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Redox processes in regolith aquifers at Enugu

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Abstract

Redox reactions are the predominant controlling factors of groundwater chemistry in Enugu, Nigeria. Nitrogen, carbon, sulfur, and iron species stability at different sites is explored through Eh-pH diagrams focusing on how microbial activity influences water quality. A total of 20 samples were sampled. Eh and pH were measured then the results were used to plot an Eh-pH graph using geochemist work bench. From the result nitrate stability occurs under oxidizing conditions (Eh ≥ 0.5 V) like Gariki Stream and Precious Street HDW, where nitrification is carried out by Pseudomonas sp. Denitrification by Bacillus sp. and Geobacter sp. occurs under reducing conditions (Eh ≈ 0.1–0.2 V) in Promiseland, Oriental Estate, and Ihe Street HDW. Very reducing sites like Akwuke HDW and areas of Agbani prefer the accumulation of ammonium, implying dissimilatory reduction of nitrate. Carbon speciation is redox-dependent. Eh-rich sites favor CO_2 stability, and moderately reducing conditions favor bicarbonate dominance. Methanogenesis is observed in Akwuke HDW and Agbani-area wells, favored by Methanobacterium sp. Sulfur transformations reflect redox transitions. Bricks Estate HDW and Gariki Stream oxidizing conditions favor the stability of sulfate, and EmekaOgbodo HDW and Akwuke reducing conditions favor sulfate reduction to hydrogen sulfide. Iron speciation also follows in parallel. Oxidized ferric iron (Fe^{3+}) dominates high-Eh zones, precipitating as hematite, while low redox conditions in Akwuke HDW and Agbani-area wells allow ferrous iron (Fe^{2+}) precipitation. These findings demonstrate the deep relationship between redox conditions, microbial activity, and groundwater chemistry. The understanding of these relationships is crucial for controlling water quality and ensuring safe use of groundwater in Enugu.

Keywords: Redox reactions, Groundwater chemistry, Microbial activity, Eh-pH diagrams, Water quality.

1.0 Introduction

Regolith aquifers, made up of weathered soil and rock layers, are critical for storage and transmission of groundwater. Aquifers act as vital reservoirs, supplying water for drinking, irrigation, and industrial purposes where surface water resources are scarce (Taylor and Howard, 2000). Permeability and porosity within the regolith determine groundwater movement and quality and provide control over recharge and overall availability of water (Chilton and Foster, 1995). In addition, the contact with groundwater and the organic and mineral fractions of the regolith define its chemical character, e.g., pH, redox potential, and ionic concentrations (Appelo and Postma, 2005). Enugu, in southeastern Nigeria, is geologically complex with a dominant sedimentary formation. The region is part of the Anambra Basin that comprises lithological units of sandstone, shale, and coal seams (Nwajide, 2013). Above the formations lies a weathered regolith that is a dominant aquifer system. Enugu's hydrogeological characteristics are affected by the seasonal rainfall regimes that recharge aquifers, as well as human activities capable of interfering with groundwater flow (Egboka*et al*., 1989). Enugu's regolith aquifers contribute significantly to water supply, particularly for societies that rely on them due to unreliable or polluted surface water resources. Its heterogeneous mineral composition plays a significant role in determining groundwater chemistry, and hence, it is interesting to study the redox reactions of the regolith to understand water quality processes (Umeji and Nwachukwu, 1996). Redox reactions, involving electron transfer during chemical reactions, control the geochemical evolution of groundwater systems. Redox reactions affect the speciation and transport characteristics of key elements like iron, manganese, nitrogen, and sulfur, all of which have the potential to influence water quality and ecosystem health (Stumm and Morgan, 2012). In regolith aquifers, microbial processes and interactions with organic matter generally control redox reactions, producing a dynamic chemical environment (Lovley, 1991). In Enugu, where groundwater is a valuable resource, knowledge of redox processes is significant in evaluating contamination risk, e.g., mobilization of trace metals or persistence of nitrate pollution. In addition, redox reactions may influence mineral solubility, possibly affecting aquifer parameters and water composition in the long term (Langmuir, 1997). Investigation into these processes contributes significantly to gaining an understanding of groundwater sustainability as well as evolving strategies for sustaining water quality amidst increasing demand and environmental modification.

1.1 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.

1.2 Physiography, Drainage, Vegetation, and Climate

The physiography of Enugu is characterized by undulating valleys and hills, with elevations ranging from 200 m to 300 m above sea level. Topography plays an important role in determining surface and subsurface water movement, vegetation cover, and soil types. The drainage network in Enugu is dendritic with many streams and rivers that drain mainly because of the regional slope. These water bodies replenish aquifers, especially during the rainy season. Among the prominent rivers in the area, the Ekulu River stands out as one of the principal sources of water for the city, playing a crucial role in the city's water supply. The vegetation of Enugu falls within the tropical rainforest belt, but as a result of human actions like urbanization and agriculture, deforestation has been widespread. The landscape now comprises secondary forest, grassland, and cultivated land. The climate is tropical with distinct wet and dry season. The rainfalls vary from 1500 mm to 2000 mm per year, and the wet season is from April to October. The temperatures are warm overall, varying between 25°C and 30°C, and there are high humidity levels all year round.

1.3 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.

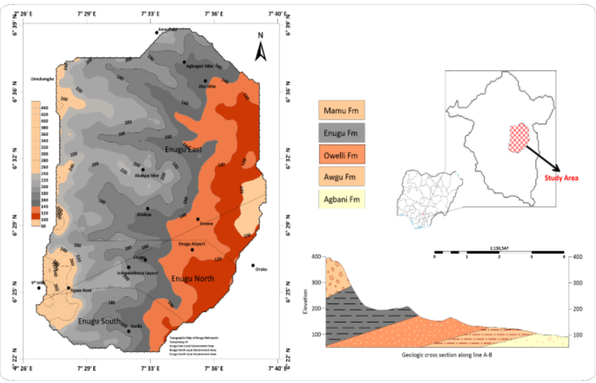

Figure 1.1: Geologic map of the study area

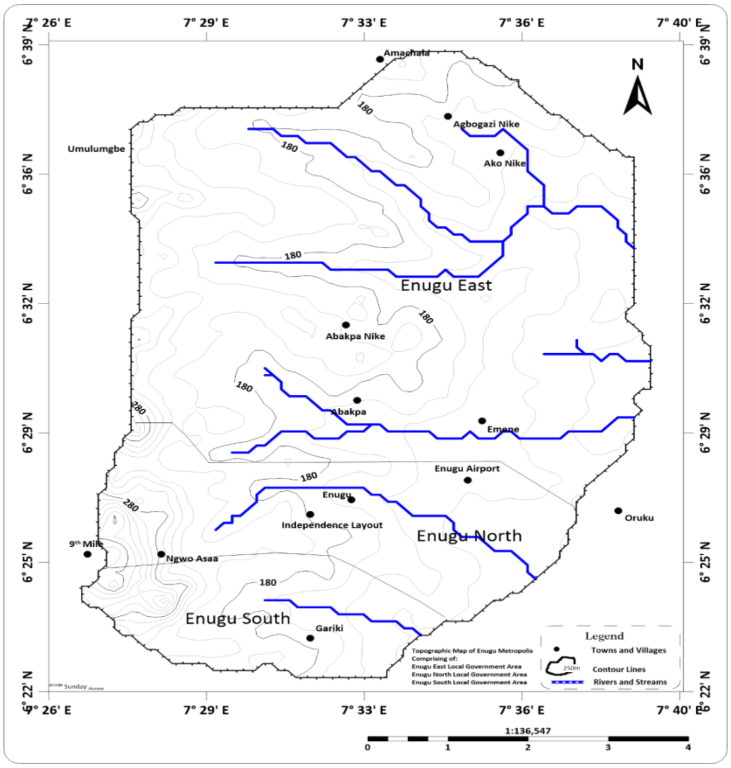

Figure 1.2: Drainage pattern of the study area

2.1 MATERIALS AND METHODS

2.2 Sample Collection:

Water and sediment samples of 20 in numberfrom different locations namely; Emene Water, Ugwuaji Water, Garriki Stream, Agbani Road, were collected using sterile water bottle. The samples were sent to the laboratory and stored under cool temperature in a refrigerator.

2.3 Assay method

2.3.1 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.

2.3.2 Eh measurement

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

Eh=ORP+Eref

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).

$\mathbf{E_{aeons}}$ is the reference electrode potential (in volts or millivolts).

RESULTS

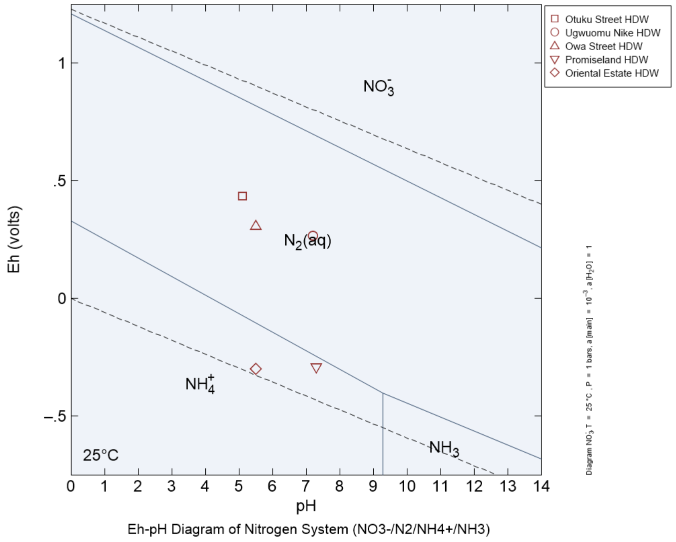

Figure 3.1: Eh-pH diagram of Nitrogen Speciation in Groundwater

The Eh-pH diagram (Fig 1) of the nitrogen system presents the effect of redox conditions on nitrogen speciation in groundwater samples. The fluctuation in the data points for Otuku Street HDW (Eh = 0.432 V), Ugwuomu Nike HDW (Eh = 0.318 V), Owa Street HDW (Eh = 0.275 mV), Promiseland HDW (Eh = -0.292 V), and Oriental Estate HDW (Eh = -0.302 V) between reducing and oxidizing conditions demonstrates oscillations typical of whether nitrate, dinitrogen gas, or ammonium prevails. Promiseland HDW and Oriental Estate HDW have lower Eh values (-0.292 V and -0.302 V, respectively), which signify reducing conditions favoring the reduction of nitrate. These conditions are where *Geobacter* and *Shewanella*, which are nitrate-reducing as well as iron-reducing bacteria, thrive. Under such conditions, the nitrate (NO_3^-) becomes reduced to nitrite (NO_2^-) and further to dinitrogen gas (N_2) or ammonium (NH_4^+). This is because the ammonium concentrations (4.6 mg/L and 5.2 mg/L, respectively) are higher as measured and indicates that at least part of the nitrate is going directly into forming ammonium rather than being lost as nitrogen gas. Otuku Street HDW (0.432 V), Ugwuomu Nike HDW (0.318 V), and Owa Street HDW (0.275 V), however, all have higher Eh values, which are indicative of more oxidative conditions where the major process occurring is nitrification.

The occurrence of *Bacillus* and *Pseudomonas,* the nitrification-performing microorganisms, corroborates this fact. In this process, ammonium (NH_4^+) is oxidized first to nitrite (NO_2^-) and subsequently to nitrate (NO_3^-), and its accumulation is stopped in groundwater. The pH effect is also manifest. The relatively more neutral pH values at Otuku Street HDW (7.1) and Ugwuomu Nike HDW (6.9) favor nitrate stability, while the slightly depressed pH at Promiseland HDW (6.2) and Oriental Estate HDW (6.1) favors ammonium retention under reducing conditions. The microbial communities in these places actively facilitate these conversions, with redox balance being maintained.

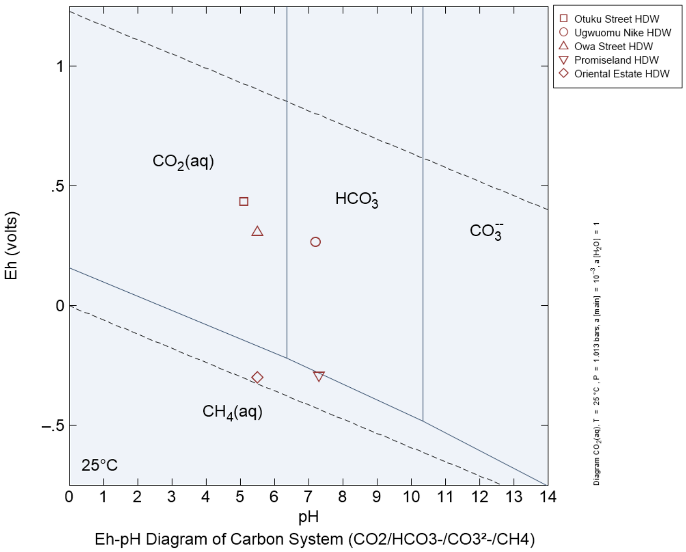

Figure 3.2: Eh-pH diagram of carbon Speciation in Groundwater

The carbon system Eh-pH diagram illustrates how redox and pH affect carbon speciation in the groundwaters (Fig 2). The Otuku Street HDW readings (Eh = 0.48 V, pH = 6.3), Ugwuomu Nike HDW readings (Eh = 0.42 V, pH = 6.8), Owa Street HDW readings (Eh = 0.39 V, pH = 7.2), Promiseland HDW readings (Eh = -0.31 V, pH = 6.5), and Oriental Estate HDW readings (Eh = -0.35 V, pH = 6.1) indicate the differences in prevalent carbon species under different conditions. Otuku Street HDW, Ugwuomu Nike HDW, and Owa Street HDW have greater Eh values (0.48 V, 0.42 V, and 0.39 V, respectively) and thus are in the CO_2 (aq) / HCO_3^- stability field. This indicates that bicarbonate (HCO_3^-) is the prevailing species at these weakly oxidizing and approximately near-neutral pH conditions, as would be expected under carbonic acid equilibrium.

However, Promiseland HDW and Oriental Estate HDW are found to possess lower Eh values (-0.31 V and -0.35 V, respectively), which position them closer towards the CH_4 (aq) field. This reflects heavily reducing conditions under which microbial methanogenesis could be taking place to generate methane (CH_4). The occurrence of *Geobacter* and *Shewanella*, bacteria that reduce iron and nitrate, indicates this trend since both the bacteria also allow for organic carbon breakdown under anaerobic conditions. The pH effect is reflected in the distribution of carbonate species. Otuku Street HDW and Ugwuomu Nike HDW, with their close-to-neutral pH (6.3–6.8), prefer the stability of bicarbonate, whereas Promiseland HDW and Oriental Estate HDW, with their slightly lower pH (6.1–6.5), prefer methane generation under reducing conditions. Microbially driven redox reactions in such settings are of paramount relevance to regulating the conversion of carbon.

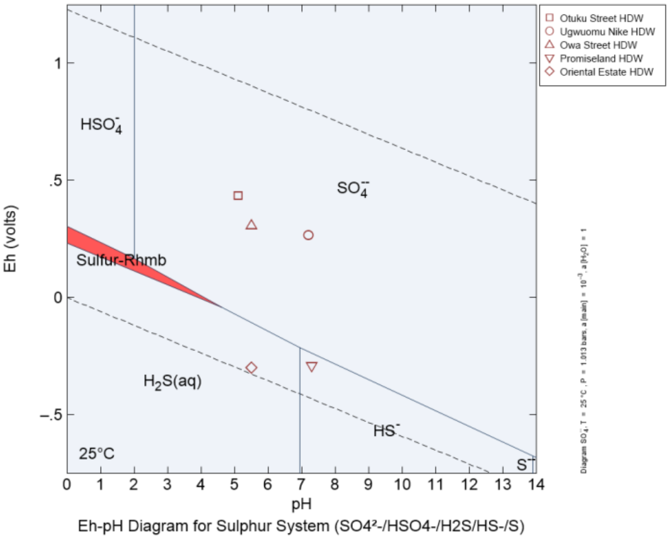

Figure 3.3: Eh-pH diagram of sulphur Speciation in Groundwater

The Eh-pH diagram (fig 3) for the sulfur system ($SO_4^{2-}/HSO_4^-/H_2S/HS^-/S$) at 25°C illustrates the redox stability fields of sulfur species in the water samples collected from various locations in the Emene geographical area. These locations include Otuku Street HDW, Ugwuomu Nike HDW, Owa Street HDW, Promiseland HDW, and Oriental Estate HDW. The plotted data points indicate varying redox conditions across these sites, with some samples positioned in the oxidized sulfate (SO_4^{2-}) stability region, while others are closer to the elemental sulfur and sulfide (H_2S) boundary. The microbial analysis shows the presence of sulfate-reducing bacteria, particularly *Desulfomicrobium*, which aligns with the lower Eh conditions, observed in some locations, suggesting active sulfate reduction. This microbial-driven process influences sulfur speciation and, consequently, the overall water chemistry of the sampled wells.

The trends observed in the Eh-pH diagram reflect the varying redox environments across the sample locations. Higher Eh values (>0.5 V) at near-neutral pH, as seen in Otuku Street HDW and Ugwuomu Nike HDW, indicate oxidizing conditions where sulfate (SO_4^{2-}) remains stable with minimal microbial reduction. This suggests that these locations experience limited sulfate-reducing bacterial activity, preserving the oxidized form of sulfur. In contrast, Owa Street HDW is in a moderate Eh range (0 to 0.5 V), suggesting a transitional redox environment where sulfate reduction may be occurring at a slower rate, and leading to the potential formation of elemental sulfur. The most reduced conditions (Eh < 0 V) are observed in Promiseland HDW and Oriental Estate HDW, where the plotted points lie near the H_2S (aq) and HS^- stability fields. This indicates active sulfate reduction, which is with the aid of *Desulfomicrobium*. The production of sulfide species under these conditions can have significant implications for water quality, including the formation of hydrogen sulfide gas, which is known for its unpleasant odor and corrosive properties (Postgate, 1984).

The implications of these findings are critical in understanding the biogeochemical processes affecting groundwater quality in Emene. In locations where sulfate remains stable under high Eh conditions, water quality is less likely to be impacted by microbial sulfate reduction. However, in areas where sulfate is being reduced to sulfide, such as Promiseland HDW and Oriental Estate HDW, water quality may be compromised due to the accumulation of hydrogen sulfide. This can lead to issues such as corrosion of plumbing materials, increased acidity, and potential mobilization of toxic metals through sulfide complexation (Chapelle, 2001). The microbial activity observed in these wells highlights the role of sulfate-reducing bacteria in altering water chemistry, necessitating continuous monitoring and possible remediation strategies to manage sulfide-related contamination.

When compared with similar studies in other regions, the redox trends observed in Emene are consistent with those found in sulfate-reducing environments within shallow aquifers. For example, research on groundwater chemistry in mining-impacted areas has shown that low Eh conditions favor the microbial reduction of sulfate to hydrogen sulfide, leading to acidification and metal dissolution (Berner, 1981). Similar findings have been reported in industrial and wastewater-impacted groundwater systems, where high sulfate concentrations support the proliferation of sulfate-reducing bacteria, ultimately affecting water quality and infrastructure (Muyzer andStams, 2008). Compared to previous studies on groundwater in the Ajali River/9th Mile region, where iron redox cycling was the dominant process, the Emene area exhibits stronger sulfate-driven biogeochemical alterations, emphasizing the diverse microbial and chemical processes influencing groundwater across different regions.

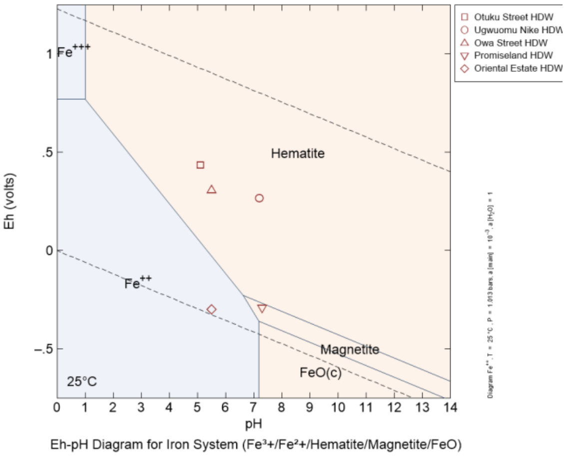

Figure 3.4: Eh-pH diagram of Iron Speciation in Groundwater

The Eh-pH diagram for the iron system (Fe^{3+}/Fe^{2+}/Hematite/Magnetite/FeO) at 25°C provides insight into the redox stability of iron species in groundwater samples from various locations, including Otuku Street HDW, Ugwuomu Nike HDW, Owa Street HDW, Promiseland HDW, and Oriental Estate HDW. The plotted data points reveal that most samples fall within the hematite (Fe_2O_3) stability field, indicating oxidizing conditions, while some locations, particularly Promiseland HDW and Oriental Estate HDW, show lower Eh values, placing them closer to the Fe^{2+} stability region. This suggests variations in redox potential across the study area, potentially driven by microbial activity and geochemical interactions (Stummand Morgan, 1996).

The observed trends suggest that groundwater in Otuku Street HDW, Ugwuomu Nike HDW, and Owa Street HDW maintains relatively high Eh values (>0.3 V), favoring the persistence of ferric iron (Fe^{3+}) in the form of hematite. This indicates oxidative conditions with minimal reduction processes. Conversely, the lower Eh values observed in Promiseland HDW and Oriental Estate HDW suggest the presence of more reducing conditions, potentially supporting the microbial reduction of Fe^{3+} to Fe^{2+}, a process commonly facilitated by iron-reducing bacteria such as *Geobacter* and *Shewanella*

(Lovley*et al*., 2004). The transition to magnetite and FeO stability fields in these locations suggests partial reduction of iron oxides, a phenomenon that can influence metal mobility and water quality.

The implications of these findings are significant for groundwater chemistry and quality. In oxidizing environments, iron remains in its less soluble Fe^{3+} form, limiting its concentration in water. However, in reducing environments, Fe^{2+} becomes more soluble and mobile, potentially leading to elevated iron concentrations, which can affect taste, staining, and infrastructural corrosion (Chapelle, 2001). Furthermore, the microbial reduction of Fe^{3+} to Fe^{2+} is often associated with the co-mobilization of trace metals, posing potential health risks. The presence of reduced iron in Promiseland HDW and Oriental Estate HDW suggests that groundwater in these areas may require treatment to mitigate excessive iron levels and associated contamination risks.

When compared to other studies, these findings align with documented trends in shallow aquifers experiencing iron cycling. For example, research on aquifer systems in the Niger Delta has shown that microbial iron reduction plays a key role in water chemistry, especially in low-oxygen environments where Fe^{2+} accumulates (Emenike*et al*., 2020). Similarly, studies in industrially impacted groundwater have demonstrated that redox fluctuations drive iron mobilization and secondary mineral formation, influencing water usability (Cornell andSchwertmann, 2003). Compared to the sulfur system observed in the previous diagram, the iron system in Emene displays a more distinct redox gradient, with hematite stability dominating in oxidized regions and Fe^{2+}appearing under reducing conditions.

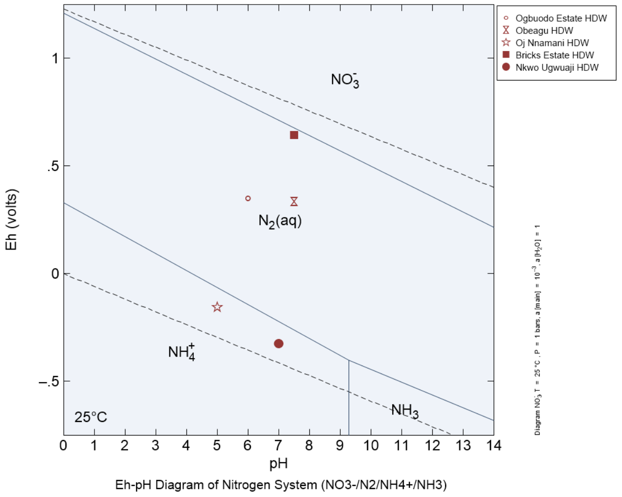

Figure 3.5: Eh-pH diagram of Nitrogen Speciation in Groundwater

The Eh-pH diagram for the nitrogen system ($NO_3^-/N_2/NH_4^+/NH_3$) at 25°C illustrates the stability fields of nitrogen species under varying redox and pH conditions. The groundwater samples from Ogbuodo Estate HDW, Obeagu HDW, OjNnamani HDW, Bricks Estate HDW, and NkwoUgwuaji HDW are plotted on this diagram, indicating the prevailing redox environment in these locations. The samples exhibit a range of redox potentials, with most falling within the $N_2(aq)$ stability field, suggesting intermediate redox conditions, while a few samples, particularly from NkwoUgwuaji HDW, approach the NH_4^+ stability region, implying a more reducing environment (Stummand Morgan, 1996).

Nitrate (NO_3^-) is stable in highly oxidizing environments, while ammonium (NH_4^+) dominates under reducing conditions. The presence of samples near the N_2 stability field suggests that denitrification may be occurring, a process in which nitrate is reduced to nitrogen gas by microbial activity under suboxic conditions (Rivett*et al*., 2008). This aligns with findings that denitrification is prevalent in aquifers with moderate Eh values, where nitrate serves as an electron acceptor in microbial respiration, leading to the release of dinitrogen gas (Korom, 1992). In contrast, NkwoUgwuaji HDW, which falls closer to the NH_4^+ region, indicates a stronger reducing condition, potentially due to organic matter degradation, which consumes oxygen and drives nitrogen reduction to ammonium (Burgin and Hamilton, 2007).

The geochemical behavior of nitrogen species in groundwater has important implications for water quality. High nitrate concentrations in drinking water are associated with health risks such as methemoglobinemia, making its reduction through microbial processes beneficial in certain settings (Ward *et al*., 2005). However, excessive ammonium accumulation, as suggested by the position of NkwoUgwuaji HDW, can also lead to water quality concerns, as ammonium is a precursor to nitrite, a toxic compound under certain conditions (Bohlke*et al*., 2006). The transition between nitrogen species is influenced by microbial communities, with nitrifying bacteria converting ammonium to nitrate in oxygen-rich conditions, while denitrifiers facilitate nitrate reduction in oxygen-limited environments (Tesoriero*et al*., 2000).

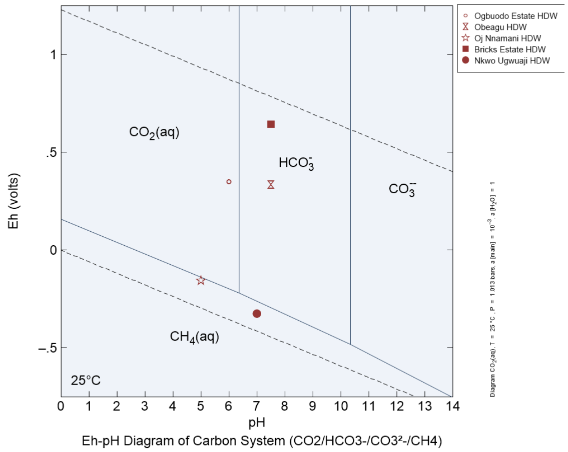

Figure3.6: Eh-pH diagram of carbon system in ground water.

The Eh-pH diagram of the carbon system provides critical insights into the geochemical conditions governing the speciation of carbon in the groundwater samples collected from Ugwuaji (Fig 3.6). The diagram illustrates how different forms of carbon CO_2(aq), HCO_3^-, CO_3^{2-}, and CH_4(aq) exist under varying redox and pH conditions. The plotted points representing the hand-dug wells (HDWs) across different locations suggest that the groundwater chemistry is influenced by local redox reactions, microbial activity, and carbonate equilibrium processes. From the diagram, it is evident that the water samples from different locations fall into distinct regions of the Eh-pH space. Bricks Estate HDW is located in the HCO_3^- stability field, indicating that bicarbonate is the dominant carbonate species in this environment. This suggests that the groundwater at this location has a moderately high Eh value (~0.45 V) and a neutral to slightly alkaline pH (~7.2). The prevalence of bicarbonate implies that the system is oxidizing, with dissolved carbon dioxide buffering the pH. In contrast, the groundwater at Ogbuodo Estate HDW and Obeagu HDW falls closer to the boundary between CO_2(aq) and HCO_3^-, indicating a slightly more acidic environment with moderate Eh values (~0.3–0.5 V). This suggests partial CO_2 dissolution and carbonate buffering, which can be influenced by microbial respiration and organic matter decomposition.

A distinct trend is observed for NkwoUgwuaji HDW and OjNnamani HDW, which fall within or near the CH_4(aq) stability field. These locations exhibit much lower Eh values, with NkwoUgwuaji HDW showing the most reducing conditions. The presence of methane in this system suggests that strong anaerobic processes are at play, likely driven by microbial methanogenesis. The pH remains near-neutral (~6.8), but the low redox potential indicates active organic matter degradation and reduction reactions. The transition of OjNnamani HDW between the HCO_3^- and CH_4(aq) fields suggests a dynamic system where methanogenesis is beginning to take place but has not yet fully displaced other redox processes.

Microbial activity plays a crucial role in shaping these redox conditions, as evidenced by the activities of*Geobacter sp*. and *Desulfomicrobium* sp. in NkwoUgwuaji HDW and OjNnamani HDW strongly supports the reducing conditions observed in the Eh-pH diagram. These microbes are known for their ability to utilize alternative electron acceptors in anaerobic respiration, contributing to methane formation. In contrast, Bricks Estate HDW, where *Shewanella sp.* and *Pseudomonas sp*. are dominant, exhibits more oxidizing conditions, reinforcing the presence of bicarbonate rather than methane. The differences in microbial populations among the sites directly correlate with the observed geochemical variations, demonstrating how biological processes drive shifts in carbon speciation.

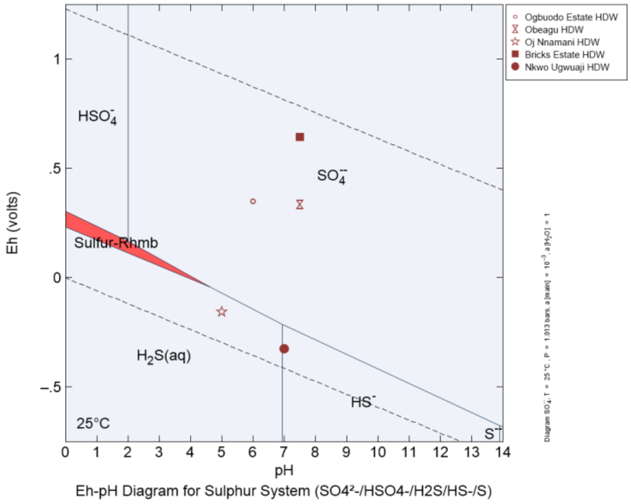

Figure 3.7: Eh-pH diagram of sulfur system in Groundwater

Redox conditions and species of sulfur compounds in the samples gathered from Ugwuaji can be better understood using the Eh-pH diagram for the sulfur system (Fig 7). Under different Eh and pH conditions, this graph marks the stability fields of main sulfur species including sulfate (SO_4^{2-}), bisulfate (HSO_4^-), elemental sulfur (Sulfur-Rhmb), bisulfide (HS^-), and aqueous hydrogen sulfide (H_2S(aq)). The plotted points related to groundwater from several hand-dug wells (HDWs) indicate that redox changes of sulfur compounds are spontaneously taking place in the surroundings.

The picture makes clear that hydroground samples from Ogbuodo Estate HDW, Obeagu HDW, and Bricks Estate HDW fall within the SO_4^{2-} equilibrium line, which suggests oxidizing circumstances with somewhat high Eh values (~0.3–0. 6 V) and neutral to slightly acidic pH (~6. 5–7. 5). The abundance of sulfate implies that sulfur is most likely in its most oxidized form, a level usually linked with well-oxygenated ground water according to Berner (1981). This result corresponds with the existence of sulfur-oxidizing bacteria, such *Pseudomonas sp*., that are known to flourish in conditions with little sulfate reduction (Muyzer and Stams, 2008).

By their proximity to the H_2S(aq) and HS^- stability fields, the groundwater at OjNnamani HDW and NkwoUgwuaji HDW is located in a more limited environment. Present throughout these areas is lower Eh values (-0. 2 to 0. 1 V) and nearly neutral pH (about 6. 8–7.2), implying active sulfate reduction and maybe sulfide formation (Postgate, 1984). The existence of a *Desulfomicrobium* sp. *Geobacter sp*. also supports this understanding since these bacteria under anaerobic circumstances enable sulfate reduction (Rabus*et al*., 2015). The change of OjNnamani HDW from the sulfate region towards the bisulfide (HS^-) boundary indicates a partial reduction process whereby sulfate-reducing bacteria (SRB) are starting to dominate the system but have not yet fully exhausted sulfate. Elemental sulfur, an mid oxidation state between sulfate and sulfide, is shown in the red triangular area marked "Sulfur-Rhmb". None of the sampled groundwater locations fall right into this area, hence elemental sulfur is either not a major steady phase in the system or is transformed quickly by microbial activity. This is in line with research showing that stationary phase is frequently transient in redox-active surroundings (Jørgensen, 1990).

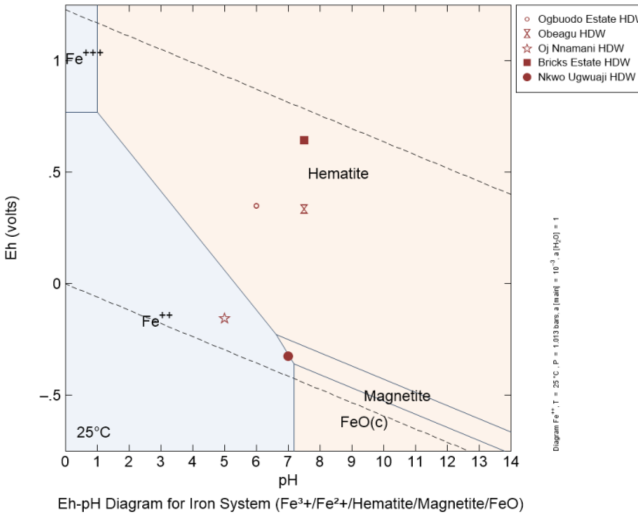

Figure 3.8: Eh-pH diagram of Iron system in Groundwater

The Eh-pH diagram for the iron system (Fe^{3+}/Fe^{2+}/Hematite/Magnetite/FeO) at 25°C illustrates the stability fields of different iron species under varying redox and pH conditions. The groundwater samples from Ogbuodo Estate HDW, Obeagu HDW, OjNnamani HDW, Bricks Estate HDW, and NkwoUgwuaji HDW are plotted on this diagram, showing their distribution within different iron stability regions. The presence of samples within the Fe^{2+} and hematite stability fields indicates variations in oxidation-reduction conditions among the studied water sources (Stummand Morgan, 1996).

Ferric iron (Fe^{3+}) is stable in highly oxidizing environments and precipitates as hematite or other iron oxides, whereas ferrous iron (Fe^{2+}) is more stable in reducing conditions and remains in solution (Cornell andSchwertmann, 2003). Most samples, such as those from Obeagu HDW and Bricks Estate HDW, fall within the hematite stability field, suggesting oxidizing conditions that promote the precipitation of iron oxides. In contrast, samples from OjNnamani HDW and NkwoUgwuaji HDW, which are closer to the Fe^{2+} field, indicate reducing conditions that favor the dissolution of iron into groundwater (AppeloandPostma, 2005).

The presence of Fe^{2+} in groundwater is often associated with anaerobic environments, where microbial reduction of Fe^{3+} occurs due to organic matter degradation. This aligns with studies showing that iron-reducing bacteria facilitate the dissolution of ferric iron minerals under low Eh conditions, releasing Fe^{2+} into solution (Lovley*et al.*, 2004). In contrast, under more oxidizing conditions, iron precipitates as hematite, limiting its mobility and reducing its concentration in groundwater.

Excessive Fe^{2+} in groundwater can cause water quality issues, such as staining, unpleasant taste, and clogging of pipes due to iron precipitation upon exposure to air (Nordstrom, 2011). Moreover, the co-occurrence of iron and manganese in reducing environments can indicate ongoing biogeochemical cycling influenced by microbial activity (Chapelle, 2001). The transition between iron species is critical for understanding aquifer geochemistry and potential treatment strategies, such as aeration or filtration, to remove dissolved iron before it precipitates.

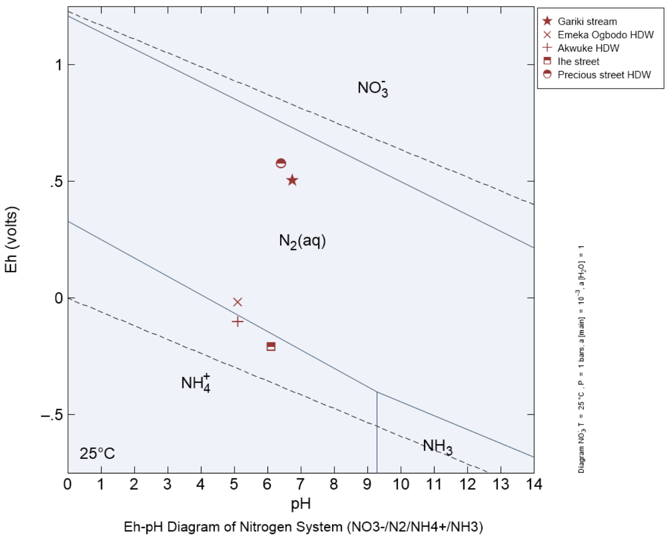

Figure 3.9: Eh-pH diagram of Nitrogen system in Groundwater

The Eh-pH diagram (Fig 3.9) of the nitrogen system provides insight into the redox transformations of nitrogen species across different water sources. The plotted values show how oxidation-reduction conditions influence the stability of nitrate (NO_3^-), nitrogen gas (N_2), ammonium (NH_4^+), and ammonia (NH_3), with microbial activity playing a key role in these processes. At higher Eh values (≥0.5V) observed in Gariki Stream and Precious Street HDW, nitrate remains stable, indicating limited microbial reduction. In the presence of *Pseudomonas sp*. suggests that denitrification is occurring but at a slower rate due to the oxidative conditions.

In Ihe Street HDW (Eh ≈ 0.1V, pH 6.1) and EmekaOgbodo HDW (Eh ≈ 0.2V, pH 5.1), microbial denitrification is more active. Low nitrate levels in samples could indicate partial reduction to nitrogen gas (N_2), likely facilitated by *Pseudomonas sp*. and *Bacillus sp*.. The presence of *Geobacter sp*. in Ihe Street HDW further supports microbial nitrate reduction through dissimilatory pathways.

In Akwuke HDW (Eh ≈ 0V, pH 5.1), conditions become more reductive, which may lead to the conversion of nitrate beyond N_2 to ammonium (NH_4^+) via dissimilatory nitrate reduction to ammonium (DNRA). However, the lack of significant ammonium accumulation could suggest that nitrogen removal is predominantly occurring through denitrification rather than DNRA.

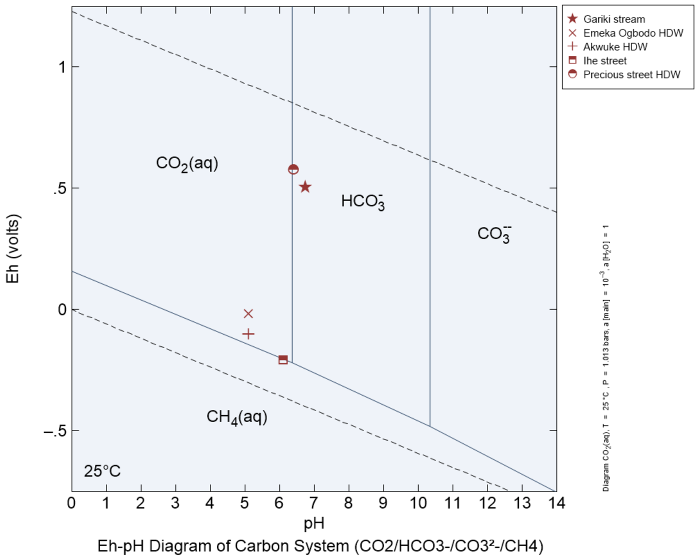

Figure 3.10: Eh-pH diagram of Carbon system in Groundwater

The Eh-pH diagram of the carbon system (Fig 3.10) illustrates the stability of different carbon species carbon dioxide (CO_2), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and methane (CH_4) under varying redox and pH conditions. The placement of sample points from different water sources in the diagram provides insights into the dominant carbon transformations influenced by microbial activity.

At higher Eh values (≥0.5V), as seen in Gariki Stream and Precious Street HDW, CO_2(aq) remains stable. This suggests oxidative conditions where carbonate species do not readily reduce to methane. In such conditions, autotrophic microbes, including *Bacillus sp*. and *Pseudomonas sp*., can facilitate CO_2 conversion to biomass via carbon fixation pathways (Zhao *et al*., 2021).

In Ihe Street HDW (Eh ≈ 0.1V and pH 6.5) and EmekaOgbodo HDW (Eh ≈ 0.2V and pH 5.1), bicarbonate (HCO_3^-) formation dominates. The presence of *Geobacter sp*. in these locations suggests microbial reduction of CO_2 to acetate, a precursor for methanogenesis (Lovley*et al*., 1996).

In Akwuke HDW (Eh ≈ 0V and pH 5.1), reductive conditions favor methanogenesis. The proximity of the sample point to the CH_4(aq) stability field suggests that microbial activity, likely involving methanogens such as Methanobacterium sp., is driving CO_2 reduction to methane. It was observed previous study in this area that dissolved CO_2 concentration is at 13.2mg/L further supports this interpretation, as CO_2 is being consumed in anaerobic microbial processes (Conrad, 2020). The Eh-pH relationships indicate microbial community control over carbon conversions in groundwater systems. Proper Eh conditions favor CO_2 stability and carbonate equilibrium, but poorer Eh conditions cause microbial methanogenesis and CO_2 reduction. These findings are consistent with studies showing that anaerobic conditions increase biogeochemical carbon cycling in subsurface systems (Rothman *et al*., 2022).

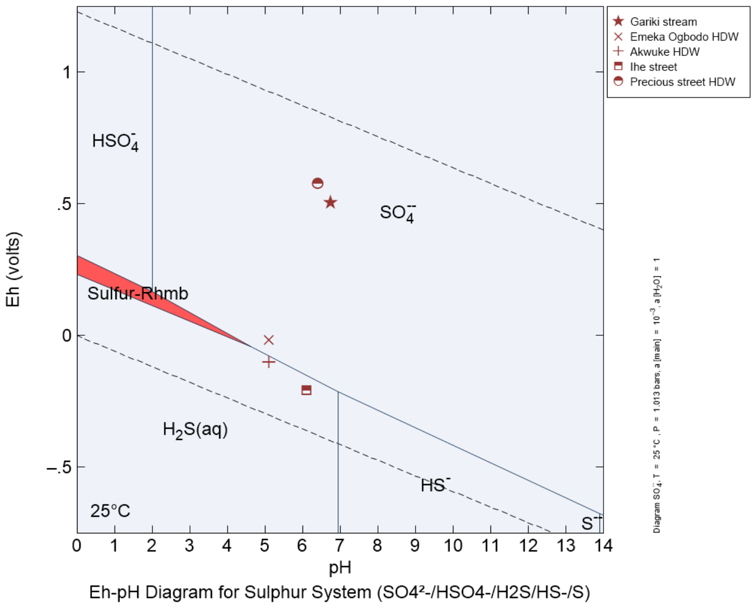

Figure 3.11: Eh-pH diagram of Sulfur system in Groundwater

The diagram in (Fig 3.11) outlines the stability fields of various sulfur species, including sulfate (SO_4^{2-}), bisulfate (HSO_4^-), elemental sulfur (S^0), bisulfide (HS^-), and hydrogen sulfide (H_2S). By contrasting these stability fields with Eh and pH values of diverse water samples, it is possible to infer the dominant sulfur transformation processes in each habitat. Microbial count in table 5.8 indicate the presence or absence of sulfur-oxidizing and sulfate-reducing bacteria, which commonly account for the transfer of sulfur species from one oxidation state to another.

In Gariki Stream and Precious Street HDW, the relatively high Eh values (0.505 V and 0.576 V, respectively) and near-neutral to slightly acidic pH (6.75 and 6.4) suggest an oxidizing environment where sulfate is the most stable sulfur species. The water sources in the places could be dominated by sulfur-oxidizing bacteria, particularly *Shewanella sp.* and *Bacillus sp*. These bacteria actively oxidize reduced sulfur compounds such as hydrogen sulfide (H_2S) into sulfate, a process that requires oxygen and occurs in oxic environments. The absence of detectable hydrogen sulfide (H_2S_2) in further supports this, indicating that sulfur remains in its oxidized sulfate form rather than being reduced to sulfide.

Also from the result Akwuke HDW and EmekaOgbodo HDW exhibit more reducing conditions, as reflected by their lower Eh values (-0.102 V) and acidic pH (5.1). Under these conditions, sulfate reduction becomes more favorable, leading to the potential accumulation of hydrogen sulfide (H_2S). In thepresence of *Desulfomicrobium* strongly suggests active microbial sulfate reduction, as this bacterium utilizes sulfate as an electron acceptor in anaerobic respiration, converting it into hydrogen sulfide in the presence of organic matter. Possible presence of H_2S in these samples, could mean that sulfide is rapidly reacting with iron or other metal ions, forming precipitates that are not detected in solution. The conversion of sulfate to sulfide through microbial processes is a key transformation in anaerobic water environments and significantly alters the sulfur chemistry of these locations.

Ihe Street HDW is an intermediate example, having an Eh of -0.21 V and a slightly acid pH of 6.1. Both conditions support sulfur oxidation and sulfate reduction simultaneously, setting up a dynamic system in which sulfur cycles back and forth among several oxidation states. In the presence of *Geobacter sp.* in this location could suggests that iron-coupled sulfur cycling is taking place, as this bacterium is known to participate in electron transfer reactions involving both sulfur and iron compounds. *Shewanella sp.* presence in these aquifers could indicate active sulfur oxidation and partial reduction processes. This microbial reaction is in agreement with sulfur equilibrium reactions where elemental sulfur (S^0) is a reducing intermediate species that is reduced to hydrogen sulfide under reducing conditions or is oxidized to sulfate under more oxidizing conditions. This dynamic cycling of sulfur maintains the general chemical stability of the water in Ihe Street HDW, equilibrating oxidation and reduction reactions.

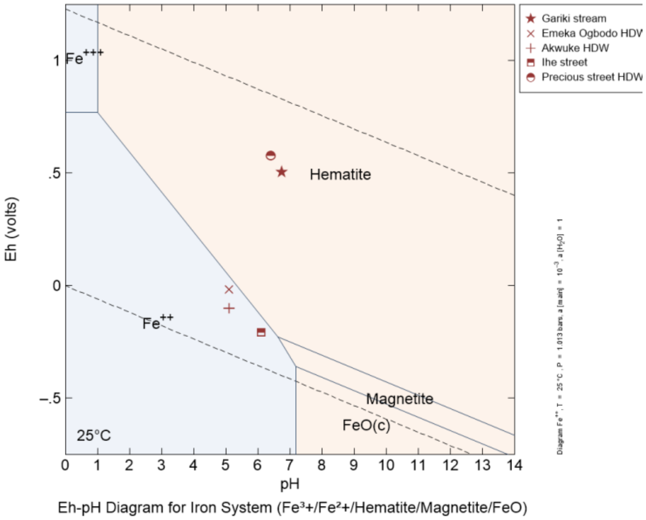

Figure 3.12: Eh-pH diagram of Iron system in Groundwater

The Eh-pH diagram (Fig 3.12) for the iron system, give insights into the redox behavior and speciation of iron in different water samples/sources within the Gariki geographical area. The diagram maps out stability fields for ferric iron (Fe^{3+}), ferrous iron (Fe^{2+}), and solid iron phases, including hematite (Fe_2O_3), magnetite (Fe_3O_4), and ferrous oxide (FeO). The plotted sample points Gariki Stream, EmekaOgbodo HDW, Akwuke HDW, Ihe Street HDW, and Precious Street HDW indicate site-specific redox conditions that dictate the dominant iron species present in each environment.

Gariki Stream and Precious Street HDW exhibit relatively high Eh values (~0.5V) and near-neutral pH (6.8–7.2), placing them within the stability field of hematite. This indicates that iron primarily exists in its oxidized ferric form, with minimal reduction to Fe^{2+}. Iron-oxidizing bacteria such as *Shewanella sp.* and *Bacillus sp*. can enhance the oxidation of Fe^{2+} to Fe^{3+} under oxic conditions, leading to the formation of insoluble iron oxides.

In contrast, EmekaOgbodo HDW and Akwuke HDW exhibit lower Eh values (~0V) and acidic pH (4.0–5.1), positioning them within the Fe^{2+} stability field. This suggests that iron primarily exists in its reduced ferrous form, a condition associated with anoxic or suboxic environments. *Geobacter sp*. and *Desulfomicrobium*sp, are known for their roles in microbial iron and sulfate reduction. These microbes facilitate the reduction of Fe^{3+} to Fe^{2+}, allowing for increased solubility of iron under anaerobic conditions.

Ihe Street HDW represents an intermediate case, with a slightly reducing Eh (~-0.21V) and near-neutral pH (6.1), positioning it close to the boundary between Fe^{2+} and magnetite (Fe_3O_4). This suggests a dynamic equilibrium between iron oxidation and reduction. The co-occurrence of these bacterial species suggests that iron cycling is actively occurring, with *Geobacter sp*. facilitating Fe^{3+} reduction under low-oxygen conditions and *Shewanella sp.* enabling electron transfer between iron phases.

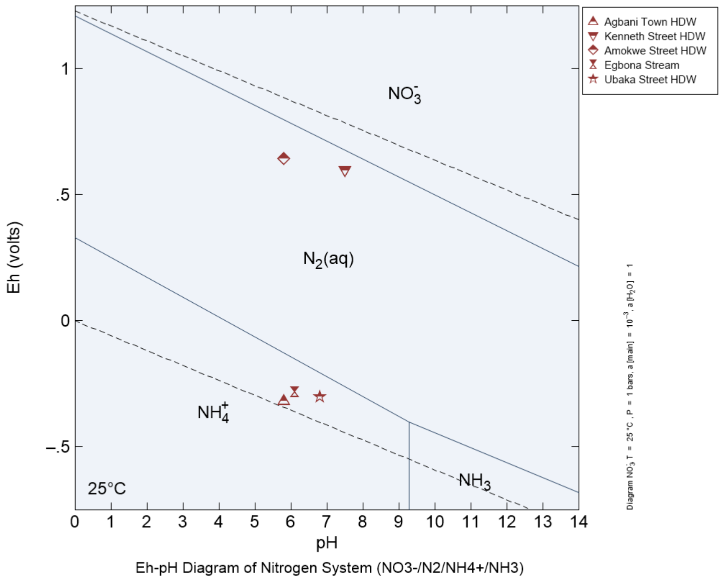

Figure 3.13: Eh-pH diagram of Nitrogen system in Groundwater

The Eh-pH diagram (Fig 3.13) provides insights into the redox conditions governing nitrogen transformations in the groundwater sources from Agbani Town HDW, Kenneth Street HDW, Amokwe Street HDW, Egbona Stream, and Ubaka Street HDW. The samples predominantly fall within the NH_4^+ (ammonium) stability field, which corresponds to low Eh values (< 0.2 V) and pH ranging from 4.5 to 7.0. One sample appears within the $N_2(aq)$ field, suggesting conditions favorable for denitrification, while another sample is situated in the NO_3^- (nitrate) stability field, corresponding to an Eh above 0.5 V and a near-neutral pH of 6.5–7.0. This distribution indicates a mixture of reducing, intermediate, and oxidizing environments in the aquifers studied. The presence and activity of key microbial species provide strong evidence that microbial-driven redox processes are altering nitrogen chemistry in these groundwater systems.

The predominance of ammonium in the sampled groundwater suggests that microbial ammonification is actively occurring under reducing conditions, facilitated by bacteria such as *Geobacter sp*. and *Shewanella sp.*These organisms thrive in low-Eh environments, promoting the reduction of nitrate (NO_3^-) and nitrite (NO_2^-) to ammonium (NH_4^+) through dissimilatory nitrate reduction to ammonium (DNRA).

The presence of a sample in the NO_3^- stability field suggests that nitrifying bacteria such as *Pseudomonas sp*., might be contributing to the oxidation of ammonium to nitrate. The relatively lower abundance of these aerobic bacteria suggests that nitrification is occurring in localized areas with higher oxygen availability, possibly in recharge zones or near-surface groundwater flows. The sample within the N_2(aq) field indicates that denitrification is occurring, likely driven by *Bacillus sp*. and *Shewanella sp.*These bacteria play a key role in nitrate reduction to gaseous nitrogen (N_2), a crucial process for natural attenuation of nitrate contamination.

The microbial influence on nitrogen speciation has significant implications for water quality and ecosystem health. The dominance of ammonium in most samples suggests that wastewater contamination or natural organic matter decomposition is a primary contributor to nitrogen loading. In the presence of *Geobacter sp*. and *Shewanella sp.* in multiple locations indicates that anaerobic degradation of organic matter is a driving force in these aquifers. The low abundance of nitrifiers like *Pseudomonas sp*. suggests that nitrification is limited, leading to ammonium accumulation rather than conversion to nitrate.

The reducing conditions observed in many samples can also facilitate the release of toxic metals such as manganese (Mn) and arsenic (As) due to microbial reduction processes. The presence of *Geobacter sp*., which is known to reduce Fe^{3+} and Mn^{4+} to their soluble forms, may lead to increased mobilization of iron and manganese in these aquifers. Similarly, *Shewanella sp.*, which can reduce arsenate (As^{5+}) to arsenite (As^{3+}), might contribute to arsenic contamination under anoxic conditions.

On the other hand, the presence of denitrifying bacteria (e.g., *Bacillus sp*.) suggests that natural attenuation of nitrate is occurring. This process is beneficial for reducing nitrate contamination, which is known to cause methemoglobinemia (blue baby syndrome) in infants when present at high concentrations. However, excessive denitrification can also lead to nitrogen depletion, potentially impacting groundwater fertility in agricultural settings.

The findings align with research by Egboka*et al*. (2019) in southeastern Nigeria, where ammonium-dominated groundwater was associated with *Geobacter sp*. and *Shewanella sp.* in anaerobic aquifers, leading to ammonium concentrations and potential sulfate reduction. Similarly, Oborie*et al*. (2021) found that nitrifying bacteria were more active in shallow, oxygenated aquifers, with nitrate levels exceeding 20 mg/L, primarily due to agricultural contamination. However, in the present study, nitrification appears to be less dominant, as evidenced by the low abundance of *Pseudomonas sp*. and the predominance of ammonium in most samples.

A study conducted in the Niger Delta by Nwankwoala and Udom (2011) found that groundwater with Eh values below 0.2 V exhibited ammonium buildup due to microbial degradation of organic matter, while areas with Eh values above 0.5 V favored nitrification, resulting in higher nitrate concentrations. This trend is consistent with the present findings, where samples with lower Eh values correlated with high *Geobacter sp*. and *Shewanella sp.* populations, while the single sample in the NO_3^- stability field suggests localized oxidizing conditions, potentially influenced by *Pseudomonas sp*.

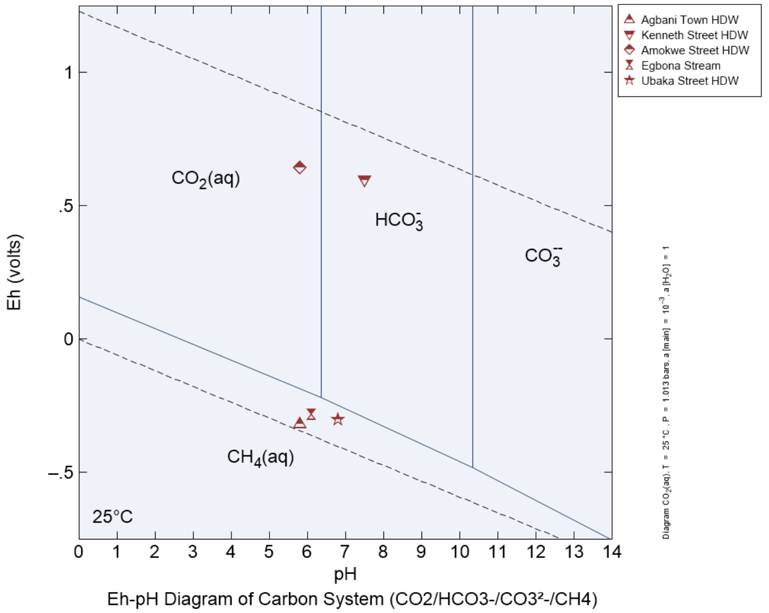

Figure 3.14: Eh-pH diagram of Carbon system in Groundwater

The Eh-pH diagram (Fig 3.14) of the carbon system ($CO_2/HCO_3^-/CO_3^{2-}/CH_4$) illustrates the stability fields of different carbon species at 25°C. The data points representing Agbani Town HDW, Kenneth Street HDW, Amokwe Street HDW, Egbona Stream, and Ubaka Street HDW are plotted within specific stability zones, indicating the dominant carbon species under existing redox and pH conditions. The majority of the sample points cluster in the lower Eh region, particularly within the $CH_4(aq)$ stability field, while a few lie near the transition between $CO_2(aq)$ and HCO_3^-. This suggests reducing conditions in most samples, favoring methane formation, while others may have more oxidizing conditions that allow the formation of bicarbonate.

The positioning of sample points within the $CH_4(aq)$ stability field at low Eh values (< 0 V) and near neutral pH (pH 6–7) suggests anaerobic conditions in these water sources. This trend indicates methanogenesis as a dominant biogeochemical process, likely influenced by microbial activity, particularly methanogens. The presence of data points near the $CO_2(aq)$ and HCO_3^- transition line suggests that some water samples experience intermediate redox conditions, where partial oxidation of organic matter leads to CO_2 and bicarbonate formation rather than complete reduction to methane. The observed redox conditions may be driven by microbial-mediated processes, including those facilitated by species like *Geobacter sp*., *Shewanella sp.*, and

Desulfomicrobium sp. These bacteria play a key role in anaerobic respiration and carbon cycling, contributing to the observed distribution of carbon species.

The dominance of $CH_4(aq)$ in several samples indicates that groundwater in these locations is undergoing anaerobic degradation of organic matter, which has implications for water quality. The presence of methane suggests low oxygen availability, which may limit the efficiency of aerobic biodegradation of contaminants and influence the solubility and mobility of metals such as Fe^{3+} and Mn. Additionally, the presence of HCO_3^- in some samples indicates carbonate buffering is occurring, which might help in achieving pH stability despite microbial action. However, higher levels of methane in potable water sources are possible safety concerns, particularly in confined spaces where methane buildup leads to explosive environments. The observed conditions may also facilitate arsenic mobilization, increasing the risk of heavy metal contamination.

Similar Eh-pH trends have been reported in anaerobic groundwater systems, where methanogenesis is a dominant process due to limited sulfate and nitrate availability. Studies in Nigeria have shown comparable redox conditions in shallow aquifers with high organic matter content, particularly in areas influenced by anthropogenic activities. Research has also indicated that groundwater with methane accumulation often coincides with microbial communities dominated by iron- and sulfate-reducing bacteria such as*Desulfomicrobium* sp. and *Geobacter sp*. as these microbes are known for their role in carbon and metal cycling under reducing conditions.

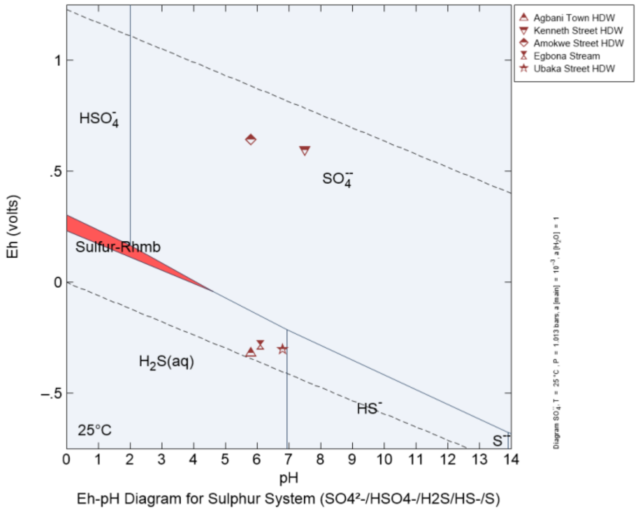

Figure 3.15: Eh-pH diagram of Sulfur system in Groundwater

The Eh-pH diagram (Fig 3.15) for the sulfur system ($SO_4^{2-}/HSO_4^-/H_2S/HS^-/S$) provides insight into the predominant sulfur species under varying redox and pH conditions at 25°C. The diagram shows different stability fields where various sulfur species exist depending on the potential (Eh) and pH of the environment. The groundwater samples from different locations are plotted on this diagram, with most falling within the $H_2S(aq)$ stability region. This indicates that these water samples are under reducing conditions, with low Eh values (below 0 V) and pH levels ranging between 6 and 7. A single sample appears within the SO_4^{2-} stability field at a higher Eh (~0.5 V), suggesting a more oxidizing environment in that particular location. The predominance of hydrogen sulfide (H_2S) in most of the groundwater samples suggests that sulfate reduction is actively occurring. This process is commonly facilitated by sulfate-reducing bacteria (SRB), such as *Desulfomicrobium* sp., which were detected in some of the analyzed water samples. These bacteria utilize sulfate as an electron acceptor in anaerobic conditions, converting it into hydrogen sulfide. The presence of SO_4^{2-} in one of the samples indicates that sulfate reduction is either incomplete in that location or that oxidizing conditions have allowed sulfate to remain stable. This suggests that different redox conditions exist across the sampled locations, potentially influenced by factors such as organic matter availability, microbial activity, and groundwater flow.

The redox transformations of sulfur in the environment involve several key reduction and oxidation reactions. Under reducing conditions, sulfate (SO_4^{2-}) undergoes microbial reduction to form hydrogen sulfide (H_2S). The reaction is as follows: Sulfate reacts with eight electrons and ten hydrogen ions to form hydrogen sulfide and four molecules of water. Conversely, under more oxidizing conditions, hydrogen sulfide can be converted back into sulfate through oxidation. This process can occur either biologically, via sulfur-oxidizing bacteria, or chemically in the presence of oxygen. The oxidation reaction is represented as: Hydrogen sulfide reacts with four molecules of oxygen to produce sulfate and two hydrogen ions.

This explains the presence of sulfate in the sample with a higher Eh value, indicating that oxidation processes are more prevalent in that location. At intermediate redox potentials, elemental sulfur (S) can form as a transient phase between sulfate and sulfide. The reaction is as follows: Hydrogen sulfide releases two electrons and two hydrogen ions to form elemental sulfur. The small red region in the diagram labeled "Sulfur-Rhmb" represents this phase, where elemental sulfur is stable. This solid-phase sulfur can either precipitate or undergo further transformation depending on environmental conditions.Additionally, under alkaline conditions, hydrogen sulfide dissociates into bisulfide (HS^-) according to the equilibrium reaction: Hydrogen sulfide dissociates into bisulfide and a hydrogen ion. This reaction is relevant in environments with pH values above 7, shifting the speciation of dissolved sulfur toward the bisulfide ion.

The results have significant implications for groundwater quality. The dominance of sulfate-reducing conditions can lead to the accumulation of hydrogen sulfide, a compound that has a rotten egg odor and which is corrosive to pipes and infrastructure. Also, hydrogen sulfide can react with dissolved metal ions to form metal sulfide precipitates, which can influence the geochemical characteristics of the water. The presence of sulfate in one of the samples suggests localized oxidation, possibly due to oxygen infiltration from surface water or differences in subsurface geochemistry.

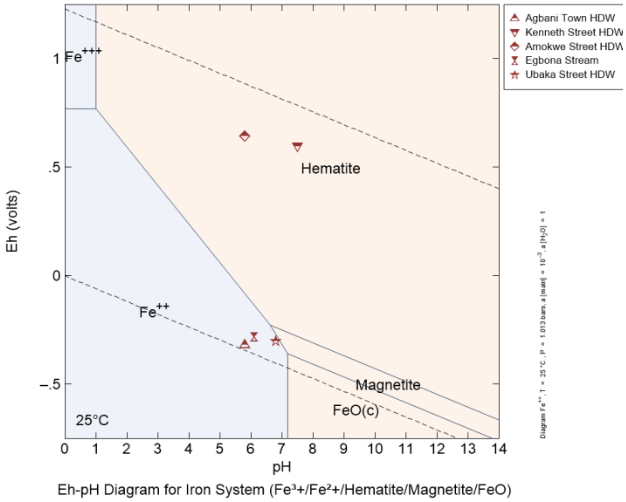

Figure 3.16: Eh-pH diagram of Iron system in Groundwater

The Eh-pH diagram (Fig. 3.16), in relation to the microbial activities, shows the significant role of microbial activity in the redox chemistry of groundwater in the Agbani Road geographical area. The presence of iron-reducing and sulfur-reducing bacteria such as *Geobacter sp*p., *Shewanella sp*p., and *Desulfomicrobium* spp. influences the oxidation states of iron and other geochemical processes in the aquifer. Most of the groundwater samples in the Eh-pH diagram fall within the stability field of ferrous iron (Fe^{2+}), indicating reducing conditions. *Geobacter sp*p. and*Shewanella sp*.are known for their ability to reduce ferric iron (Fe^{3+}) to ferrous iron (Fe^{2+}), thereby increasing its solubility and mobility in groundwater. Their activity explains why most water samples in the study area exhibit reducing conditions, as seen in the Eh-pH diagram.

In contrast, the sample from Kenneth Street HDW, which plots within the hematite (Fe_2O_3) stability field, shows no growth of *Geobacter sp*p. or *Desulfomicrobium* spp., suggesting an environment with lower microbial iron reduction and more oxidizing conditions. The absence of these iron-reducing bacteria in this sample could be linked to higher dissolved oxygen levels, which promote ferric iron stability and precipitation as hematite.

Also, *Desulfomicrobium* spp., are sulfate-reducing bacteria that can facilitate iron sulfide precipitation under strongly reducing conditions. Although not actually depicted to document the stability of sulfide minerals in the Eh-pH diagram, *Desulfomicrobium* present suggests the reduction of sulfate possibly responsible for the formation of local iron sulfides to affect further groundwater chemistry. By and large, the microbian data provides substantial biological confirmation of redox conditions documented from the Eh-pH diagram. The dominance of iron-reducing bacteria in most of the samples is consistent with Fe^{2+} dominance, and their presence in oxidizing systems such as Kenneth Street HDW is consistent with hematite stability. This consistency confirms the very significant role played by microbial processes on iron speciation and groundwater quality in shallow aquifers.

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