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Spatio-temporal evaluation of urbanization impacts on groundwater quality and the risk of human exposure to nitrate-contaminated groundwater

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ABSTRACT

Background: The study investigates how spatial factors linked to urbanisation in Owerri, Nigeria, contribute to groundwater contamination. It also evaluates the associated public health risks, particularly from poorly designed private boreholes in environmentally sensitive areas.

Methodology: Groundwater was sampled in two seasons across a ~100 km^2 area and analysed for major ions and DOC using ion chromatography and a Shimadzu TOC analyser, respectively. Water Quality Index (WQI) and Synthetic Pollution Index (SPI) were used to evaluate the drinking suitability of groundwater. A non-cancer risk model assessed age-specific health risks. Parameter relationships and variations were analysed using correlation and ANOVA, with sampling locations mapped using a handheld GPS.

Results: Findings showed nitrate (NO_3^-) as a critical contaminant having exceeded the World Health Organization's (WHO) permissible limit (PL) of 50 μg ml^{-1} in c.12 % and 26 % of boreholes in the respective seasons. DOC exceeded the WHO limit in about 83 % of sites during the rainy season but dropped to 2 % in the dry season. Nitrate pollution aligned with urban density patterns, while water quality declined from rainy to dry season, with 70 % to 25 % (WQI) and 13 % to 43 % (SPI) classified as good. Hazard quotients above 1 were recorded in 17 % to 32 % of the population during the rainy season and doubled in the dry season, indicating heightened health risks.

Conclusion: The study revealed significant seasonal variation in NO_3^- and high DOC levels, posing health risks to young children, and recommends Integrated Vulnerable Zone Management (IVZM) for safe water and sustainable urban planning in line with SDG 3.

1. Introduction

Urbanization continues to exert a myriad of stresses on the natural environment. In sub-Saharan Africa, approximately 250 million people reside in urban centres [1], usually relying on groundwater for their domestic and agricultural water supplies [2]. The expansion of urban populations leads to environmental contamination from diverse sources [3,4], including groundwater pollution via seepage [1,5]. The adverse impacts of heavy rainfall on groundwater quality and public health have been documented previously [6,7]. Hence, periodic groundwater quality monitoring and assessment are crucial for effective policies to avert the associated health hazards [8].

One key indicator of catchment pollution is nitrate (NO_3^-), whose concentration in groundwater above the World Health Organization (WHO) safe limit of 50 μg ml^{-1} could pose significant health risks to both children and adults [1,8–10]. Although NO_3^- can naturally occur in urban groundwater, its elevated values indicate pollution from diverse sources [11–14]. Aquifers contaminated with NO_3^- take a longer time to recover, thereby posing prolonged deleterious health conditions such as infantile methemoglobinemia, mouth ulceration, and reproductive toxicity [10,12,15–20]. Methemoglobinemia commonly occurs when groundwater NO_3^- levels are high, with infants under six months old being especially vulnerable due to their immature enzyme systems that cannot efficiently convert methaemoglobin back to haemoglobin [16]. Thus, methemoglobinemia reduces the oxygen carrying capacity of the blood, giving a blue pigment, which can lead to serious hypoxic

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conditions in infants (blue baby syndrome) via reduced oxygen supply to tissues, causing symptoms like bluish skin and, in severe cases, developmental harm or death [9,10,21]. This underscores the urgent need to enforce strict NO_3^- limits in drinking water, especially to protect infants, with important public health and regulatory implications.

Limited water quality monitoring schemes, lack of data-driven policies, and absence of appropriate legislation on groundwater governance prevent the employment of appropriate groundwater assessment and protection practices in developing nations [22,23]. The assessment of groundwater quality for drinking purposes and delineation of human health risk zones using multiple techniques, including geospatial technology, has become an emerging global concern amidst urban population explosion and climate change [8,24]. For instance, hydrogeochemical assessment of groundwater in certain regions of India, using zonation maps, showed spatial differences in water quality when compared to WHO standards. The findings suggest that groundwater should be pretreated before use, while recommending artificial recharge mechanisms to be implemented during dry seasons to help dilute contaminants and reduce health risks [9,25,26].

Although previous studies have applied both the water quality index (WQI) and synthetic pollution index (SPI) to assess groundwater quality using standard procedures [27], their findings may still be influenced by variations in geogenic background, climate, and human activities [28–30]. Similarly, quantification of human health risk of exposure to contaminated drinking water using hazard estimation models recommended by the US Environmental Protection Agency (USEPA) [31] would advance knowledge of the deleterious health effects of drinking contaminated water. Previous studies using Total Hazard Indices (THI) for non-carcinogenic risk have highlighted children's vulnerability to water-related illnesses, thereby supporting the development of effective policies to protect groundwater quality and promote public health [9,32].

Using these WHO-recognized tools [33,34] widely helps raise awareness and improve access to clean water and sanitation worldwide. For instance, research findings from Lanzhou, Northwest China, indicated that only 4 % of good-quality groundwater was suitable for human consumption, and attributed the condition to the impacts of urbanization and the migration of contaminants into groundwater [35]. While [36] observed that urban growth, settlements expansion and vegetation losses significantly degraded groundwater quality within the Lahore region of Pakistan by approximately 35 % in 17 years, [37] noted that groundwater contamination in Awka and Nnewi urban cities of Nigeria varied by location, and recommended more robust assessment of groundwater quality for comprehensive and reliable analysis of variation in groundwater contamination via geogenic, and natural processes. However, no study has applied a spatiotemporal analytical framework that integrates robust groundwater sampling and NO_3^- contamination to model public health exposure risk across urban density gradients in sub-Saharan Africa. Only a few related studies have provided partial insights into groundwater contamination trends based on urban demographic flux and exposure sampling in sub-Saharan Africa, but they lacked spatiotemporal, urban density gradients, or exposure health modelling [38–43]. Nevertheless, producing quality groundwater data in most sub-Saharan urban areas remains challenging due to limited access to domestic boreholes needed for monitoring [1,44].

Previous research in Owerri Metropolis showed that groundwater in urbanized areas with shallow aquifers is highly vulnerable to surface contamination [45–47]. This study focused on Owerri, Southeast Nigeria (05°21′–05°30′ N, 06°57′–07°03′ E) (Fig. 1), an administrative hub with about 400,000 residents and a population density of ~1400 persons/km^2 [48,49]. The city accommodates a diverse migrant population, whose activities often contribute to improper waste disposal. The

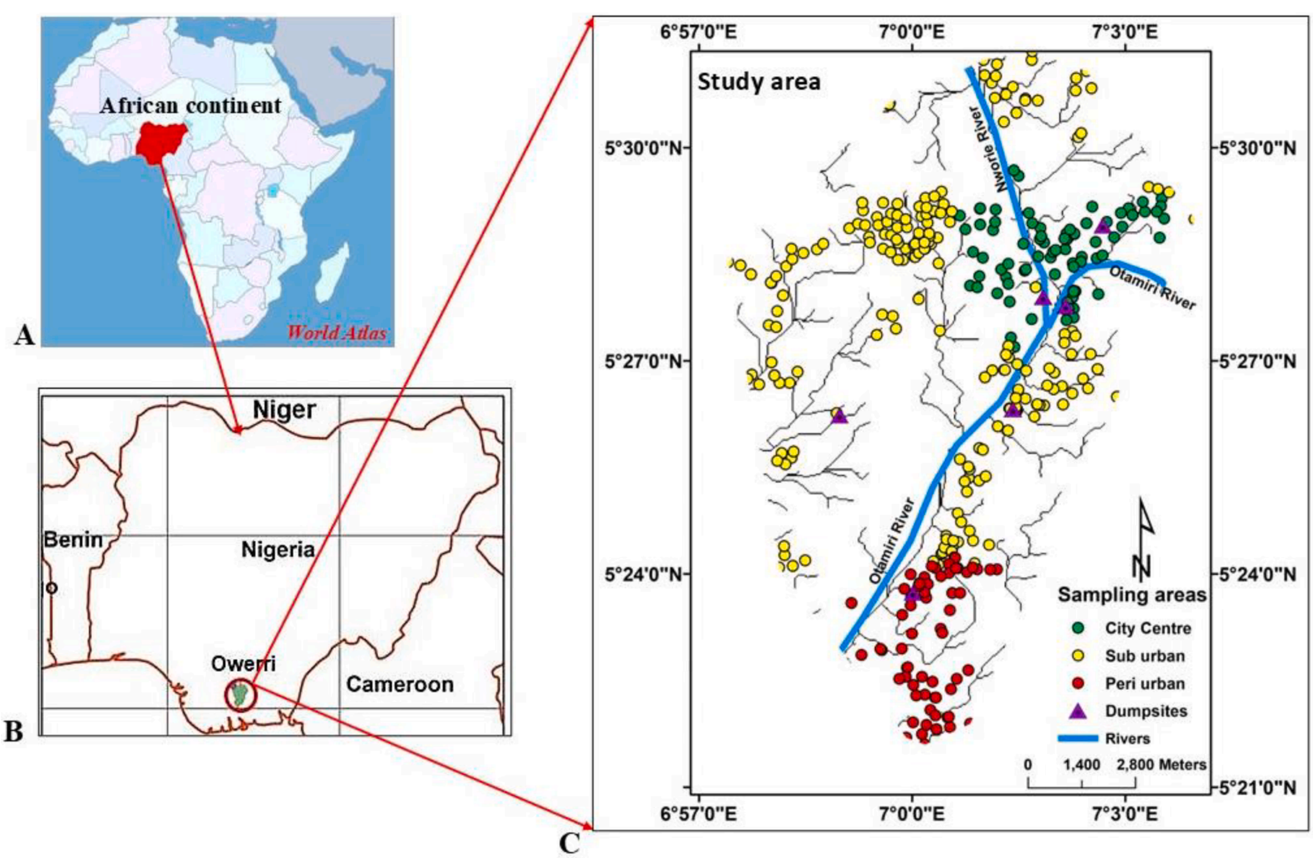

Fig. 1. (A) Geographical location of Nigeria in West Africa, (B) Owerri (circled) in the southeast of Nigeria, and **(C)** Owerri study area and sampled private domestic groundwater boreholes within the Imo River Basin.

area spans ~740 km^2 with an aquifer depth of ~24 m, and annual recharge of ~2.5 billion m^3 [50–53]. With rainfall of 1990–2200 mm/year, temperatures of 24–33 °C, and flat terrain prone to flooding, conditions favour pollutant migration, particularly along the Otamiri and Nworie rivers.

Due to the lack of detailed empirical studies on groundwater vulnerability and exposure risks, this study is essential for addressing the ongoing challenges of sustainable urban planning and access to clean drinking water in a growing sub-Saharan African city. Nevertheless, previous studies misrepresented groundwater quality by relying on random samples from too few sites, which were inadequate for capturing large-scale pollution trends in such a complex urban area [54–56].

This study, therefore, seeks to close this gap by linking groundwater pollution patterns to urban density using robust sampling and groundwater datasets, thereby providing a more detailed and reliable assessment of the anthropogenic and natural influences on groundwater quality. It aims to spatially assess factors that potentially affect groundwater contamination risk due to urbanisation and evaluate the public health implications of exposure to contaminated groundwater, using standard methods. It specifically targets the following objectives: 1. generate a robust groundwater chemistry dataset using samples directly extracted from 356 domestic groundwater boreholes under two contrasting meteorological conditions, (rainy and dry seasons); 2. extrapolate larger-scale groundwater pollution trends according to the urban density pattern, and 3. estimate exposure patterns of humans to critical contaminants in groundwater, focusing on age susceptibility to potential adverse health conditions.

2. Methods

2.1. Groundwater sampling and field measurement

A bi-seasonal sampling approach was developed based on the Owerri urban density pattern (city centre > suburban > peri-urban), as described in [57]. A semi-systematic sampling approach was adopted, i.e. minimum interval of 250 m between each of the 270 sampled boreholes, was applied for groundwater collection during the initial (rainy season) field campaign (June to September 2015), with a follow-up sampling of 116 boreholes during the dry season (December 2016 to February 2017) (Fig. 1). Thirty of the 116 boreholes sampled in the dry season were previously sampled during the rainy season but selected for repeated sampling due to rainy season NO_3^- concentrations of above 50 μg ml^{-1}, hence considered polluted, since high NO_3^- is a pollution indicator variable [58,59]. The 86 additional dry-season samples were collected around 30 boreholes with high NO_3^- levels during the rainy season to evaluate the spread of pollution in the Owerri aquifer. All groundwater sampling in the dry season was conducted in the early mornings (6:30 – 10:00 am) and late evenings (4:30 – 6:30 pm) to minimize the potential impacts of temperature and evaporation on pH, dissolved oxygen (DO), and the concentration of other parameters, providing more consistent and reliable field measurements. Sampling was avoided during and immediately after intense rainfall in the rainy season to ensure sampling consistency and prevent the impacts of hydrological changes and alterations in groundwater chemistry due to advection. Groundwater data generated for the 30 boreholes sampled during both field campaigns allow for direct seasonal comparisons. Geographic coordinates of sampling points were measured in the 1984 Geographical Coordinate System using a hand-held GPS equipment made by Garmin International, Inc., USA.

Groundwater samples were extracted from boreholes using submersible pumps, preceded by initial well purging informed by three consecutive pH measurements as a purge adequacy parameter, i.e., once the measurements stabilized within 0.1 pH units. *In-situ* measurements for temperature (°C), pH, electrical conductivity (EC; μs cm^{-1}), and DO (μg ml^{-1}) were completed using a Hanna Instrument (HI) 9828. Instrument calibration followed the HI guidelines and was performed every six samples, using the HI 9828–25 quick calibration standard solution for a single-point calibration of the pH, EC and DO saturation datasets, while the equipment was factory calibrated for temperature. Groundwater pumping was set to flow slowly and steadily to minimize aeration while collecting samples directly from boreholes. Samples were collected in 1-litre plastic bottles, pre-washed with deionized water, and then rinsed with sample water. Groundwater samples were rendered sterile by syringe filtration through separate 0.2 μm Minisart® NML Plus (cellulose acetate/glass-fibre) syringe filters (Sartorius Stedim Biotech, Germany). Ten ml of each groundwater sample was first flushed to waste through a 0.2 μm syringe filter before being filtered into 50 ml metal-free centrifuge tubes.

2.2. Experimental analyses

Groundwater ion concentrations were determined using a Thermo Scientific Dionex ICS-5000 ion chromatography system, which included the measurement of concentrations of NO_3^- and NH_4^+. Calibration standard solutions for seven anions (Thermo Fisher, product no 056933) and six cations (Thermo Fisher, product no 046070) were prepared at four concentrations. The ranges were 0.025–2.50 μg ml^{-1} for cations and 0.02–2.00 μg ml^{-1} for anions, using 18.2 MΩ ultrapure deionised water. A 1 ml aliquot of the deionised water was syringe-filtered into an ion chromatography vial and analysed as a blank. Dissolved organic carbon (DOC) concentrations were determined in 105 randomly selected samples using a Shimadzu TOC-V CPN series analyser, as explained in [60].

2.3. Quality assurance/validation

Before analysis, the Dionex ICS-5000 Chromatography System was calibrated using Thermo Scientific Dionex seven-combined anion (Product No 056933) and six cation-II (Product No 046070) standard solutions. The calibration coefficients of determination (R^2) for anions ranged from 0.9997 (Cl^-; $y = 0.4729x$) to 1.0000 (NO_3^-; $y = 0.2646x$). For cations, R^2 values ranged from 0.9936 (NH_4^+; $y = 0.2362x$) to 0.9993 (Li; $y = 1.2057x$). All groundwater samples were analysed alongside a Certified Reference Material (CRM) solution (LGC 6020). In each batch of 90 groundwater samples, three randomly selected samples were repeatedly distributed and analysed to evaluate precision or experimental measurement consistency.

CRM recoveries for measured ions were between 90 and 110 %. For example, the expected NO_3^- concentration was ~28.2 μg ml^{-1}, with a measured value of 28.3 μg ml^{-1} (SD = 0.63 μg ml^{-1}; %RSD = 2.24). Similarly, the expected Cl^- concentration was 33.1 μg mL^{-1}, with a measured value of 33.3 μgml^{-1} (SD = 0.99 μg ml^{-1}; %RSD = 2.96). These results conform to USEPA Method 300.0 (9.3) standards [61,62], confirming method accuracy. Replicate samples showed <5 % RSD, demonstrating high analytical precision, reproducibility, and reliability for interpretation and decision-making. Limit of Determination (LOD) and Limit of Quantification (LOQ) defined as 3 × SD and 10 × SD, respectively, where SD is the standard deviation of 5 measured blanks (prepared with Millipore water, 18.2 MΩ at 25 °C), ensuring maximum analytical sensitivity and reliability.

2.4. Groundwater quality indices

This study used two common indices, (a) the Water Quality Index (WQI) [63] and (b) the Synthetic Pollution Index (SPI) [33,64,65], to assess groundwater quality based on six physicochemical parameters (pH, EC, NO_3^-, NH_4^+, DOC, Cl^-); chosen due to their potentially harmful concentrations in both wet and dry seasons. (see Supplementary Table 1).

2.4.1. Water quality index

The Water Quality Index (WQI) model (Eq. (1)), originating in 1970 and modified in 1998, has been recognized by the World Health Organisation [33,66] as a valuable tool for assessment of general groundwater quality:

$$WQI = \sum Qi\ Wi \Big/ \sum_{i}^{n} wi \tag{1}$$

Where, Wi = relative weight of parameter (parameter weight/total weight)

Qi = quality rating scale

n = total number of parameters

The Weighted Arithmetic Index method developed by [67] has been employed. Parameters were weighted ranging from 1 to 5 in the increasing order of impact on drinking water quality, with the highest weightage of 5 assigned to nutrients [66] (Supplementary Table 2).

Eq. (2) shows the relative weight (Wi), calculated with respect to the respective health-based standard according to the WHO standard:

$$Wi = wi \Big/ \sum_{i}^{n} wi \tag{2}$$

where,

Wi = relative weight wi= weight of each parameter

n = number of parameters

Each parameter was assigned a quality rating scale (qi) based on the ratio of its measured concentration in groundwater to the health-based standard set by NSDWQ/WHO as applied in [33,64,65] (Supplementary Table 2) and multiplied by 100 (Eq. (3)):

$$qi = (C_m / C_s) * 100 \tag{3}$$

where C_m and C_s represent the concentration (μg ml^{-1}) of the i^{th} parameter measured and the WHO-recommended standard value, respectively.

A sub-index value (SI) (Eq. (4)) generated as a product of the relative weight (Wi) and quality rating scale (qi), is then summed to obtain the water quality index (WQI) (Eq. (5)):

$$SI = Wi * qi \tag{4}$$

$$WQI = \sum SI \tag{5}$$

2.4.2. Synthetic pollution index

The Synthetic Pollution Index (SPI) is used to assess groundwater suitability for drinking and its link to water-related diseases [33,34,37,64,65]. Thus, the following equation (Eq. (6)) was used to assess the groundwater quality and safety for human consumption.

$$SPI = \sum ni\ (Ci\ / C_s)\ \times\ Wi \tag{6}$$

where Ci and C_s represent concentrations (μg ml^{-1}) of the i^{th} parameter as measured and the WHO recommended standard, respectively, while Wi is the computed relative weight (Supplementary Table 2).

2.5. Statistical analyses

Spearman's correlation analysis was conducted to assess relationships that could suggest the source of elevated groundwater NO_3^- and other contaminants. Datasets were found not to be normally distributed, following the Kolmogorov-Smirnov test. A two-way analysis of variance (ANOVA) was applied to assess the difference in NO_3 concentration in groundwater by seasons and urban density regions in the study area, as applied in related studies [11]. Datasets were transformed by log_{10} to assume normality before ANOVA. All statistical analyses were carried out using the Origin Lab 2019 software.

2.6. Measurement of septic tank (potential pollution source) to borehole distances

Distances between wells and potential pollution sources were extracted from the coordinates of the target points (borehole to septic tank), using the near (analysis) tool in ArcMap. Before the extraction of a distance, the coordinates originally recorded in decimal degrees (Geographical Coordinate System (GCS) 1984) were projected to the x-y Projection Coordinate System (PCS) WGS,1984_UTM, ZONE 32N in metres using the data management's projection and transformation feature tool in ArcMap 10.5.

2.7. Risk assessment of human exposure to nitrate-contaminated groundwater

Due to health risks the USEPA, associated with high NO_3^- levels, Nigeria's drinking water standard and global agencies, such as the WHO, the EU, and the USEPA, have set 50 μg ml^{-1} as the maximum safe NO_3^- concentration [68]. The extensively applied non-cancer risk evaluation method [9,57,61,69–72] has been adopted in estimating exposure patterns of humans to groundwater NO_3^- contamination.

The daily exposure dose (ED) shown as Equation 7 was calculated following [73], to predict exposure risks of four different age categories to elevated NO_3^- in Owerri groundwater:

$$\text{Exposure dose (ED)} = (C_n \times IR \times EF)/BW \tag{7}$$

Where:

ED = Exposure dose (μg g^{-1} day^{-1})

C_n = Nitrate concentration (μg ml^{-1})

IR = Ingestion rate of water (litres day^{-1})

EF =Exposure factor (unitless)

BW = Body weight (kg)

The exposure factor applied here was 1, representing daily exposure to NO_3^- through groundwater ingestion [73]. The ratio of the exposure dose and toxicity reference dosage of 1.6 μg g^{-1} day^{-1} [74–76] has been used to estimate the hazard quotient (HQ) across the three urban regions, with public health (toxic) risk being identified if HQ > 1.00 [77]. Age categories used were A (Adult = 47.6 years), T (Teen = 19 years), C (Child = 11 years), Tod (Toddler = 4 years). Nigerian life expectancy and body weight for adults were adopted [78]. The average water ingestion rate (IR) (litres $person^{-1}$ day^{-1}) was adopted from the dietary reference intake for water by life stage group: Adult = 3.2, Teen = 3.2, Child = 2.25, Toddler = 1.7 litres [79]

3. Results and Discussion

3.1. General descriptive analysis of study area groundwater physicochemical parameters

Whereas some analytes showed measurable values during analysis, others, such as PO_4^+ NO_2-, Fl^-, SO_4^- NH_4^+, displayed concentrations below lower limits of detection – as such, they are not reported. Nevertheless, a statistical summary of key physicochemical parameters relevant to this article is presented as median and range, as values were not normally distributed (Supplementary Table 1). pH showed a slightly acidic trend with median values of 5.4 (4.0 – 7.2) and 6.9 (5.1 – 8.9) in the rainy and dry seasons, respectively, and could be attributed to the prevalent acidic rain and predominantly coarse sandy soil with low buffering capacity that causes more acidic recharge to reach groundwater, lowering its pH. Additionally, studies have linked pH fluctuations across seasons to redox effects, as reducing conditions increase pH, while oxidizing conditions decrease it [80,81]. Furthermore, due to the near-surface lithology of the urbanisation-induced developing areas, microbial decomposition of organic substances arising from indiscriminately dumped waste, human faeces within shabbily dug pit latrines (and septic tanks), as well as agricultural farmland waste, generate organic acids that eventually leach through the porous soil into groundwater, especially during the rainy season. Nitrate concentrations exceeded the WHO guideline of 50 μg ml^{-1} in groundwater samples from boreholes located less than 1 m from existing septic tanks (Supplementary Table 2), indicating rapid infiltration of untreated effluent into the area's shallow water table. This reflects a failure to maintain adequate safeguard distances between water sources and sanitation systems, contrary to international best practices, which recommend a minimum setback of 15 to 30 m [66] to prevent contamination. Hence, an urgent need for in-depth hydrogeological vulnerability mapping, water quality monitoring frameworks, and improved sanitation-well separation policies across the area for sustainable water resource management.

The mildly acidic conditions indicate low aquifer buffering capacity, making groundwater more prone to acidification, metal leaching, and contamination from human activities, especially during the rainy season, posing health risks to consumers [66,67]. Similar studies have also attributed low pH in groundwater sited close to point pollution sources to several factors, including the release of amino acids, production of sulphuric acid from oxidation of sulphide minerals, as well as acid mine drainage and release into the groundwater [68,69].

Electrical conductivity (EC) increased from a median value of 31.0 μS cm^{-1} to 53.5 μS cm^{-1} in the rainy and dry seasons, respectively, which may stem from low recharge, higher temperatures, and solute concentration in groundwater consistent with studies linking dry season heat to groundwater degradation [82,83]. This pattern, more evident in low-lying areas, suggests that reduced dry-season recharge limits dilution, increasing ion concentrations and EC through greater bedrock interaction. Higher temperatures further intensify solute buildup via evaporation and microbial activity, degrading groundwater quality; consistent with studies linking low recharge to increased ion release [75,84].

Nitrate median values were 12.5 μg ml^{-1} in the rainy season, and 23.9 μg ml^{-1} in the dry season (Fig. 2). However, whereas about 23 % of sampled sites recorded less than the 0.54 μg ml^{-1} limit of detection (LOD) for NO_3^- in the rainy season, only 4 % were below the LOD during the dry season. This indicates seasonal contaminant buildup due to limited recharge and increased NO_3^- mobilization. The reduction in sites below the detection limit (23 % to 4 %) signals worsening groundwater quality in the dry season and highlights the influence of hydrogeological and land use interactions. Therefore, there is a need for frequent post-rainfall sampling to detect peak NO_3^- levels and enable timely interventions. By identifying hotspots for urban and agricultural pollution, this method can allow targeted interventions to safeguard human health and water quality, such as buffer zones, modified fertiliser applications, and limited groundwater use in high-risk locations and times [85,86]. The increase in NO_3^- concentration during the dry season may be due to higher temperatures and lower humidity enhancing evapotranspiration, reduced dilution from limited rainfall, and a lowered water table that creates more oxidizing conditions in the aquifer, which suppresses denitrification and allows NO_3^- to persist [82,87]. Thus, the rapid increase in boreholes from population growth and more frequent groundwater pumping during the dry season has contributed to higher NO_3^- levels, particularly in alluvial aquifers near river channels. Seasonal NO_3^- dilution has been widely reported as a natural phenomenon that can occur within different catchments [18,88–90].

The sampling period was chosen to reflect the hydrological and biochemical processes that could potentially influence the groundwater

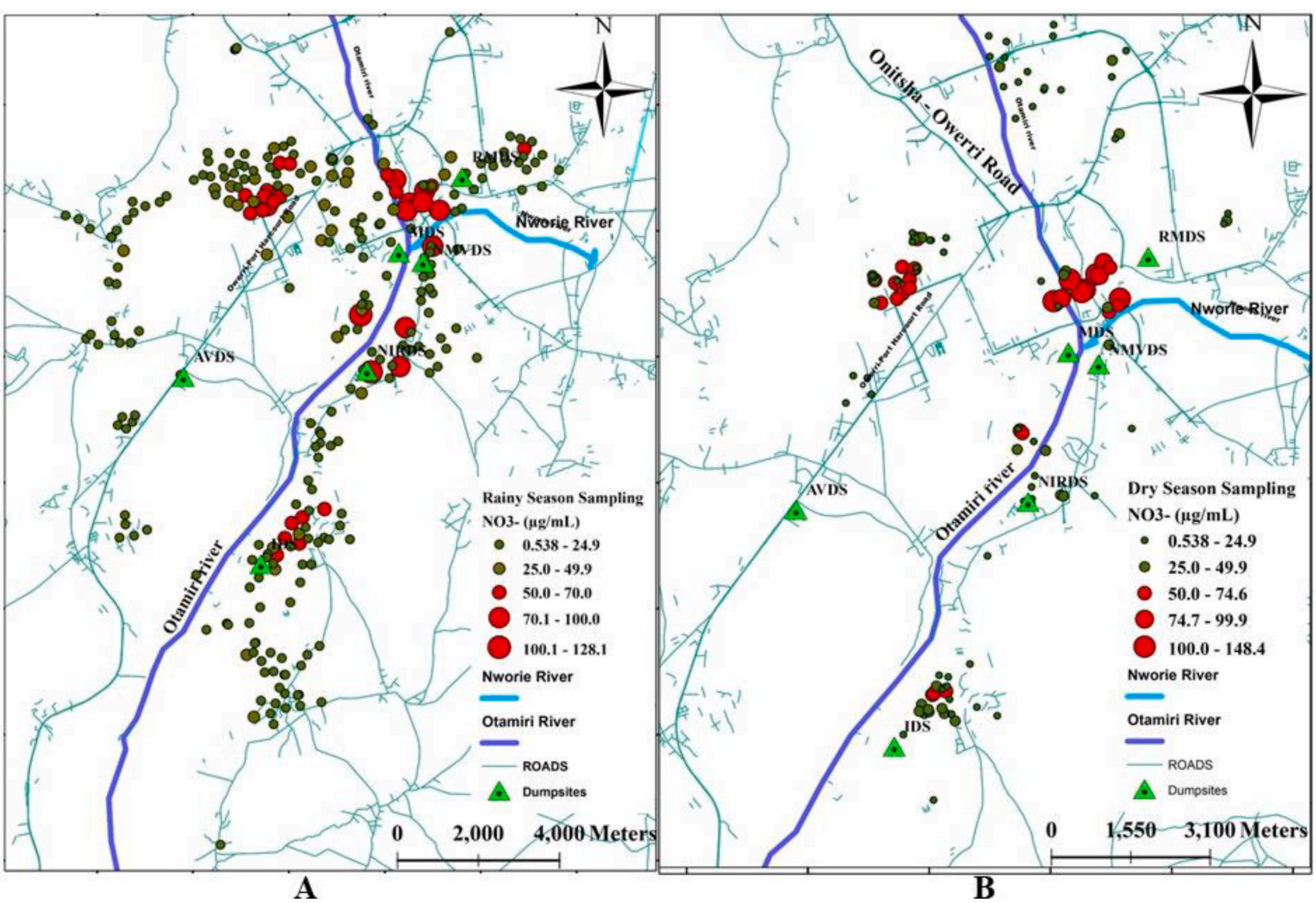

Fig. 2. Spatial distribution of NO_3^- concentrations in groundwater during the rainy (A) and dry (B) seasons in Owerri, Nigeria. Red dots indicate locations where NO_3^- levels exceeded the WHO limit of 50 μg ml^{-1}, while black dots represent sites with concentrations within the safe limit.

quality. Thus, approximately 38 % (11 boreholes) of the 30 repeated sites sampled in the month of July, being the commencement of heavy rain and seepage flow, showed elevated values of NO_3^- and DOC. This suggests a greater risk of groundwater contamination from the release of DOC and nitrogen compounds (e.g., NO_3^-, NH_4^+), especially within shallow areas, including unused plant nutrients from the dry season, leading to seasonal changes in water quality. Studies have shown that initial rains can potentially enhance the migration of accumulated NO_3^- and other suspended contaminants within the unsaturated zone into the aquifer [91,92]. The remaining sites subsequently sampled between the months of August to October showed lower NO_3^- concentration, inferring a dilution effect on the groundwater properties.

Ammonium also exhibited a similar fate as NO_3^-, with a median value range of 0.03 μg ml^{-1} to 0.67 μg ml^{-1} in groundwater during the rainy and dry seasons, respectively. Interestingly, the presence of NH_4^+ in groundwater during dry periods indicates reductive conditions that limit its conversion to NO_3^-, while evapoconcentration and a declining water table further promote these reducing zones [93,94]. This suggests inhibited microbial oxidation caused by low oxygen levels, which influences nitrogen transformation dynamics in the vadose zone and possible human activities, particularly in shallow aquifer dynamics [95–97], highlighting the need for adaptive groundwater quality management.

Conversely, only 17 % of sampled sites (46 boreholes) in the rainy season recorded DOC below the MCL of 5 μg ml^{-1}, with up to 98 % (114 boreholes) in the dry season showing the same pattern. This may be because the dropping water table and resulting low oxygen levels in the vadose zone during the dry season allow microbes to consume DOC as they break down accumulated organic matter in the aquifer. In addition, surface runoff during the rain leaches DOC from vegetation, plant litter, and decomposed waste and percolates into the groundwater. This result implies that the DOC concentration in groundwater is driven by climatic change as well as biogeochemical processes, which agrees with studies' postulation that the stability of DOC in shallow aquifers is largely dependent on the biogeochemical processes within the soil organic horizon [98,99]. Whilst the concentration trend of NO_3^- can be viewed as an index of wastewater pollution, elevated DOC concentration during the rainy season could infer increased groundwater recharge and interaction with soil organic matter [100,101]. The area is underlain by the Benin Formation, with an estimated thickness of about 800 m at its epicentre and is characterized by coastal plain sands interbedded with clay, gravel, and sandstone layers [52]. Thus, elevated values of NO_3^- and DOC recorded in the rainy season could be credited to runoff water interactions with the characteristic porous soil (>90 % quartz sand), of the study area during percolation. Runoff that follows heavy rain can contain as much as 150–400 μg ml^{-1} of NO_3^- [101], and NO_3^- can easily migrate to aquifers repelling soil electrostatic force to regulate flow, diffusion, and dispersion processes [19,39].

Groundwater chemical composition in the respective urban regions of the study area varied significantly in both sampling seasons (Table 1, Supplementary Table 1, Fig. 3). Groundwater was less acidic in the dry season, due to increased temperature, water-rock interactions, and solids dissolution, which enhanced ionic content and alkalinity. Hence, EC showed a higher concentration trend in the dry season, which aligned with the urbanisation gradient (city centre> sub-urban > peri-urban). This trend reflects compounded anthropogenic inputs from indiscriminate open solid-waste dumping, urban runoff, septic tank leakage, and water–rock interactions. Dense neighbourhoods contribute elevated dissolved ions (Na^+, Cl^-, K^+) to shallow aquifers via leaking sewers and surface runoff, sustaining high EC year-round. It implies that groundwater EC decreases as urban density declines (Table 1). The observed seasonal variation in EC was not considered central to this study objectives, as it does not constitute a significant human exposure risk. Rather, EC was treated as an indicator variable for assessing the potential presence of elevated NO_3^- levels in groundwater. The trend reflects reduced anthropogenic inputs and pollution loads, improved water quality from fewer dissolved ions (nutrients or contaminants), and greater infiltration and dilution, resulting in lower health risks in less dense areas. Thus, EC measurement serves as a valuable tool for monitoring sustainable urban groundwater management.

Peaks during the rainy season are often linked to the “first-flush” release of stored salts and dissolved constituents [102,103], while dry-season spikes are associated with extended water–rock contact from pumping stresses, reduced dilution, and altered flow paths, which enhance mineral dissolution and cation exchange [104,105]. Priority interventions include sewer integrity programs (leak detection and rehabilitation), green–gray stormwater controls to intercept first-flush dissolved ions, regulated groundwater abstraction, and land-use management in dense urban hotspots. Seasonal monitoring immediately after intense rainfall to capture dissolved ion pulses and during the late dry season to detect concentration peaks should be integral to contaminant surveillance and groundwater quality management.

Although groundwater NO_3^- concentrations were less than the detection limit (0.53 μg ml^{-1}) in c. 17 % (66 boreholes) of sampled boreholes, it was identified as the critical contaminant, given concentrations above the WHO threshold of 50 μg ml^{-1} [7] in ca. 10 % (27 boreholes), and 24 % (28 boreholes) of rainy and dry season samples, respectively. Nitrate concentrations were also significantly higher in the dry season, signifying a probable dilution effect during the rainy season.

The strength of correlations between measured groundwater parameters differed between seasons (Table 2), but the consistently strongest inter-relationships were between NO_3^- and EC (positive correlations) and between NO_3^- and DO and pH (negative correlations). A strong negative correlation was also evident between NO_3^- and DOC, but only for the dry season. Seepage flow through the vadose zone during high-intensity rain events (including monsoons) triggers biogeochemical processes in groundwater and alteration of the concentration of DOC and the chemical balance of nitrogen species [3] in groundwater. Ammonium levels were higher in boreholes located in suburban areas along drainage paths during the rainy season, due to rainwater carrying surface runoff, waste leachate, and underground flows, confirmed by elevated DOC levels. Accumulated NH_4^+ can degrade water quality and pose health risks. Regular testing of these boreholes is essential to implement safeguards and prevent pollution.

Table 1

Descriptive statistics (median, with upper and lower quartiles in brackets) of major groundwater parameters, comparing three borehole categories of urbanisation and two sampling seasons (rainy and dry) in Owerri, Nigeria. The last two columns (U= Urbanisation category and S= Season) show F-values from a general linear model on $\log_{10}$-transformed and stars represent p-values, where n.s. = non-significant, * = < 0.05, ** = < 0.01, and *** = < 0.001: the interaction term was never significant and hence removed from the model. BDL represents values below detection limit.

Parameters (μgmL^{-1})	City centre		Sub-urban		Peri-urban		U	S
	Rainy	Dry	Rainy	Dry	Rainy	Dry		
EC	62.0 (35.5–143)	196 (34.9–266)	28.0 (15.0–74.0)	46.3 (30.6–127)	16.0 (13.0–32.0)	37.6 (21.2–170)	19.7***	21.2 ***
pH	3.8 (3.5–4.2)	6.6 (6.5–7.6)	3.8 (3.6–4.1)	7.0 (6.6–7.9)	3.7 (3.5–3.9)	6.8 (6.5–7.4)	3.94*	1930***
DO	7.0 (5.4–8.7)	6.1 (5.2–6.5)	7.5 (3.7–10.6)	6.5 (6.1–6.9)	11.3 (10.0–12.6)	6.5 (6.2–7.0)	44.2***	101***
DOC	6.6 (6.2–7.4)	2.8 (2.3–3.5)	7.7 (6.6–8.0)	3.0 (2.7–3.4)	7.7 (6.7–8.2)	3.1 (2.9–3.6)	3.20*	485***
NH_4^+	BDL (BDL–0.002)	BDL (BDL–0.019)	BDL (BDL–BDL)	BDL (BDL–BDL)	BDL (BDL–0.007)	BDL (BDL–0.014)	1.35n.s.	4.03*

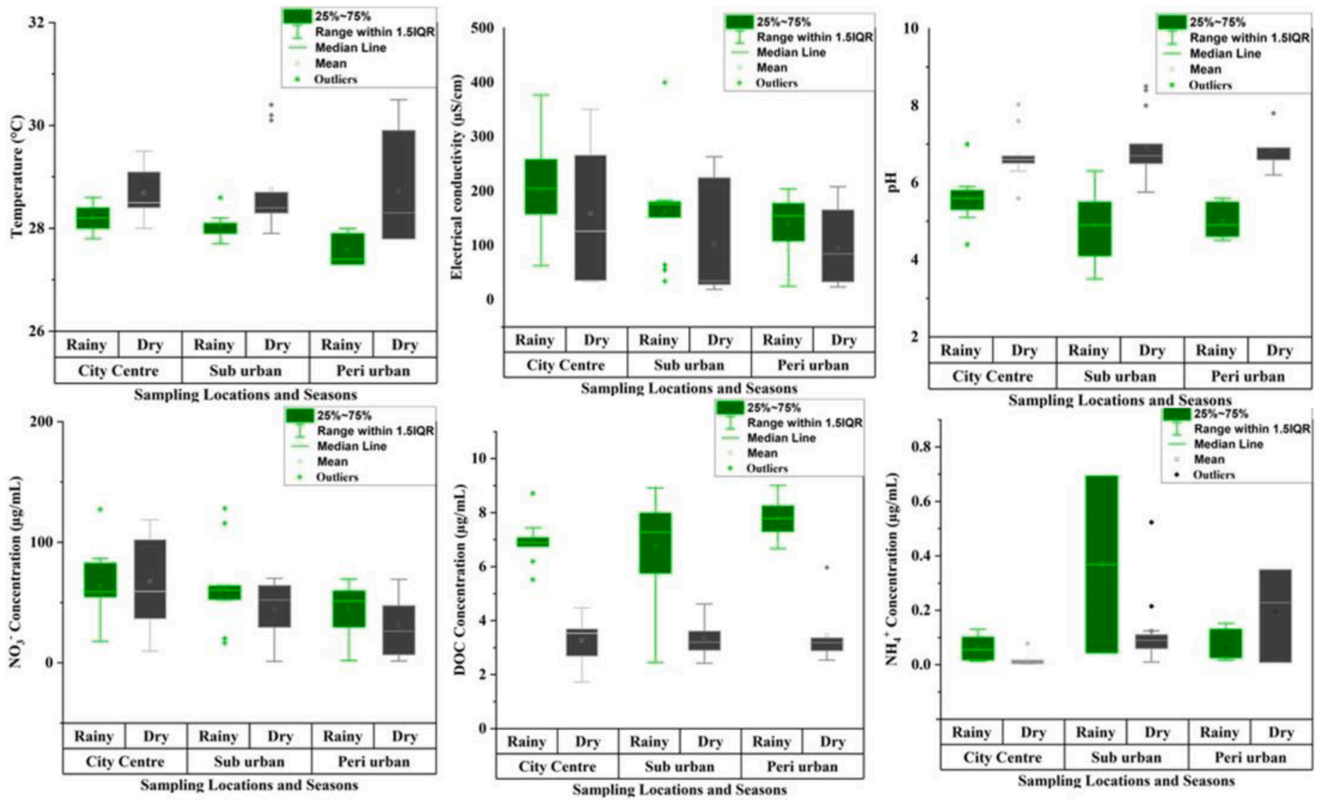

Fig. 3. Groudnwater parameter patterns across the three urbanisation categories in the rainy (green coloured) and dry (gray-coloured) seasons in Owerri, Nigeria.

Table 2
Correlations (Spearman's) between groundwater parameters in Owerri, Nigeria. Correlations in the bottom left of the table are for the wet season, with those in the top right for the dry season. Stars represent p-values of * = < 0.05, ** = < 0.01 and *** = < 0.001.

Parameters	Temperature	DO	EC	pH	DOC	NO_3	NH_{4+}
Temperature	-	−0.15	0.22 *	−0.26 **	0.08	0.18	0.16
DO	−0.20 ***	-	−0.17	0.41 ***	−0.12	−0.22 *	−0.10
EC	0.42 ***	−0.27 ***	-	−0.28 **	−0.11	0.43 ***	−0.02
pH	0.17 ***	0.06	−0.03	-	−0.02	−0.27 **	0.01
DOC	−0.40 ***	0.13	−0.24	−0.01	-	−0.54 ***	−0.16
NO_3	0.38 ***	−0.22 ***	0.86 ***	−0.12 *	−0.21	-	0.21 *
NH_4	−0.15 *	0.05	0.07	−0.07	0.50 ***	0.09	-

Studies have shown that higher concentration of NH_4^+ in groundwater signifies steady input of waste products from the breakdown of organic materials [106]. Reduced concentration of NH_4^+could be related to the corresponding elevated NO_3^- measured in the dry season due to oxidation of NH_4^+ (nitrification) by fluctuation of the water table during the frequent abstraction of groundwater.

3.2. Spatial and temporal variability of nitrate in groundwater

Overall difference among NO_3^- concentration in groundwater in boreholes across seasons in the respective regions was considered statistically significant, for seasons ($F = 7.40$, $p < 0.05$) and regions ($F = 26.8$, $p < 0.05$). There was no significant interaction between regions and seasons. Whereas city centre and sub-urban regions showed no statistically significant difference, the differences between peri-urban and city centre ($t = 7.87$, $p < 0.05$) as well as peri-urban and suburban ($t = 4.55$, $p < 0.05$) respectively, were statistically significant.

Though the scenario appeared similar to findings recorded in the analyses of locational and seasonal influences on groundwater variables in the floodplain of a headwater catchment of Rio Calaveras, New Mexico, USA [107], the latter lacked integrated human exposure and urban gradient risks analysis. Also, related studies on the climate–sanitation–groundwater nexus in peri-urban, Botswana, [42], and linking NO_3^- contamination sources to land uses in Dakar's sub-urban area [41], only identified human exposure pathways to NO_3^- contamination and not density gradients. Furthermore, the study by [38], which applied DRASTIC models using large-scale land use, hydrogeological, and population density data to model changes in groundwater pollution risks in Africa, was deficient in incorporating exposure risk analysis across intra-urban density gradients. An integrated hydrogeological investigation, combining Vertical Electrical Sounding with GIS-based DRASTIC modelling, delineated a three-tier groundwater vulnerability regime within the Owerri study area, with 49 % classified as highly vulnerable, 45 % as moderately vulnerable, and 6 % as low vulnerability [108,109]. Field inspections revealed that most boreholes were substandard in construction and terminated at shallow depths (<24 m), thereby increasing aquifer susceptibility to contaminant ingress. Consequently, groundwater quality in the area is often poor and unsafe for drinking because the shallow water table promotes salt buildup through capillary rise and evaporation [109], lowers pH via carbonic acid formation and rapid infiltration of acidic recharge, and reduces natural buffering due to short residence time and limited contact with carbonate minerals [110,111]. These results highlight the amplifying role of poorly planned urban density, typical of many sub-Saharan African cities, in accelerating groundwater quality degradation and associated public health risks.

3.3. Analyses of groundwater quality based on WQI and SPI

3.3.1. Water quality index

The overall water quality index for the 270 and 116 sampled boreholes in the rainy and dry seasons across the study area varied in space and season, as displayed in Fig. 4, and was analysed based on the recommended quality standards (Supplementary Table 4). Approximately 70 % and 25 % of groundwater in sampled boreholes was in excellent condition for human consumption without any treatment in the rainy and dry seasons, respectively. Furthermore, 19 % and 54 % of groundwater in the respective seasons (rainy and dry) was categorized as good for drinking only after disinfection. However, about 8 % and 16 % of groundwater samples were in the poor category and must undergo pretreatment and disinfection before human consumption. One % and 3 % of groundwater samples fall within the extremely poor group that requires primary and secondary treatment before drinking by humans. Remarkably, groundwater samples from about 0.70 % (index values range of 125 to 131) in the rainy season and 0.86 % (index value up to 189) of sampled boreholes in the rainy and dry seasons, respectively, were unfit for human consumption.

3.3.2. Analysis using the SPI

Similar categorisation of groundwater quality using similar description and recommendations as applied in water quality index shows (Fig. 5) that approximately 34 % and 19 % fall within the excellent group in the rainy and dry seasons based on the SPI technique. Besides, whereas about 24 % of samples fall within the good quality category in the rainy season, 59 % were in the same category during the dry season. Approximately 10 % and 20 % of samples were in the poor water quality category during the rainy and dry seasons, respectively, while about 0.7 % of sampled groundwater was in the extremely poor-quality category only in the rainy season. No sample was categorised as unfit using this technique, unlike in the WQI method.

The WQI and SPI assessments reveal the hydrogeological influence on groundwater quality, especially due to their sandy near-surface lithology and locations. Uncontrolled urban expansion and the conversion of hitherto pristine farmlands to human settlements, with the attendant demand for groundwater, led to the construction of shallow and shabbily designed domestic boreholes along drainage pathways and close to the draining riverbanks, thereby increasing the vulnerability of such boreholes to pollution via advection.

3.4. Estimated exposure dosage of nitrate in groundwater

The estimated exposure doses (ED) and ensuing hazard quotient were typically highest in the child and toddler categories. Results shown in Table 3 and Fig. 6 present toddlers as most susceptible to contamination risks in groundwater.

Approximately 17 %, 20 %, 24 %, and 32 % of adults, teenagers, children, and toddlers had an HQ greater than one for the wet season, with these percentages doubling during the dry season. This infers that all age categories appear susceptible to potential hazards from NO_3^--contaminated water in the dry season (Fig. 6) as characterized by HQ > 1.00.

This analysis indicates increasing groundwater pollution health risks

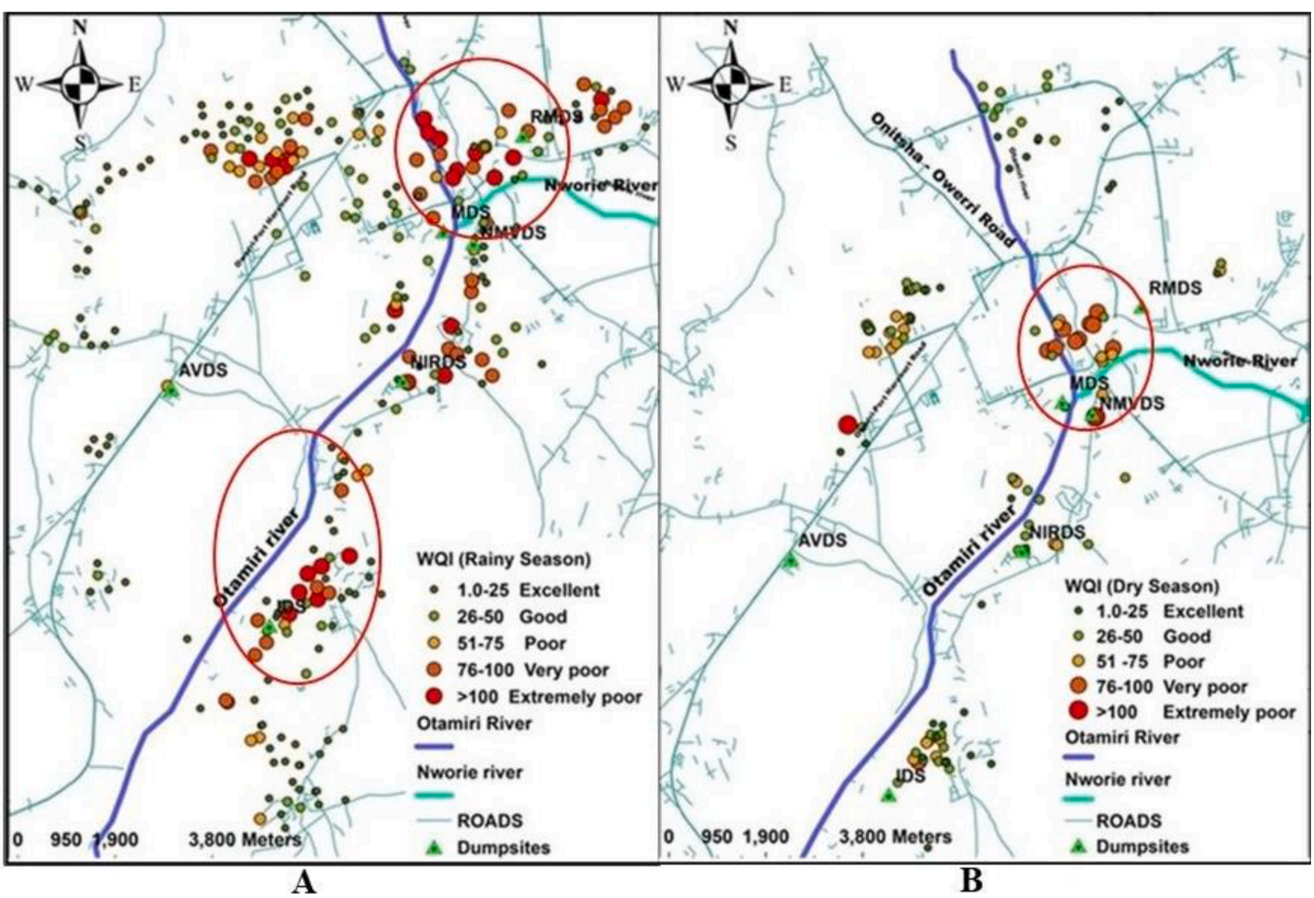

Fig. 4. Spatial variation of Water Quality Index (WQI) across the study area in Owerri, Nigeria, during the rainy (A) and dry (B) seasons, highlighting poorer quality zones near the river confluence and along riverbanks in red circles. Sampling stations are marked with graduated symbols color-coded according to WQI categories as shown in the map legend.

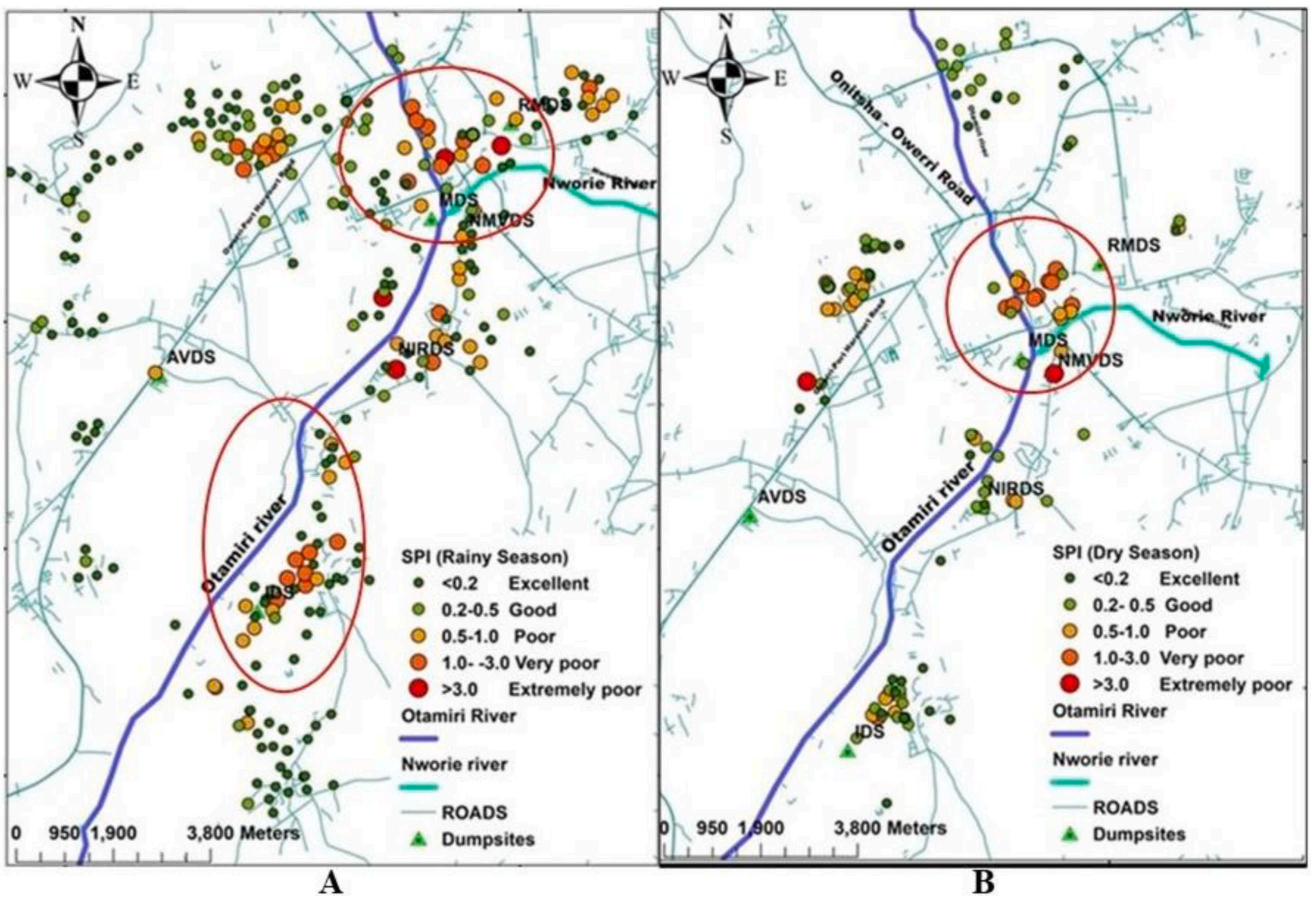

Fig. 5. Spatial variation of Synthetic Pollution Index (SPI) across the study area in Owerri, Nigeria, during the rainy (A) and dry (B) seasons. Sampling stations are marked with graduated symbols, color-coded according to SPI categories as shown in the map legend.

Table 3
Estimated hazard quotient (HQ) for exposure to groundwater nitrate in Owerri, Nigeria, for four different age categories (Adult = 47.6 years; Teen =19 years; Child =11 years; Toddler =4 years) with respect to the recommended toxicity reference dose value of 1.6 μg/g/day. Exceedance probability presents the percentage at which HQ exceeds the recommended safe limit in each age category.

Age Category	Hazard Quotient (HQ)						Exceedance probability (%)	
	Rainy			Dry			Rainy	Dry
	Median	Min.	Max.	Median	Min.	Max.		
Adult	0.353	0.015	3.63	0.615	0.001	4.20	17	38
Teen	0.418	0.018	4.29	0.729	0.001	4.87	20	41
Child	0.533	0.023	5.48	0.930	0.001	6.34	24	48
Toddler	0.804	0.034	8.25	1.400	0.002	9.56	32	57

for younger age groups. Red-coloured boxes fade with decreasing susceptibility to exposure hazards, while the coloured circles represent the distribution trend. Such an exposure rate suggests incidences of human ailments associated with drinking of NO_3^--contaminated water, such as methemoglobinemia, which affects children. Methemoglobinemia (blue-baby syndrome) results from elevated NO_3^-'s interference with the blood's ability to distribute oxygen in the body, leading to cyanosis, breathing difficulty, and death in severe cases [112,113]. Infants less than 4 months old are more susceptible to methemoglobinemia than other ages because the alkaline pH of the infants' gastric system is conducive to enhanced bacterial conversion of ingested NO_3 to a more harmful nitrite (NO_2^-) [112]. Also, a high rate of fluid intake by infants due to body weight increases the chances of infection through contaminated water; hence, children have a higher percentage of foetal haemoglobin, which could be easily oxidised to methemoglobinemia. Nevertheless, there is a limited presence of bacteria that can convert any produced methemoglobinemia to normal haemoglobin in children, as found in adults [112,113].

Moreover, there is poor awareness of potential health risks associated with unguided water treatment mechanisms, as approximately 45 % of residents interviewed during field sampling admitted occasional disinfection of extracted groundwater by only chlorination and boiling. These approaches could rather complicate the problem of NO_3^- in groundwater as chlorine easily reacts with humic substances in the already elevated DOC to form the carcinogenic trihalomethane and haloacetic acids associated with reproductive and developmental problems [114]. Furthermore, boiling NO_3^--contaminated groundwater would rather increase NO_3 concentrations as water evaporates during boiling, making it more harmful to health, especially for infants and pregnant mothers [115].

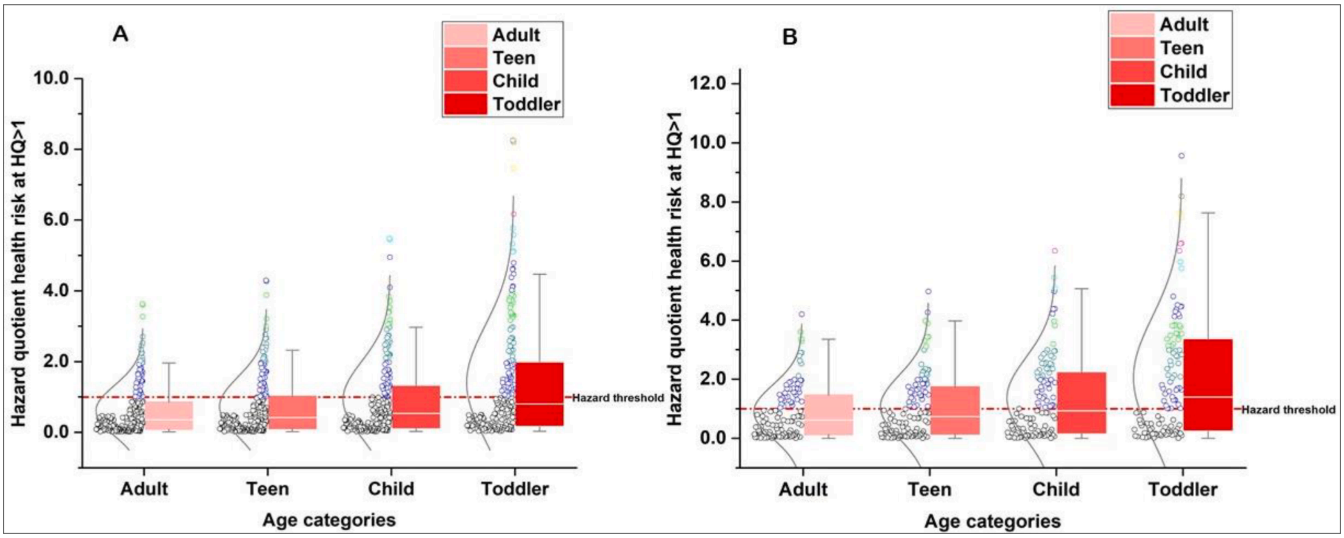

Fig. 6. Estimated hazard quotient (HQ) health risk of exposure to elevated groundwater nitrate in Owerri, Nigeria, for different age classifications. Groundwater samples in approximately 17 %, 20 %, 24 %, 32 %, and 38 %, 41 %, 48 %, and 57 % of sampled boreholes have HI>1 for Adult, Teen, Child, and Toddler, for the rainy **(A)** and dry **(B)** seasons, respectively.

4. Study significance, limitations, and insights for further research

This research provides valuable insights into the impacts of urbanization on groundwater quality and human health risks, with significant global implications for sustainable groundwater management practices and the achievement of SDGs 3 (Good Health and Well-being), 6 (Clean Water and Sanitation), and 11 (Sustainable Cities and Communities). Furthermore, the study's comprehensive health risk assessment, highlighting age-related susceptibility to NO_3^- contamination, underscores the global urgency of monitoring and mitigating NO_3^- pollution in groundwater to safeguard public health, particularly among vulnerable groups. The results call for integrated strategies that combine adequate infrastructure development, effective pollution control, and robust monitoring and assessment frameworks, especially in rapidly urbanizing regions worldwide.

Interestingly, the study systematically employed robust and integrated sampling techniques to unravel the impacts of urban density patterns on groundwater resources, and by extension, the potential deleterious health effects; thus, covering a research gap necessary for inclusive, safe, resilient, and sustainable human settlements. However, the study could not incorporate bacteriological analyses; hence, the public health concerns associated with contaminated groundwater, such as cholera, typhoid, and diarrhoea, were presumably underestimated. Vulnerable groups may be at risk if pollution is not properly captured by relying just on chemical criteria. This may cause stakeholders to make erroneous safety assumptions, postponing necessary sanitary measures. To close this gap, microbial tests (such as *Escherichia coli*, total coliforms, and faecal streptococci) should be a component of future research to monitor seasonal trends of groundwater contamination according to urban density patterns, especially after rains. Above all, a similar study is recommended on a broader scale, especially within the densely populated sub-Saharan African urban areas.

5. Conclusions

This research paper investigates the impact of urbanization on groundwater quality in Owerri, Nigeria, focusing on potential contaminants and associated human health risks. Through bi-seasonal sampling and analysis, the study identifies pollution pathways and assesses water suitability for consumption using quality indices. CRM recovery for critical parameters ranged from 90 % to 110 %, aligning with USEPA Method 300.0 standards and confirming the dataset's accuracy. Nitrate contamination was found in 10 % and 24 % of boreholes in the respective seasons, indicating a significant seasonal effect on groundwater quality, with no notable interaction between region and season. Additionally, 83 % of boreholes exceeded the DOC MCL (5 μg ml^{-1}) during the rainy season, likely due to advective contamination. Besides, NO_3^- seasonal variation was consistent with the urban density trend. This study reveals that young children are most at risk from NO_3^--contaminated groundwater, underscoring the need for targeted water management that aligns with SDG 3 (good health and well-being). By linking age-specific health risks to NO_3^- exposure and showing how borehole design and location affect contamination, the research offers critical insights for urban planning and groundwater protection in Owerri. It recommends an Integrated Vulnerable Zone Management (IVZM) approach to safeguard water resources, in line with global best practices and the UN's call for sustainable human settlements.

Use of AI-Assisted tools

The author cautiously used Grammarly, Undermind, and ChatGPT tools only to improve the language and readability of the revised manuscript.

Ethical statement

The authors declare that the dataset used in the article was generated from the PhD work of the corresponding author, hence is original with all ethical principles and standards duly observed.

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CRediT authorship contribution statement

Joseph I. Nwachukwu: Writing – original draft, Visualization, Validation, Software, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Leon J. Clarke:** Writing – review & editing, Validation, Supervision, Software, Project administration, Methodology, Formal analysis, Data curation, Conceptualization. **Francis Q. Brearley:** Writing – review &

editing, Supervision, Software, Project administration, Methodology, Conceptualization. **Elias Symeonakis:** Writing – review & editing, Supervision, Software, Project administration, Methodology, Conceptualization. **Chika V. Nwachukwu:** Writing – review & editing, Software, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jtemin.2025.100265.

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