with an atomic absorption spectrophotometer (AAS) with the aid of the UNICAM 969 AA-SPECTROMETER – SN (12083) under the standard operating conditions. Distilled water was used throughout the analysis, whereas digestion of the samples was achieved using nitric acid. The rainwater samples were digested as described by Baird *et al.* (2012). Concentrated nitric acid (5 mL) was added to 100 mL of each sample in a 250 mL glass beaker and heated to a volume of approximately 40 mL. Another 5 mL of nitric acid was added, and the mixture was heated for 10 min before cooling. The beakers were rinsed on the sides with 5 mL nitric acid and then filtered into a 50 mL conical flask, and deionized water was added to reach the mark. A blank solution was prepared in the same way as the rainwater samples and analyzed. A blank sample was analyzed with three standards after every 12-sample analysis to maintain the accuracy of the measurements. The analysis was conducted using a 3111A alpha standard and N – A and A – A flames in the spectrophotometer. The samples were exposed to ultraviolet wavelengths ranging from 217.0 to 357.9 nm for the detection of each metal (Table SS of the supplementary material). The measurement time of the AAS was 4 seconds, and the detection limits were 0.0010 mg L^{-1} for Pb, Mn, and Mg; 0.0050 mg L^{-1} for Ni, Cr, Zn, and Cu; 0.0020 mg L^{-1} for Fe and Ca; and 0.1000 mg L^{-1} for Al. Standard solutions of all eight chemical elements were prepared using analytical-grade chemicals, reagents, and a dilution factor of 1000 mg L^{-1} (Anake *et al.* 2020).

2.3.1. Chemical water quality evaluation based on comparison with existing drinking water standards

Owing to the increasing degradation and depreciation of ground and surface water quality, many developing and developed countries continue to struggle to maintain and monitor water quality (Tenebe *et al.* 2016; Emenike *et al.* 2018; Omole *et al.* 2018; Tenebe *et al.* 2018; Uddin *et al.* 2021). The reduction in the quality of water from conventional sources has led to an increase in the consideration of unconventional water sources such as rainwater, reclaimed water, brackish water, and seawater. The water obtained from these sources is constantly subjected to water quality testing and monitoring. In an attempt to protect humans from the chronic and acute effects of drinking contaminated water, toxicologists and regulatory agencies in different countries have worked together to create standards that serve as guidelines to limit the concentration of potentially toxic species in drinking water, regardless of its primary source. The concentrations of the chemical elements measured in the rainwater samples were recorded and compared with the allowable limits set by the WHO, US EPA, and NSDWQ. The percentage deviation from the allowable limits was also recorded, and the information obtained was used to conduct a human health risk assessment due to the consumption of harvested rainwater.

2.4. Human health risk assessment

The data employed for the human health risk assessment were the mean values of triplicate samples recorded from each location after testing. Human health risk assessment was conducted to evaluate eight of the ten elements detected in the water samples tested. This is because only those eight elements present a potential health risk to humans when consumed above certain quantities. Calcium and magnesium were excluded from the analysis, as the detected concentrations were not considered toxic to consumers. The human health risk assessment performed in this study was carried out using HERisk software, an enhanced version of the

HHRISK code (Neris *et al.* 2019, 2021). The application of this software is essential for carrying out a spatio-temporal risk assessment, which presents a more detailed and accurate health risk assessment (Emenike *et al.* 2020a, 2020b). Temporal evaluation is only possible because the program changes the age-dependent parameter values over the exposure time. Neris *et al.* (2021) offer a more in-depth and detailed explanation of the spatio-temporal risk assessment methodology used in the HERisk code. Briefly, the software used modified the equations provided by the US EPA. The code calculates the risks for nine different initial ages (IA) of exposure to contaminants (1, 2, 3, 6, 11, 16, 18, 21, and 65 years). These IAs were chosen based on some of the age groups defined by the U.S EPA (2011) and served as the basis for the code to define the age-dependent parameter values depending on the resident age at a given time *t*.

Residents of the study region use rainwater for consumption and body hygiene during the rainy season, which occurs between April and October. Therefore, two routes of human contamination (intake and dermal contact with water) by eight potentially toxic elements (Al, Cu, Cr, Fe, Mn, Ni, Pb, and Zn) were considered. The daily intake dose was calculated using Equation (1), whereas the dermal contact dose was calculated using Equation (2) (US EPA 1989, 2004; Neris *et al.* 2019). The risk assessment was performed for a residential scenario, and the experimental concentrations of chemical species were considered constant over time to permit human health risk assessment:

$$D_{ing}{}^{IA}(t) = \sum_{t=\Delta t}^{ED} \frac{C_w(t) \cdot IR(i) \cdot EF(i) \cdot \Delta t}{BW(i) \cdot AT} \tag{1}$$

$$D_{der}^{IA}(t) = \sum_{t=\Delta t}^{ED} \frac{C_w(t) \cdot CF_1 \cdot SA(i) \cdot PC \cdot ET(i) \cdot EV(i) \cdot EF(i) \cdot \Delta t}{BW(i) \cdot AT} \tag{2}$$

where: $D_{ing}{}^{IA}(t)$ is the daily intake dose at time t for initial age IA (mg kg^{-1} d^{-1}), $C_w(t)$ is the chemical species concentration in water at time t (mg L^{-1}), $IR(i)$ is the water ingestion rate for age group i (L d^{-1}), $EF(i)$ is the exposure frequency for age group i (d y^{-1}), Δt is the time variation (y), $D_{der}{}^{IA}(t)$ is the daily absorption dose at time t for initial age IA (mg kg^{-1} d^{-1}), CF_1 is the volumetric conversion factor (L cm^{-3}), $SA(i)$ is the skin surface area available for contact with water for age group i (cm^2), PC is the Dermal permeability of the chemical species (cm h^{-1}), $ET(i)$ is the water exposure time while showering for age group i (h event^{-1}), $EV(i)$ is the event frequency for age group i (events d^{-1}), $BW(i)$ is the body weight for age group i (kg), AT is the averaging time (d) and ED is the exposure duration (y). Age-related parameters, such as the water ingestion rate (IR), body weight (BW), skin surface area (SA), and the water exposure time while showering (ET), vary over the exposure time as the residents grow old.

The probability of a resident developing life-long cancer by being exposed to chronic carcinogenic species (potential carcinogenic risk (CR)) and the non-carcinogenic effects caused by ingestion or dermal contact with harmful chemical species (non-carcinogenic hazard quotient (HQ)) were calculated using Equations (3) and (4) (US EPA 2005, 2007):

$$HQ^{IA}(t) = \frac{D^{IA}(t) \cdot BAF}{RfD} \tag{3}$$

$$CR^{IA}(t) = D^{IA}(t) \cdot SF \cdot BAF \cdot ADAF \tag{4}$$

where ^{IA} is the dose at time t for initial age IA (mg kg^{-1} d^{-1}), BAF is the chemical species dose fraction that is absorbed by the organism (bioavailability factor), RfD is the reference dose of the chemical species (mg kg^{-1} d^{-1}), $ADAF$ is the age-dependent adjustment factor, and SF is the slope factor (mg kg^{-1} d^{-1})$^{-1}$, which converts estimated daily doses averaged over a lifetime directly into the probability of an individual developing cancer.

Owing to the utilization of the two exposure routes, it was necessary to calculate the aggregated hazard index (HI_{agg}) and aggregated potential carcinogenic risk (CR_{agg}) using Equations (5) and (6), respectively (US EPA 1989):

$$HI_{agg}^{IA}(t) = HQ_{ingestion}^{IA}(t) + HQ_{dermal}^{IA}(t) \tag{5}$$

$$CR_{agg}^{IA}(t) = CR_{ingestion}^{IA}(t) + CR_{dermal}^{IA}(t) \tag{6}$$

For the overall risk assessment incorporating the risks arising from all exposure routes and all chemical species (n), the total hazard index (HI_{tot}) and the cumulative potential carcinogenic risk (CR_{cum}) were calculated using Equations (7) and (8):

$$HI_{tot}^{IA}(t) = \sum_{j=1}^{n} HI_{agg,\ j}^{IA}(t) \tag{7}$$

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

The parameter values used to calculate the intake and absorption doses are shown in Table SY of the supplementary material, whereas Table SZ reports the *RfD*, *SF*, *BAF*, and *ADAF* values used to perform the risk calculations.

Non-carcinogenic risks were classified as negligible ($HI_{tot} < 0.1$), low ($1 > HI_{tot} \geq 0.1$), medium ($4 > HI_{tot} \geq 1$), and high ($HI_{tot} \geq 4$), whereas carcinogenic risks were classified as negligible ($CR_{cum} < 1{\cdot}10^{-6}$), low ($1{\cdot}10^{-4} > CR_{cum} \geq 1{\cdot}10^{-6}$) and high ($CR_{cum} \geq 1{\cdot}10^{-4}$) (US EPA 1989; Li *et al.* 2014). CR_{cum} values greater than $1{\cdot}10^{-4}$ imply that more than 1 in 10,000 residents present the possibility of developing cancer Samuel *et al.* (2018).

3. RESULTS AND DISCUSSION

3.1. Physical characteristic of analyzed samples

Acidic rainwater has been linked to the leaching of metals from roof materials. This acidity can be attributed to SO_2 and NO_2 emissions into the atmosphere (Obi-udu *et al.* 2021). Another potential contributor to increased rainwater pH is the weathering of roofing materials (Tengan & Akoto 2022). This could increase dissolved solids and cause the replacement of hydrogen ions with metal ions during the interaction of rainwater with roof surface materials (Appaih 2008). The pH also determines the extent of metal solubility in water. At lower pH levels, metals dissolve more easily in water, thereby increasing the risk of higher metal intake by consumers (Namieśnik & Rabajczyk 2010; Wang *et al.* 2021). The pH level of water can also have a direct impact on the taste and effectiveness of chlorine disinfection. Highly acidic water ($pH < 4$) has been linked to brain damage, retarded growth in children, and eye and skin damage (Rogers 2013; Dirisu *et al.* 2016). The pH values obtained for the samples range from 7.7 to 9.0. This implies that the samples collected were mostly neutral and slightly alkaline and, as such, may have little potential to cause leaching of roofing and storage tank materials.

Electrical conductivity (EC) does not have a direct impact on human health but serves as an indicator of the presence of ions in water, which could impact the taste quality of water (Yohanna *et al.* 2021). The EC values recorded for all the rainwater samples from the different sampling locations range from 0.12 to 180 µs/cm, which are well below the WHO guidelines for drinking and potable water of 700 µs/cm (WHO 2004). The variations in EC levels could be due to differences in roofing materials, age of roofing materials in different catchment systems, and type of storage tank used in each sampling location. The presence of ions in the collected samples could be attributed to the combustion of fossil fuels, soil dust, and incineration of farm residues in the environment. The increase in EC levels in some samples has been reported to be related to the presence of dissolved inorganic solids of Cl^-, $Na+$, $NO3^-$, and $PO4\ 3^-$ deposited on the roof surface materials and the breakdown of metal ions from the roofing materials over time (Adedeji *et al.* 2014; Desye *et al.* 2021).

All TDS values recorded from the sample testing were below the 500 mg/L limit in the WHO drinking water standard (WHO 2011a, 2011b). The dissolved solids in rainwater can be attributed to atmospheric gases present in the environment (Kerkez *et al.* 2016; Igwe *et al.* 2021). TDS has not been linked to human health risks; however, it serves as an indicator of the presence of inorganic contaminants and can affect the aesthetic quality – taste and hardness – of water. Low TDS levels in water have been reported to cause water to taste flat (Rozelle & Wathen 1993; WHO 2003a, 2003b, 2003c; Singh & Das 2021).

3.2. Chemical quality assessment of rainwater

The 54 sampling locations were grouped into districts based on their proximity (Table 1). According to various government agencies, water is considered safe for domestic use if it contains the same or lower concentrations of a contaminant, as outlined in the regulatory standards for drinking water. The WHO guidelines do not provide

Table 1 | Classification of rainwater sampling locations into districts

District	Notable landmark	Rainwater samples in district	Total no of samples in district
1	Along Benin-Auchi road Near St. Nicholas Street, Onigbinde Crescent, Efe Block Road, Princeton hostel	1, 2, 3, 4, 5, 6, 7, 9, 10, 11, 12, 17, 20, 21, 22, 23, 24, 25, 33, 34, 51, 52, 53, 54	24
2	Along Ihumudumu-Ujumen Road, Oshagale Street, Divine Royalty Hotel	8, 13, 14, 15, 16, 18, 19	7
3	Ugoelen Extension Road, Oviobe Street, Near Ezekiel College of Theology	26, 27, 28, 29, 30, 31, 32, 35, 36, 37, 38	11
4	Emando, Close to Ihumudumu-Ujumen Road, Eromon St, Afua St, Eguare Road, Ukhun-Idoa Road	44, 45, 46,47, 48, 49, 50	7
5	Ehimen Street, Musco Emuli Road	39, 40, 41, 42, 43	5

limits for Fe, Mn, and Zn concentrations in drinking water. The WHO mentioned that Fe, Mn, and Zn are not commonly found in drinking water samples, and these elements do not pose a threat to humans when consumed from drinking water sources; therefore, there is no need to set regulatory standards for these chemical elements (WHO 2004). The US EPA standards do not include limits for Ni because its occurrence in US drinking water is rare, and as such, it has become unregulated and regulatory limits for Ni are under revision. The NDWQS contains regulatory limits for all the chemical elements discussed in this study. The concentrations of chemical elements detected in this study were compared to the allowable limits provided in the regulatory standards (Table 2), while the potential toxicity of the chemical elements without a basis for comparison across all the standards was evaluated in-depth using human health risk assessment. This was essential for determining the risk of exposure due to the prolonged consumption of rainwater with the detected concentration levels of these chemical species.

Table 2 | Mean values of PTE concentrations detected in each district in comparison to regulated allowable limits

					Mean values (mg L^{-1})				
S/N	Element	USEPA MCL (mg L^{-1})	WHO MCL (mg L^{-1})	NDWQS MCL (mg L^{-1})	District 1	District 2	District 3	District 4	District 5
1	Fe	0.3	–	0.3	0.224	0.146	0.29	0.537	0.363
2	Zn	5	–	3	0.082	0.023	0.075	0.114	0.095
3	Cu	1.3	2	1	1.975	*ND	1.167	2.676	1.595
4	Pb	0	0.01	0.01	0.322	0.168	0.244	0.198	0.173
5	Mn	0.05	–	0.2	0.166	0.196	0.282	0.412	0.345
6	Cr	0.1	0.05	0.05	0.183	*ND	*ND	0.133	0.269
7	Ni	–	0.07	0.02	0.046	0.048	0.048	0.058	0.044
8	Al	0.2	0.2	0.2	0.002	*ND	0	0	0

*ND, not detected; MCL, Maximum Contaminant Level.

PTEs have been found to accumulate in the human body, leading to negative health effects (Ali *et al.* 2019). PTEs have the potential to destroy macromolecules and cellular functions in the human body when transported within cells and tissues. Figure 3(a)–3(h) presents a graphical outlook of the information presented in Table 2. Cu was not detected in samples obtained from District 2. However, all other districts contained levels of Cu and Pb that exceeded the set regulatory limits (Figure 3(b) and 3(c)). These levels of contamination can be attributed to corrugated metal rooftops used in areas that have experienced different levels of rust over time (Emenike *et al.* 2019; Tenebe *et al.* 2018). The exploratory activity of crude oil in the environment is another likely source of Pb and Cu contamination (Anake *et al.* 2020; Imarhiagbe & Osarenotor 2020). The most likely mode of transportation of the elements to the community is via air deposits. High exposure to Cu has been associated with

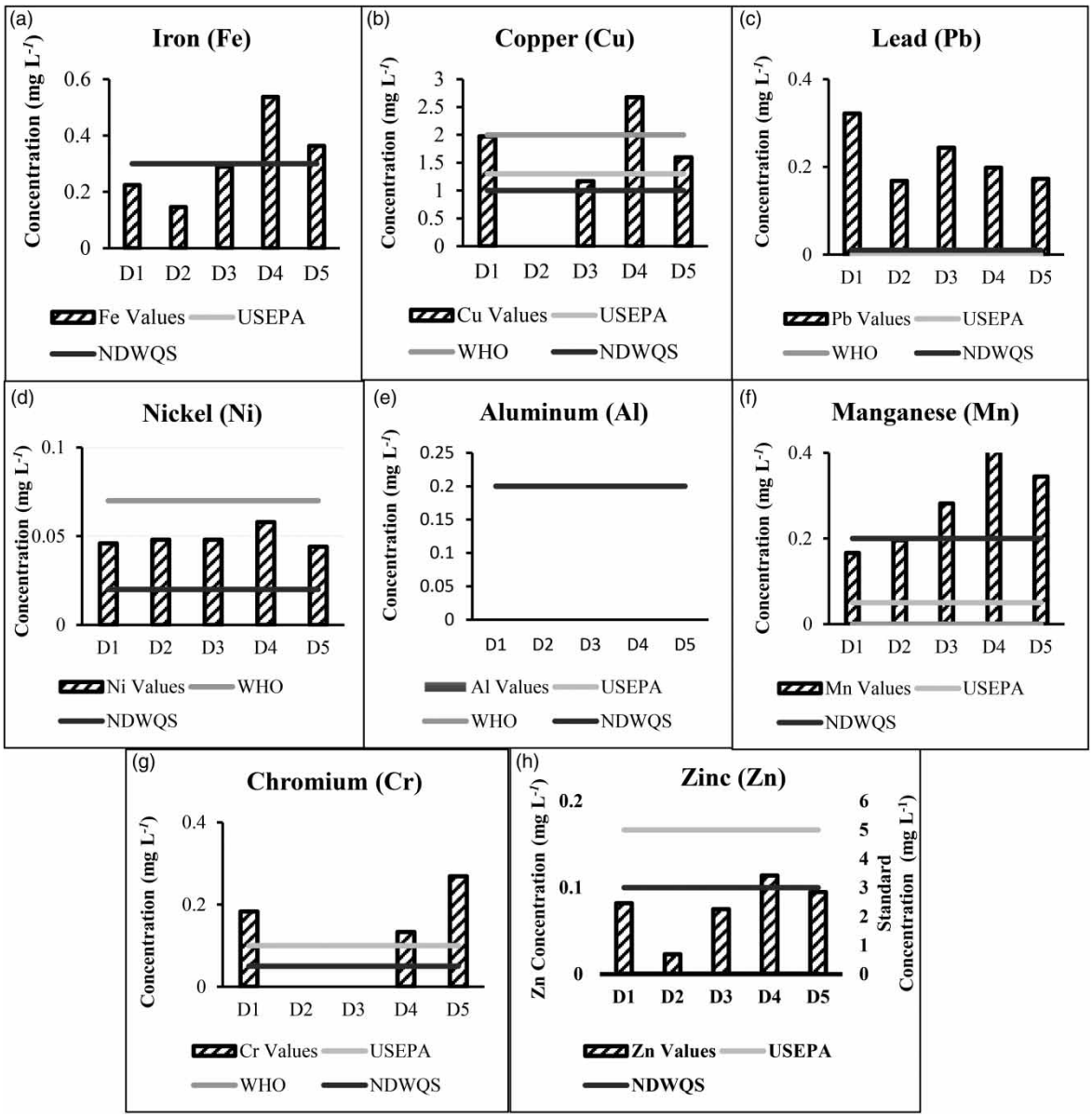


Figure 3 | (a–h): Graphical representation of PTEs concentrations in rainwater samples in comparison to set regulatory standards (WHO, US EPA, NDWQS).

liver and kidney damage, anemia, immunotoxicity, and developmental toxicity in humans (Omole *et al.* 2015; Anake *et al.* 2020; Jalil *et al.* 2022). Exposure to Pb has been found to result in a reduced intelligence quotient, convulsions, mental retardation, behavioral challenges, and mortality (WHO 2019). Pb concentrations in human blood below 25 μg/dL have been reported to harm fetuses in pregnant women (David 2005). Chronic Pb exposure can result in gene mutations, neurological and hematological disorders, kidney function disruption, endocrine and reproductive challenges and, eventually, cancer (Iavicoli *et al.* 2009).

Cr and Pb are classified as group 1 carcinogens by the International Agency for Research on Cancer and can cause cancer in humans when consumed above certain limits (IARC 2012). These metals can cause DNA damage, cell death, and oxidative stress, thereby increasing the cancer-related risks in consumers. Chromium was undetected in samples obtained from Districts 2 and 3, but all other samples exceeded the limits set by all regulatory standards (Figure 3). The absence of Cr can be attributed to the nature of the storage tanks. For samples retrieved from Districts 2 and 3, plastic storage tanks were used, unlike concrete storage wells present in other districts. Exposure to high Cr concentrations is associated with genotoxic and carcinogenic effects (Zhang *et al.* 2011; Lidiková *et al.* 2021).

Although zinc is associated with metal roofing sheets, all the samples except those from District 4 contained Zn at levels lower than the USEPA and NDWQS limits (Figure 3). The presence of Zn may be due to fuel combustion and application of zinc-containing fertilizers and pesticides in the environment (Mohan *et al.* 2021). Trace amounts of Zn and Fe are required for genetic development and immune function in humans. However, acute and chronic toxicities have been reported when consumed at concentrations above the set safe limits (Kubala 2018). It was observed that all samples obtained from Districts 4 and 5 contained Fe levels above the USEPA and NDWQS limits (Figure 3(a)), while samples from District 3 contained Fe levels that were barely below the threshold set by the USEPA and NDWQS. The samples obtained and tested from Districts 1 and 2 had concentrations lower than the set standards. These Fe levels can be attributed to the nature of the roof catchment systems used for rainwater harvesting. Previous studies have shown that a large amount of iron is present in the soil cover of the Ekpoma community (Okeke *et al.* 2011; Tenebe *et al.* 2020) and this iron concentration can be transferred to rooftops in the form of dust particles that end up in storage tanks owing to a lack of filtration systems before storage (Nnaji *et al.* 2017, 2019; Emenike *et al.* 2019). The presence of Fe could also be due to atmospheric deposition of Fe emissions from motor vehicles and particulate matter dissolved by rainwater (Wang *et al.* 2014; Tenebe *et al.* 2018; Tengan & Akoto 2022).

All samples contained nickel concentrations higher than the NDWQS limit of 0.02 mg L^{-1} but lower than the 0.07 mg L^{-1} allowable limit of the WHO (Figure 3(d)). All samples analyzed contained very low levels of aluminum (Figure 3(e)) and high levels of manganese (Figure 3(f)) when compared to the set regulatory limits.

3.3. Human health risk assessment

The results of the non-carcinogenic risk assessments for all sampling points (SP) are shown in Figure 4 and Table SQ (see Supplementary Material). The calculations carried out by HERisk showed a significant decrease in the total hazard index (HI_{tot}) during children's development, reaching the minimum values when residents reached between the ages of 16 and 18 years (Figure 4(b)). A comparison between the calculated risks for age

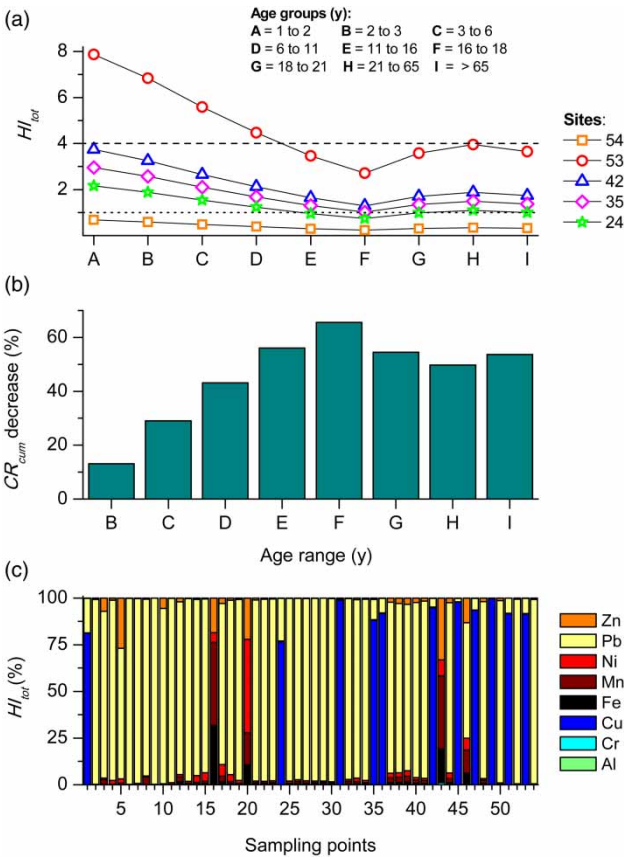


Figure 4 | (a): HI_{tot} values for each age group in five sites that presented different risk intensities; (b) HI_{tot} variation compared to values found for children up to two years old (age group A); (c) Contributions of each chemical species for HI_{tot} values.

groups A and F (see Figure 4 caption) showed a ~65% decrease in non-carcinogenic risk values. Upon entering adulthood, the risk increases (~10%) and remains constant until old age. Mathematically, this behavior can be explained almost entirely by the IR/BW ratio. The BW variation during growth was greater than the water IR variation, resulting in a decrease in risk until adulthood. In contrast, from the age of 16 years, the BW values stabilized while water IR increased, resulting in a further increase in non-carcinogenic risks for adults. The HI_{tot} values for the various age groups increased in the following order: $F < E < G < I < H < D < C < B < A$.

Evaluations of the studied sites showed that 15% of the sites did not present non-carcinogenic risks for all age groups ($HI_{tot} < 0.1$), 48% presented low risks, and only 6% presented medium risks. The other 31% of places had different ratings for some age groups. Although there were no places with high risks for all age groups, some localities presented high risks for children. Location 45 showed high risks for children up to three years old, places 47 and 49 up to six years old, and locations 51 and 53 for children up to 11 years old. For the other age groups, the risk was moderate. The calculated risks in places 8 and 44 were negligible only for residents between 11 and 21 years old, while at place 4, they were negligible for residents between 11 and 18 years old. On the other hand, location 1 presents a medium risk for children up to 11 years old ($1.93 \geq HI_{tot} \geq 1.10$) and a low risk for the other age groups. Other sites such as 14, 15, 18, 37, 38, and 39 showed low risk for children up to six years of age. Lastly, children up to 11 years old and adults (≥21 years old) were subject to medium risks at sites 24 and 31 ($2.16 \geq HI_{tot} \geq 1.00$), while the other residents were at low risk.

Among the sites evaluated, sampling points 16, 20, and 43 proved to be the safest ($HI_{tot} \leq 0.01$) considering the contamination routes by water ingestion and dermal contact with water. On the other hand, location 53 was the most harmful with the highest HI_{tot} value (7.87) found in the study area, encountered for the age group of 1–2 years. Also, for residents of other age groups the limit of quantification living in this location, the risks (HI_{tot}) remain medium/high, ranging from 6.84 (age group B) to 2.71 (age group F). Evaluating the non-carcinogenic risks associated with the two exposure routes, it is evident that the water ingestion route provides the greatest risks for residents; one route is responsible for more than 98% of the risks for all age groups and sampling points.

Among the chemical species evaluated in the non-carcinogenic risk calculations, Al and Cr did not contribute to the risks, accounting for less than 0.01% of the HI_{tot} values at all locations (Figure 4(c)). This could be attributed to the high number of sampling points without concentrations above the limit of quantification (LQ) and the high reference doses (RfD) of these chemical species. On the other hand, the chemical species that contributed the most to the risks were Pb, accounting for more than 90% of the HI_{tot} values in almost all sites evaluated, except at the sampling points where Cu concentrations were quantified (sites 1, 24, 31, 35, 36, 42, 45, 47, 49, 51, and 53). However, localities where Pb is the principal source of contamination show at most low risk ($HI_{tot} < 1$).

The most harmful chemical species in this study was Cu. Whenever quantified in water samples, its risk contribution is higher than 75%, whereas Pb contributes less than 23%. In addition, the only sampling points that presented medium or high risk ($1 \leq HI_{tot}$) were those with Cu concentrations > LQ. Although Cu is less harmful than Pb ($RfD_{Cu} = 1.00 \times 10^{-2}$ and $RfD_{Pb} = 3.60 \times 10^{-3}$), the Cu fraction that is absorbed by the organism by water intake ($BAF_{cu} = 60\%$) is much higher that of Pb ($BAF_{Pb} = 11\%$), resulting in a greater amount of Cu absorbed into the bloodstream and higher risks to human health. The other chemical species, Fe, Mn, Ni, and Zn, showed a low contribution to the non-carcinogenic risks found (≤7%), with the exception of sampling points 16, 20, 43, and 46, where the Pb concentrations were lower than the LQ.

Risks associated with the consumption of Cu-contaminated water include nausea, abdominal pain, or vomiting (Pizarro *et al.* 1999). In contrast, Pb ingestion can affect the urinary, gastrointestinal, and central nervous system. Symptoms include headache, dizziness, violence, memory loss, extensor muscle problems, anemia, kidney failure, gastrointestinal inflammation, vomiting, and diarrhea (Williams *et al.* 2000; Azevedo & Chasin 2003; Martin 2006). Generally, the increasing chemical species contribution order for the HI_{tot} value was $Al < Cr < Fe < Ni < Zn < Mn < < Pb < Cu$.

The results of the carcinogenic risk assessments for all SP are shown in Figure 5 and Table ST (Supplementary Material). Cumulative carcinogenic risks (CR_{cum}) after a total exposure time of 26 years indicated that only 33% of the evaluated sites had negligible carcinogenic risks despite the IA of exposure to contaminants, whereas the other 61% were sites with low carcinogenic risks to residents. In SP4, the only residents who did not present carcinogenic risks were the elderly ($IA = 65$). On the other hand, location 44 showed significant (i.e., low) carcinogenic risks for residents whose initial age of exposure to contaminants was one year. Finally, Site 8

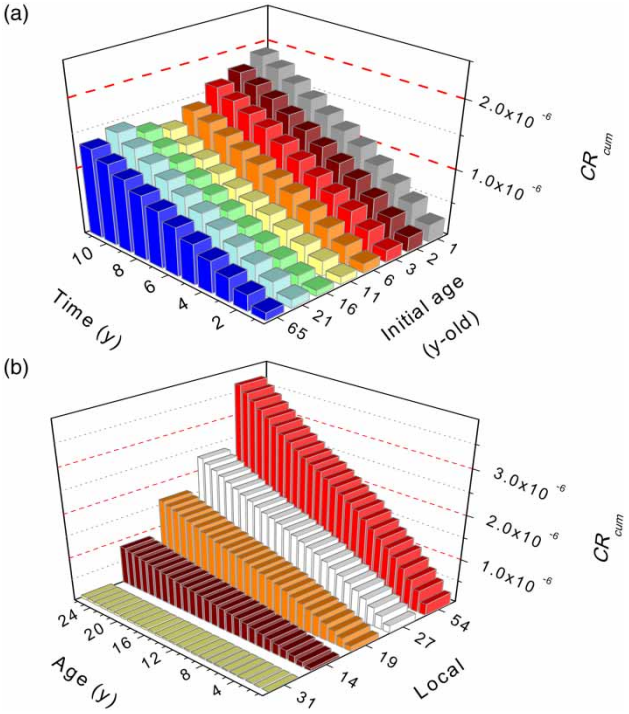


Figure 5 | (a): Comparison of CR_{cum} Spatio-temporal evolution for different initial ages of exposure to the contaminants (SP54) (b) CR_{cum} Spatio-temporal evaluation for five sites with different intensities of carcinogenic risks (IA = one-year-old).

presented low carcinogenic risks when contamination began within the first three years of age (IA $\leq$ 3) or in the adult stage at 21 years of age.

Unlike the results of the non-carcinogenic risks, site 54 showed the highest CR_{cum} values for residents, ranging from 3.70×10^{-6} when contamination began in the first year (IA = 1) and 3.17×10^{-6} when the contamination started at the IA of 65 years old. For adults, the average lifetime probability of developing cancer is one in approximately 300,000 individuals at this site. In contrast, localities 16, 20, 43, and 49 showed no carcinogenic risk once Pb concentrations were below LQ. Site 31 had the lowest carcinogenic risk among localities with quantifiable Pb concentrations (>LQ), resulting in a probability of developing cancer of less than one in ~15,600,000 residents.

A detailed spatiotemporal analysis of carcinogenic risks calculated for site 54 (Figure 5(a)) showed that when residents were exposed to contaminants from the age of one year, the carcinogenic risks were not negligible even after only five years of exposure. Similarly, for residents where exposure begins at two or three years of age, six years of exposure is required, while for the remaining IA ($\geq$6), 8–10 years of contaminant exposure are expected to be classified as low ($CR_{cum} \geq 1.00\times10^{-6}$).

The spatiotemporal evaluation of carcinogenic risks when IA = one-year-old (Figure 5(b)) showed that of the 36 localities that presented carcinogenic risks, 44% went from negligible to low risks after 5–10 years of exposure to the contaminants. Another 25% need residents to be exposed for 11–15 years, while 31% of the localities need more than 15 years of exposure for the risks to be no longer negligible. The carcinogenic risks calculated are entirely derived from Pb, as it is the only quantified PTEs with carcinogenic potential via dermal or ingestion routes. Also, in the same way as the non-cancer risk, the exposure route by drinking contaminated water is the principal source of carcinogenic risks for residents, representing approximately 98.8% of the risks in the entire study area.

4. CONCLUSION

Many studies have proven that the major sources of RHRW contamination include roofing materials, emissions from fossil fuel use, and industrial and agricultural activities. These anthropogenic sources affect the quality of rainwater, thus increasing the need for rainwater quality monitoring and evaluation to ensure the safety of human consumption. A comparison of PTE concentrations in the samples tested with existing standards revealed that approximately 75% of the samples contained PTEs at levels exceeding the allowable limits for these elements

in drinking water. Pb is considered a carcinogenic element by the US EPA, and high concentrations of this element were present in the water samples tested. High doses of Cu were measured in some of the water samples tested, and the consumption of high doses of Cu resulted in Cu toxicity. These results indicate that consumers in the community are at a potential risk of developing cancer and other diseases, such as liver damage from long-term consumption of water. Most of the contamination was due to the nature of the materials used in roof harvesting systems, which primarily included slightly to significantly rusted iron sheets. Additionally, owing to the ability of rainwater to dissolve chemical elements, leaching can contaminate stored water in concrete tanks, which is common in the Ekpoma community. Human activities in the locality, such as crude oil exploration, transportation, and agriculture, may have impacted the quality of harvested rainwater due to sediments on rooftops being transported by air.

Human health risk assessment indicated that children are the most susceptible to risks, with the age group between 1–2 years-old the most affected. The risks decreased significantly (up to 60%) until the adult stage of 18 years and remained constant thereafter. SP53 showed the highest non-carcinogenic risk, while sites 16, 20, and 43 were the safest. The chemical species that contributed the most to the high and medium HI_{tot} values were Cu, whereas Pb generated only low health risks. Only low carcinogenic risks associated with Pb were observed in the study area, with site 54 being the most affected. However, spatiotemporal evaluation indicated that in 44% of all localities, the CR_{cum} values were no longer negligible after 5–10 years of exposure to PTEs. Among the two exposure routes considered, water ingestion was responsible for $>$ 98% of the CR_{cum} and HI_{tot} values.

Continued consumption of contaminated water can result in exposure to various health problems in the bodies of consumers in Ekpoma. Therefore, it is recommended that rainwater harvesting systems be improved to collect clean and good-quality water by implementing the first flush method, as well as utilizing covered storage tanks made of high-density polyethylene or other materials that would not dissolve upon contact with rainwater. Filtration and plant-based adsorption systems should also be included to adsorb any PTEs that may have escaped the first flush. These improvements will very likely lower the health risk to consumers who depend solely on rainwater. In addition, more research is necessary to investigate the health risks and levels of exposure to other known drinking water sources used in this community, such as dug wells and river water. Future studies should also aim to investigate prevalent water-related diseases in the community and determine their specific connection with roof-harvested rainwater, as this research work has set a baseline for such studies.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no competing interests that could have influenced this study. The authors are not affiliated with or involved with any organization or entity with any financial or non-financial interest in the subject matter or materials discussed in this paper.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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