

SULFUR SPECIATION IN REGOLITH AQUIFERS AT ENUGU, SOUTHEASTERN NIGERIA

Ezeugwu Innocent Onyebuchi*, Ozoko Daniel Chukwuemeka and Iyi Emmanuel Chibuike

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

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

Received: 2016-09-14

Accepted: 2016-10-27

Published online: 2016-11-01

Abstract

This study investigates the geochemical behavior and microbial interactions influencing sulfur speciation in regolith aquifers across Enugu, Southeastern Nigeria. A total of 30 groundwater samples from multiple locations such as Centenary, 9th mile, Ologo, Trans-Ekulu, New-artizan and Amechi were analyzed using Eh-pH diagrams for the sulfur system ($\text{SO}_4^{2-}/\text{HSO}_4^-/\text{HS}^-/\text{H}_2\text{S}/\text{S}$). From the result, the Eh-pH plots revealed diverse redox environments ranging from oxidizing to strongly reducing conditions. It was observed that, Winners Estate HDW and similar sites which were plotted in the oxidizing zone dominated by SO_4^{2-} , while Ezenweke Street HDW and similar sites displayed reducing conditions where sulfur exists predominantly as HS^- or H_2S . These redox environments suggest varying degrees of microbial activity, particularly sulfate-reducing bacteria, influencing sulfur transformations. The presence of reduced sulfur species in some samples indicates potential risks such as corrosion, odor issues, and the mobilization of toxic trace metals like arsenic and manganese. The study shows and buttress on the importance of redox-sensitive monitoring for effective groundwater management and public health protection in urban and peri-urban settings.

Keywords: Sulfur speciation, Microbial Sulfur Cycling, Redox Reactions, Groundwater geochemistry, Sulfate-reducing bacteria, Regolith aquifers.

INTRODUCTION

Sulfur is a chemically versatile element that exists in a wide range of oxidation states in natural waters, making it a key player in subsurface redox reactions. In groundwater systems, sulfur commonly occurs as sulfate (SO_4^{2-}), sulfide (H_2S), elemental sulfur (S^0), and other intermediate species. These forms are not just passively present—they're actively transformed through complex biogeochemical processes, many of which are microbially driven (Langmuir, 1997; Appelo and Postma, 2005).

Microorganisms play a central role in sulfur cycling within aquifers. Sulfate-reducing bacteria (SRB), such as species from the *Desulfovibrio* and *Desulfomicrobium* genera, reduce sulfate to hydrogen sulfide under anaerobic conditions, using organic matter or hydrogen as an energy source (Zhang *et al.*, 2019). Conversely, sulfur-oxidizing bacteria like *Thiobacillus* can convert reduced sulfur species back into sulfate, especially in zones where oxygen or nitrate is available. These microbial processes significantly influence the speciation, mobility, and eventual fate of sulfur in groundwater systems. In regolith aquifers, deeply weathered profiles typically overlying crystalline

bedrock such as microbially mediated redox processes are often enhanced due to the presence of organic-rich zones, fluctuating water tables, and variable oxygen availability. The Enugu region in southeastern Nigeria presents a prime example of such an environment. It hosts widespread lateritic regolith aquifers that serve as major water sources for urban and peri-urban communities (Ezeh, 2004). However, the shallow and unconfined nature of these aquifers also makes them particularly vulnerable to contamination and redox alterations driven by both natural and anthropogenic factors (Nwankwoala and Udom, 2011).

One of the often-overlooked outcomes of microbial sulfur cycling in groundwater is its impact on water quality. For instance, hydrogen sulfide generated by sulfate-reducing bacteria imparts a characteristic "rotten egg" odor, contributes to corrosion of plumbing materials, and indicates anoxic conditions that can facilitate the mobilization of toxic metals like arsenic or manganese (Burton *et al.*, 2007). Moreover, shifts in sulfur speciation can alter the pH and redox status of aquifers, influencing the solubility of other contaminants and minerals. Despite its importance, sulfur speciation particularly the microbial influence on its transformation is poorly understood in Nigerian groundwater systems. Past studies in the Enugu area have focused primarily on major ions, trace metals, and general hydrochemistry (Egboka *et al.*, 1989; Edet and Okereke, 2005), with limited attention given to the microbial ecology or redox-sensitive species like sulfur.

This study addresses this gap by exploring sulfur speciation in regolith aquifers of Enugu, with a particular emphasis on the microbial processes driving these transformations. The key objectives are to: (i) identify the dominant sulfur species and their concentrations across different sites; (ii) evaluate redox conditions and their influence on sulfur cycling; and (iii) assess the role of microbial communities in shaping sulfur dynamics in these shallow aquifers.

REVIEW OF LITERATURE

Sulfur speciation in groundwater has become increasingly important to comprehend in recent years due to its ramifications on water quality, redox status of aquifers, and microbial ecology. Numerous studies across the globe have documented the existence of sulfur in a redox dynamic cycle, oscillating between oxidized species like sulfate (SO_4^{2-}) and reduced species like sulfide (H_2S), with several intermediate species like thiosulfate ($\text{S}_2\text{O}_3^{2-}$) and elemental sulfur (S^0) (Luther *et al.*, 2011). These processes are not just abiotic reactions that drive them but also, and often more significantly, by microbial activity (Muyzer and Stams, 2008).

Globally, microbial regulation of sulfur cycling in aquifers has been the subject of intensive study. For instance, in their article on wetland and shallow aquifer systems, Burton *et al.* (2007) illustrated that sulfate-reducing bacteria (SRB) could effectively alter sulfur chemistry through the reduction of sulfate to sulfide in anoxic conditions. Likewise,

Tesoriero *et al.* (2015) found that presence and ongoing concentrations of sulfide in groundwater directly related to the availability of organic carbon and microbial activity, particularly in alluvial and regolith aquifers with fluctuating redox conditions. Moreover, Zhang *et al.* (2019) have summarized sulfur transformation processes in subsurface environments, highlighting the significance of microbially catalyzed redox gradients, particularly in shallow groundwater systems. In sub-Saharan Africa, however, studies specifically addressing sulfur speciation are limited. Much of the available groundwater literature from Nigeria has focused on general hydrochemistry, pollution, and metal concentrations. Egboka *et al.* (1989), for example, discussed groundwater contamination and pollutant transport in southeastern Nigeria but did not delve into sulfur dynamics. Similarly, Ezeigbo (1989) and Edet and Okereke (2005) concentrated on ionic characteristics and hydrochemical facies in the Imo River Basin and southeastern Nigeria, respectively, with no mention of sulfur speciation or microbial sulfur transformations.

Despite the absence of focused sulfur studies, some clues point to its relevance in local contexts. Ezeh (2004) and Nwankwoala and Udom (2011) both reported anoxic groundwater conditions and the presence of hydrogen sulfide odors in shallow aquifers, hinting at active sulfate reduction. Nwankwoala (2013) also observed signs of microbial contamination and sulfur-related corrosion in Niger Delta groundwater systems, although these were not directly linked to sulfur speciation. These findings suggest that microbial sulfur cycling may be active but remains under-investigated in Nigerian aquifers.

Recent international studies have taken a more integrated approach by examining both the geochemical and microbiological drivers of sulfur speciation. For instance, Luther *et al.* (2011) emphasized the need to quantify intermediate sulfur species as indicators of ongoing redox reactions. Kuenen (2008) also highlighted the role of sulfur-oxidizing bacteria in natural attenuation and bioremediation, especially in environments experiencing oxygen-nitrate fluctuations. Yet, applying these methods in African regolith systems particularly in regions like Enugu where weathered profiles are deeply developed has not been widely attempted.

Regolith aquifers, such as those found in Enugu, offer a unique setting for sulfur transformation studies due to their layered lithology, iron-rich matrix, and variable saturation levels. These systems are often unconfined and interact closely with surface inputs, organic matter, and microbial communities, which are ideal conditions for coupled sulfur and iron cycling (Appelo and Postma, 2005). However, there is still a lack of local studies integrating sulfur speciation, redox chemistry, and microbial analysis in these environments.

While international literature has extensively documented sulfur dynamics in groundwater systems particularly the role of microbes in sulfate reduction and sulfide oxidation, there is a significant research gap in Nigerian contexts. The few studies that hint at sulfur activity have not directly investigated its speciation or microbial

associations. Therefore, there is a pressing need to study sulfur speciation in Enugu's regolith aquifers to better understand how sulfur behaves in these settings and how it impacts water quality, especially in the presence of microbial communities.

Location of the Study Area

Enugu, the main city of south-east Nigeria, lies within latitudes 6°22'N and 6°39'N, and longitudes 7°26'E and 7°40'E. It has an area of approximately 79 square kilometers (Egboka *et al.*, 1989). As the administrative and commercial hub of Enugu State, the city is replete with history that has been inextricably intertwined with its coal mines, which have been the driving force for motivation in its development. Enugu is situated within the Anambra Basin, a major sedimentary basin in Nigeria. The topography of the city has been influenced by a combination 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.

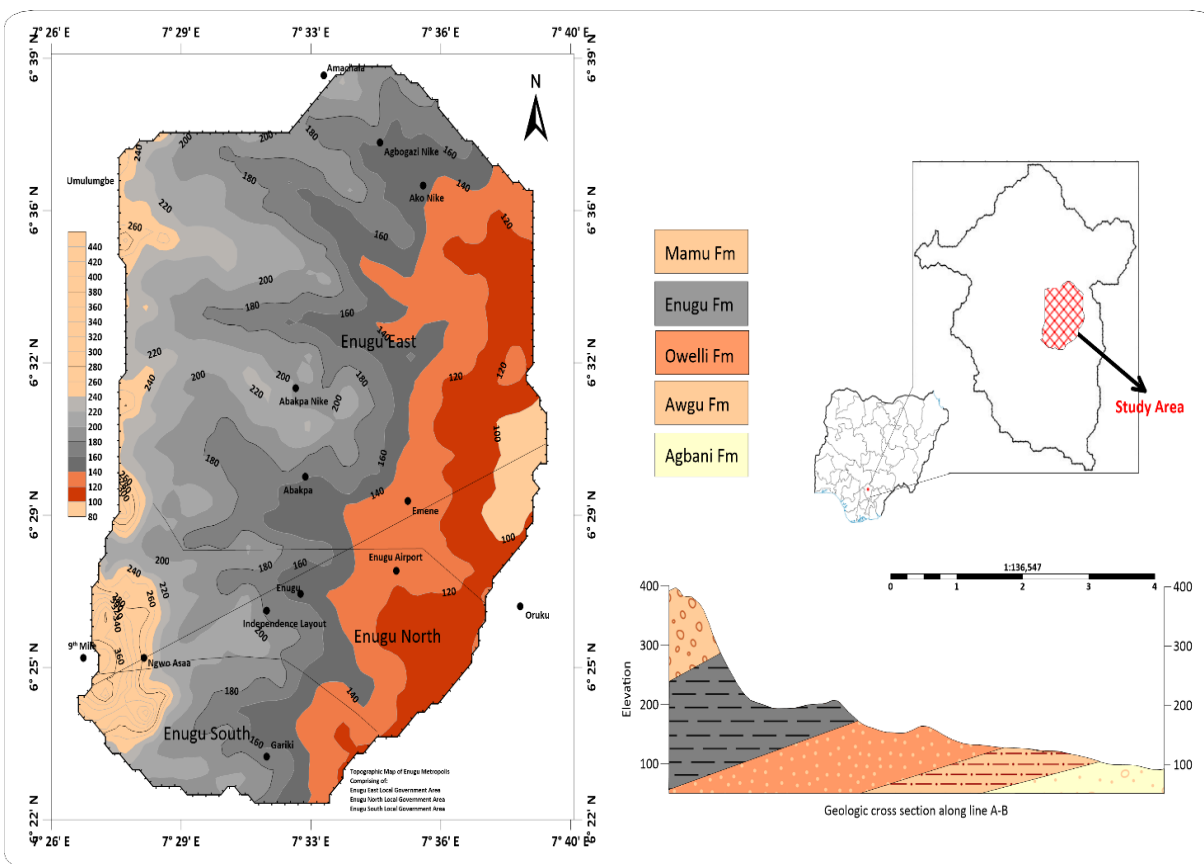


Figure 1: Geologic map of the study area

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

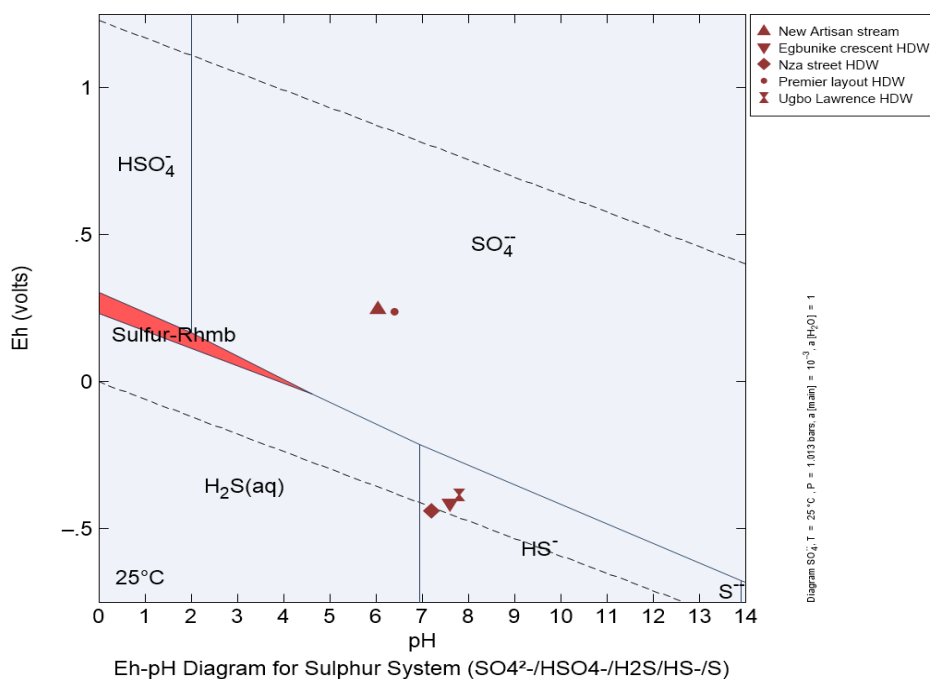


Figure 2: Eh-pH diagram of Sulphur system in Groundwater

The Eh-pH diagram presented provides valuable insight into the sulfur speciation within regolith aquifers across several locations in Enugu, including New Artisan Stream, Egbunike Crescent HDW, Nza Street HDW, Premier Layout HDW, and Ugbo Lawrence HDW. The plotted samples predominantly cluster within the stability field of sulfate ions (SO_4^{2-}), indicating that the majority of these aquifers are characterized by oxidizing conditions. These conditions support the stability of fully oxidized sulfur species and suggest that there is limited biological or chemical reduction of sulfate in most of the groundwater sampled. Specifically, the samples from New Artisan and Premier Layout HDWs exhibit Eh values above 0.3 V and pH values ranging from approximately 6 to 7.5, reinforcing their placement in the oxidizing zone of the diagram.

Interestingly, a subset of samples—particularly those from Egbunike Crescent and Nza Street HDWs—lie closer to or within the transitional zone between the sulfate field and the fields associated with elemental sulfur (S^0) and hydrogen sulfide (H_2S). These samples exhibit slightly lower Eh values (approaching 0 or slightly negative), with near-neutral pH. Their positioning suggests the presence of microenvironments within the aquifers that may experience temporal or spatial fluctuations in redox potential. Such redox variability can be attributed to microbial activity, especially which of sulfate-reducing bacteria (SRB), which thrive under anoxic conditions and convert sulfate into sulfide (H_2S or HS^-). This microbial-driven process is commonly found in aquifers with organic-rich sediments or limited oxygen replenishment (Muyzer and Stams, 2008).

The presence of samples in the H_2S and HS^- fields, though less frequent, is particularly significant. It implies that certain zones within the Enugu regolith aquifer system may be undergoing active sulfate reduction, a process that not only alters sulfur speciation but also influences groundwater chemistry more broadly. For instance, sulfate reduction often results in the release of dissolved iron and manganese from sediments, which can degrade water quality and contribute to well clogging and infrastructure corrosion (Burton *et al.*, 2007; Tesoriero *et al.*, 2015). Moreover, the generation of H_2S although not always detectable through odor alone can pose health risks and make groundwater unsuitable for domestic use if concentrations are high. These findings emphasize the importance of understanding redox zonation when evaluating groundwater suitability.

Comparing this study with others conducted both within Nigeria and globally reveals several parallels. Similar sulfur behavior has been observed in shallow aquifers elsewhere, where fluctuating redox conditions and microbial processes govern the dominant species of sulfur in groundwater (Luther *et al.*, 2011; Zhang *et al.*, 2019). In Nigeria, studies by Ezeh (2004) and Nwankwoala and Udom (2011) reported occurrences of sulfurous-smelling groundwater in certain localities, often attributing the phenomenon to the presence of H_2S from natural degradation of organic matter or microbial sulfate reduction. However, those studies did not provide quantitative redox data. This current

study thus contributes a more nuanced and data-driven understanding by directly correlating Eh and pH values with the likely sulfur species present, offering a geochemically grounded basis for interpreting field observations.

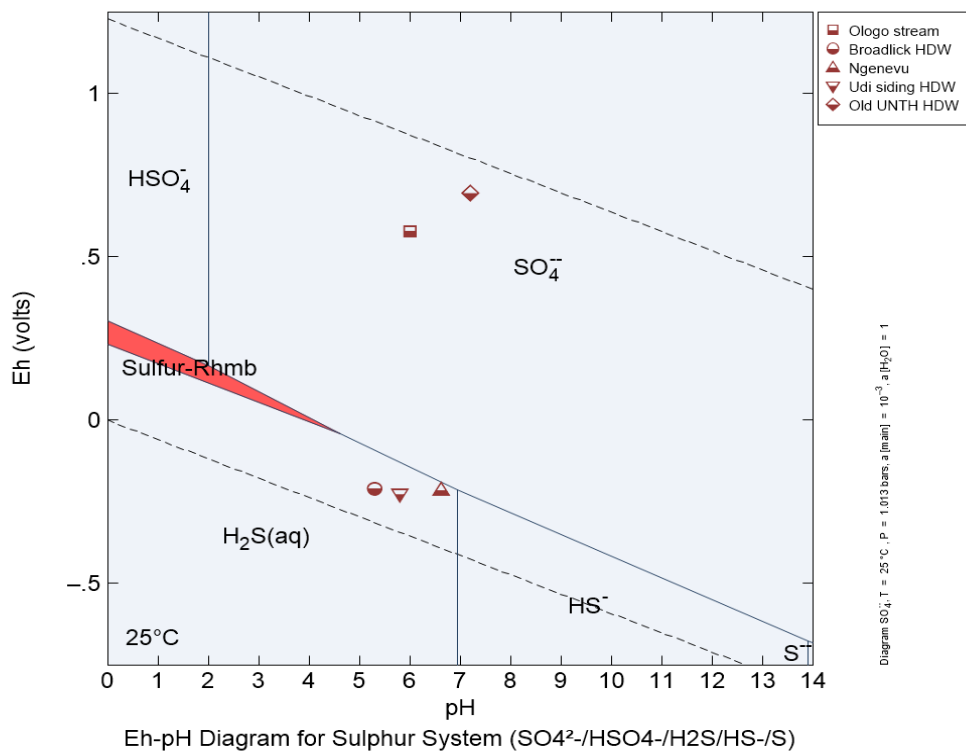


Figure 3: Eh-pH diagram of Sulfur system in Groundwater

The Eh-pH diagram for sulfur speciation at additional Enugu aquifer sites—Ologo Stream, Broadlick HDW, Ngenevu, Udi Siding HDW, and Old UNTH HDW—further reveals the redox complexity of the subsurface environment. In this figure, a more distinct spread of data points is evident across oxidizing and reducing conditions, reflecting the dynamic redox landscape of regolith aquifers in these locations. Most notably, the sample from Ologo Stream, situated well within the sulfate (SO_4^{2-}) field with an Eh value above 0.5 V and pH near neutral, suggests an environment dominated by oxidized sulfur species and minimal microbial reduction activity. This oxidizing condition may be due to relatively shallow water tables, open exchange with the atmosphere, or limited organic carbon availability that would otherwise fuel anaerobic microbial processes.

In contrast, samples from Broadlick HDW, Ngenevu, and Udi Siding HDW plot close to or within the $\text{H}_2\text{S}(\text{aq})$ field. These samples have Eh values close to or slightly below 0 V, with pH values ranging between 5.5 and 7. This positioning suggests the influence of sulfate-reducing conditions, likely driven by microbial communities such as *Desulfovibrio*

and *Desulfotomaculum* species. These bacteria use sulfate as a terminal electron acceptor in anaerobic respiration, reducing it to hydrogen sulfide (H₂S) (Muyzer and Stams, 2008).

The presence of H₂S in groundwater is an important indicator of anoxic conditions and typically correlates with zones of organic matter decomposition and iron mobilization (Tesoriero *et al.*, 2015; Luther *et al.*, 2011). These processes not only influence the chemical form of sulfur but can also contribute to unpleasant odors and the deterioration of water quality in domestic wells. The sample from Old UNTH HDW is particularly interesting, as it plots firmly within the SO₄²⁻ stability field despite its proximity to the more reduced zones. This suggests that while the site may experience occasional redox variability, the overall system remains moderately oxidized. Such variability can be attributed to factors such as recharge events, subsurface heterogeneity, or fluctuating groundwater levels, all of which affect oxygen availability and microbial activity (Appelo and Postma, 2005).

The broader implication of these findings is that sulfur cycling in Enugu's regolith aquifers is not uniform across the landscape. While some locations maintain stable oxidizing conditions, others demonstrate clear signs of microbial sulfate reduction. This variability has important consequences for water quality management, especially in areas where H₂S production may render water sources unsuitable for drinking or lead to infrastructure corrosion. Furthermore, understanding these redox patterns helps anticipate interactions with other elements such as iron, manganese, and arsenic, which often become more mobile under reducing conditions (Burton *et al.*, 2007).

When compared to other studies across sub-Saharan Africa and beyond, these results are consistent with observations in similar regolith-dominated aquifers, where microbial sulfate reduction occurs in organic-rich or poorly aerated zones (Zhang *et al.*, 2019; Ezeh, 2004). Notably, Nwankwoala and Udom (2011) also reported sulfurous odors in groundwater across parts of southeastern Nigeria, attributing them to anaerobic microbial activity. However, this present study, by incorporating Eh-pH data, offers a clearer geochemical framework to substantiate those field observations and identify the dominant sulfur species at play.

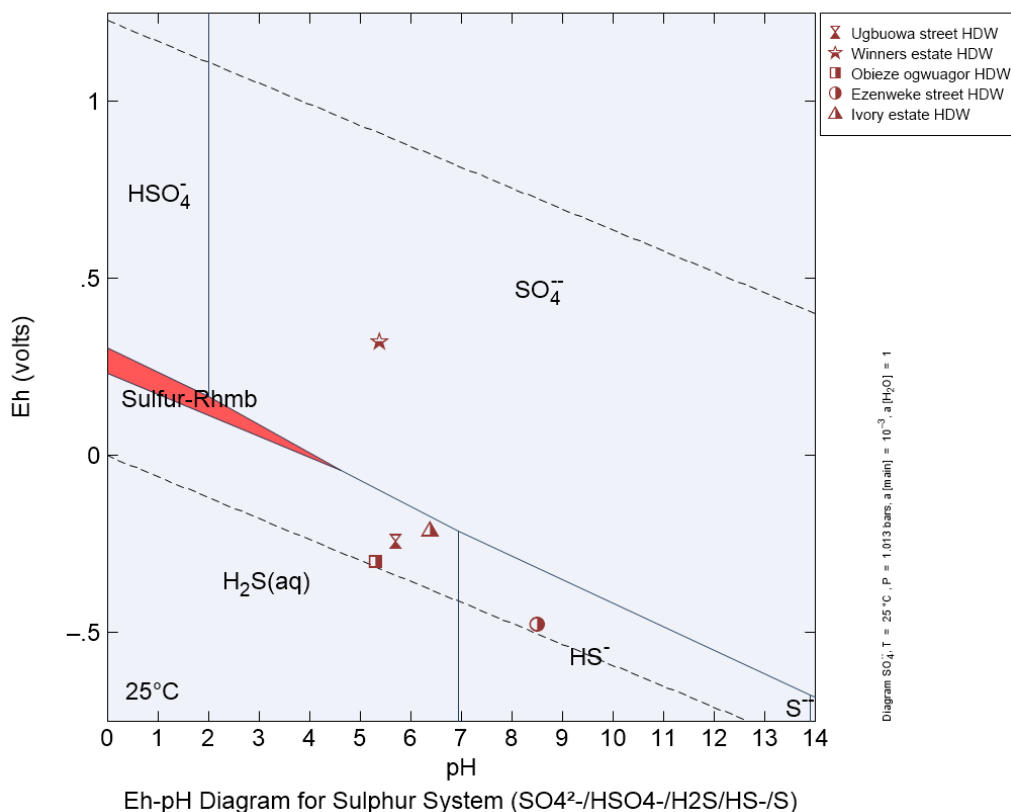


Figure 4: Eh-pH diagram of Sulfur system in Groundwater

The Eh-pH diagram for the sulfur system ($\text{SO}_4^{2-}/\text{HSO}_4^-/\text{HS}^-/\text{H}_2\text{S}/\text{S}$) provides important insights into the redox conditions and sulfur speciation in the groundwater of selected locations within Enugu Metropolis. The five sampled sites Ugbuowa Street HDW, Winners Estate HDW, Obieze Ogwuagor HDW, Ezenweke Street HDW, and Ivory Estate HDW exhibited diverse redox environments, ranging from oxidizing to reducing conditions. Winners Estate HDW, for example, plots clearly in the oxidizing sulfate (SO_4^{2-}) domain, indicating that sulfate is the stable sulfur species in this location. In contrast, Ezenweke Street HDW is positioned in the strongly reducing HS^- field with a high pH and low Eh, suggesting conditions favorable for microbial sulfate reduction. The remaining three locations such as Ugbuowa, Obieze, and Ivory fall close to the transition zone between $\text{H}_2\text{S}(\text{aq})$ and HS^- , indicating mildly reducing environments that could support the activity of sulfate-reducing bacteria.

A closer look at the trends reveals a clear pattern: groundwater from more open or oxygen-exposed environments like Winners Estate tends to retain its oxidizing character, favoring the stability of sulfate ions. This may reflect recent recharge, better aquifer ventilation, or less organic pollution. On another vein, sites like Ezenweke and

Ivory Estate, which lie in more reducing zones, are likely characterized by limited oxygen availability, stagnation, and organic matter accumulation, creating anoxic conditions that facilitate the microbial reduction of sulfate to sulfide. Such environments are often associated with the metabolic activity of sulfate-reducing bacteria (SRB), such as *Desulfovibrio spp.*, which utilize organic carbon sources under anaerobic conditions to reduce SO_4^{2-} to H_2S (Muyzer and Stams, 2008). This biogeochemical transformation is typical in shallow aquifers where residence times are longer and oxygen is depleted due to microbial respiration (Postma and Jakobsen, 1996).

The implications of these findings are multifaceted. In reducing environments, particularly where sulfide species like H_2S or HS^- dominate, there is a risk of unpleasant odor, corrosion of plumbing infrastructure, and potential mobilization of toxic metals such as arsenic and manganese (Appelo and Postma, 2005; Zhang *et al.*, 2019). These metals become more mobile under anoxic and reducing conditions, increasing the likelihood of contamination in drinking water sources. Additionally, the presence of H_2S can be hazardous to health at high concentrations and often indicates organic pollution, possibly from septic tanks or latrine seepage. This highlights the importance of regular monitoring and management of groundwater quality, especially in densely populated and peri-urban areas where sanitation infrastructure is often inadequate. Furthermore, understanding redox conditions is crucial for predicting the behavior of contaminants and for designing appropriate remediation strategies.

When compared with other studies, the results from these Enugu samples show consistency with previous hydrogeochemical assessments in similar Nigerian settings. Ezeh (2004) noted signs of sulfurous odor and turbidity in hand-dug wells within Enugu, which he attributed to microbial sulfate reduction which aligns with the finding from Ezenweke and Obieze. Also, Okereke *et al.* (2012) reported evidence of reducing groundwater conditions in Port Harcourt and Owerri, linked to organic pollution and anaerobic microbial activity. On a broader scale, research by Tesoriero *et al.* (2015) in the U.S. highlighted how temporal changes in redox conditions within aquifers can shift sulfur speciation, leading to episodic occurrences of sulfide and metal mobilization. This underscores the dynamic nature of groundwater systems and the influence of both geogenic and anthropogenic factors on redox chemistry.

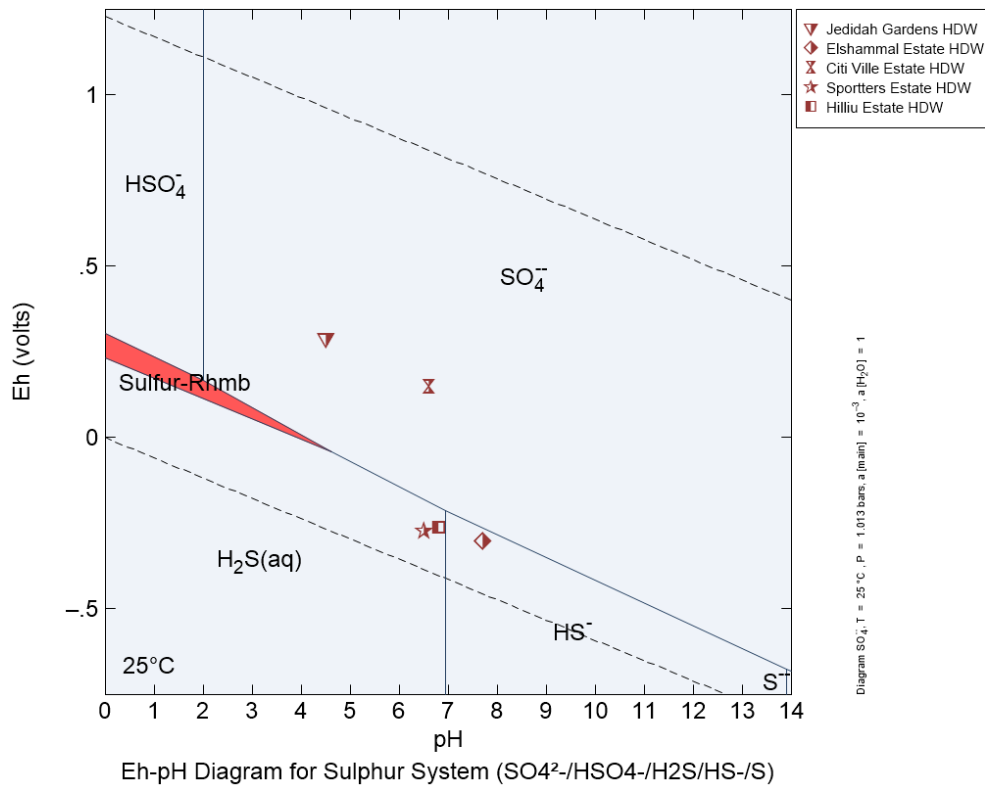


Figure 5: Eh-pH diagram of Sulfur system in Groundwater

The Eh-pH diagram for the sulfur system provides crucial insights into the prevailing redox and acidity conditions in the hand-dug wells (HDWs) sampled from various residential areas, namely Jedidah Gardens, Elshammal Estate, Cit Ville Estate, Sportters Estate, and Hilliu Estate. These wells, plotted based on their measured redox potential (Eh) and pH, fall within distinct regions of sulfur species stability, ranging from sulfate (SO_4^{2-}) in oxidizing conditions to hydrogen sulfide (H_2S) in reducing conditions. The majority of the samples are concentrated between the Sulfur-Rhombic (elemental sulfur), sulfate, and aqueous hydrogen sulfide fields, indicating a complex interplay of geochemical processes, particularly those influenced by microbial activity.

Jedidah Gardens HDW and Cit Ville Estate HDW are located within the sulfate (SO_4^{2-}) stability field, which is characteristic of oxidizing environments. In such conditions, sulfur tends to exist in its most oxidized form as sulfate, suggesting the presence of sufficient dissolved oxygen or alternative electron acceptors. This condition is generally unfavorable for the activity of sulfate-reducing bacteria (SRB), which require anoxic or suboxic conditions to thrive. On the other hand, the data points from Sportters Estate HDW and Hilliu Estate HDW fall closer to the $\text{H}_2\text{S}(\text{aq})$ field, indicative of reducing environments where hydrogen sulfide predominates. These conditions are typically

associated with microbial sulfate reduction, a process carried out by SRB such as *Desulfovibrio* and *Desulfotomaculum* species. These bacteria utilize sulfate as a terminal electron acceptor in the absence of oxygen, producing H₂S as a metabolic byproduct (Muyzer and Stams, 2008). The presence of H₂S not only marks microbial activity but also highlights the potential for odor issues, corrosion of pipes, and health risks if the gas accumulates in confined spaces.

The positioning of Elshammal Estate HDW near the sulfur-rhombic field suggests a transitional redox environment. This intermediate state may result from partial oxidation of H₂S or incomplete reduction of sulfate, often occurring where fluctuating redox conditions support both sulfur-oxidizing and sulfur-reducing microorganisms. For instance, sulfur-oxidizing bacteria such as *Thiobacillus* spp. can convert elemental sulfur to sulfate under aerobic conditions, while SRB perform the reverse in anaerobic niches (Friedrich *et al.*, 2005). These dynamic interactions highlight the microbial mediation of sulfur speciation in groundwater systems and underscore the ecological balance between oxidation and reduction processes.

The implications of these findings are significant, particularly in assessing groundwater quality and potential health impacts. Elevated levels of H₂S, as suggested in Sportters and Hilliu Estates, could indicate ongoing sulfate reduction, which is often accompanied by the mobilization of trace metals such as iron and manganese due to reductive dissolution. Furthermore, the generation of sulfide can influence the pH and redox stability of other contaminants, making these environments more chemically reactive. In contrast, oxidizing wells like those in Jedidah Gardens and Cit Ville may support fewer microbial transformations but could be more susceptible to nitrate contamination, which often co-occurs in well-oxygenated groundwater (Christensen *et al.*, 2000).

Comparatively, these observations are in line with other groundwater studies. For example, Böttcher *et al.* (2005) documented zones of microbial sulfate reduction in coastal aquifers, closely aligned with Eh-pH stability diagrams similar to the one presented here. Likewise, Postgate (1984) emphasized that SRB become dominant in low Eh environments, especially when pH is neutral to slightly alkaline, which corresponds well with the observed conditions in Hilliu and Sportters Estates. These microbial processes are not only crucial for understanding the biogeochemical cycling of sulfur but also for designing effective groundwater monitoring and remediation strategies.

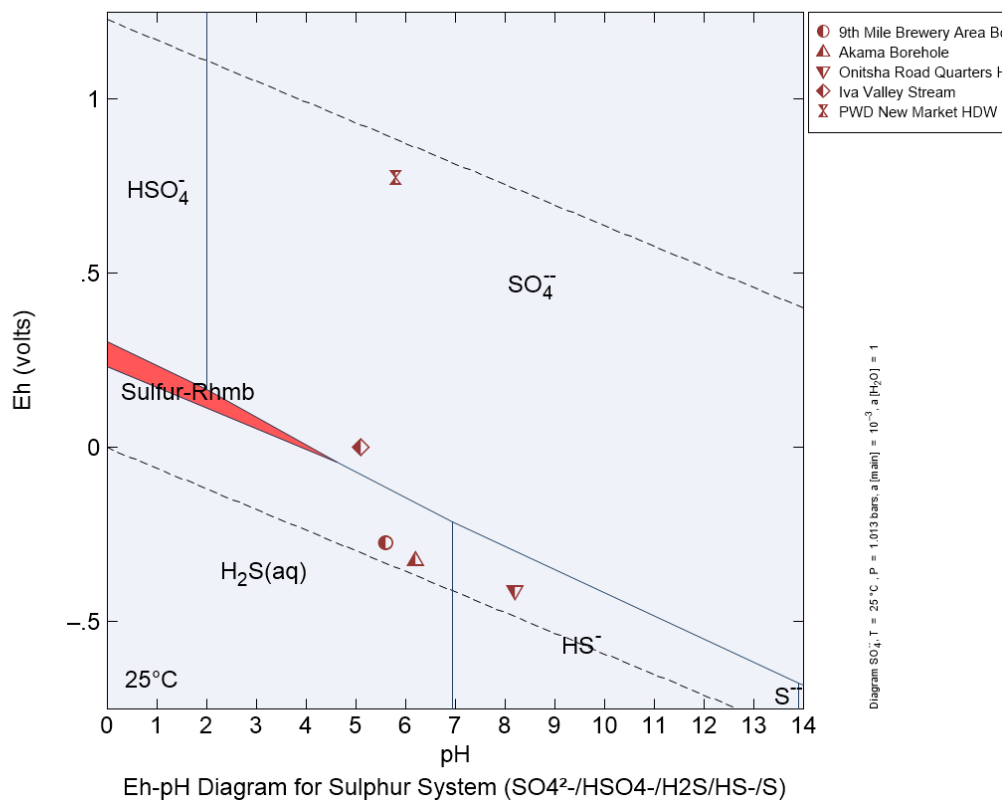


Figure 6: Eh-pH diagram of Sulphur system in Groundwater

The Eh-pH diagram for the sulfur system in this analysis depicts data from various groundwater and surface water sources, including the 9th Mile Brewery Area Borehole, Akama Borehole, Onitsha Road Quarters HDW, Iva Valley Stream, and PWD New Market HDW. This diagram is particularly informative in assessing the redox and acidity conditions influencing sulfur speciation in these water bodies. The data points plot across regions corresponding to sulfate (SO₄²⁻), aqueous hydrogen sulfide (H₂S(aq)), and in some cases near elemental sulfur (Sulfur-Rhmb), highlighting the geochemical diversity of the sampled environments.

The sample from Iva Valley Stream is located within the SO₄²⁻ stability field, characterized by a relatively high Eh and moderate pH. This suggests the environment is oxidizing, promoting the persistence of sulfate, which is the fully oxidized and most stable form of sulfur under such conditions. Environments like these typically suppress sulfate-reducing bacteria (SRB) due to the abundance of oxygen or other electron acceptors, thereby reducing the formation of reduced sulfur species like H₂S. In contrast, the Akama Borehole, 9th Mile Brewery Area Borehole, and Onitsha Road Quarters HDW cluster within the H₂S(aq) stability field, with lower Eh values indicative of reducing conditions that

support microbial sulfate reduction. Such reducing conditions are often the result of organic matter degradation and oxygen depletion, which promote the activity of SRB such as *Desulfovibrio*, *Desulfobacter*, and *Desulfotomaculum* species that convert sulfate to H₂S (Muyzer and Stams, 2008).

Notably, the PWD New Market HDW lies near the boundary between the SO₄²⁻ and H₂S(aq) fields, implying a transitional environment that could support both oxidative and reductive microbial processes. Such conditions are ideal for the coexistence of both sulfur-reducing and sulfur-oxidizing microbes. Bacteria like *Thiobacillus* and *Beggiatoa* are known to oxidize reduced sulfur species back to sulfate under semi-aerobic conditions (Friedrich *et al.*, 2005), thereby maintaining a dynamic sulfur cycle influenced by redox fluctuations. The presence of hydrogen sulfide in Akama and 9th Mile Boreholes suggests that these groundwater sources are undergoing active microbial sulfate reduction. This biogeochemical process not only lowers redox potential but can lead to the release of other associated elements like iron, manganese, and arsenic due to the reductive dissolution of metal oxides (Christensen *et al.*, 2000). The generation of H₂S is also of concern from a public health and water quality standpoint, as it can produce foul odors, cause taste issues, and in higher concentrations, pose toxicity risks.

Comparative studies affirm these findings. For instance, research by Böttcher *et al.* (2005) in coastal aquifers showed that zones with low Eh and neutral to slightly acidic pH values were hotspots for microbial sulfate reduction. Similar patterns are observed in this dataset, particularly in the 9th Mile and Akama Borehole samples. Postgate (1984) also emphasized that the ecological dominance of SRB in anoxic, slightly acidic-to-neutral environments is a consistent indicator of active biogeochemical sulfur cycling, aligning well with the observed data distribution on this diagram.

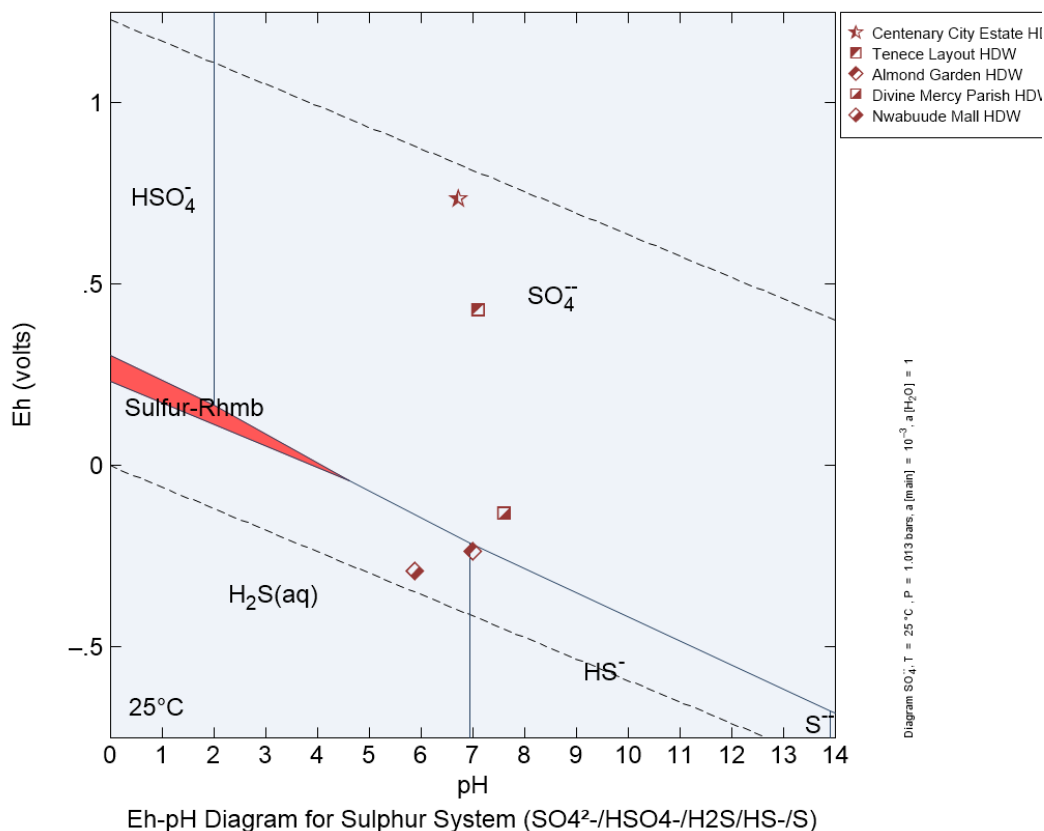


Figure 7: Eh-pH diagram of Sulfur system in Groundwater

The Eh-pH diagram for the sulfur system ($\text{SO}_4^{2-}/\text{HSO}_4^-/\text{H}_2\text{S}/\text{HS}^-/\text{S}$) presents a thermodynamic perspective on the stability fields of various sulfur species under varying redox potentials and acidity. The plot integrates data from hand-dug wells (HDWs) at Centenary City Estate, Tenece Layout, Almond Garden, Divine Mercy Parish, and Nwabuude Mall within Enugu metropolis. The samples cluster across distinct regions of the diagram, signifying variable redox and pH regimes that govern sulfur speciation and, importantly, microbial community structure and functionality. The Centenary City Estate HDW, located deep within the SO_4^{2-} field, reflects a strongly oxidizing and moderately acidic environment ($\text{Eh} \sim 0.7 \text{ V}$, $\text{pH} \sim 6.5\text{--}7$). Such geochemical conditions inhibit the survival of sulfate-reducing bacteria (SRB) and instead favor sulfur-oxidizing bacteria (SOB), such as *Paracoccus pantotrophus*, *Acidithiobacillus ferrooxidans*, and *Thiomonas intermedia*, which catalyze the oxidation of reduced sulfur compounds to sulfate (Kelly *et al.*, 2000; Kappler *et al.*, 2021). These microbes thrive in oxygenated aquifers, utilizing oxygen or nitrate as electron acceptors, and play a crucial role in maintaining water quality by limiting the accumulation of reduced sulfur species (Baldwin *et al.*, 2020). High sulfate levels under these conditions may originate from natural mineral dissolution or anthropogenic sources such as fertilizers or sewage leachate.

In contrast, samples from Nwabuude Mall and Almond Garden HDWs fall closer to or within the $\text{H}_2\text{S}(\text{aq})$ stability field, indicating significantly reducing conditions ($E_h \sim -0.2$ to -0.3 V) and near-neutral pH. These environments are favorable for SRB activity, including genera like *Desulfobacter*, *Desulfotomaculum*, and *Desulfovibrio*, which use sulfate as a terminal electron acceptor in anaerobic respiration, reducing it to H_2S (Santos *et al.*, 2015; Rabus *et al.*, 2013). The presence of H_2S can be associated with odor issues and potential corrosion of water infrastructure, but more critically, it signals active anaerobic microbial metabolism that may also mobilize toxic trace metals like arsenic and iron via reductive dissolution (Islam *et al.*, 2004; Hug *et al.*, 2008). These biogeochemical transformations are often exacerbated in organic-rich, stagnant zones where oxygen diffusion is limited.

The wells at Divine Mercy Parish and Tenece Layout HDWs occupy transitional zones between SO_4^{2-} and $\text{H}_2\text{S}(\text{aq})$ fields. These intermediate redox conditions suggest dynamic sulfur cycling, likely governed by a combination of SOB and SRB. In such microaerophilic environments, microbial consortia may switch between oxidative and reductive metabolism depending on localized oxygen and substrate availability (Canfield *et al.*, 2010). Studies have shown that redox transitions in shallow aquifers often correlate with fluctuating water tables, organic matter input, and seasonal recharge, influencing microbial community composition and activity (Fang *et al.*, 2017). Mixed microbial activity in these transitional zones may promote sulfur disproportionation reactions, where elemental sulfur (S^0) is both oxidized and reduced, contributing to complex sulfur speciation and reactivity (Finstler, 2008).

These geochemical and microbiological variations have broader implications for groundwater management. Reducing conditions that foster SRB activity can increase concentrations of sulfide and dissolved metals, while oxidizing zones support higher sulfate levels and potentially lower microbial diversity. Moreover, the cycling of sulfur is not isolated—it interlinks with carbon, nitrogen, and metal cycles, influencing the overall biogeochemical fingerprint of the aquifer (Sivan *et al.*, 2014). Hence, monitoring Eh-pH parameters, in conjunction with microbial profiling, provides a more holistic assessment of groundwater quality and stability.

Conclusion and Recommendation

This study highlights how the chemistry of groundwater in Enugu is closely tied to the redox conditions that control sulfur speciation. In areas like Winners Estate, where the environment is more oxidizing, sulfate is the dominant sulfur species, while in locations such as Ezenweke Street and Ivory Estate, reducing conditions favor the formation of hydrogen sulfide and bisulfide. These reduced sulfur forms not only affect the taste and smell of the water but also raise concerns about corrosion and the potential release of toxic metals like arsenic and manganese. These findings point to the influence

of both natural microbial processes and human activities, such as poor waste management, on groundwater quality. To safeguard water resources, there is a need for regular monitoring of redox-sensitive elements and deeper investigations into the microbial communities involved in sulfur cycling. Improving sanitation infrastructure, protecting recharge zones, and raising public awareness will also go a long way in ensuring safer drinking water for communities across Enugu.

References

- Appelo, C. A. J., and Postma, D. (2005). *Geochemistry, Groundwater and Pollution* (2nd ed.). CRC Press.
- Baldwin, B. R., Tornabene, T. G., and Gulati, M. (2020). "Microbial sulfur oxidation in shallow groundwater environments: implications for water quality." *Journal of Environmental Quality*, 49(4), 943–954.
- Böttcher, M. E., Thamdrup, B., Gehre, M., and Theune, A. (2005). "Stable sulfur isotopes indicate net sulfate reduction in near-surface groundwater flow." *Chemical Geology*, 215(1–4), 133–147.
- Burton, E. D., Bush, R. T., and Sullivan, L. A. (2007). Reductive transformation of iron and sulfur in wetland sediments: Implications for water quality. *Environmental Chemistry*, 4(3), 137–147.
- Canfield, D. E., Thamdrup, B., and Kristensen, E. (2010). *Aquatic Geomicrobiology*. Elsevier.
- Christensen, T. H., Bjerg, P. L., Banwart, S. A., Jakobsen, R., Heron, G., and Albrechtsen, H. J. (2000). "Characterization of redox conditions in groundwater contaminant plumes." *Journal of Contaminant Hydrology*, 45(3–4), 165–241.
- Edet, A. E., and Okereke, C. S. (2005). Hydrogeological and hydrochemical characteristics of the regolith aquifer, southeastern Nigeria. *Journal of African Earth Sciences*, 41(3), 221–234.
- Egboka, B. C. E., Nwankwor, G. I., Orajaka, I. P., and Ejiofor, A. O. (1989). Principles and problems of environmental pollution of groundwater resources with case examples from developing countries. *Environmental Health Perspectives*, 83, 39–68.
- Ezeh, H. N. (2004). Hydrogeological and geotechnical parameters as aid to groundwater potential mapping in Enugu State, Nigeria. *Global Journal of Geological Sciences*, 2(2), 243–254.
- Ezeigbo, H. I. (1989). Groundwater quality problems in parts of Imo River Basin, southeastern Nigeria. *Journal of Mining and Geology*, 25(1), 1–9.
- Fang, Y., Yao, J., Zhang, X., and Yuan, S. (2017). "Impact of seasonal recharge on microbial redox dynamics in a shallow aquifer." *Science of the Total Environment*, 599–600, 742–750.
- Finster, K. (2008). "Microbiological disproportionation of inorganic sulfur compounds." *Journal of Sulfur Chemistry*, 29(3), 281–292.

- Friedrich, C. G., Rother, D., Bardischewsky, F., Quentmeier, A., and Fischer, J. (2005). "Oxidation of reduced inorganic sulfur compounds by bacteria: emergence of a common mechanism?" *Applied and Environmental Microbiology*, 71(5), 2331–2347.
- Hug, S. J., Leupin, O. X., and Berg, M. (2008). "Arsenic in groundwater: Natural processes and mitigation." *Applied Geochemistry*, 23(11), 2888–2905.
- Islam, F. S., Gault, A. G., Boothman, C., Polya, D. A., Charnock, J. M., and Lloyd, J. R. (2004). "Role of metal-reducing bacteria in arsenic release from Bengal delta sediments." *Nature*, 430(6995), 68–71.
- Kappler, A., Bryce, C., Mansor, M., Lueder, U., Byrne, J. M., and Swanner, E. D. (2021). "An evolving view on biogeochemical cycling of iron." *Nature Reviews Microbiology*, 19(6), 360–374.
- Kelly, D. P., Shergill, J. K., Lu, W. P., and Wood, A. P. (2000). "Oxidative metabolism of inorganic sulfur compounds by bacteria." *Antonie van Leeuwenhoek*, 77(3), 297–315.
- Kuenen, J. G. (2008). Colourless sulfur bacteria and their role in sediment biogeochemistry. In J. T. Hollibaugh (Ed.), *Pollution and Marine Ecology* (pp. 187–204). Academic Press.
- Langmuir, D. (1997). *Aqueous Environmental Geochemistry*. Prentice Hall.
- Luther, G. W., Findlay, A. J., MacDonald, D. J., Owings, S. M., Hanson, T. E., Beinart, R. A., and Girguis, P. R. (2011). Thermodynamics and kinetics of sulfide oxidation by oxygen: A look at inorganically and biologically mediated reactions. *Aquatic Geochemistry*, 17, 325–356.
- Muyzer, G., and Stams, A. J. M. (2008). "The ecology and biotechnology of sulphate-reducing bacteria." *Nature Reviews Microbiology*, 6(6), 441–454.
- Muyzer, G., and Stams, A. J. M. (2008). The ecology and biotechnology of sulphate-reducing bacteria. *Nature Reviews Microbiology*, 6(6), 441–454.
- Nwankwoala, H. O. (2013). Hydrochemical characteristics and quality assessment of groundwater in parts of the Niger Delta. *Journal of Academic Research International*, 4(6), 186–198.
- Nwankwoala, H. O., and Udom, G. J. (2011). Hydrochemical facies and ionic ratios of groundwater in Port Harcourt, Southern Nigeria. *Research Journal of Chemical Sciences*, 1(3), 87–101.
- Postgate, J. R. (1984). *The Sulphate-Reducing Bacteria*. Cambridge University Press.
- Rabus, R., Venceslau, S. S., Wohlbrand, L., Voordouw, G., Wall, J. D., and Pereira, I. A. C. (2013). "A post-genomic view of the ecophysiology, catabolism and biotechnological relevance of sulfate-reducing prokaryotes." *Advances in Microbial Physiology*, 62, 55–321.
- Santos, A. L., Coelho, F., and Almeida, J. S. (2015). "Microbial diversity and metabolic pathways in sulfide-rich groundwater environments." *Frontiers in Microbiology*, 6, 1380.

- Sivan, O., Antler, G., Turchyn, A. V., and Yechieli, Y. (2014). "Geochemical evidence for iron-mediated anaerobic oxidation of methane." *Geochimica et Cosmochimica Acta*, 137, 267–277.
- Tesoriero, A. J., Puckett, L. J., and Gurdak, J. J. (2015). Vulnerability of groundwater quality to human activity and climate change. *Current Climate Change Reports*, 1(2), 53–69.
- World Health Organization (WHO). (2017). *Guidelines for Drinking-Water Quality* (4th ed., incorporating the 1st addendum). WHO Press, Geneva.
- Zhang, W., Lyu, M., Song, Y., and Chen, X. (2019). Sulfur cycling and speciation in subsurface environments: A review of current knowledge and future perspectives. *Earth-Science Reviews*, 194, 32–50.
<https://doi.org/10.1016/j.earscirev.2019.03.005>