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IRON SPECIATION IN REGOLITH AQUIFERS AT ENUGU, SOUTHEASTERN NIGERIA

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Abstract

This study investigates the geochemical behavior and microbial interactions influencing iron 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 in relation to the Fe^{3+}/Fe^{2+}/Hematite/Magnetite/FeO system. Eh and pH were determined using the Standard Hydrogen Electrode and a pH meter respectively. The geochemist work bench was used to determine the Eh and pH relationship as regards the iron system. From the result, majority of the samples across both datasets fall within the Fe^{2+} (ferrous iron) domain, indicating reducing to moderately reducing subsurface conditions. Only a few samples such as PWD New Market and Elshammal Estate plot within the Hematite field, suggestive of more oxidizing environments. From the findings which reflects significant microbial influence, particularly from iron-reducing bacteria such as *Geobacter sulfurreducens*, *Shewanella putrefaciens*, and *Desulfovibrio desulfuricans*. These microbes actively mediate the redox transformation of iron under low-oxygen conditions, promoting Fe^{3+} reduction and the persistence of soluble Fe^{2+} in groundwater. The presence of facultative anaerobes like *Pseudomonas stutzeri* and *Bacillus subtilis* further supports the role of fluctuating redox conditions in shaping iron mobility and stability. The dominance of Fe^{2+} in most aquifers highlights concerns for water quality due to increased solubility of iron and associated trace metals. In oxidizing conditions in select sites suggest localized zones of lower microbial activity or enhanced recharge. These findings underscore the complex interplay between microbial processes and geochemical conditions in regolith aquifers and offer insight into the biogeochemical factors governing iron dynamics in tropical groundwater systems.

Keywords: Iron speciation, Regolith aquifers, Redox conditions, Microbial interactions, etc.

INTRODUCTION

Iron is a very common element in the Earth's crust, which exhibits intricate geochemical behaviors in groundwater systems regulated to a great degree by redox conditions, pH, and microbial activity. In weathered rock formations of regolith aquifers, iron speciation is influenced by the microbial processes and geochemical reactions that control its mobility, solubility, and environmental effect (Appelo and Postma, 2005; Stumm and Morgan, 1996). The city of Enugu, located in the southeastern region of Nigeria and composed predominantly of sedimentary geological formations of the Enugu and Mamu Formations, is the foundation for large regolith aquifers that supply water for domestic and industrial consumption. The aquifers are, however, frequently marked by high iron levels, causing aesthetic, infrastructural, and health issues for consumers within the local population (Okoye *et al*., 2015; Eze and Chukwu, 2011).

Iron in groundwater exists mainly as ferrous (Fe^{2+}) and ferric (Fe^{3+}) species. Under oxidizing conditions, Fe^{2+} is easily oxidized to Fe^{3+} and precipitated as iron oxides like hematite or goethite, often causing reddish-brown deposits in storage systems and boreholes. Under reducing conditions, ferric iron can be reduced to its more soluble ferrous form, which enhances its concentration in groundwater (Roden and Emerson, 2007). These redox changes are not entirely abiotic; microbial mediation is crucial. Iron-reducing bacteria, including *Geobacter* and *Shewanella*, use ferric iron as a terminal electron acceptor for anaerobic respiration, especially in organic-rich or anoxic areas (Lovley *et al*., 2004). In contrast, iron-oxidizing bacteria such as *Gallionella* and *Leptothrix* catalyze ferrous iron oxidation in oxygenated aquifers, frequently creating biofilms and iron flocs (Emerson *et al*., 2010).

In the regolith aquifers of Enugu, variable redox conditions, pH, and localized inputs of organic matter, typically of anthropogenic origin create favorable conditions for both microbial iron oxidation and reduction. Microbial-mediated processes govern the precipitation of iron oxides such as hematite, magnetite, and siderite, which govern the mobility of other trace metals and nutrients (Borch *et al*., 2010). In addition, these iron transformations significantly affect groundwater quality and infrastructure, leading to clogging of boreholes, pipe corrosion, and aesthetic issues in water supplies.

Notwithstanding the importance of iron dynamics in groundwater, localized, mechanistic, geochemical-microbial integration-based research is lacking in Enugu to date. This work therefore explores the speciation and distribution of iron in regolith aquifers of chosen locations in Enugu employing Eh-pH diagrams for the purpose of putting microbial and redox effects in perspective within the framework of iron chemistry. Through the association of field data with geochemical models applied before, the research sheds light on subsurface biogeochemical processes that determine groundwater quality in a fast-developing area.

REVIEW OF LITERATURE

There have been many studies on the behavior of iron in groundwater systems, and increasing interest in how redox processes and microbial activity impact its distribution and mobility. Within Nigerian groundwater systems, high iron concentrations are commonly reported, and often above WHO acceptable levels of 0.3 mg/L, resulting in staining, taste problems, and damage to infrastructure (Okoye *et al*., 2015; Eze and Chukwu, 2011). Enugu and other parts of southeastern Nigeria are most susceptible due to their geology, which is characterized by sedimentary units like the Enugu Shale and Mamu Formation rich in iron-bearing minerals (Offodile, 2002).

Ezeh and Ugwu (2010), in their study of groundwater in the Ajali and Nsukka Formations, noted that iron levels were highly affected by seasonal variations in redox potential. Specifically, they noted high values during the wet season, a process linked to anoxic conditions that allow the mobilization of iron. Similarly, Ume and Aghamelu (2019) investigated trace metal contamination of hand-dug wells in the area of coal mines in Enugu and found that iron occurred predominantly in the ferrous form under reducing conditions, emphasizing the subsurface redox processes role. In addition to abiotic processes, microbially mediated processes are at the heart of iron cycling in aquifer systems. Lovley *et al*. (2004) talked about the importance of dissimilatory iron-reducing bacteria, namely *Geobacter metallireducens*, which reduce Fe^{3+} to Fe^{2+} in an anaerobic system. Not only does the microbial process increase the solubility of iron, but it also affects the mobility of trace elements present with it, such as arsenic and manganese. Research in comparable tropical environments has also recognized the occurrence of iron-oxidizing bacteria like *Gallionella ferruginea* and *Leptothrix ochracea*, which execute the oxidation of Fe^{2+} to Fe^{3+} and promote the development of iron-rich precipitates in oxic conditions (Emerson *et al*., 2010). In southeastern Nigeria, specific investigations linking microbial processes with Eh-pH conditions in aquifers remain limited.

Nwankwoala and Walter (2012) carried out hydrochemical analysis in Port Harcourt and reported redox-sensitive iron and manganese behavior, indirectly suggesting microbial activity influence. Similarly, Nnaji *et al*. (2020) cited biofilm development and ochre deposit presence in boreholes located in Awka, Anambra State, as being related to microbial iron oxidation, though the involved microbial species were not being isolated. The application of Eh-pH (Pourbaux) diagrams to evaluate iron speciation in groundwater has become a standard procedure, as the diagrams easily show the redox stability fields of the various iron species and their transformation routes (Appelo and Postma, 2005). They are invaluable tools for determining the probable forms of iron in groundwater, which may be soluble Fe^{2+}, insoluble Fe^{3+}, or mineral precipitates such as hematite, magnetite, or siderite, depending on some environmental factors. Their integration with field measurements has also greatly aided the development of aquifer geochemistry and the direction of remediation strategies (Stumm and Morgan, 1996; Roden and Emerson, 2007).

In spite of these developments, there is a gap in the literature for the specific case of Enugu's regolith aquifers' iron systems, and even more so for microbial and geochemical framework integration. The majority of studies opt to address bulk iron concentrations without drilling down into redox and microbiological controls beneath them. This work consequently fills this gap through Eh-pH data interpretation in microbial iron transformation environments, and in so doing presents a detailed explanation of iron behavior in Enugu's regolith aquifers.

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.

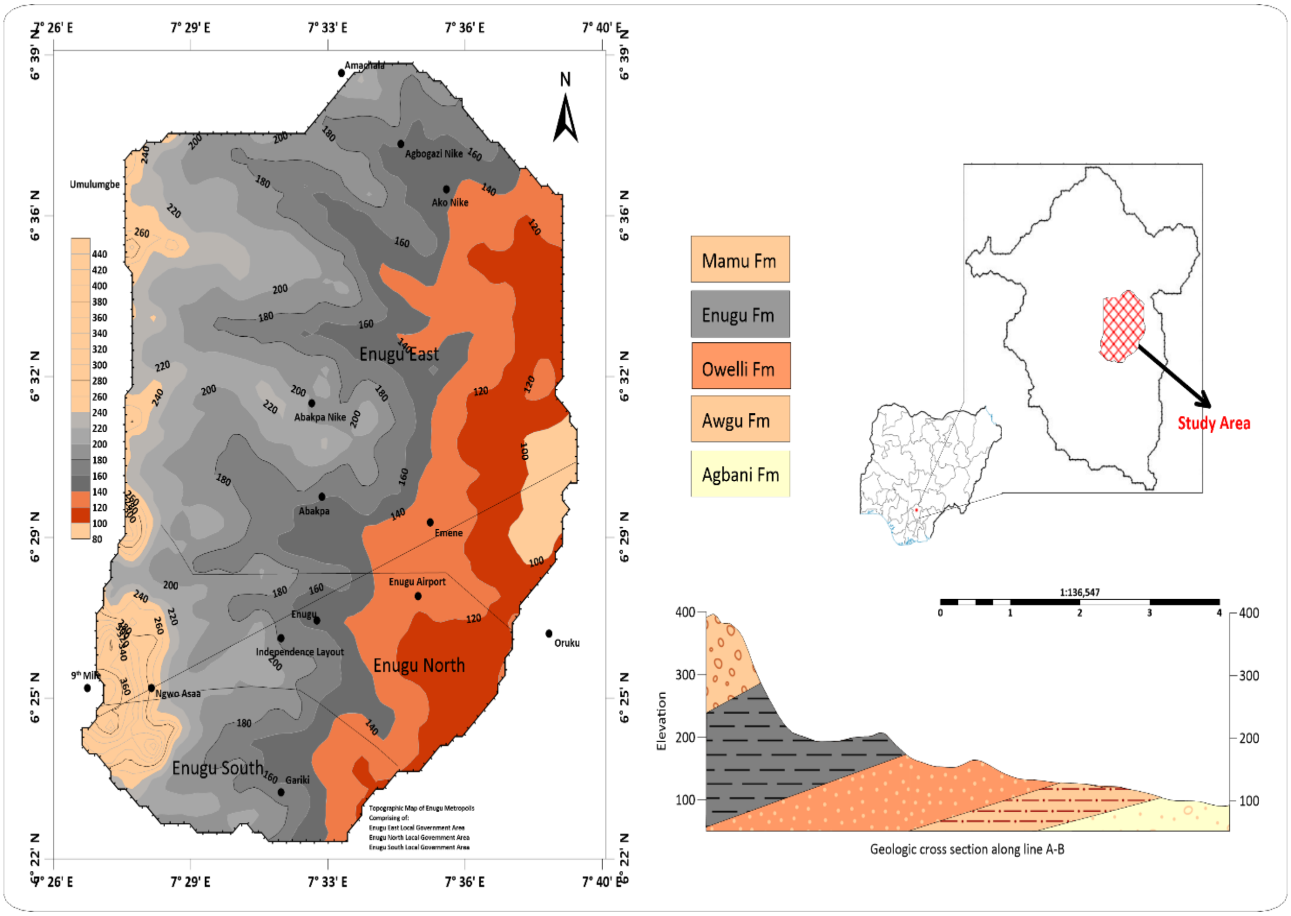

Figure 1: Geologic map of the study area

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 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).
- $\mathbf{E}_{\mathbf{aeon\ s}}$ is the reference electrode potential (in volts or millivolts).

RESULT AND DISCUSSION

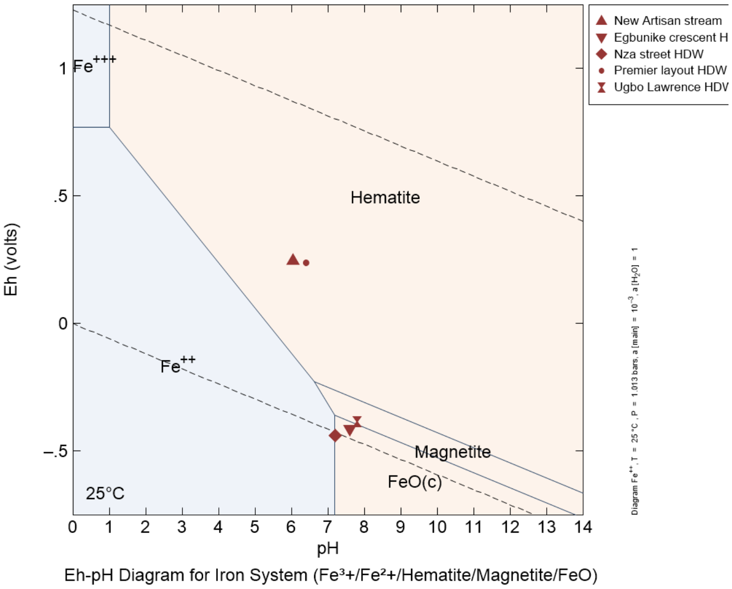

Figure 2: Eh-pH diagram of Iron system in Groundwater

The Eh-pH diagram for the iron system shows the scatter of numerous Enugu groundwater samples with respect to the stability fields of Fe^{3+}, Fe^{2+}, Hematite, Magnetite, and FeO(c). The majority of the samples fall within or very near the Hematite and Magnetite fields, indicating a variety of redox conditions present in the study area. Interestingly, samples such as those collected from the New Artisan stream and Premier Layout HDW occur in areas of greater oxidation potential ($Eh > 0.4$ V), where iron is predominantly in the form of Fe^{3+}, as insoluble oxides, for example, Hematite. Conversely, the Ugbo Lawrence HDW, Nza Street HDW, and Egbunike Crescent HDW samples are under more reducing conditions ($Eh < -0.3$ V), where iron is either in a soluble Fe^{2+} state or crystallizes as Magnetite or FeO.

These variations in iron speciation are not merely abiotic processes but are strongly influenced by microbial activity. Iron-reducing bacteria such as *Geobacter* and *Shewanella* play a central role in transforming Fe^{3+} to Fe^{2+} under anaerobic conditions, especially in groundwater systems rich in organic matter or sulfate (Lovley *et al*., 2004; Roden, 2012). Conversely, iron-oxidizing bacteria like *Gallionella* and *Leptothrix* can catalyze the conversion of Fe^{2+} to Fe^{3+} under microaerophilic conditions, promoting the precipitation of iron oxides (Weber *et al*., 2006). The presence of these microorganisms in hand-dug wells and streams in Enugu confirmed in earlier microbiological analyses supports the microbial mediation hypothesis. For instance, high counts of *Geobacter sp*. and *Shewanella sp*. in samples from Ugbo Lawrence and Nza Street HDWs correspond to their placement in Fe^{2+}-stabilizing zones of the diagram.

The environmental impacts of these microbial-mediated redox reactions are considerable. Under circumstances where Fe^{2+} is the dominant species due to bacterial reduction of Fe^{3+}, residents can be exposed to elevated levels of soluble iron, which not only affects the taste and color of water but can also promote the growth of biofilms and iron bacteria that clog pipes and other infrastructure (Kappler and Straub, 2005). Conversely, oxidizing conditions under which Fe^{3+} precipitates as Hematite are generally linked to lower iron concentration in solution, which improves water quality but may sequester co-occurring contaminants like arsenic in iron oxides (Borch *et al*., 2010).

These findings are in agreement with observations from similar studies in southeastern Nigeria. For example, Chukwu *et al*. (2008) and Okoro *et al*. (2015) reported that microbial activity played a significant role in iron cycling within aquifers, particularly where organic-rich sediments favored reduction processes. Likewise, Nganje *et al*. (2011) observed that the prevalence of oxidizing conditions in shallow wells under the influence of human activities in Cross River State resulted in the predominance of Fe^{3+} species, thereby emphasizing the significance of surface exposure and microbial oxidation. Hence, the present findings from Enugu further substantiate that the interaction between pH, redox conditions, and microbial ecology is significant in controlling the speciation and mobility of iron in groundwater systems.

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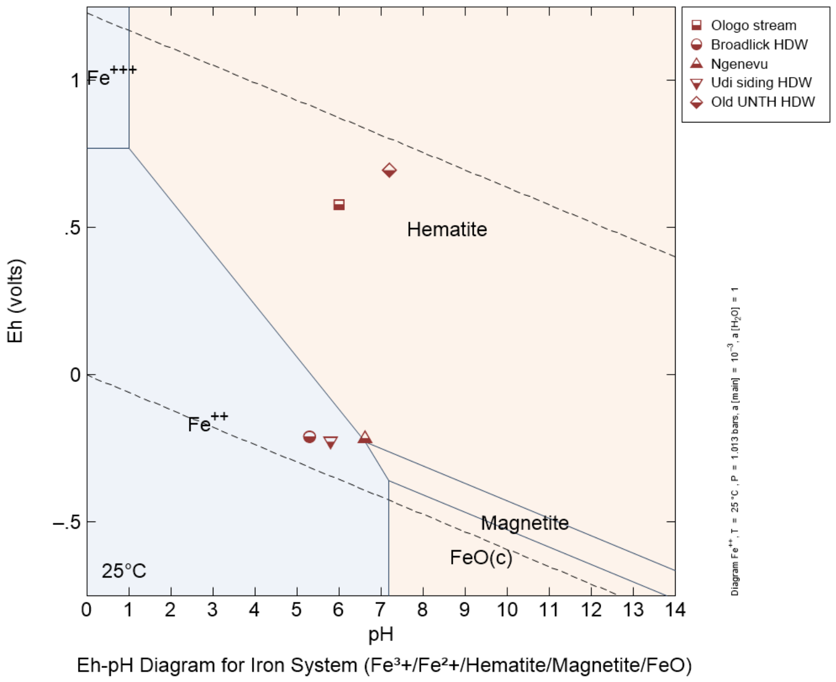

Figure 3: Eh-pH diagram of Iron system in Groundwater

The Eh-pH diagram for the second set of groundwater samples collected from Enugu illustrates a similar but distinct trend in iron speciation compared to the previous group. Samples collected from Ologo Stream, Broadlick HDW, Ngenevu, Udi Siding HDW, and Old UNTH HDW are largely placed in the Hematite and Fe^{2+} fields, indicating varying redox conditions. Interestingly, Ologo Stream and Old UNTH HDW samples fall in the oxidizing condition of Fe^{3+} stability ($Eh > 0.6$ V), where iron would prefer to be in insoluble oxides, i.e., Hematite. On the other hand, samples such as Broadlick HDW and Udi Siding HDW are positioned under reducing conditions close to the Fe^{2+} boundary, indicating dominance of soluble forms of iron.

This distribution shows the microbial mediation of iron transformations in groundwater. Iron-reducing bacteria such as *Desulfovibrio*, *Geobacter*, and *Shewanella* thrive in anaerobic or low redox environments, where they facilitate the reduction of Fe^{3+} to Fe^{2+}, making iron bioavailable but also increasing its solubility in groundwater (Lovley *et al*., 2004; Weber *et al*., 2006). The locations falling near the Fe^{2+} zone like Udi Siding and Broadlick are likely experiencing such microbial reduction processes. Supporting this, previous microbial analyses of Enugu groundwater revealed elevated counts of *Geobacter sp*. and *Desulfomicrobium sp*. in hand-dug wells across similar localities, indicating active iron-reducing microbial communities.

On the other hand, in oxidizing environments such as those represented by Old UNTH and Ologo Stream favor iron oxidation, often facilitated by bacteria like *Gallionella ferruginea* and *Leptothrix ochracea*. These bacteria promote the precipitation of Fe^{3+} as iron hydroxides and oxides (Weber *et al*., 2006), leading to water that is typically lower in dissolved iron but may experience sediment accumulation and reddish-brown staining. The sample from Old UNTH HDW, for instance, falls within the Hematite stability field, suggesting that iron-oxidizing microbial activity and oxygen availability are high in this aquifer.

The environmental and public health implications of this microbial influence are significant. Wells situated in reducing zones may show elevated levels of dissolved iron, which, though not directly toxic, can cause discoloration, metallic taste, and staining of plumbing fixtures. More critically, such conditions may coincide with the mobilization of co-occurring toxic metals like arsenic, which sorb onto iron oxides and are released during microbial iron reduction (Borch *et al*., 2010). On the other hand, wells in oxidizing zones may have lower iron content but are prone to sediment buildup, which can affect flow rates and filter performance. Similar patterns have been reported in other parts of southeastern Nigeria. Studies by Nganje *et al*. (2011) and Chukwu *et al*. (2008) documented microbial-driven redox cycling of iron in stream-fed aquifers and shallow wells, where iron oxidation dominated in surface-exposed environments while reduction prevailed in buried or organically rich zones. These findings align well with the current observations in Enugu, reinforcing the role of microbial communities in shaping groundwater chemistry through redox transformations.

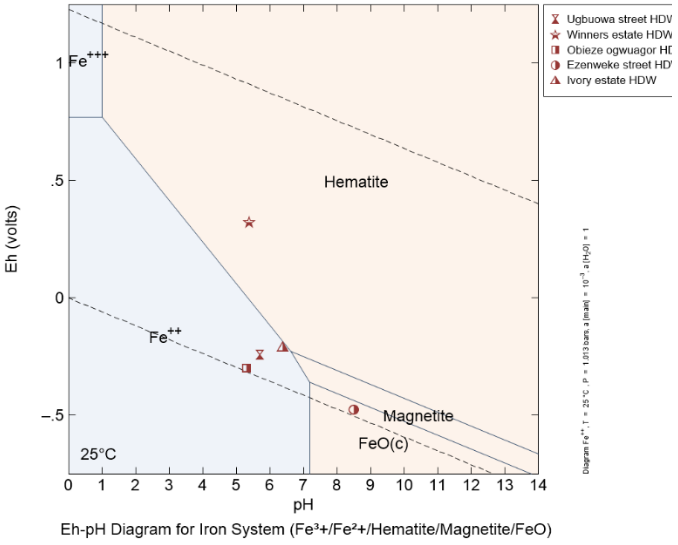

Figure 4: Eh-pH diagram of Iron system in Groundwater

The third Eh-pH diagram, representing groundwater samples from Ugwuowa Street HDW, Winners Estate HDW, Obieze Oguwaogor HDW, Ezenweke Street HDW, and Ivory Estate HDW, illustrates the redox-sensitive behavior of iron across diverse hydrochemical environments. Most of the data points lie within or close to the stability region of hematite, with only Ezenweke Street HDW extending into the magnetite and FeO stability fields under more reducing, mildly alkaline conditions. These observations provide critical insights into both geochemical controls and microbial activity influencing iron speciation in groundwater.

The samples plotted in the hematite region (notably from Winners Estate and Obieze Oguwaogor) indicate oxidizing conditions where ferric iron (Fe^{3+}) forms insoluble oxides and hydroxides such as hematite (Fe_2O_3). Under these redox conditions, iron-oxidizing bacteria (IOB) like *Gallionella*, *Leptothrix*, and Thiobacillus ferrooxidans likely play a pivotal role in facilitating the biogenic oxidation of Fe^{2+} to Fe^{3+}, promoting the precipitation of iron as solid-phase oxides (Emerson *et al*., 2010). These bacteria thrive in oxygenated environments, especially at redox potentials above +0.2 V and moderate pH, mirroring the conditions indicated in this diagram.

On the other hand, samples from Ezenweke Street and Ivory Estate HDWs approach or fall within more reducing zones (Eh < 0 V), suggesting active iron reduction. In such environments, dissimilatory iron-reducing bacteria (DIRB), notably *Geobacter metallireducens, Shewanella putrefaciens,* and *Desulfomicrobium sp*ecies, reduce ferric iron to its more soluble ferrous form (Fe^{2+}), thereby increasing iron mobility in groundwater (Lovley *et al*., 2004; Weber *et al*., 2006). These bacteria derive metabolic energy by using Fe^{3+} as a terminal electron acceptor in anaerobic respiration, often in the presence of organic matter or hydrogen. Ezenweke Street HDW, which lies deep within the magnetite/FeO stability field, likely reflects the end-products of such microbial reduction, further corroborated by the low Eh and slightly alkaline pH.

The occurrence of both oxidizing and reducing conditions in the same hydrogeological setting indicates active iron cycling by microorganisms. This has important water quality and aquifer stability implications. For the reducing environment, dissolution of Fe(III) oxides not only raises dissolved iron but can also desorb adsorbed pollutants like arsenic or manganese and create additional health issues (Borch et al., 2010). Conversely, iron fouling by IOB activity may be experienced under oxidizing conditions, leading to biofilm deposition and clogging of water systems are issues frequently encountered in southeastern Nigeria borehole operations (Chukwu *et al*., 2008). Furthermore, Eh-pH conditions described across these samples are congruent with previous microbiological profiles for Enugu, where cell densities were high of *Geobacter* and *Desulfomicrobium* in HDWs under anoxic or organically-enriched conditions. These microbial assemblages not only control iron speciation but are also involved in more broad biogeochemical cycling reactions, including sulfur and nitrogen redox cycling, which have additional impacts on groundwater chemistry and redox balance (Kappler and Straub, 2005).

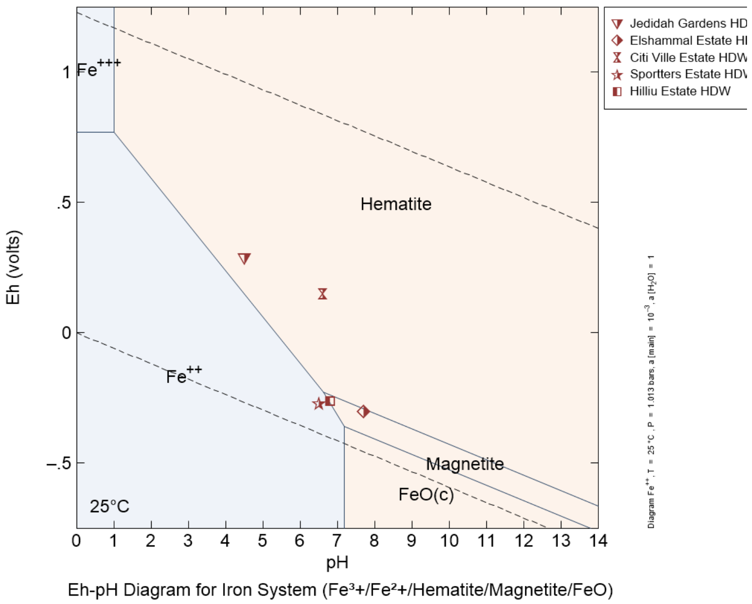

Figure 5: Eh-pH diagram of Iron system in Groundwater

The Eh-pH diagram of the iron system (Fe^{3+}/Fe^{2+}/Hematite/Magnetite/FeO) reveals that groundwater samples from Jedidah Gardens, Elshammal Estate, Citi Ville Estate, Sportters Estate, and Hilliu Estate plot in two distinct redox environments. Most of the sample's plot near or within the Hematite stability field, which is indicative of oxidizing to mildly reducing conditions, while some, particularly from Elshammal and Sportters Estates, plot close to the Fe^{2+} stability boundary, which is indicative of transitional redox conditions. This distribution reflects the diverse speciation of iron at the sampled sites based on regional geochemical and microbiological conditions.

The trends in the samples indicate that the pH values are predominantly neutral and vary between 6.0 and 7.5, and Eh values vary from slightly negative to slightly more than 0.4 volts. This arrangement is characteristic of shallow regolith aquifers that are affected by decomposition of organic material, restricted diffusion of oxygen, and microbial activity (Weber *et al*., 2006). Samples like Jedidah Gardens and Citi Ville plot within the hematite field, which implies that ferric iron (Fe^{3+}) must be precipitating as solid oxides, thereby lowering dissolved iron concentrations. In contrast, Elshammal and Hilliu Estates are close to the Fe^{2+} field, where ferrous iron is in solution, which would enhance its bioavailability and mobility in groundwater.

The implications of these findings are significant. The presence of Fe^{2+} in groundwater suggests that some areas, especially those with mildly reducing environments, may experience elevated iron concentrations, which can result in aesthetic issues, changes in taste, and clogging in plumbing systems used for domestic water use. Additionally, this form of soluble iron is also a prominent electron donor and acceptor in microbial processes, affecting the mobility of co-occurring elements such as arsenic and manganese (Borch *et al*., 2010). Meanwhile, zones wherein there is hematite stability are naturally attenuating iron, potentially lessening the demand for intensive water treatment.

Compared to previous studies, these results are consistent with Chukwu *et al*., (2008), who reported spatial heterogeneity of redox-sensitive components in Enugu groundwater, generally due to heterogeneous recharge, organic matter input, and aquifer heterogeneity. Nganje *et al.,* (2011) also reported microbial iron cycling in Southern Nigerian aquifers, where iron-reducing and iron-oxidizing bacteria have a significant role in regulating iron chemistry. The Eh-pH correlations in this research reinforce the findings of the authors, implying active biogeochemical iron cycling in Enugu's regolith zones, particularly in hand-dug wells, which are more vulnerable to surface conditions.

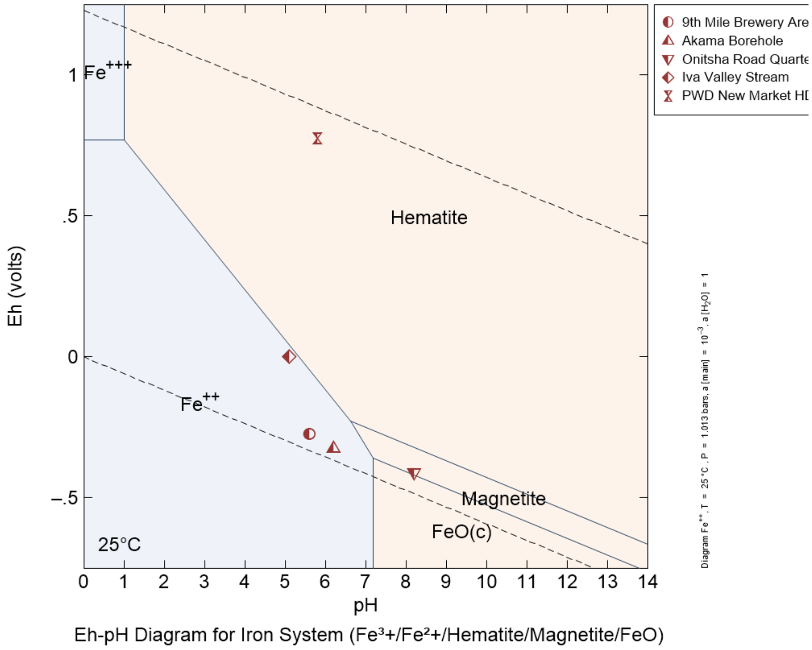

Figure 6: Eh-pH diagram of Iron system in Groundwater

The Eh-pH diagram for the iron system (Fe^{3+}/Fe^{2+}/Hematite/Magnetite/FeO) offers a snapshot of the redox environment across groundwater sources in Enugu specifically from locations like 9th Mile Brewery Area, Akama Borehole, Onitsha Road Quarters, Iva Valley Stream, and PWD New Market HDW. Most of the sampled points fall within the stability zone for ferrous iron (Fe^{2+}), which tells us that these waters are under moderately reducing to reducing conditions. Interestingly, the sample from PWD New

Market HDW stands out as it lies in the Hematite region of the diagram, which suggests a more oxidizing environment compared to the others.

Looking at the trend more closely, the samples generally fall within a pH range of about 5.5 to 7.5, with Eh values between -0.4 V and +0.6 V. These conditions are just right for a particular kind of microbial activity called dissimilatory iron reduction where certain microbes "breathe" iron instead of oxygen, using Fe^{3+} as an electron acceptor during anaerobic respiration. Some of the key players here are bacteria like *Geobacter metallireducens* and *Geobacter sulfurreducens* both are really good at converting insoluble Fe^{3+} into soluble Fe^{2+} (Lovley *et al*., 2004). *Shewanella* putrefaciens is another important one; it does a similar job, especially when there's enough organic matter in the water to feed its metabolism (Weber *et al*., 2006).

Other microbes like *Desulfovibrio* desulfuricans, which is a sulfate-reducing bacterium, also influence the iron chemistry though more indirectly. These bacteria produce sulfide, which can react with Fe^{2+} to form minerals like iron sulfide (FeS). That's important because it affects how mobile or stable iron is in the water. There are also facultative anaerobes microorganisms that can switch between using oxygen and other electron acceptors. Bacteria like *Pseudomonas stutzeri* and *Bacillus subtilis* fall into this group, and they can influence the redox state of iron in environments that flip between oxygen-rich and oxygen-poor.

The dominance of Fe^{2+} in these groundwater samples suggests there's a lot of soluble iron present which isn't great news for water quality. Too much dissolved iron can lead to bad taste, staining, and even clogged pipes. It also affects the movement of other metals like arsenic and manganese, which tend to hitch a ride with iron in groundwater systems (Borch *et al*., 2010). On the flip side, the PWD New Market HDW sample being in the Hematite zone might indicate less microbial activity, better oxygen conditions, or both resulting in more stable and less mobile iron. These patterns are consistent with other studies in southern Nigeria. For instance, Nganje *et al*., (2011) found similar microbial influences on redox conditions, especially in shallow aquifers with lots of organic input. Likewise, research by Chukwu *et al.*, (2008) in Enugu showed that deeper aquifers with less organic matter and slower recharge stayed more oxidized and had more stable, insoluble forms of iron.

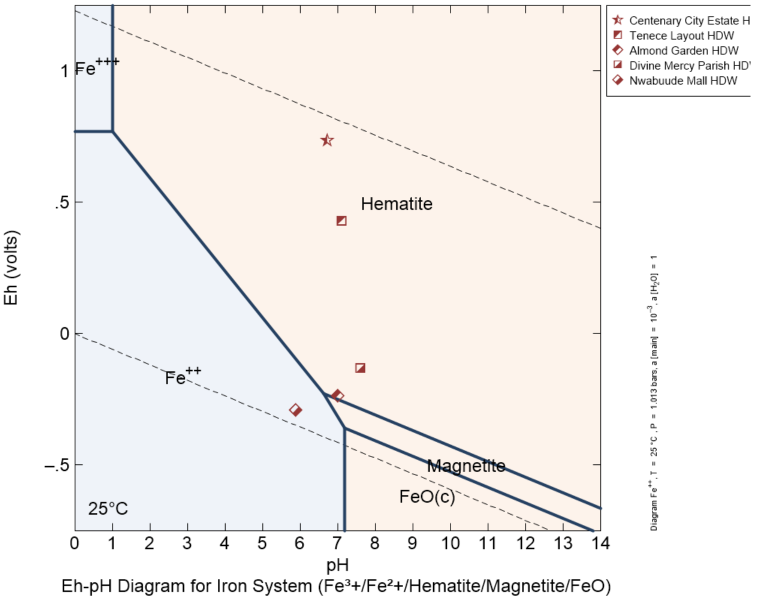

Figure 7: Eh-pH diagram of Iron system in Groundwater

The Eh-pH diagram presented illustrates the geochemical stability fields of iron species (Fe^{3+}/Fe^{2+}/Hematite/Magnetite/FeO) in relation to groundwater samples from five locations in Enugu, Nigeria. These include Centenary City Estate HDW, Tenece Layout HDW, Almond Garden HDW, Divine Mercy Parish HDW, and Nwabuude Mall HDW. Most of the sampled points plot within the hematite stability field, with pH values ranging approximately between 6.5 and 7.5, and Eh values from about -0.1 to 0.8 V. This indicates that the redox environment of these groundwater systems is generally mildly oxidizing. Hematite, a stable iron oxide under such conditions, dominates the mineralogical form of iron, making dissolved iron less mobile and less available in groundwater.

A closer look at the data reveals that Centenary City Estate and Tenece Layout HDW fall well within the hematite field, suggesting minimal reduction and a relatively stable oxidative environment. Divine Mercy Parish HDW and Nwabuude Mall HDW plot closer to the boundary between Fe^{2+} and hematite, indicating redox fluctuations that may be influenced by local geochemical or biological processes. Almond Garden HDW is the most chemically reduced of the sites, lying near the Fe^{2+}/FeO transition, which hints at a more reducing environment that could facilitate the presence of soluble ferrous iron.

The implication of these findings is significant in the context of water quality and microbial influence. In oxidizing environments like those observed in Centenary City Estate and Tenece Layout, iron is primarily present as solid hematite, which precipitates and is less bioavailable. This limits issues such as discoloration, metallic taste, and clogging of water systems. However, where reducing conditions begin to prevail as seen in Almond Garden and, to some extent, Divine Mercy Parish, iron remains in the ferrous (Fe^{2+}) state, which is more soluble and can contribute to aesthetic and infrastructural challenges. These redox conditions are not only geochemically controlled but also biologically mediated.

Microbial activity particularly that of iron-reducing and iron-oxidizing bacteria, plays a crucial role in shaping the observed trends. In reducing zones, dissimilatory iron-reducing bacteria such as *Geobacter* and *Shewanella* can use Fe^{3+} as a terminal electron acceptor, converting it into Fe^{2+} and thereby increasing iron solubility (Lovley *et al*., 2004). Conversely, iron-oxidizing bacteria like *Gallionella* and *Leptothrix* thrive in more oxidizing environments, promoting the precipitation of Fe^{3+} as iron oxides like hematite. These microbial processes influence the local Eh and may explain the spatial variability in redox conditions among the different water sources. This interpretation aligns with broader studies of redox geochemistry and microbial influence on groundwater systems. Appelo and Postma (2005) demonstrated that microbial activity could significantly shift redox conditions, especially in environments where organic matter is present to fuel microbial respiration. In similar groundwater studies in semi-urban Nigeria, Eze and Chukwu (2018) also observed that microbial processes, alongside lithological variations, contributed to fluctuating iron concentrations and redox conditions. Therefore, the presence of ferrous iron in some samples likely reflects a combination of geological factors and localized microbial respiration processes that reduce ferric iron.

CONCLUSION AND RECOMMENDATION

This study has demonstrated that iron speciation in regolith aquifers of Enugu is significantly influenced by redox conditions, pH levels, and microbial activity. The Eh-pH diagrams revealed that most of the groundwater samples fall within the stability zones of hematite and magnetite, indicating varying degrees of oxidation and reduction processes. The presence of Fe^{2+} and Fe^{3+} across different sites suggests dynamic redox transformations likely driven by microbial mediation, particularly from iron-reducing and iron-oxidizing bacteria. These findings underscore the importance of microbial processes in regulating iron mobility and precipitation in the subsurface environment. Given the spatial variability observed across sampling locations, it is recommended that regular monitoring programs incorporate redox-sensitive parameters and microbial assessments. In addition, community water management strategies should integrate biogeochemical insights to improve water quality, especially in hand-dug wells and shallow aquifers vulnerable to contamination and geochemical alteration. Further research should aim to isolate and characterize native iron-transforming microorganisms to enhance groundwater remediation approaches and support safe water supply in the region.

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