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A GROWING CONCERN OF SPATIO-TEMPORAL DISTRIBUTION OF NITRATE CONTAMINATION IN GROUNDWATER OF WARRI, NIGERIA: CAUSES, HEALTH RISKS AND MITIGATION STRATEGIES

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ABSTRACT

Groundwater accounts for one-third of the world's total potable water source. However, anthropogenic activities and natural factors have introduced pollutants into groundwater thereby compromising its quality. Nitrate, one of the most important contaminants poses a significant threat to groundwater quality, as its presence in water has resulted in serious health risks causing various lethal diseases such as digestive system cancer, methemoglobinemia and other diseases in infants, children and adults. This study investigated the nitrate contamination of groundwater in Warri and its environs, focusing on its causes, the health risks on humans, and potential mitigation strategies. 50 groundwater samples were collected from existing boreholes in the dry and wet seasons, and analyzed for nitrate concentration and its spatial and temporal distribution maps produced using geostatistical techniques. The nitrate pollution index (NPI) and the qualitative and quantitative assessment of the health risk of nitrate consumption and contact on humans of different ages and sexes (HHRA) in drinking groundwater in Warri, Nigeria was evaluated, The NO_3 concentration mean value of 0.83±0.81mg/l in the dry season and 1.06±1.08mg/l in the wet season were recorded, ranging from 0.02 mg/L to 3.27 mg/L in the dry season and 0.01 mg/L to 4.12 mg/L in the wet season. The nitrate pollution index (NPI) and health risk values were significantly low indicating that nitrate does not pose health threat in the study area currently. However, regular monitoring of nitrate levels in groundwater especially in areas with a high density of septic systems should be done in order to detect and address nitrate contamination promptly.

KEYWORDS: Drinking groundwater, groundwater quality, nitrate pollution, human health risk assessment.

1. INTRODUCTION

Groundwater is an important natural resource with high economic value and social significance that supplies almost half of all drinking water in the world (WWAP, 2009), playing a key role in food production and accounting for over 40% of the global consumptive use in agricultural irrigation (Siebert et al., 2010). Groundwater quality is closely related to people's anthropogenic activities and life (Alireza et al., 2020;) and is particularly important in areas with insufficient surface water resources (Zakhem & Hafez 2015; Tian et al., 2021). However, with population boom and industrial growth, both shallow groundwater and deep groundwater have been polluted by various contaminants (physical, chemical and bacteriological contaminants) (Sun et al., 2022). It is difficult to control the polluted groundwater because it is highly hidden and difficult to detect (Li et al., 2016). The last decades have witnessed an increased pressure on groundwater resources globally, which in which in many cases will induce abstraction beyond sustainable levels and increase levels of pollution. (Groundwater Governance, 2013). Climate change, land use and population growth are posing a variety of threats to groundwater resources globally thereby impacting both quantity and quality of the water. Warri, a bustling city located in the Niger Delta region of Nigeria, is facing a significant environmental challenge and possible nitrate contamination of its groundwater.

Nitrite and nitrate are important sources of plants and algae nutrient, nitrogen (N). in the nitrogen cycle, ammonia (NH_3) is broken down by bacterial action, nitrite is formed and is then converted to the more stable, much less toxic nitrate through a process called nitrification. Other major sources of nitrogen enrichment in soils are fertilizers, animal wastes, sewage, etc. Nitrate is one of the main groundwater pollutants and high nitrate concentrations in groundwater can cause public health risk that are chronic or acute and environmental pollution that have already become a global problem (Sousa et al., 2013). Nitrate is a chemical pollutant exists in groundwater, dissolves easily and has strong fluidity

(Gu et al., 2013; Hand et al., 2013) and it can enter underground through leaching and surface runoff (Li et al., 2015). Excessive consumption of groundwater polluted by nitrate for a long time poses serious threat to human health such as methemoglobinemia, blue baby syndrome in infants which reduces the blood's oxygen-carrying capacity, digestive system cancer, and other diseases particularly to infants and pregnant women (Sun et al., 2017). The World Health Organization (WHO) has established a permissible limit for nitrate in drinking water with a maximum acceptable concentration of 10 milligrams per liter (WHO, 2017).

Nitrate-contaminated groundwater causes harm to the human body when it enters the human body; therefore, it is necessary to evaluate the harm and degree of nitrate-contaminated groundwater. Human Health Risk Assessment (HHRA) is a systematic process used to evaluate the potential adverse health effects that may result from exposure to certain hazards, such as chemicals, pollutants, or contaminants. It is a qualitative and quantitative assessment method for the hazard degree of polluted groundwater to the human body (Ni et al., 2010; Sun et al., 2022). It involves assessing the magnitude of exposure and the potential health effects associated with that exposure. The HHRA process typically includes several steps:

i. Hazard Identification: Identifying and characterizing the potential hazards or substances of concern.
ii. Exposure Assessment: Evaluating the pathways and routes through which individuals may come into contact with the hazardous substances, and estimating the magnitude, frequency, and duration of exposure.
iii. Dose-Response Assessment: Determining the relationship between the amount of exposure and the potential health effects, using available toxicological data and scientific studies.
iv. Risk Characterization: Integrating the information from the previous steps to estimate the likelihood and severity of adverse health effects in the exposed population.
v. The results of a Human Health Risk Assessment are used to inform decision-making processes, such as setting regulatory standards, developing risk management strategies, or implementing measures to mitigate or control exposure to the identified hazards.

The last decades have witnessed an increased pressure on groundwater resources globally, which in many cases induced abstraction beyond sustainable levels and increased levels of pollution (Groundwater Governance, 2013). Climate change, land use and population growth are posing a variety of threats to groundwater resources globally thereby impacting both quantity and quality of the water. Warri, a bustling city located in the Niger Delta region of Nigeria, is facing a significant environmental challenge and possible nitrate contamination of its groundwater.

1.1 Sources of nitrate contamination

Nitrate contamination in groundwater systems is caused by various processes and sources but primarily from agricultural activities, improper waste disposal, and industrial discharges. Identifying the various sources of nitrate contamination and understanding system dynamics is fundamental to address groundwater quality problems. In general, sources of nitrate pollution can be divided into two main groups, nonpoint (diffuse) and point-source pollution. Agricultural fertilizers application is the largest nonpoint source pollution affecting groundwater quality and it is extended over a wide area, as opposed to point sources, which are single and identifiable sources of contamination mainly affecting localized areas. The diffuse sources of nitrate include long-term, widespread overuse of chemical or manure fertilizers (cropland, lawns or golf courses) and long-term leaks in sewer lines (Viers et al., 2012). Point sources include the areas of concentrated livestock confinement, leaky septic or sewer systems and areas of chemical or manure storage[17] (Haller et al, 2013). In particular, point sources may result in extremely high nitrate concentration in localized areas. As a result of decades of fertilizer application and surface spreading of animal manure, significant increases in nutrient concentrations have been documented in both private and municipal well systems (Hallberg and Keeney, 1993). Agricultural land use represents the largest diffuse pollution threat to groundwater quality on a global scale (Haller, 2013). As a result of decades of fertilizer application and surface spreading of animal manure, significant increases in nutrient concentrations have been documented in both private and municipal well systems (Hallberg and Keeney, 1993). Intensive agricultural practices, including the excessive use of nitrogen-based fertilizers, are a major contributor to nitrate contamination. Runoff from farmlands can carry excess nitrates into nearby water bodies, which eventually seep into the groundwater. Studies by Oyeku et al., (2018) and Okparanma et al., (2020) have highlighted the significant impact of agricultural practices on nitrate levels in Warri's groundwater.

Inadequate waste management practices, such as the improper disposal of human and animal waste, can introduce high levels of nitrates into the environment. In Warri, where sanitation infrastructure is often lacking, untreated sewage and septic systems can contaminate groundwater sources. A study conducted by Akpokodje et al. (2019) emphasized the role of poor waste management in nitrate pollution in the region. Nitrate contamination from collapsed septic tanks can be a significant concern for groundwater quality. When a septic tank collapses or fails, it can lead to the release of untreated wastewater, including high levels of nitrate, into the surrounding soil and potentially contaminate the underlying groundwater. Nitrates are a common component of human waste and can be present in septic tank effluent. If the septic tank is compromised, either due to structural failure or improper maintenance, the untreated wastewater can infiltrate the soil and reach the groundwater. Once in the groundwater, nitrates can persist for an extended period and potentially contaminate drinking water wells or other water sources.

Industrial activities, including oil and gas exploration and refining, chemical manufacturing, and food processing, can release nitrates into the environment. Effluents from these industries, if not properly treated, can infiltrate the groundwater, leading to contamination. A study by Ogbeibu et al., (2017) highlighted the impact of industrial activities on nitrate levels in Warri's groundwater.

1.2 Spatial distribution of nitrate contamination

The spatial distribution of nitrate contamination in groundwater is influenced by several factors. Understanding the interplay of these factors is crucial for assessing and managing nitrate contamination in groundwater. By considering these factors, policymakers, researchers, and stakeholders can develop targeted strategies to mitigate nitrate pollution and protect groundwater resources. The factors include.

a. Land use and agricultural practices:

The land use patterns in an area play a significant role in nitrate contamination. Agricultural activities, particularly the use of nitrogen-based fertilizers, can contribute to elevated nitrate levels in groundwater (Schilling et al., 2012). Areas with intensive agriculture, such as farmlands or regions with extensive livestock operations, are more likely to experience higher nitrate contamination due to runoff and leaching of excess fertilizers and animal waste (Green et al., 2008).

b. Proximity to pollution sources:

The proximity of potential pollution sources to groundwater sources affects the spatial distribution of nitrate contamination. Industries, wastewater treatment plants, landfills, and septic systems can release nitrates into the environment. If these pollution sources are located near groundwater recharge areas or shallow aquifers, there is a higher likelihood of nitrate contamination in the surrounding groundwater (Dubrovsky et al., 2010).

c. Hydrogeological factors:

The geological and hydrological characteristics of an area influence the movement and fate of nitrates in groundwater. Factors such as soil permeability, depth to the water table, and groundwater flow patterns can affect the spatial distribution of nitrate contamination. Highly permeable soils or fractured rock formations can facilitate the rapid movement of nitrates into groundwater, increasing the potential for contamination (Nolan et al., 2002).

d. Climate and Precipitation patterns:

Climate and precipitation patterns can impact the spatial distribution of nitrate contamination by influencing the transport and dilution of nitrates in the environment. In regions with high rainfall, excess water can percolate through the soil, carrying nitrates into groundwater. Conversely, in arid regions with limited rainfall, nitrates may accumulate over time due to minimal leaching and dilution (Spalding and Exner, 1993).

e. Local hydrological conditions:

Local hydrological conditions, such as the presence of rivers, streams, or wetlands, can affect the spatial distribution of nitrate contamination. These water bodies can act as pathways for the transport of nitrates from the land surface to groundwater. Areas located downstream or in close proximity to these water bodies may experience higher nitrate contamination due to the potential for direct infiltration or surface water-groundwater interactions (Schilling et al., 2012).

1.3 Effects

Health risks

In many parts of the world, groundwater is the single most important supply for the production of drinking water, particular in areas with limited or polluted surface water sources (Schmoll et al., 2006). Half of all drinking water in the world is extracted from groundwater resources (WWAP, 2009). Groundwater contamination can directly affect human health because excessive levels of nitrate in drinking water can produce negative health impacts on human well-being. Consuming water containing high nitrate concentrations can have almost immediate effect on a person (acute toxicity). High levels of nitrates in drinking water pose significant health risks, especially for vulnerable populations such as infants and pregnant women. Nitrate contamination can lead to methemoglobinemia, also known as blue baby syndrome (Uhlman and Artiola, 2011). Studies by Oyeku et al. (2018) and Okparanma et al. (2020) have reported elevated nitrate levels in groundwater, raising concerns about potential health impacts in unprotected groundwater sources. Long term exposure to high nitrate levels in excessive levels of nitrate in drinking water (concentration higher than 10 mg/L) has been found in some studies to be a risk factor that can produce negative health impacts on human well-being. Other diseases associated with nitrate consumption are cancer including gastric, colorectal, bladder, urothelial and brain tumor (Self and Waskom, 2013; CDPH, 2013). Some information suggests that ingesting nitrate-contaminated drinking water during early pregnancy may increase the risk of certain birth defects[32] (Bundy et al., 1980). In other words, it is of vital importance to regulate nitrate concentration in drinking water to minimize public health risk. Studies conducted in Australia, Canada and U.S.A. found a higher incidence of neural tube defects and cleft palates in areas where nitrate levels were elevated (Bundy et al., 1980). Additional problem related to nitrate exposure during pregnancy have raised serious concerns because research shows nitrites may cross the placenta and potentially increase methemoglobin levels in the developing fetus. Also, prolonged intake of high levels of nitrate are linked to gastric problems due to the formations of nitrosamines. It is therefore expedient to mitigate the impact of nitrate pollution in groundwater and understand the global impact of nitrate contamination.

1.4 Mitigation

One of the most important steps to reduce nitrate leaching in an area is to limit the amount of nitrogen applied. It is better to use slow-release nitrogen sources, or low rates of soluble nitrogen applied more often. In addition, the farmers should be more cautious about adding nitrogen during periods in which the ground is not yet frozen but the grass is not growing. The farmers should also avoid over-irrigation, which increases the chance of nitrate leaching. These steps will greatly reduce the chance of nitrate leaching into groundwater in the agricultural areas (Hallberg and Keeney, 1993). Nitrates are a common component of human waste and can be present in septic tank effluent. If the septic tank is compromised, either due to structural failure or improper maintenance, the untreated wastewater can infiltrate the soil and reach the groundwater. Once in the groundwater, nitrates can persist for an extended period and potentially contaminate drinking water wells or other water sources. To mitigate nitrate contamination from collapsed septic tanks, it is crucial to address the issue promptly.

This may involve repairing or replacing the septic tank, ensuring proper maintenance and regular inspections, and implementing measures to prevent untreated wastewater from reaching groundwater sources. Local health departments or environmental agencies often provide guidelines and regulations for septic system maintenance and can offer guidance on remediation actions. Regular monitoring of groundwater quality, especially in areas with a high density of septic systems, is also essential to detect and address nitrate contamination promptly. Testing private wells for nitrate levels is recommended, and if elevated concentrations are found, appropriate treatment or alternative water sources may be necessary to ensure safe drinking water.

Nitrate pollution has been addressed by governmental policy measures related to reduce atmospheric pollution and limiting nitrogen contamination of groundwater and surface water resources. It includes environmental protection policies and regulations (Sutton et al., 2011). In order to regulate the nitrate concentration to minimize public health risk, local environmental protection agency of various countries have created standards for maximum contaminant level for nitrate in drinking water supply and the World Health Organization (WHO) has published the guideline value for nitrate (NO_3) in drinking water which should not exceed 10 mg/l (WHO, 2004). The maximum contaminant level for drinking water supplies should not contain more than 10 mg/l of nitrate (as nitrogen) and 1 mg/L of nitrite (as nitrogen) (Borkovich, 2010).

Sewage system should be properly managed. Wastewater is necessary to be treated before discharged in order to minimize environmental pollution. The aim of sewage treatment is to purify the effluent by removal of harmful and hazardous substances and plant nutrients contained in sewage as solids and as dissolved matter. Sewerage networks transport wastewaters to treatment plants where organic matter, nutrients and harmful substances are removed from the sewage before the effluent is discharged back into the environment., (UNEP, 2007). Investments in robust waste management infrastructure, including sewage treatment plants and proper disposal systems, are crucial to prevent nitrate contamination from human and animal waste. Providing sufficient training and education for local administration to plan and building the adequate sewage treatment facilities in rural areas. Then, formulation and implementation of awareness campaigns for the general public to gain general recognition for the need for the installation of appropriate and environmentally sound sewage facilities.

Beneficial management practices for agriculture involves effective prevention measures to reduce the nitrate pollution is to minimize the leaching of nitrate from the soil. Furthermore, it suggests that effectively managing nitrogen is a multi-faceted task and requires an integrated approach based on the adoption of beneficial management practices (BMP) (Di and Cameron, 2002). This technique is a practical and affordable activity that can achieve the goals including protecting and conserving farm resources, facilitation the reduction of greenhouse gas emission or encourage carbon sequestration (Mussell et al, 2011). BMP techniques can be applied to minimize nitrate leaching from croplands and/or to make crops use nitrogen fertilizer as efficiently as possible. For instance, better timing and placement of fertilizers could improve efficient use[32] (Bundy et al., 1980). Many studies have shown that beneficial management practices significantly improve the potential to maximize crop yield while minimizing the quantity of nitrate leaching into groundwater (Badee, 2017). Many research projects have invested in the BMP to reduce the nitrate pollution from agricultural activities. It represents effective environmental strategies to ensure the groundwater obtained in drinking water production wells will meet the Ontario Drinking Water Standard (ODWS) for nitrogen (10 mg/L) now and in the future (Mussell et al., 2011). Promoting sustainable agricultural practices, such as precision farming techniques, organic fertilizers, and proper irrigation management, can help reduce nitrate runoff from farmlands. Public awareness campaigns and training programs should be implemented to educate farmers about the potential impacts of excessive fertilizer use and the benefits of sustainable practices. The construction of concrete pits (manure lagoons/slurry store) for storing large contaminant source (manure) is another possible way to prevent nitrate pollution in many farming areas. These facilities are proven to store manure without leaking and are actually more convenient for the farmer once they are installed. Various alternative water treatment techniques should be adopted in nitrate contaminated groundwater to reduce the concentration of nitrate before it is used as drinking water. Some of the methods are:

i. **Industrial Regulations and Monitoring:** Stringent regulations and regular monitoring of industrial discharges are essential to prevent nitrate contamination. Industries should be required to implement effective wastewater treatment systems and adhere to strict pollution control measures. Regular water quality testing should be conducted to ensure compliance with established standards.

ii. **Blending drinking water (Non-treatment technique):** Blending drinking water is a method to mix contaminated water with clean water from another source to lower overall nitrate concentration. This method is not safe for infants but is acceptable for livestock and adults (Self and Waskom, 2013). The benefits of non-treatment method is the spread of the costs of water quality monitoring in the different regions so that it significantly reduces expenses and helps to provide safe(r) drinking water to the majority of the people. The disadvantage of this method is however that it can only be applied when the nitrate contamination is limited to a specific area. Other alternatives are the use of treatment processes, such as ion exchange, reverse osmosis and biological denitrification (Haller et al., 2013).

a. **Ion exchange:** Ion exchange needs a substance such as chloride to exchange with nitrate in the water. The ion exchange unit is a tank filled with special resin beads that are charged with chloride. Once contaminated water passes over the tank, the nitrate is substituted with the chloride. The resin is recharged by backwashing it using a sodium chloride solution. Ion exchange method is very effective method, except for water that contains high amounts of sulphate. In this case the sulphate competes with nitrate in the exchange process (Self and Waskom, 2013).

b. **Reverse osmosis:** Reverse osmosis is another method that can be used to reduce nitrate concentration. Water is moved under high pressure through a membrane. The membrane contains many microscopic pores that allow only water molecules to pass through, and as such, will stop nitrate and other inorganic chemicals such as calcium and magnesium. The membrane can reject nitrate which estimates around 83-92% of the incoming nitrate. Consequently, it is important to know the original nitrate concentration in the water. If nitrate-nitrogen levels are extremely high (greater than 110 mg/l) up to 90 % may be removed. Although reverse osmosis can be an effective nitrate remover, this method is relatively expensive and removing the useful chemicals (Mahler et al., 2007).

c. **Biological denitrification:** Biological denitrification is using denitrifying bacteria and microbes so that nitrate ions are converted into its elemental state of nitrogen. Nitrate can be removed by using a chemical material like ethanol. Besides special bacteria, photosynthetic algae can be used to remove nitrates from water. This method does not produce concentrated brine streams, however, biofilm growth have to be managed. The important drawback of biological systems is requiring start-up time after prolonged periods of closure. For instance, the response of seasonal water demand needs more operator support than nonbiological systems (Mahler et al., 2007).

2. MATERIALS AND METHODS

2.1 Study area selection:

Warri is located in the western end and coastal region of the Nigerian Niger Delta. It lies between latitude 5°54′00’’N and 5°35′00’’N of the Equator and longitude 5°42′00’’E and 5°54′00’’E of the Greenwich Meridian. It is one of the major commercial cities in southern Nigeria and it has a port, a refinery and several oil fields and flow stations. The study area includes the area that covers the metropolitan city of Warri and Effurun, Orhuwhoru, Jeddo, Ukuokoko in Warri South, Uvwie, Udu and Okpe Local Government Areas, respectively. Figure 1.

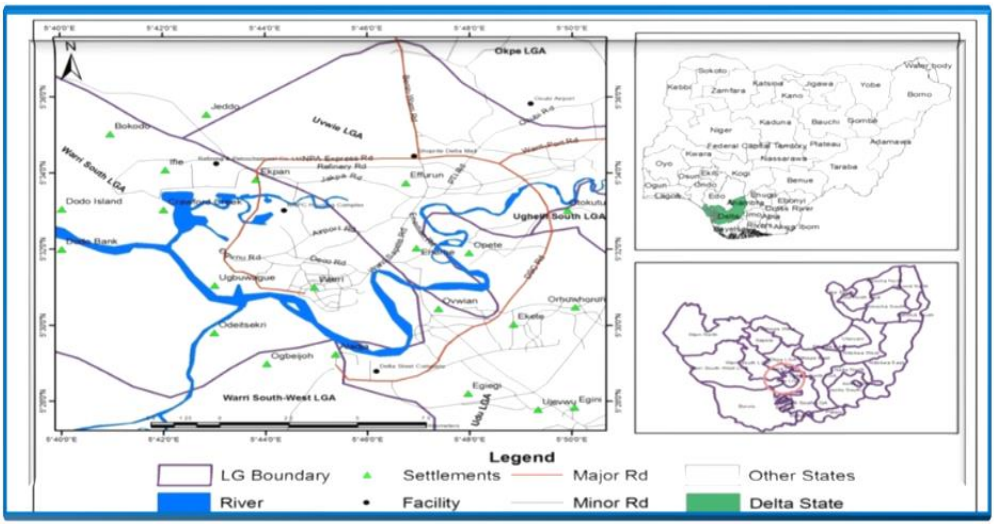


Figure 1: Map of Warri and Its environs (Google Map, 2019).

The geological formation of the study area consists of more than 90% sands and about 10% shale/clays as shown in Figure 2. The sands range in size from fine-to-medium and coarse-grained unconsolidated sands, with occasional intercalations of gravelly beds that are also poorly-sorted, sub-angular to well-rounded, and bear lignite streaks and wood fragments peat or lenses of plastic clay (Akpoborie et al., 2011). The area overlies the three major subsurface lithostratigraphic units of the Niger Delta (from the oldest to the youngest, Akata, Agbada, and Benin) Formations (Orji & Egboka, 2015). The Benin Formation is masked by the younger Holocene deposits of the Sombreiro-Warri Deltaic Plain, the Mangrove Swamp and Freshwater Swamp wetlands. The first aquifer (Benin formation which is less than 50m in thickness and is extremely vulnerable to pollution from surface sources especially due to the fact that groundwater could be encountered in this formation even at a depth of 4m or less (Akpoborie et al., 2011).

Hydraulic conductivities of the Quaternary sand vary from 3.82 x 10^{-3} to 9.0 x 10^{-2} cm/sec which indicates high aquifer potentials (Aweto et al., 2015). The water table is very close to the ground surface and varies from 0 to 4 metres (Offodile, 1991). This huge annual rainfall contributes largely in the recharging of the aquifer that has enriched the underground water source of the study area. The mean annual temperature of Warri urban is about 32.8 °C and there are high temperatures of 36 and 37 °C (Adejuwon, 2012).

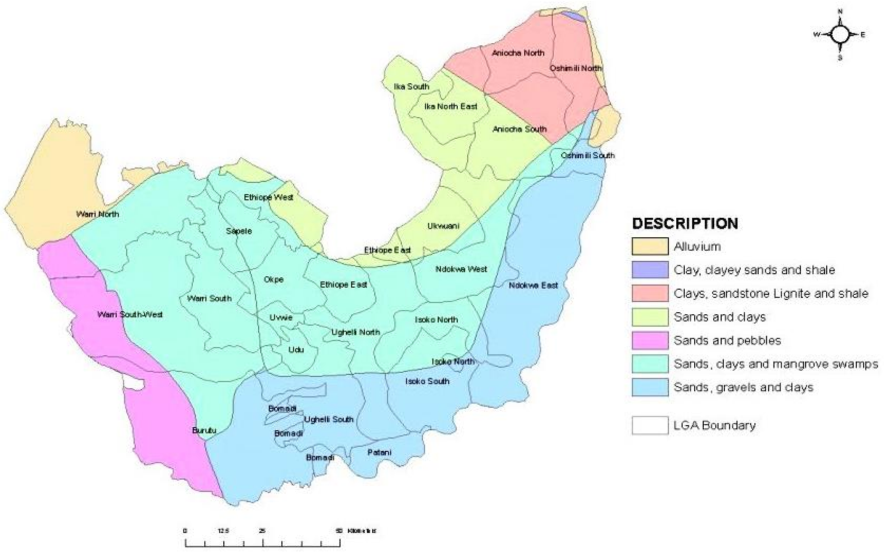


Figure 2: **Geological map of Delta State by local governments (Akpoborie et al., 2011).**

The land is gentle and rises from less than 6m above sea level in the lowlands that adjoin the sea to an average elevation of about 18m above the sea level (Olobaniyi & Efe, 2007). The flat and low-relief features of the area, often encourage flooding after rain. The climate of Warri and its environs is humid equatorial and it is influenced by two prevailing air masses; the south-west monsoon wind and the north-east trade wind. The natural vegetation of the study area along the banks is made up of mangrove plants of different species. Away from the banks, rainforest plants predominate. Tropical rainforest occurring in flat-floored valleys and adjoining low-lying areas with swamp forest that are seasonally or permanently waterlogged. The rain forest is floristically diverse and structurally complex, with several layers of trees. However, virtually all the rainforest in the area has been destroyed as a result of farming, especially shifting cultivation and the establishment of small-scale holdings of rubber tree, commercial lumbering and urbanization (Akpoborie et al., 2011). Groundwater is the major source of water and it is extracted from large number of private bore wells. There is no record of the number of private bore wells within the study area. Based on physical observation, it may be safely quoted that almost every house has one bore well (Agori, 2021).

2.2 Sampling locations:

A satellite imagery of the study area was obtained using ArcMap 10.6. The built-up areas were digitized and gridded at 1km intervals to determine the sampling points, ensure adequate coverage and uniform spacing of sampling locations. Fifty (50) sampling locations at or close to the grid intersection points were selected and established based on the areas of high and low population density, industrial or anthropogenic activities such as crude oil refining activities, open solid waste dump sites, density areas and river catchment areas. The depths of some boreholes were also determined using a plumb bulb and line.

2.3 Samples Collection and Analysis:

Water samples were collected from the 50 selected existing boreholes during the dry season (December, 2019 – January, 2020) and the wet season (June, 2020 –August, 2020) using appropriate sampling techniques. Samples were collected in clean, sterilized new high-density PET screw-capped containers of 1.5litres capacity. The PET containers and stoppers were thoroughly washed with distilled water three times and once with the water to be sampled before collecting the actual samples to avoid contamination. Multiple samples were collected from each location to account for temporal and spatial variability. The bottles were filled, allowed to overflow and immediately corked, properly labeled to avoid mix up, placed in an ice block chest and transported to the laboratory within a prescribed period of not more than three hours after collection. Collection, preservation and transportation of the water samples to the laboratory and preserved in refrigerators at $4^{o}C$ in the laboratory to keep the samples intact until analysis was carried out following the standard guidelines recommended by APHA, (2017). Nitrate concentration was determined using the colorimetry and UV Spectrophotometric methods. The results obtained from the field and laboratory analysis of water samples for dry and wet seasons were averaged and the mean values obtained to determine the spatial and temporal variation of the concentration of the parameters in both dry and wet seasons. Quality control measures were implemented throughout the laboratory analysis process to ensure accurate and reliable results. This included the use of certified reference materials, calibration of instruments, and duplication of analysis of samples.

2.4 Data analysis

The obtained data were analyzed using Microsoft Excel statistical tools. Descriptive statistics (means, standard deviations, and ranges), were calculated to summarize the nitrate concentrations in the groundwater samples. The Kriging spatial analysis techniques for mapping and geostatistical analysis was employed to identify patterns and hotspots of nitrate contamination.

2.5 Human health risk assessment.

Nitrate pollution index (NPI)

The Nitrate Pollutants Index is an indicator for assessing water pollution caused by high nitrate concentration (Obeidat, 2012). It is important and necessary to check and evaluate the percentage of nitrates in the water. NPI is measured using Equation 1 (Ali, 2013) in order to investigate groundwater pollution by nitrate and NPI classification as in Table 4.

$$NPI = \frac{Cs - HAF}{HAF} \qquad (1)$$

Where,

Cs is the concentration of nitrate and

HAF is the human acceptable value of nitrate and is taken as 10 mg/L.

Table 4: NPI threshold limits.

NPI Value	NPI Interpretation
<0	Clean (unpolluted)
0–1	Low pollution
1–2	Moderate pollution
2–3	High pollution
>3	Very significant pollution

In this study, the risk assessment was carried out in three groups of the exposed population, comprising children, females, and males. The intake of polluted groundwater can cause a severe threat to humans, primarily by two exposure routes, the ingestion of drinking water or oral route, and the dermal interaction route, (Adimalla & Qian, 2019). The US Environmental Protection Agency originally proposed this rigorous model for the assessment of human health risk (USEPA, 1997). The non-carcinogenic health risk from oral intake was calculated as follows (Karunanidhi et al. 2019).

$$CDI = \frac{C \times EF \times ED \times IR}{ABW \times AET} \qquad (2)$$

$$HQ_{Oeal} \frac{CDI}{RfD} \qquad (3)$$

Where, in Eq. (2),

CDI is referred as chronic daily intake (in mg/kg/day);

C is the concentration of groundwater nitrate (in mg/L);

IR is denoted for daily ingestion rate of groundwater (in L/day) for both males and females ingestion rate is 2.5 L/day and for children, ingestion rate is 1 L/day (USEPA, 1989).

EF is denoted for the exposure frequency (in days/year), and the exposure frequency is considered as 365 days/year for males, females, and children [53] (USEPA, 1989).

ED is denoted for exposure duration (in a year), for children 12 years, for females 67 years, and for males, 64 years have considered for this study (Adimalla, 2020, Karunanidhi, et al., 2020).

ABW is the average body weight as 65 kg, 55 kg, and 15 kg for males, females, and children, respectively (Adimalla. & Qian, 2021).

AET (The average exposure times) are 23,360 days, 24,455 days, and 4380 days for males, females, and children, respectively.

In Eq. (3),

The hazard quotient is presented as HQ.

RfD indicates reference dose of nitrate contaminant (in mg/kg/day) which is 1.6 mg/kg/day (USEPA, 1989, USEPA, 1989).

The non-carcinogenic health risk from dermal contact is calculated by the following formulae (Adimalla, & Qian, 2021, Chen, et. al., 2017; Chen, et. al., 2017; Karunanidhi, et. al., 2019).

$$DAD = \frac{C \times TC \times K_i \times CF \times EV \times ED \times EF \times SSA}{ABW \times AET} \quad (4)$$

$$HQ_{Dermal} = \frac{DAD}{RfD} \quad (5)$$

$$HI_{Total} = \sum_{i=1}^{n} \left(HQ_{Oraj} + HQ_{Dermal} \right) \quad (6)$$

Where in Eq. (4)

DAD indicates the dermal absorbed dose (in mg/kg×day);

TC is the contact time (in h/day) taken as 0.4 in h/day;

Ki represents the dermal adsorption parameters (in cm/h) taken as 0.001 cm/h; and

CF is denoted for conversion factor taken as 0.001 (Abdesselam, et. al., 2013)

EV represents bathing frequency (in times/day) and considered as two times in a day, and

SSA indicates the skin surface area (in cm^2) and values for SSA are taken as 16,600 sq. centimetres for both males and females, and 12,000 sq. centimetres for children (USEPA, 2002).

In Eq. (6),

HI is the hazard index, and non-carcinogenic human health risk

The HI value greater than one shows the potential human health risk from nitrate contamination,

HI value less than one expresses an acceptable level of health risk on human (USEPA, 2002).

Data treatment

The obtained data were analyzed using Microsoft Excel statistical tools. Descriptive statistics (means, standard deviations, and ranges), were calculated to summarize the nitrate concentrations in the groundwater samples and the sample concentration results were compared to WHO Standard of drinking water quality (BIS, 2012). ArcGIS 10.7 software was used to make distribution maps and interpolate the experimental dataset. The Kriging spatial analysis techniques for mapping and geostatistical analysis was employed to identify patterns and hotspots of nitrate contamination.

3. RESULTS AND DISCUSSION

The nitrate concentration at the sampling locations are in Table1 and Figure 3, The descriptive statistics are contained in in Table 2. The NO_3 concentration mean value of $0.83 \pm 0.81 mg/l$ in the dry season and $1.06 \pm 1.08 mg/l$ in the wet season were recorded, ranging from 0.02 mg/L to 3.27 mg/L in the dry season and 0.01 mg/L to 4.12 mg/L in the wet season. The nitrate values are less than the WHO permissible limit of 50mg/l all through the sampling stations, indicating no potential risks to human health. The range, mean, and standard deviation values revealed variations in the nitrate concentration in the study area. Nitrate in drinking water is highly deleterious to human health and it is recommended that nitrate in water for domestic use be less than 10mg/l of water. Its effect on infants below the age of six months include shortness of breath and blue-baby syndrome. High nitrate levels observed have been associated with agrochemicals and wastewater from farms and homes. Higher concentrations were clustered in high density areas, agricultural areas and some areas with industrial activities indicating localized sources of contamination. The lower concentrations are associated with natural attenuation processes or less anthropogenic influence. The nitrate concentration prediction maps for both dry and wet seasons are presented in Figure 3.

Table 1: Nitrate concentration at the sampling locations.

Locations	**Nitrate Concentration (mg/L)**		**Locations**	**Nitrate Concentration (mg/L)**	
	Dry season	**Wet season**		**Dry season**	**Wet season**
Okuokoko	0.14	0.14	Okumagba Layout	0.21	0.27
Effurun GRA	1.20	1.26	Okere Road	0.43	0.59
Army Barracks	0.27	0.28	Marine Quarters	0.55	0.75
Niger CAT	0.52	0.67	Essi Layout	0.98	1.30
Airport Road	1.95	4.12	Igbudu Market	0.72	0.95
Jakpa Road	0.82	0.96	Agbassa	0.10	0.18
Shagholoh	0.11	0.11	Bowen Avenue	0.05	0.13
Ekpan	0.02	0.04	Iyara	0.02	0.08
Urhobo College Effurun	0.15	0.16	Pessu Market	0.95	0.02
Effurun Market	1.94	2.64	Orhunworun	0.58	1.26
Ogborode	1.28	1.72	Enerhen	0.01	0.68
Ughoton	3.27	3.96	Udu Road	0.31	0.41
Jeddo	1.90	2.87	Otokutu	0.09	0.01
Ubeji 1	1.74	2.83	Bendel Estate	0.24	0.24
Ubeji 2	0.57	0.68	Upper Erejuwah	1.20	1.26
Osubi Market	2.29	0.39	Mammy Market	0.41	0.69
Osubi Airport	2.95	3.41	DSC Township	1.36	1.40
Ogbuwangue	2.64	3.05	Okumagba Estate	1.44	1.51
Warri Port	0.46	0.79	Mofor	1.10	0.18
Ogunu	0.46	0.69	FUPRE	0.98	1.19
Edjebah	2.68	3.10	Shoprite	0.53	0.55
Edjeba Housing Est.	0.91	1.19	Robbinson Plaza	0.17	0.19
Federal Govt. Coll.	1.03	0.94	Esisi Road	0.22	0.23
Ajamimogha	0.81	0.66	Robert Road	0.83	1.07
Warri GRA	0.57	0.27	PTI Road	0.17	0.29

Table 2: Groundwater nitrate descriptive statistics of domestic boreholes samples analyzed during the dry and wet seasons (where, n = number of samples collected = 50).

Parameter	Dry season (n = 50)				Wet season (n = 50)			
	Range		Mean	SD	Range		Mean	SD
	Min	Max			Min	Max		
NO_3 (mg/l)	0.02	3.27	0.83	0.81	0.01	4.12	1.06	1.08

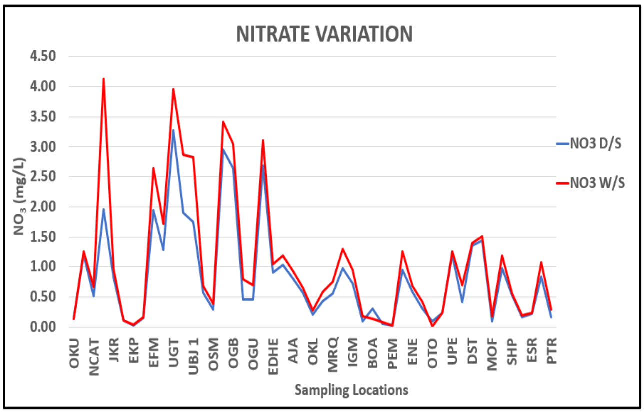
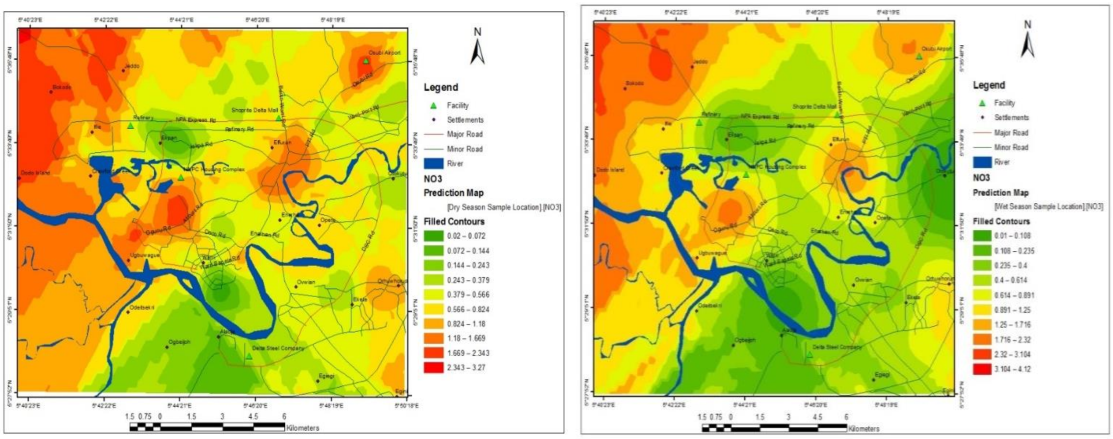


Figure 2: Nitrate variation across the study area.



(a) **(b)**

Figure 3: Spatial distribution of nitrate concentration in (a) Dry season and (b) Wet season.

Range of nitrate concentrations:

Nitrate pollution index (NPI) for this study area.

In this study area, the NPI values range from -0.998 to -0.873 with an average NPI of -0.917 in the dry season and -0.999 to -0.873 with an average NPI of -0.917 in the dry season as in Table 3.

Table 3: Nitrate pollution index in both seasons.

NPI	Dry season	Wet season
NPI_{min}	-0.998	-0.999
NPI_{max}	-0.873	-0.588
NPI_{meab}	-0.917	-0.894

From the human health risk assessment of nitrate, the research found that all samples demonstrated very low non-carcinogenic health issues on children, females and males due to low nitrate content of in groundwater, signifying a low risk to human health, Table 4. The findings of the analysis also indicate that health hazards are more dangerous to infants and children due to nitrate ingestion via oral and dermal exposure pathways.

Table 4: Summary of the estimated non-carcinogenic risks of Nitrate ingestion of drinking water and dermal exposure.

Age classes	**Mean CDI**		Mean HQ_{Oeal}		*Mean DAD*		Mean HQ_{Dermal}		HI_{Total}	
	D/S	**W/S**	**D/S**	**W/S**	**D/S**	**W/S**	**D/S**	**W/S**	**D/S**	**W/S**
Children	0.023	0.027	0.014	0.017	0.001	0.001	0.0006	0.0006	0.0146	0.0316
Female	0.015	0.019	0.009	0.012	0.002	0.0004	0.0013	0.0003	0.0103	0.0223
Male	0.001	0.001	0.007	0.007	0.0001	0.0003	0.0001	0.0002	0.0071	0.0141

*D/S = Dry season, W/S = Wet season

The results show that the exposure of nitrate due to drinking water ingestion was higher than the exposure due to dermal interactions in the study area. Te reasonable limit for non-carcinogenic health risk is≤1 (HI≤1), based on the USEPA health risk standards. If the hazard index (HI) value is>1, then the possibility of an adverse risk to human health is very high51. HI_{Total} values in the study area are varied from 0.0146 in the dry season to 0.0316 in the wet season for children, 0.0103 and 0.0223 in the dry and wet seasons respectively for women and 0.0071 and 0.0141 for men in the dry and wet seasons respectively. The findings appear to suggest that children are more vulnerable to non-carcinogenic effects in the study area owing to the intake of higher nitrate concentrations in drinking water. Many other scholars have found that due to lower body weight and personality characteristics, children are more vulnerable to chronic non-carcinogenic threats than adults.[61] The spatial distribution of the background values of nitrate (Fig. 3a and 3b) showed that the health hazard was high at the place where the significant difference between NBL and total concentrations of groundwater nitrate was noticed., which is also known as blue baby syndrome, causes infant mortality, hypertension, thyroid disorders, goiter, hives, severe cyanosis, cytogenetic defects, congenital malformations, and headaches49,65,78–82. However, in many parts of the globe where a significant populace depends entirely on groundwater resources for drinking without pre-examination of safety problems, the non-carcinogenic health risk of NO3 − in drinking water becomes a serious issue18,65,78,79,81,82. In northern India, a detailed study done74and assessed the human health risk of nitrate. Their research found that about 36% of samples demonstrated greater non-carcinogenic health issues on children due to higher content of nitrate in groundwater, signifying a tremendous risk to human health. Similarly, in southern India, a researcher3 had analyzed the issues due to groundwater nitrate. Their fndings reveal that about 60%, 57%, and 50% of groundwater samples were in the range of potential health risk for children, females, and males, respectively. Likewise, another study related to nitrate health implications was carried83 in the northern Shandong Peninsula of China, and found that about 87.6% of water samples were unft for nitrate concentration-based consumption. The findings of their analysis also indicate that health hazards are more dangerous to infants and children due to nitrate ingestion via oral and dermal exposure pathways. Tus, owing to the drinking of contaminated groundwater, the intensity of health risk steadily increases.

CONCLUSION

The concentration of nitrate was analyzed and possible health risks in the drinking water in Warri, Nigeria evaluated. Nitrate contamination of groundwater in Warri does not pose significant risks to both human health and the environment. However, the dynamic changes of NO_3^- content in groundwater need to be closely monitored in order to be able to control any possible future contamination by nitrate. Analyzing the magnitude of change in nitrate concentrations can provide insights into the impact of rainfall on nitrate contamination. Locations with significant increases in nitrate concentrations during the rainy season may indicate a higher potential for nitrate leaching and runoff from agricultural areas or other pollution sources. Preventing septic tank failures through proper maintenance and timely repairs is crucial to minimize the risk of nitrate contamination and protect groundwater quality. Regular monitoring of groundwater quality, especially in areas with a high density of septic systems, is also essential to detect and address nitrate contamination promptly. Addressing this issue requires a multi-faceted approach that involves sustainable agricultural practices, improved waste management, and stringent industrial regulations. Collaborative efforts between government agencies, industries, farmers, and the local community are crucial to safeguarding Warri's groundwater resources and ensuring a sustainable future. Testing private wells for nitrate levels is recommended, and if elevated concentrations are found, appropriate treatment or alternative water sources may be necessary to ensure safe drinking water. Correlations between nitrate and specific land use practices, such as agricultural intensity or proximity to septic systems, can help identify the primary drivers of nitrate contamination. This information can inform land management decisions and targeted interventions to reduce nitrate pollution. In studying nitrate contamination, other additional parameters that influence nitrate contamination should be investigated abd these these include:

i. **pH:** pH levels can influence the mobility and transformation of nitrate in groundwater. Low pH conditions can enhance nitrate leaching, while high pH conditions may promote denitrification processes. Monitoring pH levels helps assess the potential for nitrate contamination and its fate in the aquifer.

ii. **Electrical Conductivity (EC):** EC is a measure of the water's ability to conduct electrical current and is often used as an indicator of overall water quality. High EC values can suggest the presence of dissolved ions, including nitrates, which can indicate contamination.

iii. **Dissolved Oxygen (DO):** DO levels are important in understanding the redox conditions and potential for denitrification in groundwater. Low DO levels can indicate anaerobic conditions, which favor denitrification and the conversion of nitrate to nitrogen gas.

iv. **Ammonium (NH_4^+):** Monitoring ammonium levels is relevant as it can indicate the presence of organic matter decomposition or the incomplete nitrification of ammonium to nitrate. Elevated ammonium concentrations may suggest a potential source of nitrate contamination.

v. **Total Nitrogen (TN):** TN includes all forms of nitrogen, including nitrate, nitrite, ammonium, and organic nitrogen. Assessing TN levels provides a more comprehensive understanding of the overall nitrogen load in groundwater and its potential sources.

vi. **Stable Isotopes:** Stable isotopic analysis of nitrogen (δ15N) and oxygen (δ18O) can help identify the sources and processes influencing nitrate contamination. Different sources, such as fertilizers, animal waste, or sewage, have distinct isotopic signatures that can be used to trace the origin of nitrate.

vii. **Microbial Indicators:** Parameters such as fecal coliforms or E. coli are often measured to assess the potential for microbial contamination, which can be associated with nitrate sources like septic systems or agricultural runoff.

viii. **Other Nutrients:** Studying the concentrations of other nutrients, such as phosphorus, potassium, or carbon, can provide insights into nutrient interactions and potential synergistic effects with nitrate contamination.

These parameters, along with nitrate concentration, collectively contribute to a more comprehensive understanding of nitrate contamination sources, fate, and potential impacts on groundwater quality. The specific parameters to be studied may vary based on the research objectives, local conditions, and available resources.

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