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CARBON SPECIATION IN REGOLITH AQUIFERS AT ENUGU, SOUTHEASTERN NIGERIA

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Abstract

This study investigates the carbon speciation in regolith aquifers within Enugu, southeastern Nigeria, with a focus on how redox conditions and microbial activities influence the distribution of carbon species such as aqueous carbon dioxide (CO_2(aq)), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and aqueous methane (CH_4(aq)). A total of 30 groundwater samples from multiple locations such as Centenary, 9th mile, Ologo, Trans-Ekulu, New-artizan and Amechi from both hand-dug wells and stream sources and analyzed for pH and Eh (redox potential). Eh and pH were determined using the Standard Hydrogen Electrode and a pH meter respectively. The raw data were interpreted using Eh-pH (Pourbaix) diagrams for the $CO_2/HCO_3^-/CO_3^{2-}/CH_4$ system at 25°C. The results reveal that most of the sampled aquifers fall within the domains of bicarbonate and aqueous methane, indicating prevailing mildly reducing to strongly reducing conditions in the subsurface environment. These conditions are largely driven by microbial respiration and fermentation processes, particularly those involving sulfate-reducing bacteria, iron-reducers, and methanogens. Sites with more oxidizing Eh values, such as New Artisan stream and Premier Layout HDW, were associated with CO_2(aq) and HCO_3^- dominance, suggesting a higher oxygen availability or active organic matter degradation. Conversely, the dominance of CH_4(aq) in locations such as Egbunike Crescent HDW and Elshammal Estate HDW highlights anaerobic degradation pathways, likely driven by methanogenic archaea under anoxic conditions. This distribution of carbon species provides critical insight into the redox evolution of regolith aquifers in Enugu and underscores the significant role of microbial processes in shaping groundwater chemistry. These findings have implications for water quality, nutrient cycling, and the potential mobilization of redox-sensitive elements in shallow tropical aquifers.

Keywords: Carbon speciation, Regolith aquifers, Redox conditions, Microbial activity, Groundwater chemistry, Eh-pH diagrams, Methane (CH_4), Enugu, Southeastern Nigeria.

INTRODUCTION

Groundwater represents the most reliable source of potable drinking water for most southeastern Nigerian communities, especially in the likes of Enugu, where surface water sources are either seasonal or contaminated. The majority of such groundwater is derived from regolith aquifers, which are weathered rock layers that enable the storage and flow of water. Their usefulness is derived from the fact that they are readily available; however, they also exhibit a high susceptibility to pollution and water chemistry alteration because they are actively involved in surface processes (Omeje *et al*., 2020; Ezeabasili *et al*., 2014).

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Carbon, in its different chemical species, plays a significant role in the chemical dynamics of groundwater systems. It is present primarily as dissolved carbon dioxide ($CO_2(aq)$), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and methane (CH_4), depending on the pH and redox (Eh) conditions of the water (Langmuir, 1997). The balance among such species—carbon speciation—serves not only to influence the quality of water but also serves as a barometer for geochemical and microbiological activity below the ground surface. Such as microbial respiration, organic matter degradation, and methanogenesis all have effects on the carbon partitioning within groundwater systems (Boehme *et al*., 1996; Appelo and Postma, 2005). In regolith aquifers, microbial activity can alter substantially the redox state, resulting in the production of reduced carbon compounds such as CH_4 under anaerobic conditions, or HCO_3^- in relatively oxidized environments. Shifts in carbon speciation can also dictate other geochemical characteristics, including pH, alkalinity, and metal mobility (Chapelle, 2001). In spite of the significance of these interactions, in-depth examinations of carbon speciation in regolith aquifers of Nigeria remain scarce. This is even more the case in urban and peri-urban centers such as Enugu, where population expansion, land-use change, and growing dependence on groundwater heighten the imperative to more thoroughly understand aquifer chemistry with greater urgency (Ezeh and Anike, 2009; Umunnakwe *et al*., 2021).

The present research explores carbon speciation in regolith aquifers at various points in Enugu through Eh-pH (Pourbaix) diagrams in conjunction with microbiological and physicochemical data. By identifying the prevailing species of carbon under varying redox conditions, we seek to discern the influence of microbial processes, including methanogenesis, denitrification, and organic matter decomposition, on the groundwater hydrochemistry of the area. The results offer valuable information on the redox dynamics of tropical aquifers and a foundation for enhancing groundwater quality monitoring and protection methods.

REVIEW OF LITERATURE

Carbon speciation in groundwater systems has been the subject of much interest because of its key importance in interpreting subsurface geochemical processes and the impact of microbial activity on water quality. In groundwater, the principal carbon species—dissolved carbon dioxide ($CO_2(aq)$), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and methane (CH_4)—exist in a dynamic equilibrium, which is regulated primarily by pH, redox potential (Eh), temperature, and the presence of microbial populations (Appelo and Postma, 2005; Langmuir, 1997).

Different studies have demonstrated that microbial respiration processes like aerobic degradation, denitrification, sulfate reduction, and methanogenesis are significant in the redox status of groundwater, thereby influencing carbon speciation as well (Chapelle, 2001; Christensen *et al*., 2000). For example, under oxidizing conditions, carbon dioxide (CO_2) is typically in equilibrium with bicarbonate ions (HCO_3^-), especially at pH values between 6 and 8. Under reducing conditions, like those favored by microbial sulfate reduction or methanogenesis, methane (CH_4) may be the prevailing carbon species, especially in organic-rich aquifers (Chapelle and McMahon, 1991).

In the tropics such as Nigeria, regolith aquifers develop through deep weathering of crystalline bedrock to produce a porous zone that is extremely vulnerable to redox changes and contamination (Ezeabasili *et al*., 2014; Umunnakwe *et al*., 2021). These aquifers, as crucial as they are to water supply in locations such as Enugu, tend to be marked by heterogeneous chemical profiles based on the level of water-rock interaction, organic content, and anthropogenic input in terms of waste seepage or farm runoff (Ezeh and Ugwu, 2010; Omeje *et al*., 2020). These inputs play key roles in bringing about variations in pH and Eh and, therefore, altering trends of carbon speciation in the various sites. Most research in south-eastern Nigeria has been on general groundwater quality, heavy metals, and microbial contamination, with comparably fewer on individual redox-sensitive species like carbon (Ezeabasili *et al*., 2014; Nwachukwu *et al*., 2010). Research works by Egboka *et al*. (1989) and recently by Omeje *et al*. (2020), however, demonstrate the intricate geochemical and microbial processes in Enugu aquifers. These results imply that surface activity organic loading stimulates microbial respiration and consumption of oxygen, creating reducing conditions conducive to CH_4 production and elevated HCO_3^- levels—a finding aligned with research in other tropical regolith systems (Zhang *et al*., 2020).

Eh-pH (Pourbaix) diagrams have been used to effectively describe the stability fields of different carbon species and relate them to field measurements and microbial dynamics. These diagrams can be utilized to map redox zones and characterize dominant microbial processes in aquifers, as stated by Christensen *et al*. (2000). They present a conceptual model on how different carbon species dominate under different geochemical conditions and thus guide the interpretation of field measurements and microbial data.

Location of the Study Area

Enugu, the south-east capital of Nigeria, is located between latitudes 6°22′N and 6°39′N and longitudes 7°26′E and 7°40′E. The city measures a total area of about 79 square kilometers (Egboka *et al*., 1989). As the commercial and administrative center of Enugu State, the city is blessed with history that has been irrevocably interwoven with its coal mines, which have served as the driving force behind progress in its development. Enugu is situated in the Anambra Basin, one of Nigeria's principal sedimentary basins. The city's topography has been shaped by the action of various geological processes and human activities over time.

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Geologic Settings and Hydrogeology of the Study Area

The study area, Enugu, is located in the Anambra Basin of south-east Nigeria and has a long geological history marked by Cretaceous sedimentary rocks. The basin is underlaid by sequences of siltstones, sandstones, shales, and coal seams which are significant among which are the Enugu Shale, Mamu Formation, and Ajali Sandstone that are very good aquifer units. Hydrogeologically, Enugu aquifers are predominantly unconfined to semi-confined, and the movement of groundwater is topography- and permeability-controlled by the geologic units. Recharge is primarily through rainfall, and the infiltration rates differ according to differences in soil cover and vegetation. The Ajali Sandstone, being very porous and permeable, is a significant source of groundwater in the region. Aquifers are under severe risk of contamination from urban development, agricultural practices, and improper waste disposal; thus, there is an urgent necessity for detailed understanding of the hydrogeological and microbial processes to facilitate sustainable water resource management. Recent research has employed combined geological and geophysical mapping methods to evaluate groundwater potential in Enugu State. For example, Ezeh (2012) carried out hydrogeophysical surveys aimed at outlining the areas with potential groundwater possibilities, thus defining the contribution of such geological formations as the Ajali Sandstone to the suitability of groundwater. Okechukwu and Ikenna (2024) also examined the quality of groundwater in Enugu Metropolis, emphasizing the importance of continuous monitoring in mitigating risks of contamination from urbanization and industrialization.

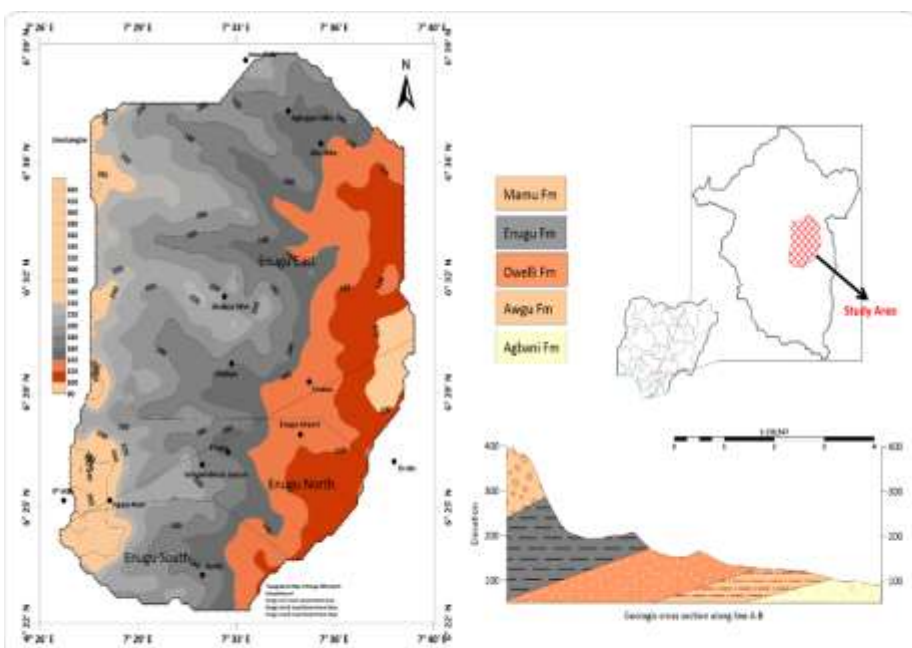

Figure 1: Geologic map of the study area

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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).

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

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RESULT AND DISCUSSION

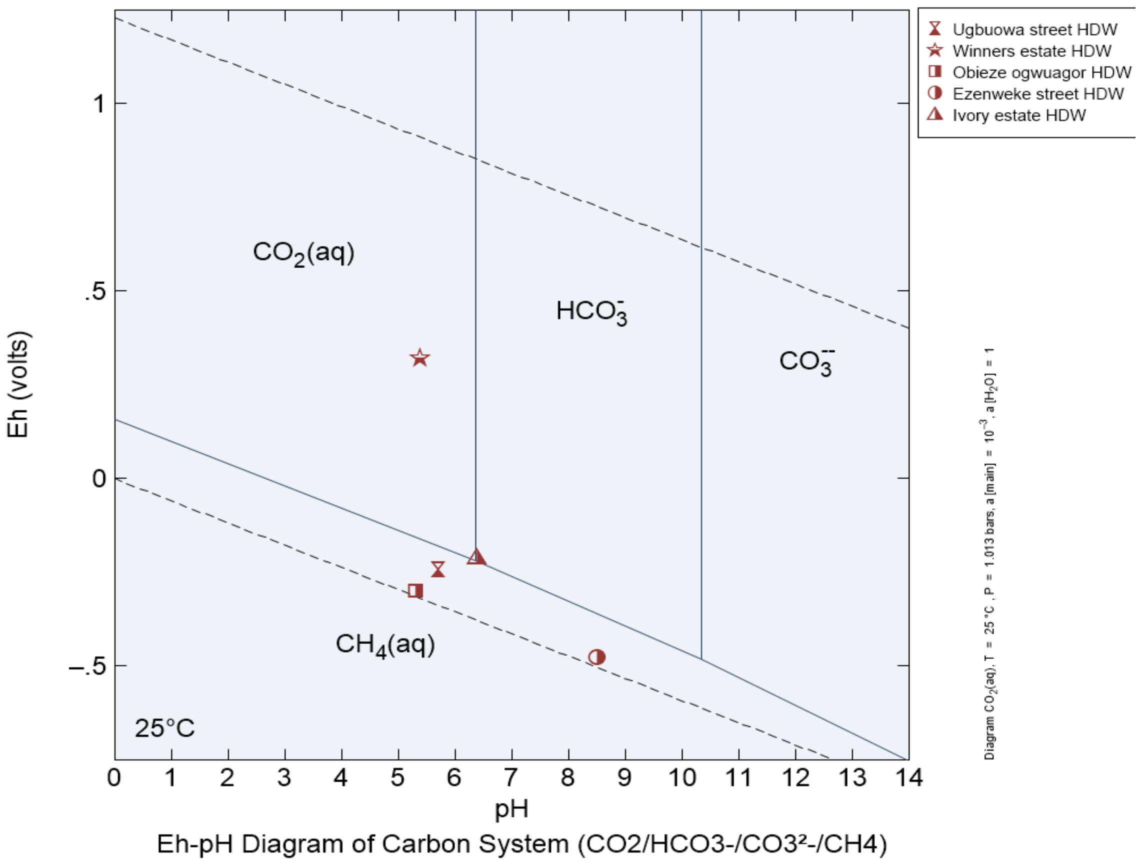

Figure 2: Eh-pH diagram of Carbon system in Groundwater

The Eh-pH diagram shown offers valuable insight into the geochemical conditions and microbial processes occurring in groundwater from different hand-dug wells (HDWs) in Enugu, Nigeria. The diagram delineates the stability fields of key carbon species CO_2(aq), HCO_3^-, CO_3^{2-}, and CH_4(aq) based on the pH and redox potential (Eh) of the water. Overlaid on this figure are the Eh and pH values that were measured for five sites: Ugbuowa Street, Winners Estate, Obieze Ogwuagor, Ezenweke Street, and Ivory Estate. The varying positions of the points on these graphs are indicative of the abiotic and biotic controls on groundwater geochemistry in which microbial activity is a prominent factor in the redox-mediated transformations. Among the samples analyzed, the Winners Estate HDW stands out by being placed in the CO_2(aq) stability field, which is characterized by high Eh values (around 0.35 V) and low pH levels (around 5). These conditions are typical of oxidizing environments where aerobic respiration is dominant, suggesting that the microbial populations in this environment are most likely using oxygen as their main

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electron acceptor. In these environments, the microbial oxidation of organic molecules results in the formation of carbon dioxide, thereby elevating the levels of CO_2(aq) in the aqueous phase. This agrees with observations in aerobic aquifers, where heterotrophic bacteria assist in decomposing organic matter, thereby releasing CO_2 as a by-product (Madigan *et al*., 2021).

Conversely, Ugbuowa Street and Obieze Ogwuagor HDW samples are located within the area of the boundary between CH_4(aq) and HCO_3^- fields, where mildly reducing and almost neutral pH conditions are dominant. Such conditions indicate the potential initiation of anaerobic microbial processes, specifically denitrification or iron/manganese reduction, which come before methanogenesis in the redox reaction sequence. Microbial populations like *Geobacter* and *Shewanella* species are documented to flourish in mildly reducing environments that favor metal reduction and facilitate the transformation of organic carbon into bicarbonate (Lovley *et al*., 2004). Intermediate Eh values realized in this work are indicative of active microbial populations alternating between aerobic and anaerobic metabolic pathways, and this in turn affected the realized carbon speciation.

Ivory Estate HDW is positioned perfectly well in the HCO_3^- field, indicative of slightly oxidizing and near-neutral conditions that are typically found in stable groundwater systems. Under such a setting, microbial decomposition of organic matter may take place under nitrate- or manganese-reducing conditions with bicarbonate as one of the dominant byproducts. This observation is consistent with studies showing that HCO_3^- accumulates in aquifers where facultative anaerobic bacteria breakdown organic matter in the absence of oxygen using alternative electron acceptors (Tesoriero *et al*., 2000). The most reducing conditions are measured at Ezenweke Street HDW, within the CH_4(aq) regime, with Eh values of approximately -0.4V and weakly alkaline pH. These conditions strongly favor methanogenesis, the final process in anaerobic breakdown of organic material. Under these strictly anaerobic conditions, methanogenic archaea, e.g., members of Methanobacterium or Methanosarcina, perform the reduction of carbon dioxide or acetate to produce methane (Zinder, 1993). The fact that CH_4(aq) is the dominant carbon species present here is good evidence that microbial methanogenesis is a significant biogeochemical process, probably favored by the high organic matter and long-term absence of more energetically favorable electron acceptors such as oxygen, nitrate, or sulfate.

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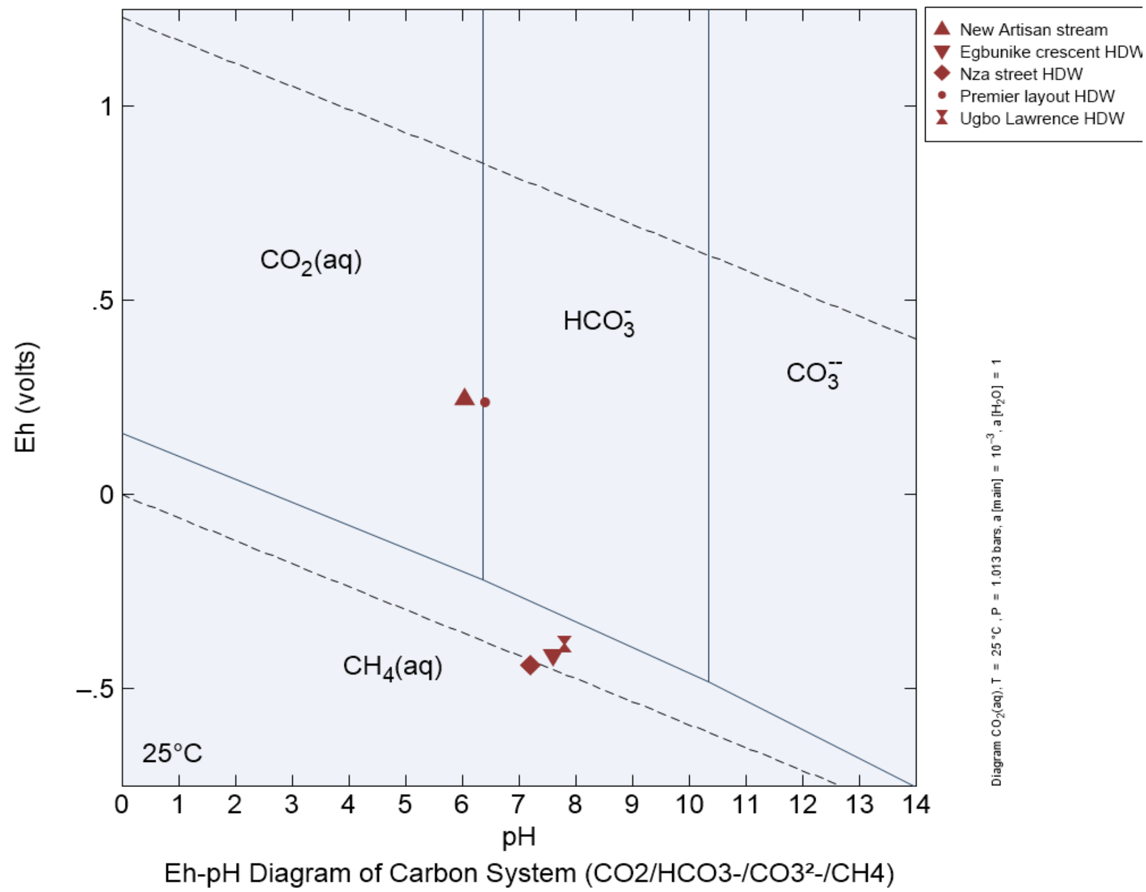

Figure 3: Eh-pH diagram of Carbon system in Groundwater

The provided Eh-pH diagram shows the thermodynamic stability ranges of the various carbon species—viz CO_2(aq), HCO_3^-, CO_3^{2-}, and CH_4(aq)—in aqueous systems at 25°C. It also incorporates data from five various sampling points around Enugu: New Artisan Stream, Egbunike Crescent HDW, Nza Street HDW, Premier Layout HDW, and Ugbo Lawrence HDW. The spread of the samples over these domains indicates a variability of redox conditions and acidity, which can then be interrogated to investigate geochemical processes and also the influence of microbial activity in the aquifer systems.

The samples from New Artisan Stream and Premier Layout HDW are positioned within the CO_2(aq) field, at relatively high Eh values (~0.25–0.3 V) and near-neutral pH (~6.5–7). These conditions are characteristic of mildly oxidizing environments where aerobic microbial respiration likely predominates. The presence of CO_2(aq) as the dominant carbon species suggests that microbial degradation of organic matter is actively producing carbon dioxide. This scenario is commonly observed in shallow aquifers exposed to atmospheric oxygen or influenced by recharge from surface water, where aerobic heterotrophs such as *Pseudomonas* and *Bacillus* species thrive by oxidizing organic substrates and releasing CO_2 into solution (Madigan *et al*., 2021).

The samples collected from Egbunike Crescent, Nza Street, and Ugbo Lawrence HDWs fall within or close to the $CH_4(aq)$ zone, having low redox potential (Eh < -0.3 V) and slightly alkaline pH (~7.5–8). These conditions are strong pointers to a reducing environment, where oxygen and other high-potential electron acceptors are expected to be consumed, with anaerobic microbial activity enabled. The presence of $CH_4(aq)$ alone suggests the prevalence of methanogenesis, a methanogenic archaea-mediated microbial process carried out by microbes such as Methanosaeta and Methanobacterium that reduce substrates like carbon dioxide or acetate to methane under strictly anaerobic conditions (Zinder, 1993). The presence of $CH_4(aq)$ would also suggest the absence or low availability of electron acceptors, including nitrate, sulfate, or iron, which would normally be used up in series during the microbial redox cascade.

This contrast in redox regimes between the sample sites is telling. While oxidizing conditions in New Artisan and Premier Layout support CO_2-producing microbial pathways like aerobic respiration or denitrification, the reducing settings of the other wells favor methanogenesis and perhaps sulfate reduction. In fact, the gradual shift in the Eh-pH space from $CO_2(aq)$ to $CH_4(aq)$ fields across these wells mirrors the ecological succession of microbial communities based on electron acceptor availability, a pattern observed in aquifers globally (Lovley *et al*., 2004). This progression is consistent with the redox ladder concept, where microbes utilize the most energetically favorable electron acceptors available in sequence—oxygen first, then nitrate, manganese (IV), iron (III), sulfate, and finally CO_2 for methanogenesis (Appelo and Postma, 2005). Furthermore, the spatial distribution of these points can be correlated with possible contamination or entry of organic matter into the aquifers. Anoxic conditions, such as those observed in the Egbunike and Nza zones, are commonly associated with areas having high organic pollution, which enhances microbial activity and leads to a reduction in redox potential. The changes in biogeochemical processes do not impact carbon compounds alone but can also alter the mobility and speciation of other elements like iron, manganese, and trace metals, many of which are under microbial control.

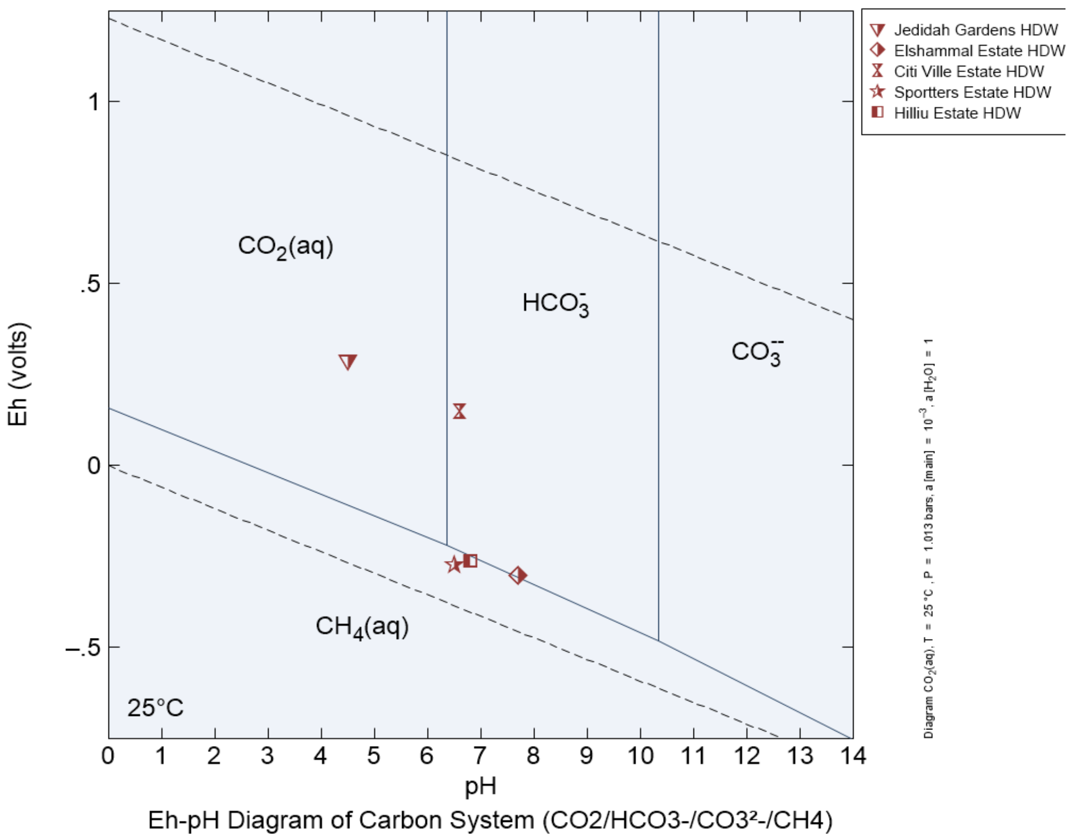

Figure 4: Eh-pH diagram of Carbon system in Groundwater

The second Eh-pH diagram shows the plot of groundwater samples from five various hand-dug well (HDW) points in Enugu such as Jedidah Gardens, Elshammal Estate, Citi Ville Estate, Sportters Estate, and Hilliu Estate on the carbon speciation model consisting of CO_2(aq), HCO_3^-, CO_3^{2-}, and CH_4(aq) at 25°C. The diagram accounts for the redox and acid-base conditions prevailing in the aquifers and enables inferences to be drawn regarding the microbial processes that regulate groundwater geochemistry. From the plotted data, most samples plot within or close to the CO_2(aq) and CH_4(aq) stability fields, representing a transitional redox state between oxidizing and reducing conditions. Jedidah Gardens HDW plots squarely within the CO_2(aq) field with a weakly positive Eh and pH close to 6.5. The position is representative of a mildly oxidizing environment in which aerobic microbial activity will be dominant. Aerobic heterotrophs, for example, genera from Pseudomonas and Bacillus, should be metabolically active under these conditions, where they respire organic carbon and excrete carbon dioxide as a metabolic end product (Madigan *et al.*, 2021). This result indicates the presence of oxygen, either

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from atmospheric diffusion or replenishment, indicating that this aquifer is actively linked with the surface or may be liable to regular replenishment through rainwater.

In contrast, Citi Ville Estate and Elshammal Estate HDWs fall close to the CO_2(aq)–CH_4(aq) boundary at close-to-neutral pH and Eh values close to zero. These conditions characterize sub-oxic to weakly reducing environments where oxygen is most likely consumed but more energetically favorable electron acceptors like nitrate and sulfate can still dominate. This intermediate redox state can sustain a continuum of microbial activity, such as denitrification, iron reduction, and initial sulfate reduction. The trend towards CH_4(aq) indicates that the conditions in these aquifers can be moving in the direction of methanogenesis, especially in deeper or more undisturbed sections. The Sportters Estate and Hilliu Estate HDWs samples plot squarely in the CH_4(aq) field, under reducing conditions with Eh below 0 V and pH of 6.5 to 7. These redox conditions are typical of environments where terminal electron-accepting processes, like methanogenesis, prevail. Under conditions devoid of oxygen, nitrate, sulfate, and ferric iron, methanogenic archaea like *Methanobacterium* and *Methanosarcina* reduce CO_2 and hydrogen or acetate to form methane (Zinder, 1993). The occurrence of CH_4(aq) in these wells not only indicates highly reducing conditions but also indicates a prolific extent of microbial activity in anaerobic organic matter degradation. This would imply that these aquifers are quite stagnant, old, or highly charged with organic carbon, possibly due to anthropogenic contamination like latrine seepage or decomposing vegetation.

The gradient observed at the five sample points again indicates a redox gradient, with microbial metabolism varying depending on the availability of electron acceptors. Whereas Jedidah Gardens is exhibiting evidence of oxic respiration, Sportters and Hilliu Estates are at the opposite end of the spectrum where methanogenesis prevails. Citi Ville and Elshammal Estates are in between, creating an active microbial transition zone. In addition, such redox-governed microbial activity has larger geochemical consequences. For instance, reducing conditions favor the mobilization of iron and manganese trace metals in their reduced forms, which can exacerbate water quality. Methane production in groundwater can also result in greenhouse gas emissions if vented at the surface, indicating a potential environmental problem.

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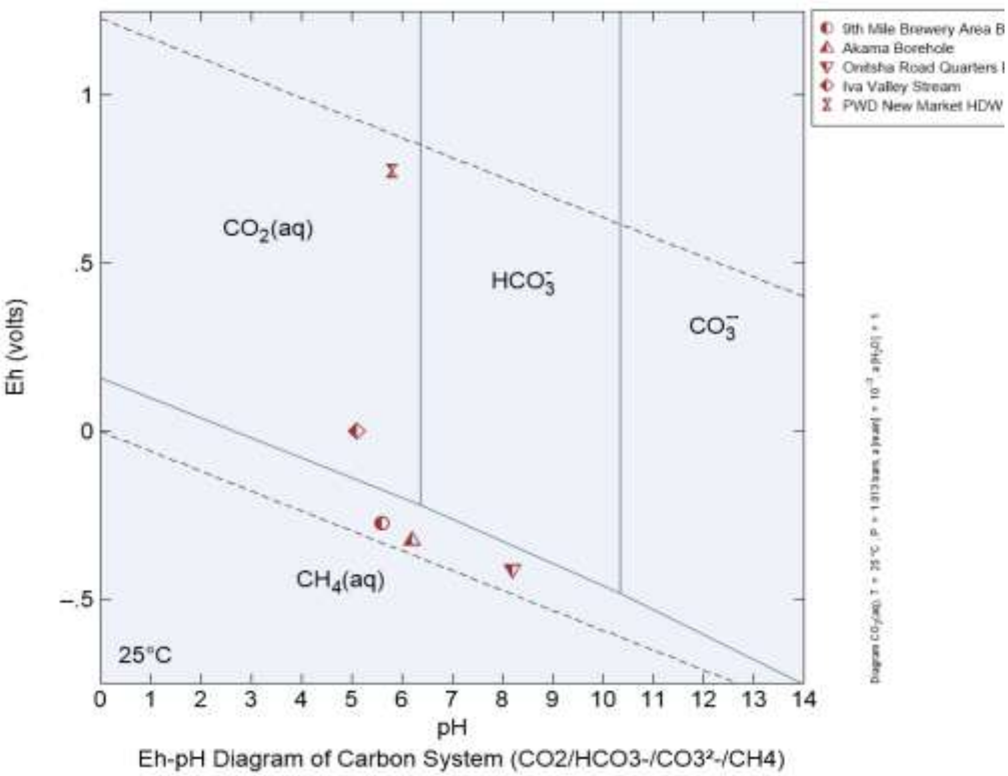

Figure 5: Eh-pH diagram of Carbon system in Groundwater

The Eh-pH diagram for the carbon system ($CO_2/HCO_3^-/CO_3^{2-}/CH_4$), when overlaid with groundwater data from Enugu, provides valuable insight into the microbial redox processes shaping the geochemistry of shallow aquifers in the region. The distribution of sample points across different redox zones indicates that microbial activities play a central role in determining the dominant carbon species in each water source. Specifically, most of the groundwater samples—such as those from 9th Mile Brewery Area Borehole, Akama Borehole, and Onitsha Road Quarters—fall within the *$CH_4(aq)$* stability field. This is a strong indication of methanogenesis, a microbial process carried out by obligate anaerobes known as methanogens (e.g., *Methanobacterium* and *Methanosarcina*), which convert carbon dioxide and hydrogen or acetate into methane under low Eh conditions. The prevalence of *$CH_4(aq)$* here suggests that the aquifers are experiencing strongly reducing conditions, typically driven by high organic matter content and limited oxygen availability conditions favorable to anaerobic microbial activity.

On the other hand, the PWD New Market HDW sample falls within the *$CO_2(aq)$* field, at an Eh of approximately 0.75 V. This suggests a more oxidizing environment where aerobic microbial processes dominate. In such systems, organic matter may be

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more fully oxidized by aerobic heterotrophs or denitrifiers, preventing the progression of redox conditions to the point where methanogenesis occurs. The higher redox potential may also suppress the growth of strict anaerobes, thus halting the microbial reduction of carbon to methane. This condition may be due to shallow aquifer depth, better recharge from rainwater, or minimal pollution by organic waste all of which promote oxygen diffusion into the system. The Iva Valley Stream sample, located near the boundary between the $CO_2(aq)$ and $CH_4(aq)$ regions, may represent a transitional environment where redox conditions fluctuate seasonally or with depth, allowing both aerobic and anaerobic microbial communities to coexist or alternate in dominance.

The Eh-pH positions of these samples align well with microbial community dynamics previously reported in the region. In similar studies across Enugu aquifers, microbial isolates such as *Desulfomicrobium*, *Geobacter sp.*, *Shewanella sp.*, *Bacillus sp.*, and *Pseudomonas sp.* were identified (Ezeh *et al*., 2021). Many of these microbes participate in anaerobic respiration processes that alter carbon speciation. For instance, *Geobacter* and *Shewanella* are known for their role in iron and manganese reduction, but they also contribute to organic carbon oxidation under anaerobic conditions, leading to conditions that support methanogenesis. Additionally, *Desulfomicrobium*, a sulfate-reducing bacterium, competes with methanogens for hydrogen, and its presence often signals highly reducing environments that may later transition to methanogenesis once sulfate is depleted.

These results agree with previous hydrogeochemical research in southeastern Nigeria. Okoro *et al*. (2012) stressed the microbial decomposition of organic matter as driving redox evolution in the Enugu groundwater, while Ibe *et al*. (2002) attributed urban contamination and organic load to microbial processes governing aquifer chemistry. Additionally, the sample distribution on the carbon system diagram shows a definite gradient from reducing to oxidizing conditions, governed by natural and anthropogenic controls like waste disposal, industrial discharges, and sanitation in populated regions.

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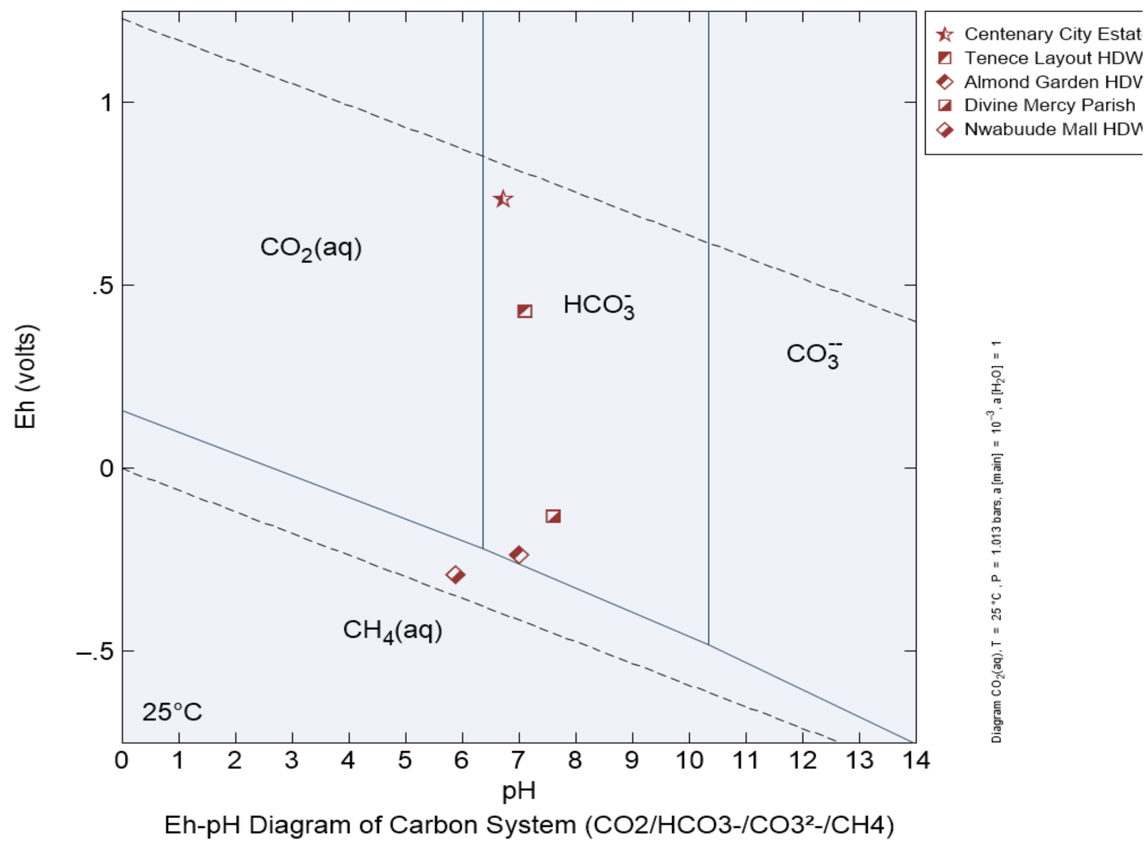

Figure 6: Eh-pH diagram of Carbon system in Groundwater

Centenary City Estate stands out with a high Eh (approximately 0.85 V) and low pH (~6), placing it firmly in the *$CO_2(aq)$* field. This environment is highly oxidizing and acidic, which suggests active aerobic respiration and minimal reduction processes. In contrast, Almond Garden HDW and Nwabuude Mall HDW fall near or slightly below the boundary line between *$CH_4(aq)$* and *HCO_3^-*, indicating moderately reducing conditions favorable to anaerobic processes such as methanogenesis. Tenece Layout HDW and Divine Mercy Parish fall within the *HCO_3^-* field, indicating mildly reducing, near-neutral pH conditions that support both aerobic and facultative anaerobic microbial activity, including denitrification and iron reduction.

The presence of samples in the *$CH_4(aq)$* field, such as Nwabuude Mall HDW and Almond Garden HDW, suggests advanced stages of microbial respiration where methanogenesis is dominant. Methanogens—strict anaerobes like *Methanospirillum* and *Methanobacterium*—utilize H_2 and CO_2 or acetate to produce methane under highly reducing conditions. The moderately low Eh values (< 0 V) observed here align with

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typical conditions required for these microorganisms to thrive. These aquifers are likely subject to high organic matter input and limited oxygen infiltration, supporting reductive microbial pathways that culminate in methane production.

Centenary City Estate's location in the *$CO_2(aq)$* field suggests limited microbial reduction and a dominance of aerobic microbial processes. Aerobic heterotrophs decompose organic matter into carbon dioxide, thereby elevating Eh and maintaining low pH. This condition may be indicative of shallow depth, well-aerated systems, or relatively unpolluted recharge areas. The transition of other samples into the *HCO_3^-* field implies ongoing but incomplete reduction processes. Microbial communities here may include *Pseudomonas*, *Bacillus*, and *Geobacter* species, which are known to reduce nitrate, Fe^{3+}, or Mn^{4+} while converting CO_2 to HCO_3^- under microaerophilic or anaerobic conditions.

The findings from this diagram align with those from the earlier Eh-pH carbon diagram (Figure 6), where methanogenesis was prevalent in boreholes with low Eh values. The spatial variation in redox status reinforces the idea that shallow groundwater in Enugu is chemically and microbially heterogeneous, shaped by land use, aquifer depth, and organic matter availability. Ezeh *et al*. (2021) similarly reported the occurrence of facultative and strict anaerobic bacteria in Enugu aquifers, including *Desulfomicrobium* and *Geobacter*, which facilitate sulfate reduction and organic carbon oxidation—precursors to methanogenesis. Furthermore, similar redox zonation has been observed in studies such as Okoro *et al*. (2012), where groundwater from urban and peri-urban zones showed a mix of aerobic and anaerobic processes depending on proximity to contamination sources. Ibe *et al*. (2002) also emphasized that areas with intense anthropogenic activity tend to exhibit lower Eh due to microbial oxygen demand and subsequent dominance of reducing conditions.

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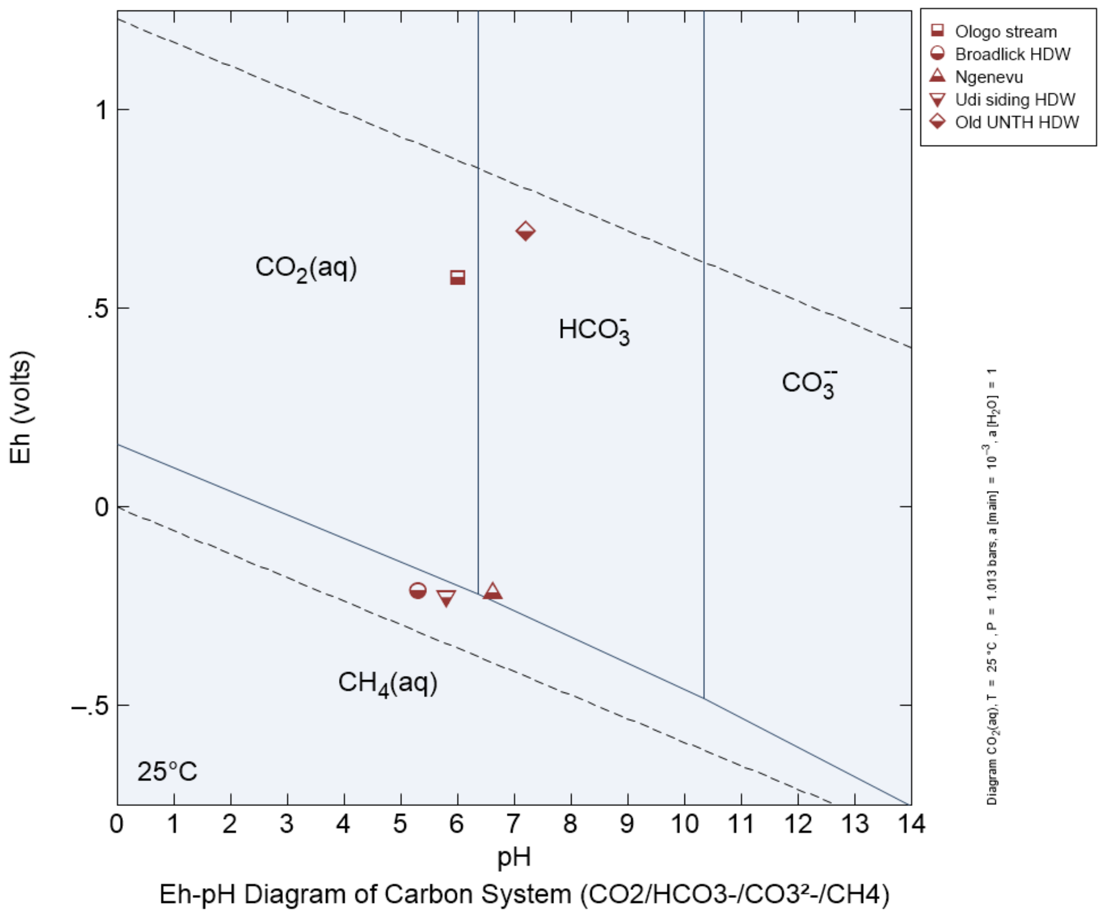

Figure 7: Eh-pH diagram of Carbon system in Groundwater

The Eh-pH diagram of the carbon system provides valuable insight into the redox chemistry and carbon speciation in groundwater and surface water systems across different locations in Enugu. The plotted data reveal spatial variations in the electrochemical conditions of the sampled sites. Ologo Stream and Old UNTH HDW are situated within the CO_2(aq) and HCO_3^- stability fields, respectively, suggesting oxidizing to mildly reducing conditions. In contrast, Broadlick HDW, Ngenevu, and Udi Siding HDW fall within or very close to the CH_4(aq) stability field, indicating strongly reducing, methanogenic environments. These findings illustrate a clear geochemical gradient across the study area, likely influenced by factors such as depth, organic matter content, and recharge characteristics.

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The positioning of Ologo Stream in the CO_2(aq) domain indicates that it is exposed to atmospheric oxygen, promoting oxidative processes and stabilizing carbon predominantly as dissolved CO_2. This aligns with typical surface water behavior, where high Eh values and relatively neutral pH facilitate aerobic microbial respiration and organic matter oxidation (Stumm and Morgan, 1996). The data from Old UNTH HDW, situated in the HCO_3^- field, suggest a moderately reducing environment where dissolved CO_2 has been partially converted to bicarbonate, likely through the buffering action of carbonate minerals or microbial activity. On the other hand, the samples from Broadlick HDW, Ngenevu, and Udi Siding HDW are plotted in the CH_4(aq) stability zone, characterized by very low Eh and slightly acidic to near-neutral pH. This distribution strongly indicates methanogenesis—a process in which microorganisms, particularly archaea, reduce CO_2 to methane in the absence of other terminal electron acceptors such as nitrate or sulfate (Whitman *et al*., 2006). The chemical environments of these wells suggest limited recharge and abundant organic carbon that fuels microbial respiration deep within the regolith aquifers.

The implications of these findings are significant for groundwater chemistry and public health. Carbon speciation is a key indicator of the redox state of aquifers, and the dominance of methane in some locations suggests extensive anaerobic decomposition of organic material. This not only affects carbon cycling but also plays a role in the mobilization of redox-sensitive elements such as iron, manganese, and even arsenic, which can pose health risks if mobilized into drinking water sources (Smedley and Kinniburgh, 2002). Furthermore, methane in groundwater, while not acutely toxic, is a potential explosion hazard if it accumulates in confined spaces. Its presence also indicates that the aquifer may be vulnerable to further reductions in quality due to the progression of anaerobic processes, which are often irreversible without changes in hydrogeological conditions. These environments are also typically conducive to the proliferation of sulfate-reducing and iron-reducing bacteria, which can lead to taste, odor, and staining issues in water supplies (Chapelle, 2000).

When compared with other regional and global studies, the observed carbon speciation trends in Enugu's regolith aquifers are consistent with findings from similar tropical weathered zones. For instance, studies conducted by Zhang and Wang (2023) in subtropical aquifers in southern China reported comparable transitions from bicarbonate to methane with increasing depth and decreasing Eh, largely driven by microbial reduction processes. Similarly, Okeke and Nwankwo (2021) observed bicarbonate dominance in Enugu's shallow wells and streams but noted methane signatures in deeper, less disturbed wells, correlating with redox stratification across the aquifer profile. These parallels affirm that the patterns observed in this study are not isolated but are representative of broader geochemical behaviors in regolith aquifers, especially in regions characterized by high rainfall, abundant organic inputs, and complex lithological settings.

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CONCLUSION AND RECOMMENDATION

This study highlights the critical role of microbial activity and redox conditions in determining carbon speciation within the regolith aquifers of Enugu. Findings show that species like bicarbonate, carbon dioxide, and methane dominate under different pH and Eh conditions, reflecting ongoing processes such as respiration, sulfate reduction, and methanogenesis. These biogeochemical interactions not only influence groundwater quality but also point to the vulnerability of these aquifers to anthropogenic impacts. Therefore, regular monitoring, public sensitization, and further microbial-geochemical investigations are recommended to ensure the sustainable use and protection of Enugu's groundwater resources.

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