

Nitrogen Speciation in Regolith Aquifers at Enugu, Southeastern Nigeria

Ezeugwu Innocent Onyebuchi^{1*}, Ozoko Daniel Chukwuemeka¹ and Dike Anselm Obichukwu²

¹Department of Geology and Mining, Faculty of Physical Sciences, Enugu State University of Science and Technology, Agbani, Enugu, Nigeria.

²Department of Applied Microbiology and Brewing, Faculty of Biological Sciences, Enugu State University of Science and Technology, Agbani, Enugu, Nigeria.

*Corresponding author's e-mail: Innocentezeugwu38@gmail.com or services@geoinnservices.com

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Abstract

This study investigates nitrogen speciation in groundwater across multiple locations in Enugu, Southeastern Nigeria, using Eh-pH diagrams to interpret dominant microbial processes influencing nitrogen transformations. A total of 30 groundwater samples from multiple locations such as Centenary, 9th mile, Ologo, Trans-Ekulu, New-artizan and Amechi were studied. Eh and pH were determined using the Standard Hydrogen Electrode and a pH meter respectively. Water samples from urban hand dug wells and streams were analyzed for redox potential and pH, and their positions were plotted against thermodynamic stability fields of nitrate (NO_3^-), ammonium (NH_4^+), ammonia (NH_3), and nitrogen gas (N_2) using geochemist work bench software. The results reveal that most groundwater samples fall within the NH_4^+ and N_2 stability fields, indicating that ammonification and denitrification are the predominant nitrogen transformation pathways. Nitrification was largely absent due to low oxygen levels, with no samples falling within the NO_3^- stability field. Sites like New Artisan Stream and several wells in the Amechi and Trans-Ekulu areas exhibited strong denitrification signatures, facilitated by bacteria such as *Pseudomonas sp.*, *Geobacter sp.*, and *Bacillus sp.* On the other hand, samples from the 9th Mile and Premier Layout areas showed evidence of ammonification under reducing conditions, with high NH_4^+ concentrations pointing to organic matter decomposition and limited oxygen availability. These microbial-mediated nitrogen processes have critical implications for groundwater quality, particularly with respect to nitrate attenuation and potential ammonia toxicity. The findings magnify the importance of redox conditions in shaping nitrogen dynamics in tropical groundwater systems and highlight the need for integrated water quality management in the face of increasing anthropogenic impact.

Keywords: Groundwater contamination, Nitrogen cycle, Nitrate pollution, Regolith aquifers, Shallow groundwater, Subsurface hydrogeochemistry, Groundwater quality, Eutrophication Microbial contamination, Anthropogenic pollution.

INTRODUCTION

Nitrogen is one of the most abundant elements in the Earth's atmosphere which plays a vital role in the biosphere. However, its excessive accumulation in groundwater systems has become a worldwide concern in terms of the environment and public health. Nitrate (NO_3^-), the most mobile and stable form of nitrogen in oxic groundwater environments, is frequently reported as a major contaminant due to agricultural runoff, domestic waste discharge, and leaching from pit latrines (Spalding and Exner, 1993;

Rivett *et al.*, 2008). Globally, nitrate-contaminated groundwater poses risks such as methemoglobinemia (blue baby syndrome), cancer, and thyroid dysfunctions, especially in developing regions where groundwater is a primary source of drinking water (Ward *et al.*, 2005). In sub-Saharan Africa, including Nigeria, increasing urbanization and land-use changes have led to intensified and increased inputs of nitrogen into shallow aquifers. The regolith aquifers, which are dominant in many parts of southeastern Nigeria, including Enugu, are especially vulnerable due to their shallow depth, weathered nature, and variable permeability (Ehirim and Nwankwo, 2010; Nwankwoala, 2011). These aquifers which are derived from weathered sedimentary and crystalline basement rocks, often act as both conduits and storage for infiltrating water and contaminants. The dynamics of nitrogen within such systems are governed by a combination of geochemical processes such as nitrification, denitrification, sorption and human activities some of which are mediated by the activities of microorganisms (Kim *et al.*, 2015).

Enugu city, located within the Anambra Basin of southeastern Nigeria, relies heavily on groundwater from hand-dug wells and shallow boreholes for domestic and agricultural use. However, with increasing population pressure, indiscriminate waste disposal, and the proliferation of latrines and septic tanks in residential areas, concerns over groundwater quality particularly nitrate pollution have escalated (Obinna *et al.*, 2018). Despite the critical reliance on these aquifers, there is limited localized information on the nitrogen system, especially on how nitrogen species vary across different depths, lithologies, and hydrochemical facies in the regolith. Most previous studies in the region have focused broadly on groundwater quality (Eze and Ugwu, 2011; Ibe and Sowa, 2015), often without a targeted investigation into nitrogen transformations and fluxes in regolith-dominated systems. There is a pressing need to understand the pathways, sources, and sinks of nitrogen in these aquifers to guide sustainable water resource management and public health interventions.

REVIEW OF LITERATURE

Interest in nitrogen dynamics in shallow groundwater, especially in regolith-rich areas like Enugu, has grown due to concerns about pollution from human activities. Nitrate contamination, fecal infiltration, and eutrophication threaten water safety in this densely populated and geologically sensitive region. Recent studies have explored both chemical and microbial processes to understand how human and natural factors influence groundwater quality.

A recent study on the eutrophication status of shallow wells in Enugu metropolis revealed significant nutrient loading in groundwater, particularly nitrate (NO_3^- -N) and phosphate (PO_4^{3-} -P), with nitrate levels ranging from 14 to 93.7 mg/L these values exceeds the World Health Organization (WHO) guidelines in many cases. Using the Trophic Level Index (TLI), Trophic State Index (TSI), and Eutrophication Index (EI), the

study found groundwater trophic states varying from oligotrophic to mesotrophic, suggesting ongoing nutrient enrichment and increasing eutrophication risk, particularly in areas with inadequate sanitation infrastructure (Afribary, 2022). An Earlier work by Ogbu and Echebiri (2003) provided foundational insights into nitrate and nitrite levels in Enugu well water. While nitrate concentrations were within WHO safety limits (mean $\text{NO}_3^- = 0.54$ mmol/L), nitrite levels (mean $\text{NO}_2^- = 0.24$ mmol/L) significantly exceeded permissible values. This pattern, coupled with the inverse relationship between NO_3^- and NO_2^- concentrations, was attributed to microbial reduction processes commonly linked to fecal contamination and anaerobic conditions in regolith aquifers.

In another study, Aniebone (2013) assessed the hydrogeochemistry of groundwater across ten locations in Enugu. Although most major ion concentrations including nitrate were within acceptable limits, all samples tested positive for *Escherichia coli* and total bacterial count, underscoring microbial pollution likely stemming from improper waste disposal and latrine seepage. This aligns with findings from Ezeh and Anike (2009), who reported seasonally variable water quality in Enugu's regolith aquifers, ranging from strongly acidic to slightly alkaline, and from soft to moderately hard. Their study also identified microbial loads capable of mediating redox transformations of nitrogen species, highlighting the role of bacteria in shaping the groundwater chemistry. The influence of industrial and mining activities on nitrogen cycling has also been documented. Egboka and Uma (1985) investigated acid mine drainage from coal mines in Enugu and reported the discharge of approximately 18.1 million liters of acidic effluent into the Ekulu River daily. This effluent, rich in iron and sulfates, facilitates oxidative and reductive reactions in the subsurface, potentially altering the speciation and mobility of nitrogen compounds. This geogenic influence, when coupled with microbial activity, contributes to the complexity of nitrogen behavior in regolith aquifers.

Further insights into groundwater potential and geological control were provided by Ogbodo and Eze (2024) through an integrated geological and geophysical study. Their work revealed the dominance of porous sandy horizons and clayey layers, which modulate groundwater flow and microbial niche stability. These lithological variations have direct implications for the retention or attenuation of nitrates and microbial communities involved in denitrification and ammonification. Finally, Nwanchukwu (2018) emphasized the impact of localized contamination particularly from petroleum hydrocarbons and metal-rich runoff on water chemistry. The study identified Na-Cl water types and elevated magnesium and manganese levels, which can suppress or stimulate specific microbial processes like nitrification, depending on redox conditions.

Location of the Study Area

Enugu, the key city of south-eastern Nigeria, falls between latitudes 6°22'N and 6°39'N, and longitudes 7°26'E and 7°40'E. It covers approximately 79 square kilometers (Egboka *et al.*, 1989). As the administrative and economic hub of Enugu State, the city is rich in history that has closely been associated with its coal deposits, which have been the stimulus for motivation in its development. Enugu is nestled within the Anambra Basin, a significant sedimentary basin in Nigeria. The city's landscape has been shaped by a blend of geological processes and human activities over time.

Geologic Settings and Hydrogeology of the Study Area

The study area, Enugu, lies in the Anambra Basin of south-eastern Nigeria and has an intensive geological past dominated by Cretaceous sedimentary rocks. The basin rests upon sequences of siltstones, sandstones, shales, and coal seams, significant amongst which are the Enugu Shale, Mamu Formation, and Ajali Sandstone that are great aquifer units. Hydrogeologically, Enugu aquifers are predominantly unconfined to semi-confined, with groundwater flow governed by topography and the permeability of the geologic units. Recharge is primarily by rain, with infiltration rates varying due to differences in soil cover and vegetation. The Ajali Sandstone, highly porous and permeable, is a significant source of groundwater in the region. The aquifers are threatened by contamination from urbanization, agriculture, and poor waste disposal, and thus an overall knowledge of the hydrogeological and microbial processes is critical for sustainable water resource management. Combined geology and geophysical mapping techniques have been used in recent studies to assess groundwater potential in Enugu State. For instance, Ezeh (2012) conducted hydrogeophysical surveys to delineate zones of possible groundwater, which emphasized the significance of formations like the Ajali Sandstone in groundwater potential. Okechukwu and Ikenna (2024) also evaluated the quality of groundwater in Enugu Metropolis, emphasizing the significance of continued monitoring to fight against contamination risks associated with urbanization and industrial processes.

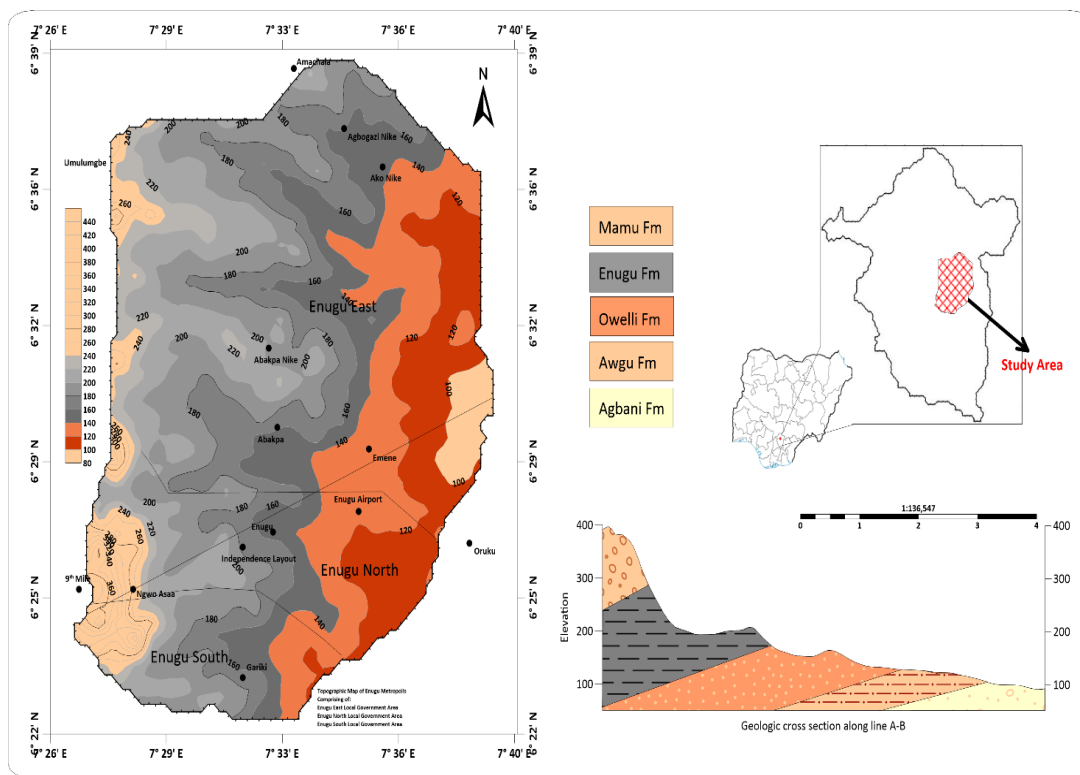


Figure 1: Geologic map of the study area

MATERIALS AND METHODS

Sample Collection

Water and sediment samples of 24 in number from different locations namely; New-artisan, 9th mile, ologo, Centenary, Trans-Ekulu and Amechi geographical areas were collected using sterile water bottle. The samples were sent to the laboratory and stored under cool temperature in a refrigerator.

Assay method

pH test

The pH of water samples was measured potentiometrically using a pH meter equipped with a temperature-compensating device, accurate to 0.1 pH units, and a range of 0 to 14, along with a reference electrode with a quartz liquid junction and a glass electrode. The electrodes were maintained according to the manufacturer's instructions, ensuring proper wetting and electrolyte levels. Buffer solutions were prepared, including potassium hydrogen phthalate (pH 4.00), phosphate buffer (pH 6.86), and borax buffer (pH 9.18), stored in polyethylene bottles, and replaced every four weeks. The electrodes were standardized using the initial buffer and verified in a second buffer within 2 pH units of the sample's expected pH. For sample measurement, the electrodes were equilibrated

with the sample, and the pH was recorded after ensuring proper stabilization. In poorly buffered solutions, multiple equilibrations were performed before final measurements. The sample was gently stirred during measurement to maintain homogeneity, ensuring accurate and reproducible pH readings.

Eh measurement

Eh values were calculated from the ORP values obtained from the field of the sampled sites using nearest equation.

$$Eh = ORP + E_{ref}$$

where:

Eh is the redox potential relative to the Standard Hydrogen Electrode (SHE) (in volts or millivolts).

ORP is the measured oxidation-reduction potential (in volts or millivolts).

E_{aeon s} is the reference electrode potential (in volts or millivolts).

RESULT AND DISCUSSION

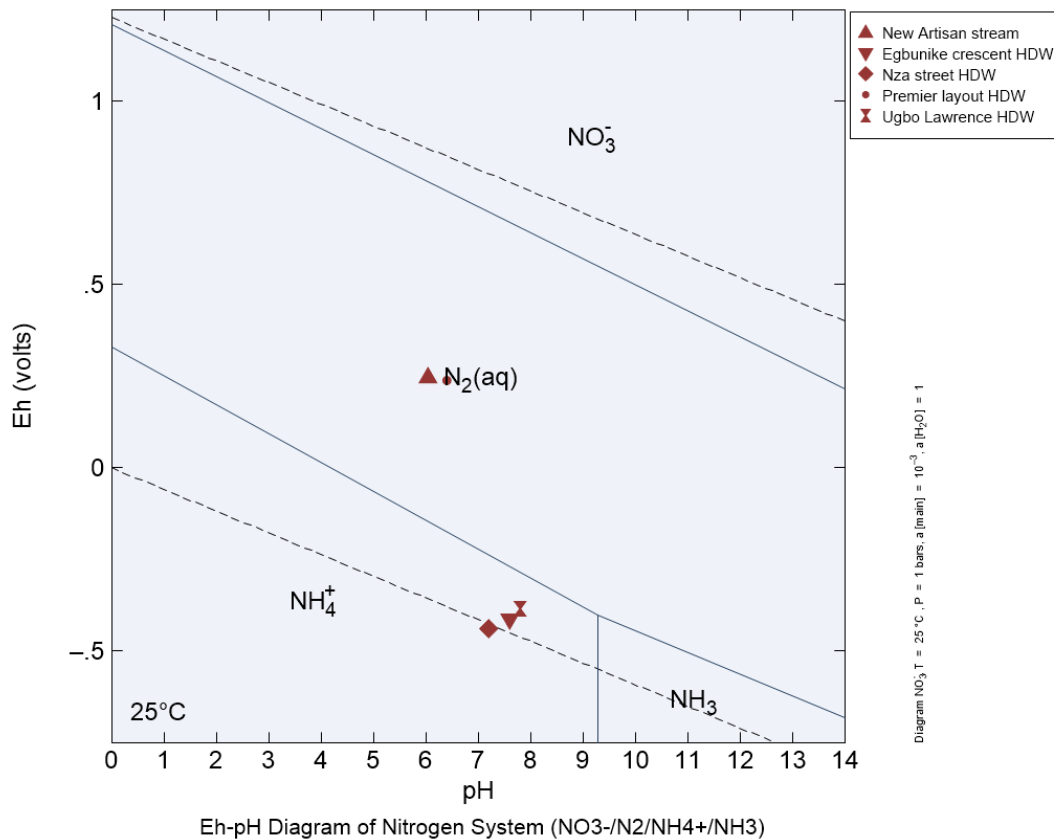


Figure 2: Eh-pH diagram of Nitrogen system in Groundwater

The Eh-pH diagram provides a visual representation of nitrogen speciation under varying redox conditions and pH levels (Figure 2). The plotted points for water samples from New Artisan Stream, Egbunike Crescent HDW, Nza Street HDW, Premier Layout HDW, and Ugbo Lawrence HDW indicate differences in nitrogen transformation pathways influenced by microbial activities. These activities are played by key players that include microbial species which are involved in nitrification, denitrification, and ammonification and in the long run control the nitrogen chemistry in the water bodies.

The data points reveal that New Artisan Stream falls within the $N_2(aq)$ stability field, suggesting active microbial denitrification, where nitrate (NO_3^-) is reduced to nitrogen gas. Denitrifying bacteria such as *Pseudomonas sp.* and *Geobacter sp.* thrive in low oxygen and high organic material conditions, converting nitrate to nitrogen gas, which is subsequently lost to the air. This depletes nitrates from pollution but can result in a loss of nitrogen from the water. In contrast, water samples from Egbunike Crescent HDW, Nza Street HDW, and Ugbo Lawrence HDW fall within the NH_4^+ stability region, indicating reducing conditions that favor ammonification over nitrification. The presence of *Bacillus sp.*, which is accompanied by decomposition of organic matter, facilitates decomposition of nitrogenous organic compounds to ammonium (NH_4^+). This is shown by elevated levels of ammonium in such wells, which reflects minimal microbial oxidation of NH_4^+ to NO_3^- . The presence of ammonium-rich groundwater can indicate sewage contamination or excessive organic matter input, which promotes anaerobic microbial activity.

For Premier Layout HDW, the data point is near the NH_3 boundary, suggesting possible ammonia volatilization at slightly higher pH values. This sample pH (6.85) is higher than New Artisan Stream (6.05); therefore, the slightest increase in pH will push the equilibrium towards ammonia gas (NH_3), causing nitrogen loss from the system. It can be further exacerbated under warm temperatures, once again altering nitrogen availability in the water. The absence of data points in the NO_3^- stability region suggests limited nitrification, a microbial process where ammonium is oxidized to nitrate. This could be due to low oxygen availability in the studied water sources, which hinders the activity of *Nitrosomonas* and *Nitrobacter*, the primary nitrifying bacteria. Moreover, the low redox conditions in water, indicated by microbial occurrence, favor denitrification and ammonification over nitrification. Partial conversion of NH_4^+ to NO_3^- can lead to ammonium accumulation, with additional effects on water chemistry and potential toxicity concerns. Microbial nitrogen cycling has significant implications for water quality. Elevated levels of ammonium are harmful to potable water since they enhance microbial growth and oxygen demand. Excessive denitrification, however, like the one that is experienced at New Artisan Stream, may reduce nitrate contamination but also contribute to nitrogen loss in water bodies to the disadvantage of aquatic life. Excessive denitrification, on the other hand, like that in New Artisan Stream, may reduce nitrate pollution but also cause nitrogen loss in water bodies at the expense of aquatic life. The

balance of such microbial processes is regulated by environmental factors such as oxygen concentrations, organic matter concentrations, and pH, which regulate nitrogen conversion in such water bodies.

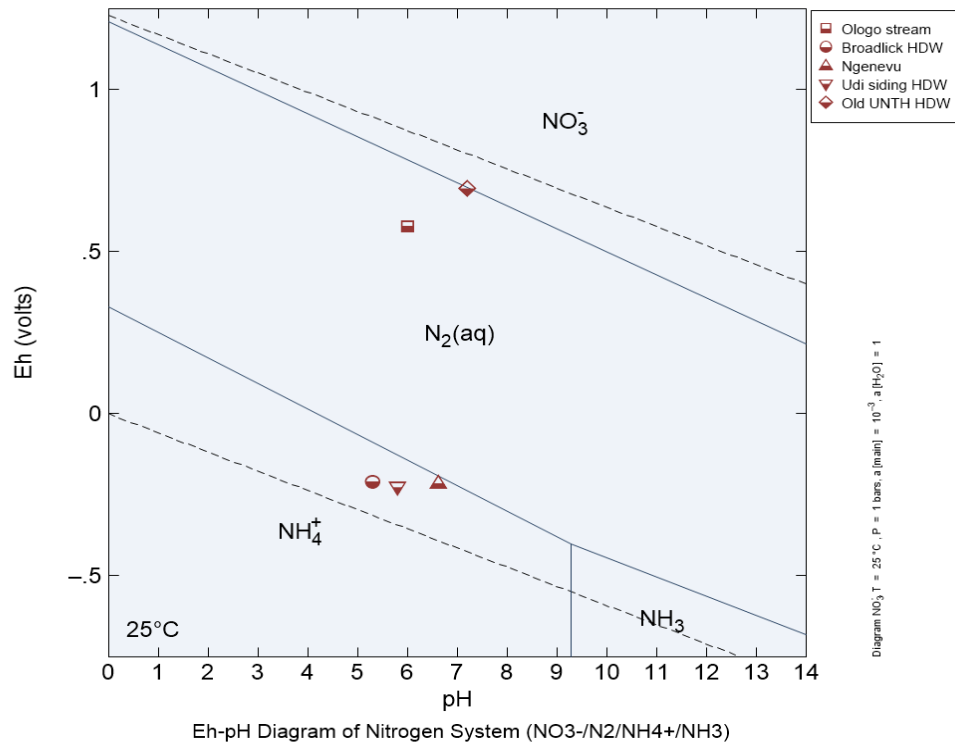


Figure 3: Eh-pH diagram of Nitrogen system in Groundwater

The Eh-pH diagram (Figure 3) of the nitrogen system illustrates how different nitrogen species, including nitrate (NO₃⁻), ammonium (NH₄⁺), and nitrogen gas (N₂), exist under varying redox (Eh) and pH conditions. The distribution of water samples from Ologo Stream, Broadlick HDW, Ngenevu HDW, Udi Siding HDW, and Old UNTH HDW within this system helps explain the microbial and geochemical processes occurring in each location. From the result in fig 3, the Ologo Stream sample is positioned in the nitrate (NO₃⁻) stability region, characterized by an Eh of 0.5 mV and a pH of 7.2. This suggests an oxidizing environment where nitrate is stable, and ammonium oxidation might be occurring. In presence of *Pseudomonas* species in Ologo Stream, which are known for their denitrifying ability, converting nitrate to nitrogen gas under anaerobic or low-oxygen conditions. This suggests that partial denitrification might be occurring, reducing nitrate levels. In contrast, Broadlick HDW, Ngenevu HDW, and Udi Siding HDW exhibit reducing conditions (Eh values from -0.2 to -0.4 mV) and slightly acidic pH of 5.8 to 6.5. These conditions favor ammonium accumulation instead of nitrification and promote sulfate reduction. The Old UNTH HDW sample, positioned near the N₂ stability region, has an Eh of 0.6 mV and an alkaline pH of 8.2. High total alkalinity provides a

buffer that helps maintain a stable pH for microbial activity. Bacteria such as *Bacillus* species, are known for their ability to metabolize nitrogen compounds, possibly playing a role in nitrate transformation. The relationship between redox conditions, pH, and microbial activity is further supported by total solids levels. The total dissolved solids (TDS) and total suspended solids (TSS) values are higher in Broadlick HDW and Udi Siding HDW, which aligns with microbial reduction of Fe^{3+} and Mn and the subsequent mobilization of these metals into solution. The possible presence of *Shewanella* and *Geobacter* supports this, as both bacteria are known for iron and manganese reduction, leading to higher Fe^{3+} and Mn concentrations.

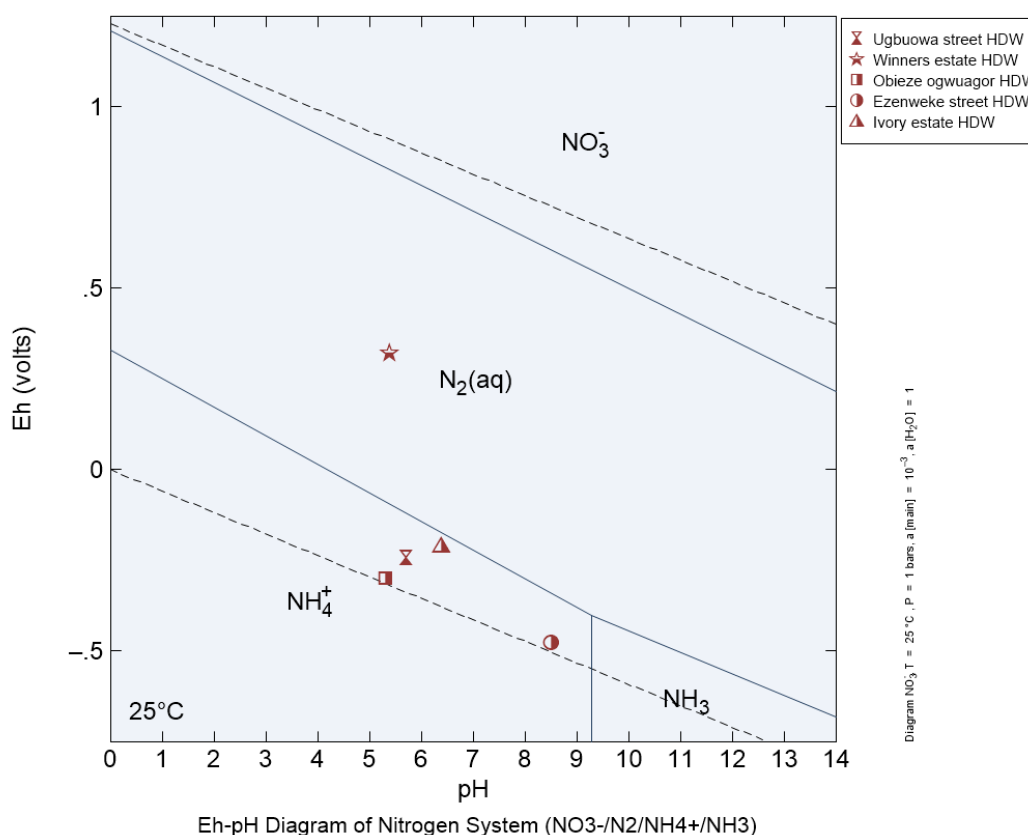


Figure 4: Eh-pH diagram of Nitrogen system in Groundwater

The Eh-pH diagram (Fig 4) for the nitrogen system provides insights into the oxidation-reduction behavior of nitrogen species in the water samples from different locations in the Trans-Ekulu geographical area. The plotted data points indicate the redox potential (Eh) and pH conditions of the water samples, showing the stability regions for nitrate (NO_3^-), molecular nitrogen (N_2), ammonium (NH_4^+), and ammonia (NH_3). The samples generally fall within the $N_2(aq)$ and NH_4^+ stability fields, indicating that nitrogen is predominantly in reduced forms. The trend observed in the diagram suggests that at

higher Eh values (above 0.5 V) and moderate pH conditions (above 6.5), nitrate (NO_3^-) is stable, which is characteristic of oxidizing environments. However, as the pH decreases and Eh drops, nitrate undergoes denitrification, converting into nitrogen gas (N_2) through microbial processes. For example, the water sample from Winners Estate HDW (pH 5.39, Eh 0.322 V) falls within the N_2 stability zone, suggesting active denitrification. Similarly, the Obieze Ogwuagor HDW sample (pH 5.3, Eh -0.302 V) lies closer to the NH_4^+ region, indicating further reduction of nitrogen to ammonium.

At lower Eh values (below 0V), nitrogen reduction proceeds further, leading to the formation of ammonium (NH_4^+). This is evident in the sample from Ugbuowa Street HDW (pH 5.7, Eh -0.244 V), which is positioned near the NH_4^+ stability zone. Such conditions are characteristic of anoxic environments where microbial activity facilitates nitrate reduction. Furthermore, in areas with extremely low Eh values and higher pH (above 8.0), ammonium may convert into ammonia gas (NH_3), as seen in the Ezenweke Street HDW sample (pH 8.5, Eh -0.479 V).

The presence of nitrogen in reduced forms has significant implications for water quality. The presence of accumulated ammonium may point to microbial activity and organic pollution, which is a cause for concern for groundwater contamination. The low Eh values in certain samples point toward limited oxygen supply, which may favor microbial nitrate reduction, thereby causing the accumulation of ammonium. Studies such as those by McMahon and Chapelle (2008) have demonstrated that nitrate reduction is prevalent in anoxic groundwater, supporting the findings in this study.

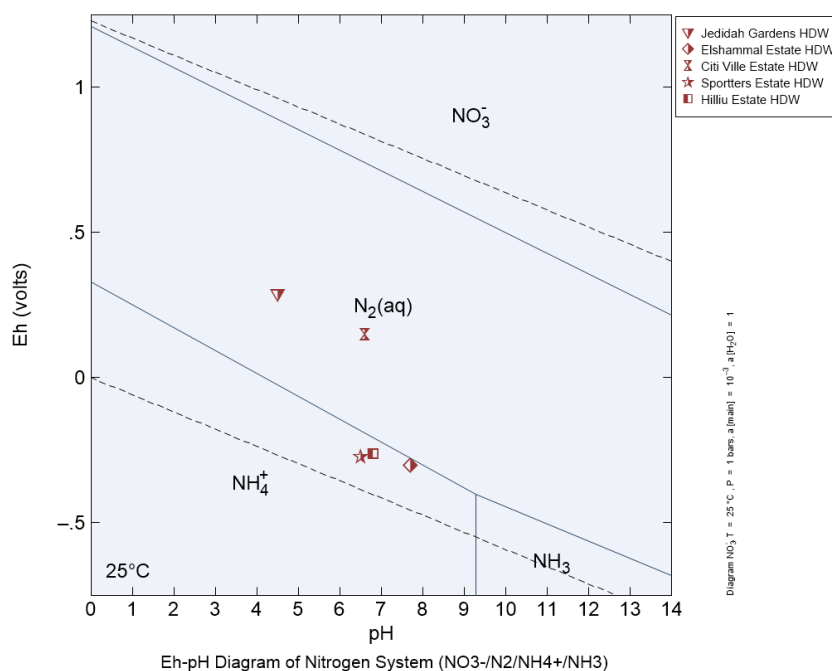


Figure 5: Eh-pH diagram of Nitrogen system in Groundwater at Amechi geographical area

The Eh-pH diagram (Figure 5) of the nitrogen system provides insight into the redox conditions and microbial influences that drive nitrogen speciation in groundwater from the Amechi area. This diagram shows the stability fields for major nitrogen species nitrate (NO_3^-), nitrogen gas (N_2), ammonium (NH_4^+), and ammonia (NH_3) as a function of redox potential (Eh) and pH at 25°C. In this diagram, the water samples from Jedidah Gardens, Elshammal Estate, and Citi Ville Estate cluster within the nitrogen gas (N_2) field, suggesting mildly reducing conditions (Eh between 0 and 0.5 V) and neutral to slightly acidic pH. These conditions are ideal for microbial denitrification, where nitrate (NO_3^-) is reduced to N_2 gas through the action of denitrifying bacteria such as *Pseudomonas*, *Paracoccus*, and *Bacillus* (Knowles, 1982; Tiedje *et al.*, 1982). This transformation implies that nitrate contamination possibly from domestic sewage or agricultural runoff is being naturally attenuated through microbial activity in these groundwater systems.

On the other hand, Sporters Estate and Hilliu Estate HDWs plot further down the Eh scale, settling within or near the ammonium (NH_4^+) field. These readings indicate strongly reducing environments (Eh < 0 V), where oxygen and nitrate have been largely depleted, allowing for the accumulation of reduced nitrogen species like ammonium. This environment supports ammonification, the microbial breakdown of organic nitrogenous matter into NH_4^+ , facilitated by heterotrophic bacteria such as *Clostridium* and *Bacillus* species (Strauss, 1993; Torsvik *et al.*, 2002).

These observations reflect the complex interplay between hydrogeological setting, organic matter availability, and microbial activity. The presence of ammonium in more reduced areas such as Sporters and Hilliu Estates could point to the stagnation of water or limited recharge, which often allows organic-rich conditions to persist. On the other hand, areas like Citi Ville Estate and Jedidah Gardens, which show nitrogen gas dominance, might represent zones of active nitrate reduction, suggesting better circulation and more dynamic redox transitions. The data also imply that nitrification the oxidation of ammonium to nitrate is largely absent, as none of the HDWs fall within the NO_3^- stability field. This may result from low oxygen concentrations, which inhibit the activity of autotrophic nitrifiers such as *Nitrosomonas* and *Nitrobacter* (Prosser, 1989). The consistent absence of nitrate across these wells highlights a naturally reducing aquifer system, likely influenced by high microbial load, warm temperatures, and the presence of electron donors from decaying organic material which are the kind of conditions commonly found in tropical aquifers like those found in southeastern Nigeria (Ezeh *et al.*, 2016; Oke and Opara, 2021).

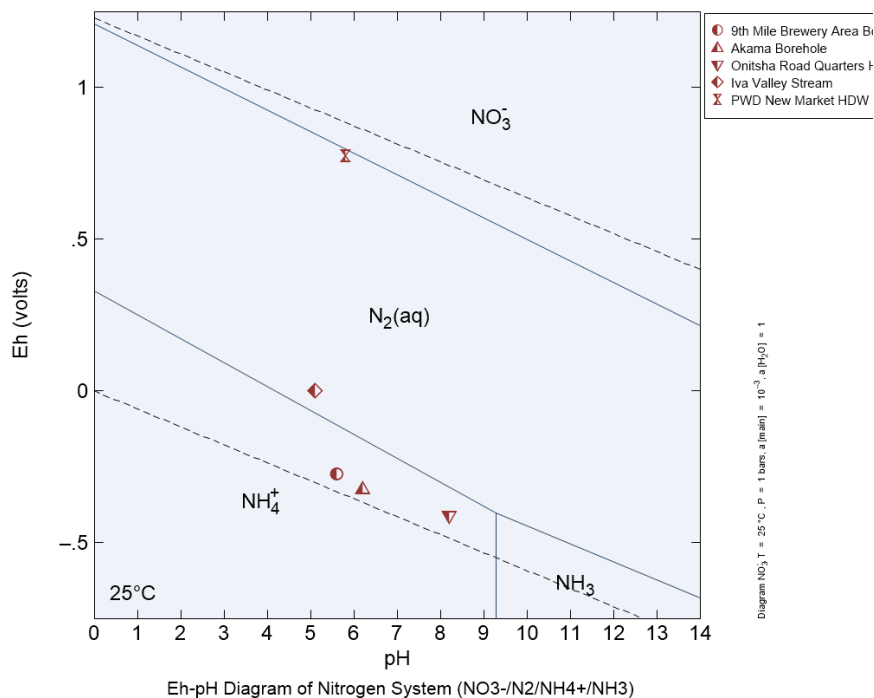


Figure 6: Eh-pH diagram of Nitrogen system in Groundwater

The Eh-pH diagram (Fig 6) of the nitrogen system for selected groundwater sources in 9th mile area in Enugu offers a robust visual interpretation of the geochemical landscape, illustrating the dominant nitrogen species under varying redox and pH conditions. From the plotted groundwater samples 9th Mile Brewery Area, Akama Borehole, Onitsha Road Quarters, Iva Valley Stream, and PWD New Market HDW it is evident that most points fall within zones that favors ammonium (NH_4^+) and nitrogen gas (N_2), with only one site (PWD New Market HDW) situated in the nitrate (NO_3^-) field. These distinctions reflect the influence of microbially mediated nitrogen transformations, which are known to be redox-sensitive (Postma *et al.*, 1991; Rivett *et al.*, 2008).

The presence of NH_4^+ as the dominant nitrogen species at locations like 9th Mile Brewery Area and Onitsha Road Quarters indicates reducing conditions ($\text{Eh} < 0 \text{ V}$), which are favorable for ammonification. This process, also called mineralization, involves the microbial breakdown of organic nitrogen into ammonium and is primarily carried out by heterotrophic bacteria such as *Bacillus* and *Clostridium* spp. (Tiedje *et al.*, 1982; Strauss, 1993). In environments with low oxygen and high organic content, ammonification dominates the nitrogen cycle. Also, *Desulfomicrobium* a sulfate-reducing bacterium identified in similar regolith environments can co-occur in these anoxic zones, consuming sulfate and generating sulfide, which further lowers redox potential and enhances conditions favorable for ammonium stability (Muyzer and Stams, 2008; Oyetibo *et al.*, 2020).

On the other hand, samples from Iva Valley Stream and Akama Borehole cluster near the $N_2(aq)$ field on the diagram, suggesting that denitrification is the dominant microbial process. This pathway involves the stepwise reduction of nitrate to nitrogen gas, usually under suboxic conditions. Denitrifying bacteria such as *Pseudomonas*, *Shewanella*, and *Paracoccus* spp. are known to thrive under these intermediate redox conditions, using nitrate as an alternative terminal electron acceptor when oxygen is limited (Knowles, 1982; Zumft, 1997). The positioning of these sites within the N_2 stability field, combined with moderate Eh values and circumneutral pH, supports the notion that active denitrification is naturally attenuating nitrate levels in the groundwater. This process is critical for protecting water quality, especially in regions prone to nitrate contamination from anthropogenic sources. In contrast, the PWD New Market HDW site falls within the oxidizing NO_3^- field ($Eh > 0.8$ V), suggesting limited denitrification and possible active nitrification. Nitrification, an aerobic two-step process involving the oxidation of ammonium to nitrate, is typically mediated by autotrophic bacteria such as *Nitrosomonas* and *Nitrobacter* spp. (Prosser, 1989; Ward, 2013). The occurrence of nitrate at this site may be attributed to rapid recharge with oxygenated water or exposure to nitrate-rich surface inputs such as fertilizer leachate or wastewater. Similar observations have been made in urban groundwater systems where shallow depths and minimal subsurface attenuation promote nitrate persistence (Oke and Opara, 2021). Taken together, the spatial distribution of nitrogen species across these locations reveals how microbial activity strongly influenced by Eh and pH governs nitrogen transformations in Enugu’s regolith aquifers. These aquifers, often composed of highly weathered lateritic materials, provide diverse redox niches that facilitate microbially driven biogeochemical processes (Ezeh *et al.*, 2016).

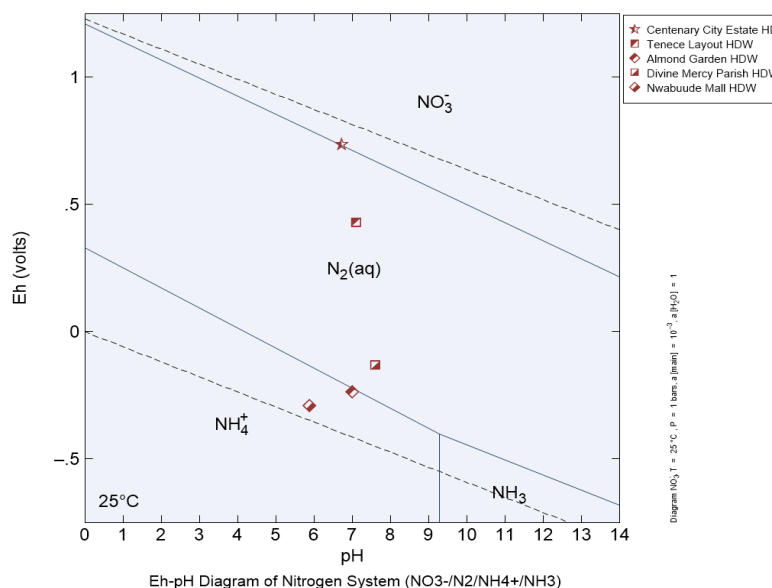


Figure 7: Eh-pH diagram of Nitrogen system in Groundwater

The Eh-pH diagram (Figure 7) for the nitrogen system provides critical insight into the dominant forms of nitrogen present in groundwater within the Centenary area of Enugu. The diagram plots the redox potential (Eh) against pH, identifying stability fields for various nitrogen species namely nitrate (NO_3^-), nitrogen gas (N_2), ammonium (NH_4^+), and ammonia (NH_3). Five hand-dug wells (HDWs) are represented: Centenary City Estate, Tenec Layout, Almond Garden, Divine Mercy Parish, and Nwabuude Mall. These points occupy distinct regions on the diagram, reflecting varied subsurface redox conditions and pH levels.

Notably, Centenary City Estate HDW (marked with a star) falls within the nitrate (NO_3^-) stability field, suggesting that this groundwater is relatively oxidizing ($E_h > 0.7$ V) and supports nitrification, the microbial conversion of ammonium to nitrate. Nitrifying bacteria such as *Nitrosomonas* and *Nitrobacter* thrive in such environments, utilizing oxygen as a terminal electron acceptor (Ward, 2013; Prosser, 1989). The presence of NO_3^- could be indicative of surface contamination from fertilizers or domestic wastewater, especially given the shallow nature of most HDWs and potential for infiltration in urban landscapes (Rivett *et al.*, 2008; Oke and Opara, 2021).

The other four sites Tenec Layout, Almond Garden, Divine Mercy Parish, and Nwabuude Mall HDWs are situated within or near the nitrogen gas (N_2) and ammonium (NH_4^+) fields, revealing more reducing conditions ($E_h \approx 0$ to -0.2 V) with slightly acidic to neutral pH. This chemical environment supports denitrification and ammonification. Denitrification is a microbial process that reduces nitrate to N_2 gas, typically carried out by facultative anaerobes such as *Pseudomonas*, *Paracoccus*, and *Shewanella* species in low-oxygen conditions (Knowles, 1982; Zumft, 1997). The proximity of some data points in places such as Nwabuude Mall and Divine Mercy Parish to the NH_4^+ field also suggests that ammonification the microbial breakdown of organic matter into ammonium is occurring, likely due to the activity of heterotrophs like *Bacillus* and *Clostridium* (Tiedje *et al.*, 1982; Strauss, 1993).

The presence of ammonium and nitrogen gas rather than nitrate in most locations implies a natural attenuation of nitrate via microbial reduction or restricted oxygen availability in the subsurface. This is particularly important in tropical regolith aquifers like those in Enugu, where organic matter and microbial activity can lead to rapid redox shifts (Ezeh *et al.*, 2016). Moreover, sulfate-reducing bacteria such as *Desulfomicrobium*, which have been previously reported in the Enugu groundwater system, may also contribute to these reducing conditions, further suppressing nitrate stability and supporting ammonium retention (Muyzer and Stams, 2008; Oyetibo *et al.*, 2020).

CONCLUSION AND RECOMMENDATION

The study of nitrogen systems in the regolith aquifer in Enugu shows how microbial processes and nitrogen species interact to affect groundwater quality. Nitrification, denitrification, and ammonification are influenced by the aquifer's redox conditions, leading to variations in nitrogen levels across different sites. To better manage nitrogen contamination, it's recommended that monitoring continues, with a focus on sustainable agricultural and waste disposal practices. Public awareness and stronger land-use policies are key to protecting groundwater, and regular water quality checks should be conducted to track changes in nitrogen dynamics.

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