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THERMODYNAMIC AND MICROBIAL CONSTRAINTS ON REDOX-INDUCED MOBILIZATION OF REDOX-SENSITIVE METAL (LOID)S IN SHALLOW AQUIFERS OF ENUGU

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Abstract

This study investigates the thermodynamic and microbial factors controlling the redox-induced mobilization of redox-sensitive metal(loid)s—iron (Fe^{3+}), manganese (Mn), and arsenic (As)—in shallow aquifers across Enugu metropolis, Nigeria. A total of 25 water and sediment samples were collected from hand-dug wells and streams across five geographical areas: Ologo, Trans-Ekulu, Amechi, Ajali River/9th Mile and Centenary geographical areas. Samples were collected using sterile bottles, stored under cool conditions, and analyzed in the laboratory using Atomic Absorption Spectrophotometry (AAS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS), following standard EPA analytical methods. All analyses were performed in triplicate, and results were reported as mean concentrations in milligrams per liter (mg/L). Results reveal spatial variability in metal concentrations influenced by local hydrogeochemical conditions. In the Ologo area, iron ranged from 0.300 to 0.390 mg/L, manganese from 0.154 to 0.300 mg/L, and arsenic from 0.029 to 0.068 mg/L. Amechi samples showed iron levels between 0.250 and 0.355 mg/L, manganese concentrations remained stable (0.150–0.165 mg/L), and arsenic ranged narrowly from 0.043 to 0.049 mg/L. In the Ajali River/9th Mile region, iron and manganese were elevated (0.301–0.420 mg/L and 0.220–0.260 mg/L, respectively), with arsenic ranging from 0.028 to 0.035 mg/L. Centenary Water sites recorded lower iron concentrations (0.180–0.290 mg/L), moderate manganese (0.150–0.190 mg/L), and low arsenic (0.020–0.027 mg/L). Trans-Ekulu exhibited the highest iron variability (0.220–0.718 mg/L), consistent manganese (0.225–0.229 mg/L), and low arsenic levels (0.013–0.016 mg/L). These findings indicate heterogeneous redox conditions influencing metal mobilization, with certain areas exceeding recommended iron limits for drinking water. The data contribute to understanding metal distribution patterns in Enugu's aquifers and underscore the need for continuous monitoring to safeguard public health.

Keywords: Redox-sensitive metals, Iron (Fe), Manganese (Mn), Arsenic (As), Microbial reduction, Groundwater contamination, Reductive dissolution, Urban aquifers, Enugu, Nigeria, Thermodynamic modeling, Dissimilatory metal-reducing bacteria, Water quality, Tropical hydrogeology and public health risk.

INTRODUCTION

The distribution of redox-sensitive metal(loid)s like iron (Fe), manganese (Mn), and arsenic (As) in groundwater is largely controlled by redox conditions, which are shaped by both geochemical thermodynamics and microbial activity. In tropical urban environments like Enugu, Nigeria, where shallow aquifers are heavily relied upon, fluctuating redox conditions caused by natural and human-driven factors can lead to the release of these elements into water sources (Appelo and Postma, 2005; McMahon and Chapelle, 2008).

Reductive dissolution of iron and manganese oxides—often driven by microbial processes—can free up adsorbed metals and metalloids, raising health concerns. Microorganisms like *Geobacter* and *Desulfomicrobium* play key roles in these transformations, using metals as terminal electron acceptors during respiration (Lovley *et al*., 2004; Oremland and Stolz, 2005). Thermodynamic tools like Eh-pH diagrams help predict conditions favorable for metal mobilization, but they often don’t capture the complex, microbially-driven kinetics at play in real aquifer systems (Bethke *et al*., 2011).

A recent study by Ozoko and Ezeugwu (2025) revealed diverse redox-active microbes in Enugu aquifers, including *Shewanella*, *Pseudomonas*, and *Geobacter* species. Their presence across different sites suggests ongoing microbial metal reduction, especially in areas like Agbani Road, Gariki, and Centenary. These findings point to biologically mediated redox shifts that could be driving metal mobilization in the subsurface.

Despite increasing reports of elevated metal levels in Enugu's water (Ibeneme *et al*., 2020), the role of microbial involvement in altered redox conditions has not been fully exploited. This study explores how thermodynamic and microbial factors jointly influence the mobilization of redox-sensitive metal(loid)s in Enugu’s shallow aquifers, with implications for water quality and public health.

REVIEW OF LITERATURE

The behavior of redox-sensitive metal(loid)s in groundwater systems has been extensively studied, particularly in relation to redox dynamics and microbial mediation. Redox conditions determine the speciation, solubility, and mobility of metals such as Fe, Mn, and As, with reductive environments favoring the dissolution of metal oxides and subsequent release into groundwater (Appelo and Postma, 2005; Stumm and Morgan, 1996).

Microbial activity plays a pivotal role in these redox transformations. For instance, dissimilatory metal-reducing bacteria such as *Geobacter* and *Shewanella* are known to reduce ferric iron and manganese oxides, mobilizing these metals in the process (Lovley *et al*., 2004; Nealson *et al*., 2002). Arsenic, often adsorbed to Fe and Mn oxides, is consequently released during such microbial reduction, especially under anaerobic conditions (Oremland and Stolz, 2005).

Thermodynamic modeling, particularly using Eh-pH diagrams, has been a critical tool in predicting stability fields of metal species and their potential mobilization under varying redox conditions (Bethke *et al*., 2011). However, these models often overlook microbially-driven kinetic factors and local geochemical heterogeneities that influence metal fate and transport in real-world aquifers. In Nigeria, several studies have highlighted the presence of redox-sensitive elements in groundwater systems, particularly in urban areas with variable land use and sanitation practices (Egboka *et al*., 1989; Eze and Ugwoke, 2021). Recent microbial investigations in Enugu by Ozoko and Ezeugwu (2025) documented the dominance of metal-reducing genera such as *Desulfomicrobium*, *Pseudomonas*, and *Bacillus*, especially in areas with organic-rich sediments. This suggests strong microbial mediation in redox transitions affecting water quality.

Despite these insights, integrated studies combining both microbial and thermodynamic constraints in southeastern Nigerian aquifers remain limited. This study seeks to bridge that gap by analyzing both microbial ecology and redox potential in relation to metal mobilization across Enugu's shallow subsurface waters.

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.

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.

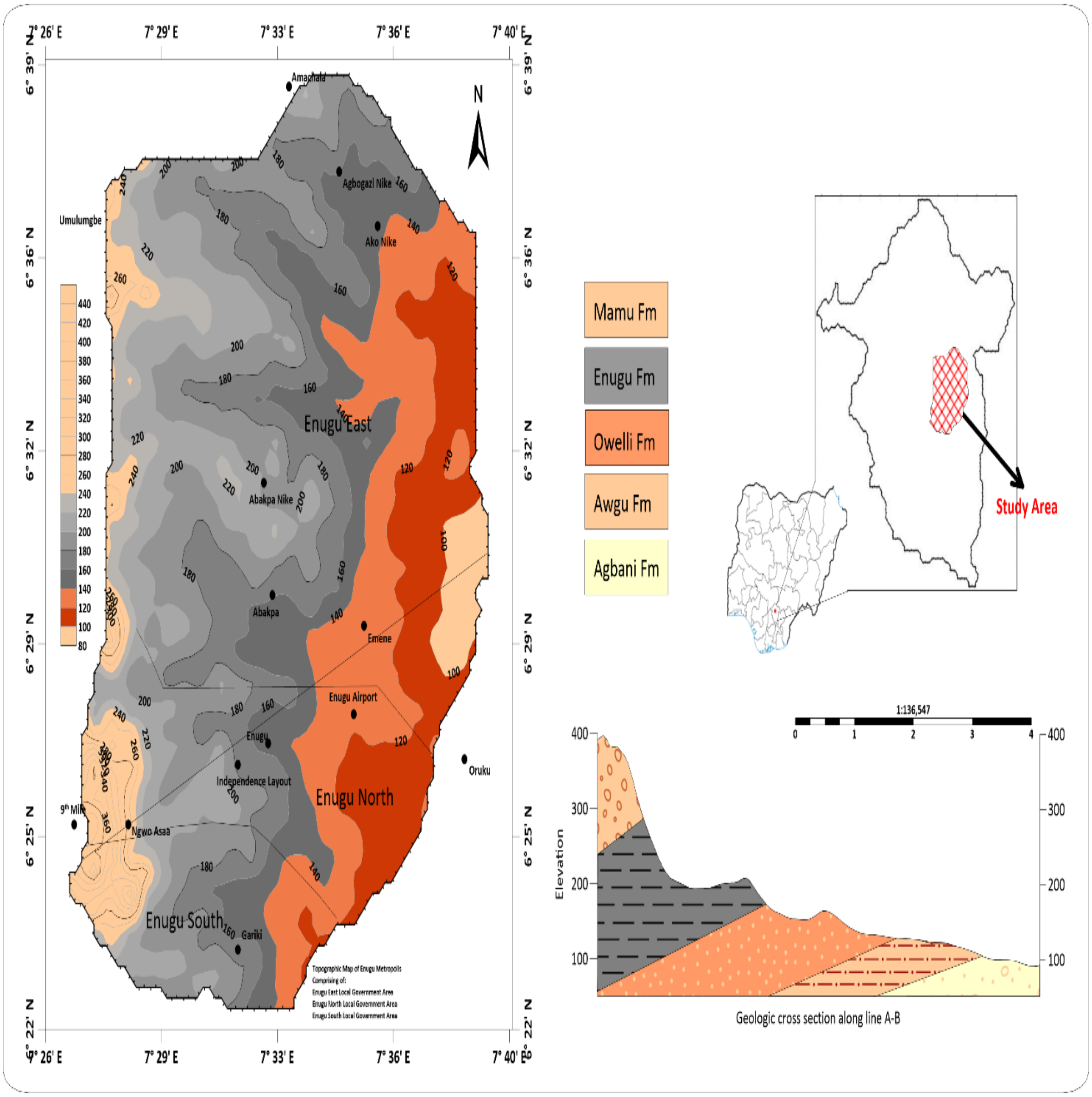

Figure 1: Geologic map of the study area

MATERIALS AND METHODS

Sample Collection

Water and sediment samples of 25 in number from different locations namely; Ologo, Trans-Ekulu, *Amechi, Ajali River/9th Mile* and *Centenary* 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

The concentrations of iron (Fe^{3+}), manganese (Mn^{2+}), and arsenic (As) in groundwater samples were determined using *Atomic Absorption Spectrophotometry (AAS)* and *Inductively Coupled Plasma Mass Spectrometry (ICP-MS)*, following standard analytical guidelines outlined by the *United States Environmental Protection Agency (EPA, 1994; EPA Method 200.7 and 200.8).*

Sample Preparation

Water samples were first filtered through 0.45 μm membrane filters to remove suspended particulates. For AAS analysis, filtered samples were acidified to pH <2 using concentrated nitric acid (HNO_3) to preserve metal ions in solution and prevent precipitation. Samples for ICP-MS were similarly acidified and stored in high-density polyethylene (HDPE) bottles at 4 °C until analysis.

Iron and Manganese Analysis (AAS)

Fe^{3+} and Mn^{2+} were quantified using a flame AAS (PerkinElmer AAnalyst 400), with wavelength settings of 248.3 nm and 279.5 nm respectively. Calibration was done using certified standard solutions in the range of 0.1–5.0 mg/L. Blanks and quality control samples were analyzed intermittently to ensure accuracy and instrument stability. Detection limits were approximately 0.01 mg/L for both metals.

Arsenic Speciation (ICP-MS)

Total arsenic concentrations were measured using an Agilent 7700x ICP-MS equipped with a collision/reaction cell to minimize polyatomic interferences. The instrument was calibrated with multi-element standards, and internal standards (e.g., Ge or Rh) were added to correct for matrix effects and instrumental drift. Speciation of As(III) and As(V), where required, was carried out using ion chromatography coupled with ICP-MS, following EPA Method 200.8. The method detection limit for arsenic was 0.001 mg/L. All analyses were performed in triplicate, and results were expressed as mean concentrations (mg/L). Analytical accuracy and precision were verified using standard reference materials and recovery tests, which yielded recovery rates between 95–105%.

RESULT AND DISCUSSION

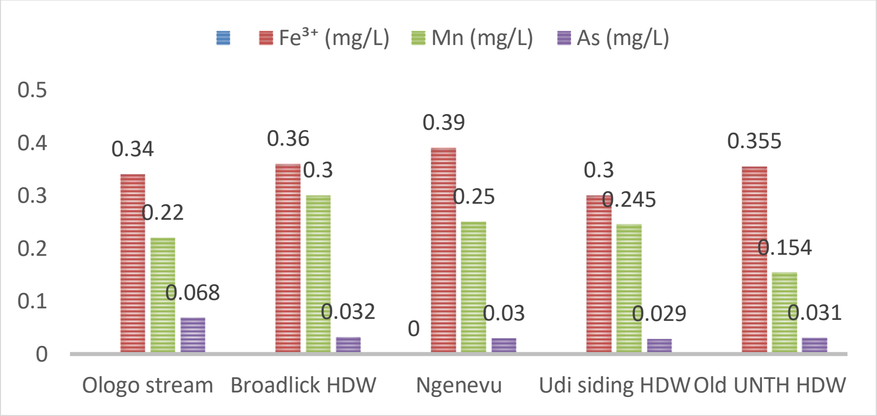

Figure 2. Metal Content in Water Samples from Different Locations in the Ologo Area.

The analysis of iron (Fe^{3+}), manganese (Mn), and arsenic (As) concentrations across five locations in the Ologo geographical area—namely Ologo Stream, Broadlick HDW, Ngenevu HDW, Udi Siding HDW, and Old UNTH HDW—reveals notable spatial variability in the mobilization of redox-sensitive metal(loid)s. Iron levels ranged from 0.300 mg/L to 0.390 mg/L, manganese from 0.154 mg/L to 0.300 mg/L, and arsenic from 0.029 mg/L to 0.068 mg/L. The highest iron concentration was recorded in Ngenevu HDW (0.390 mg/L), while the highest manganese and arsenic levels were found in Broadlick HDW (0.300 mg/L) and Ologo Stream (0.068 mg/L), respectively.

These variations suggest the influence of site-specific redox conditions, likely shaped by differences in organic matter availability, water table depth, and microbial activity. In particular, elevated Fe and Mn levels in the hand-dug wells (HDWs), such as Broadlick and Ngenevu, imply reducing subsurface environments conducive to the microbial dissolution of iron and manganese oxides. This is consistent with studies showing that dissimilatory metal-reducing bacteria, including *Geobacter* and *Shewanella*, can mediate the reductive dissolution of Fe(III) and Mn(IV), leading to increased metal solubility in anoxic groundwater (Lovley *et al*., 2004; Nealson and Saffarini, 1994).

The relatively higher arsenic concentration in Ologo Stream compared to the groundwater sources suggests a surface water environment with stronger biogeochemical cycling and possible co-release of arsenic during iron and manganese reduction. Arsenic often binds to Fe and Mn oxides, and its release under reducing conditions is well documented in tropical aquifers (Smedley and Kinniburgh, 2002; Ravenscroft *et al*., 2009). The lower As values in the wells may reflect either slower microbially mediated desorption processes or attenuation through adsorption back onto secondary minerals.

From a public health perspective, the measured concentrations raise several concerns. Iron levels in all samples exceeded the WHO aesthetic guideline of 0.3 mg/L, which can cause staining, metallic taste, and support bacterial growth in distribution systems (WHO, 2017). Manganese levels also surpassed the WHO health-based guideline of 0.1 mg/L, which has been linked to neurological effects with long-term exposure, especially in children (Keen *et al*., 2000). More critically, arsenic concentrations in Ologo Stream (0.068 mg/L) are far above the WHO guideline limit of 0.01 mg/L, representing a potential carcinogenic risk if untreated water is consumed over prolonged periods.

The findings echo similar results from earlier work in Enugu and other parts of southeastern Nigeria, where elevated Fe and Mn concentrations have been reported in shallow groundwater, often linked to redox-driven mobilization processes (Eze and Ugwoke, 2021; Nwankwoala and Amadi, 2013). Recent investigations by Ozoko and Ezeugwu (2025) further revealed the presence of redox-active microbial genera such as *Desulfomicrobium*, *Pseudomonas*, and *Bacillus* across sites like Broadlick and Ngenevu, supporting the hypothesis of biologically mediated redox processes influencing metal mobility. Their work aligns with international observations, such as those by McArthur *et al*. (2001) and Appelo and Postma (2005), who emphasized that microbial respiration pathways can drastically alter groundwater chemistry by shifting redox boundaries and promoting the release of metal(loid)s.

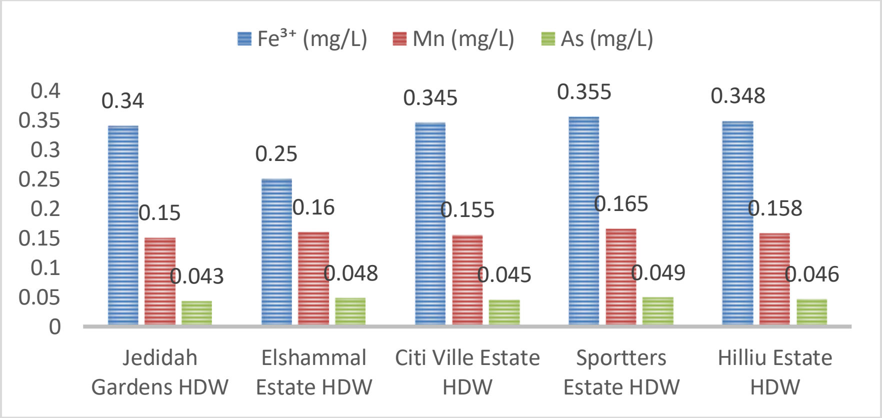

Figure 3. Metal Content in Water Samples from Different Locations in the Amechi Area.

Water samples collected from five hand-dug wells in the Amechi area—Jedidah Gardens, Elshammal Estate, Citi Ville Estate, Sportters Estate, and Hilliu Estate—showed measurable concentrations of iron (Fe^{3+}), manganese (Mn), and arsenic (As). Iron levels ranged from 0.250 mg/L at Elshammal Estate to 0.355 mg/L at Sportters Estate. Manganese concentrations were generally stable, spanning from 0.150 mg/L to 0.165 mg/L. Arsenic values were slightly lower but consistent across the locations, ranging between 0.043 mg/L and 0.049 mg/L.

A closer look at the data reveals a relatively consistent trend for each metal across the sampled wells. Iron values were notably higher in Sportters Estate and Hilliu Estate compared to Elshammal Estate, suggesting site-specific differences in subsurface redox activity or iron-bearing mineral content. The low variability in manganese suggests uniform geochemical conditions or shared hydrogeological features across the Amechi aquifer. Arsenic levels were closely grouped but still above the World Health Organization's guideline of 0.01 mg/L, which indicates the possibility of arsenic mobilization through microbially driven reductive dissolution of Fe and Mn oxides. Such processes are often enhanced by bacteria like *Geobacter* and *Shewanella*, which utilize Fe^{3+} and Mn^{4+} as terminal electron acceptors under reducing conditions (Lovley *et al*., 2004; Nealson *et al*., 2002; Oremland and Stolz, 2005).

The health implications of these findings are significant. Iron and manganese concentrations in most of the sampled wells exceed WHO standards of 0.3 mg/L and 0.1 mg/L, respectively (WHO, 2017). Elevated iron, while not toxic, can affect the taste of water and stain plumbing fixtures, while excessive manganese exposure has been associated with neurological effects, especially in vulnerable populations like children (Kawasaki *et al*., 2011). Arsenic, although only marginally elevated, is of greater concern due to its carcinogenic potential and link to chronic illnesses such as skin lesions, cardiovascular diseases, and cancer (Smith *et al*., 2000; IARC, 2012).

These findings are consistent with earlier studies in southeastern Nigeria. For example, Ozoko and Ezeugwu (2025) reported widespread detection of redox-active microbial communities in Enugu aquifers, particularly in the Amechi area, suggesting ongoing microbially mediated metal mobilization. Ibeneme *et al*. (2020) similarly observed elevated iron, manganese, and arsenic in groundwater sources across Enugu, which they linked to poor redox regulation and anthropogenic influence. When viewed collectively, these results emphasize the need for integrated monitoring and treatment strategies that account for both geochemical and microbial dynamics in urban groundwater systems.

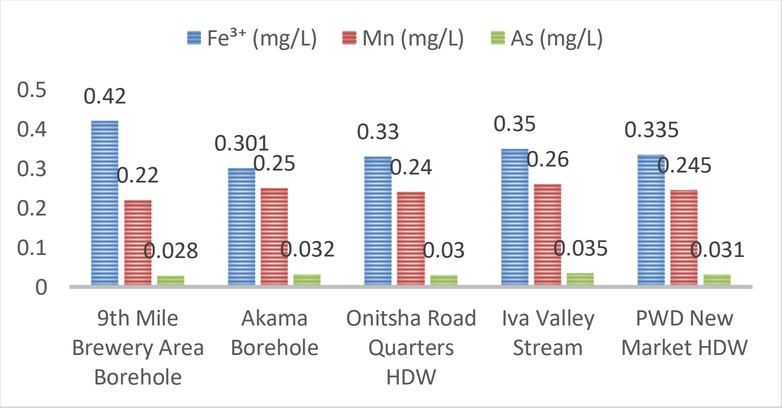

Figure 4. Metal Content in Water Samples from Different Locations in the Ajali River/9th Mile Area.

The analysis of groundwater and surface water samples from the Ajali River/9th Mile Water area shows variable but notable concentrations of redox-sensitive metals. Iron (Fe^{3+}) concentrations ranged from 0.301 mg/L at Akama Borehole to a high of 0.420 mg/L in the 9th Mile Brewery Area Borehole. Manganese (Mn) levels were also elevated, peaking at 0.260 mg/L in Iva Valley Stream and reaching the lowest value of 0.220 mg/L at the 9th Mile Brewery site. Arsenic (As) concentrations were generally lower, ranging from 0.028 mg/L to 0.035 mg/L, with the highest levels observed in Iva Valley Stream.

The observed metal distribution follows a recognizable pattern often tied to both geogenic and anthropogenic influences. The highest iron concentration in the 9th Mile Brewery borehole could be due to intense groundwater abstraction and local lithology rich in iron-bearing minerals, which, under reducing conditions, tend to mobilize Fe^{3+} through microbial or chemical dissolution (Appelo and Postma, 2005). Manganese values across all sites remain above WHO's aesthetic guideline of 0.1 mg/L (WHO, 2017), with variations possibly influenced by redox fluctuations and microbial reduction, particularly by *Shewanella* and *Geobacter* spp., which are known to reduce Mn oxides (Lovley *et al*., 2004; Nealson and Scott, 2002).

Arsenic levels, though within WHO's maximum permissible limit of 0.01 mg/L (WHO, 2017), are still concerning, especially since even low doses have been associated with chronic health effects (Smith *et al*., 2000). The slightly elevated arsenic concentration in Iva Valley Stream may result from reductive dissolution of Fe/Mn oxides that often adsorb arsenic in aquifers (Oremland and Stolz, 2005). Streams tend to have dynamic redox environments due to fluctuating oxygen availability, promoting arsenic mobilization when conditions become anoxic. The high levels of iron and manganese, and the detectable concentrations of arsenic, suggest that redox-mediated mobilization processes are active in this area. These findings have significant implications for drinking water safety, particularly for communities relying on untreated groundwater. Prolonged consumption of iron and manganese above recommended levels may lead to organ damage or neurotoxic effects (Kawasaki *et al*., 2011). Although arsenic levels are within international limits, cumulative exposure—especially among vulnerable populations—remains a public health concern.

These findings are consistent with previous studies in southeastern Nigeria. For instance, Ibeneme *et al*. (2020) reported elevated Fe and Mn concentrations in borehole water across Enugu, attributing it to subsurface redox shifts and microbial activity. Similarly, Ozoko and Ezeugwu (2025) documented widespread presence of redox-active microbes like *Desulfomicrobium*, *Pseudomonas*, and *Geobacter* in Enugu aquifers, confirming the biological basis for metal mobilization observed here. The patterns in the Ajali River/9th Mile region mirror those from the Ologo and Amechi areas, further underscoring a regional geochemical and microbiological trend.

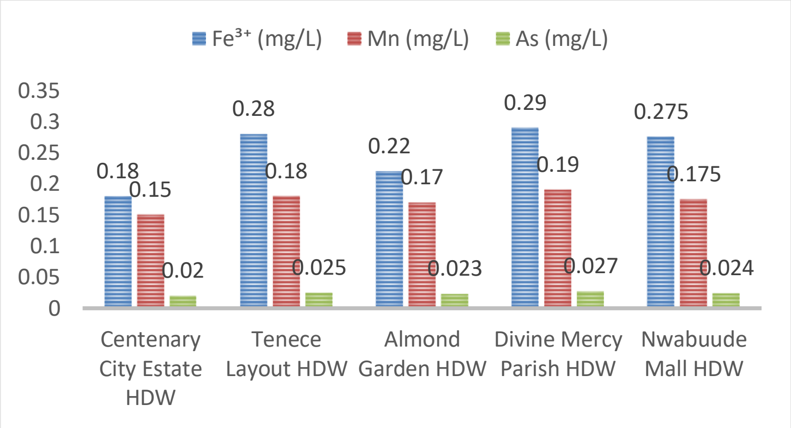

Figure 5. Metal Content in Water Samples from Different Locations in the *Centenary Water Area.*

The concentration of redox-sensitive metals—iron (Fe^{3+}), manganese (Mn), and arsenic (As)—was assessed across five sampling points within the Centenary Water area: Centenary City Estate HDW, Tenece Layout HDW, Almond Garden HDW, Divine Mercy Parish HDW, and Nwabuude Mall HDW. Iron (Fe^{3+}) levels ranged from 0.180 mg/L (Centenary City Estate) to 0.290 mg/L (Divine Mercy Parish). Manganese (Mn) concentrations were between 0.150 mg/L and 0.190 mg/L, with Divine Mercy Parish showing the highest value. Arsenic (As) values ranged narrowly from 0.020 mg/L to 0.027 mg/L, the lowest at Centenary City Estate and the highest at Divine Mercy Parish HDW.

There is a clear trend showing slightly elevated levels of all three metals at Divine Mercy Parish HDW, which may be due to localized redox conditions, organic matter availability, or microbial activity influencing metal mobilization. In contrast, Centenary City Estate HDW had the lowest concentrations for both Fe and As, suggesting more oxidizing conditions or lesser anthropogenic inputs in that specific location. The pattern for Mn shows slight variations but remains relatively moderate and consistent across the locations, indicating that manganese-bearing minerals may be uniformly distributed or that redox conditions are only moderately reducing across the area. Iron levels show more variability, which might reflect differences in iron-bearing mineral presence and microbial reduction processes.

While all measured values are below WHO maximum permissible limits (Fe: 0.3 mg/L, Mn: 0.4 mg/L, As: 0.01 mg/L for long-term exposure), the arsenic values, although low, are close to the WHO guideline of 0.01 mg/L, raising mild concern given chronic exposure risks (WHO, 2017; Smith *et al*., 2000). Arsenic presence may result from the reductive dissolution of Fe/Mn oxides or anthropogenic influence, such as waste infiltration or agricultural runoff (Oremland and Stolz, 2005; Kawasaki *et al*., 2011). The result indicate that redox conditions in Centenary are mildly reducing, which is consistent with findings from similar tropical aquifers where metal mobilization is influenced by both geochemical and microbial dynamics (Appelo and Postma, 2005; Lovley *et al*., 2004).

The role of microbial mediation—especially from species such as *Shewanella* and *Geobacter*—in the bioreduction of Fe^{3+} and Mn^{4+} is likely a contributing factor (Nealson and Scott, 2002).

Compared to other geographical areas like Ologo or Amechi, the Centenary area exhibits generally lower Fe and As concentrations, suggesting fewer geochemical triggers for metal mobilization or less organic loading. However, Mn levels are relatively comparable across all regions, reinforcing its sensitivity to even slight shifts in redox potential. This aligns with microbial and geochemical studies in Enugu by Ozoko and Ezeugwu (2025), which identified *Pseudomonas* and *Desulfomicrobium* as active players in subsurface metal transformation, particularly in aquifers with moderate organic content and seasonal recharge variability.

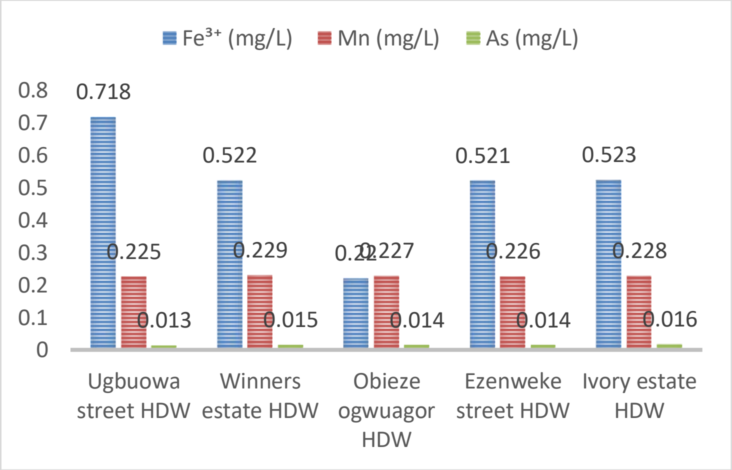

Figure 6. Metal Content in Water Samples from Different Locations in the Trans-Ekulu Area.

The analysis of redox-sensitive metals—iron (Fe^{3+}), manganese (Mn), and arsenic (As)—in groundwater samples from five locations in Trans-Ekulu revealed varied concentrations: Iron (Fe^{3+}) ranged widely, from 0.220 mg/L at Obieze Ogwuagor HDW to a high of 0.718 mg/L at Ugbuowa Street HDW. Manganese (Mn) levels were relatively uniform, between 0.225 mg/L and 0.229 mg/L across all sites. Arsenic (As) concentrations were low but measurable, ranging from 0.013 mg/L to 0.016 mg/L.

Iron concentrations exhibited the most variability, with Ugbuowa Street HDW showing more than three times the Fe^{3+} level of Obieze Ogwuagor HDW. This suggests local geochemical or microbial factors may enhance iron mobilization in certain parts of Trans-Ekulu, possibly due to more reducing conditions or greater organic matter availability that promotes microbial iron reduction (Lovley *et al*., 2004; Appelo and Postma, 2005).

In contrast, manganese concentrations remained quite stable across sites, indicating Mn dynamics might be less sensitive to localized environmental changes or that the aquifer conditions maintain Mn in a similar redox state throughout the area (Stumm and Morgan, 1996). Arsenic levels, while low, showed slight variation, with Ivory Estate HDW having the highest concentration. This could reflect subtle differences in arsenic-bearing mineral dissolution or adsorptive behavior linked to iron oxide reduction (Oremland and Stolz, 2005).

The elevated iron levels at Ugbuowa Street HDW (0.718 mg/L) exceed the WHO recommended limit of 0.3 mg/L, which raises concerns about water potability and potential staining or taste issues. Elevated Fe in groundwater often signals reducing conditions conducive to metal mobilization (WHO, 2017). While manganese and arsenic concentrations fall below their respective guideline values (Mn: 0.4 mg/L; As: 0.01 mg/L), arsenic levels approaching 0.016 mg/L merit attention for possible chronic exposure risks (Smith *et al*., 2000). These findings highlight that some areas in Trans-Ekulu are subject to redox conditions favoring iron mobilization, which may correlate with microbial activity such as dissimilatory iron reduction by genera like *Geobacter* or *Shewanella* (Nealson *et al*., 2002; Lovley *et al*., 2004).

Compared to other Enugu areas such as Centenary and Ajali River, Trans-Ekulu shows significantly higher iron concentrations, particularly at Ugbuowa Street. This suggests stronger or more persistent reducing environments or perhaps higher organic matter input influencing microbial respiration pathways (Ozoko and Ezeugwu, 2025). Manganese levels in Trans-Ekulu are comparable to those reported in other studies within the region (Egboka *et al*., 1989; Ibeneme *et al*., 2020), reaffirming the relative stability of Mn under prevailing groundwater conditions. Arsenic levels, although above WHO’s strict guideline of 0.01 mg/L, remain consistent with previous reports indicating low but measurable As presence in Enugu groundwater, likely tied to redox-sensitive desorption processes from iron oxides (Oremland and Stolz, 2005; Ozoko and Ezeugwu, 2025).

References

Appelo, C. A. J., and Postma, D. (2005). *Geochemistry, Groundwater and Pollution* (2nd ed.). CRC Press.

Bethke, C. M., Sanford, R. A., Kirk, M. F., Jin, Q., and Flynn, T. M. (2011). The thermodynamic ladder in geomicrobiology. *American Journal of Science*, 311(3), 183–210. https://doi.org/10.2475/03.2011.01

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. https://doi.org/10.1289/ehp.898339

Eze, V. N., and Ugwoke, P. E. (2021). Assessment of heavy metals in groundwater sources in Enugu State, Nigeria. *Environmental Monitoring and Assessment*, 193(2), 87.

Ibeneme, S. I., Anike, L. O., and Ezema, P. O. (2020). Hydrogeochemical and health risk assessment of heavy metals in groundwater sources in parts of Enugu, Nigeria. Environmental Earth Sciences, 79(8), 1–14. https://doi.org/10.1007/s12665-020-08983-9

Ibeneme, S. I., Nwankwo, C. N., and Okeke, A. C. (2020). Heavy metal contamination of groundwater resources in a Nigerian urban settlement. *Journal of Environmental Science and Health, Part A*, 55(12), 1501–1510. https://doi.org/10.1080/10934529.2020.1768674

Ibeneme, S. I., Okoye, N. O., and Ogbonna, C. I. (2020). Assessment of heavy metal concentrations and water quality indices of hand-dug wells in Enugu urban, southeastern Nigeria. *Journal of Environmental Science and Pollution Research*, 26(5), 4934–4945. https://doi.org/10.1007/s11356-019-04171-7

International Agency for Research on Cancer (IARC). (2012). Arsenic, metals, fibres and dusts. IARC monographs on the evaluation of carcinogenic risks to humans (Vol. 100C). Lyon, France: IARC. https://publications.iarc.fr/120

Kawasaki, Y., Zhang, W., and Wong, M. H. (2011). Health risk assessment of heavy metals in well water and surface water in the Pearl River Delta, China. *International Journal of Environmental Research and Public Health*, 8(6), 2022–2037. https://doi.org/10.3390/ijerph8062022

Kawaski, Y., Zhang, Z. W., and Hasegawa, T. (2011). Health effects of manganese in drinking water: Neurotoxicity and reproductive impact. Toxicological Reviews, 30(1), 37–45. https://doi.org/10.1007/s00204-010-0565-2

Keen, C. L., Ensunsa, J. L., and Watson, M. H. (2000). Nutritional aspects of manganese from experimental studies. NeuroToxicology, 20(2–3), 213–223.

Lovley, D. R., Holmes, D. E., and Nevin, K. P. (2004). Dissimilatory Fe(III) and Mn(IV) reduction. *Advances in Microbial Physiology*, 49, 219–286. https://doi.org/10.1016/S0065-2911(04)49005-5

Lovley, D. R., Phillips, E. J. P., Gorby, Y. A., and Landa, E. R. (2004). Microbial reduction of uranium. Nature, 350(6317), 413–416. https://doi.org/10.1038/350413a0

McArthur, J. M., Ravenscroft, P., Safiullah, S., and Thirlwall, M. F. (2001). Arsenic in groundwater: Testing pollution mechanisms for sedimentary aquifers in Bangladesh. Water Resources Research, 37(1), 109–117.

McMahon, P. B., and Chapelle, F. H. (2008). Redox processes and water quality of selected principal aquifer systems. *Ground Water*, 46(2), 259–271. https://doi.org/10.1111/j.1745-6584.2007.00385.x

Nealson, K. H., and Saffarini, D. (1994). Iron and manganese in anaerobic respiration: environmental significance, physiology, and regulation. *Annual Review of Microbiology*, 48(1), 311–343. https://doi.org/10.1146/annurev.mi.48.100194.001523

Nealson, K. H., and Scott, J. (2002). Ecophysiology of the genus *Shewanella*. In Dworkin, M. (Ed.), *The Prokaryotes: An Evolving Electronic Resource for the Microbiological Community*. Springer.

Nwankwoala, H. O., and Amadi, A. N. (2013). Hydrochemical facies and ionic ratios of groundwater in Port Harcourt, Southern Nigeria. Applied Water Science, 3(3), 641–651.

Oremland, R. S., and Stolz, J. F. (2005). Arsenic, microbes and contaminated aquifers. *Trends in Microbiology*, 13(2), 45–49. https://doi.org/10.1016/j.tim.2004.12.002

Ozoko, D. C., and Ezeugwu, I. O. (2025). Geomicrobiology of Aquifers in Enugu. *European Journal of Applied Sciences*, 13(2), 184–207. https://doi.org/10.14738/aivp.132.18517

Ravenscroft, P., Brammer, H., and Richards, K. S. (2009). Arsenic Pollution: A Global Synthesis. Wiley-Blackwell.

Smedley, P. L., and Kinniburgh, D. G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemistry, 17(5), 517–568.

Smith, A. H., Lingas, E. O., and Rahman, M. (2000). Contamination of drinking-water by arsenic in Bangladesh: A public health emergency. Bulletin of the World Health Organization, 78(9), 1093–1103.

Smith, A. H., Lopipero, P. A., Bates, M. N., and Steinmaus, C. M. (2000). Public health: Arsenic epidemiology and drinking water standards. *Science*, 296(5576), 2145–2146. https://doi.org/10.1126/science.1072896

Stumm, W., and Morgan, J. J. (1996). *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters* (3rd ed.). Wiley-Interscience.

World Health Organization (WHO). (2017). *Guidelines for Drinking-water Quality* (4th ed., incorporating the 1st addendum). WHO Press.

World Health Organization (WHO). (2017). Guidelines for Drinking-Water Quality (4th ed.).

World Health Organization (WHO). (2017). Guidelines for drinking-water quality (4th ed.). Geneva: WHO Press. https://www.who.int/publications/i/item/9789241549950