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Assessing the cause of increasing iron concentration in the eutrophication of Lagos coastal water

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Abstract

Iron (Fe) has been found to play a significant role in the surface waters biogeochemical cycles of some macronutrients responsible for eutrophication. Thus, the need to assess the cause of increasing concentration of Fe in the eutrophication of the economically important Lagos coastal waters. Top and bottom water samples were obtained from ten (10) study stations along the Lagos coastal water system, spanning Lagos Central to Lagos East, between November 2019 and March 2020. Physicochemical parameters including pH, Dissolved Oxygen (DO), Oxidation-Reduction Potential (ORP), Total Dissolved Solids (TDS), Turbidity and Salinity were measured in-situ while iron concentrations were determined by spectrophotometric method. The data showed average pH, DO, ORP, TDS, turbidity and salinity of 7.56 ± 0.24; 11.99 ± 2.58 mg L^{-1}; 52.25 ± 42.01 mV; 9.45 ± 2.92 g L^{-1}; 54.92 ± 21.91 NTU and 10.13 ± 2.76 ppt respectively while average Fe concentration was 0.67 ± 0.32 mg L^{-1} for both top and bottom water layer. The locations with elevated concentrations of Fe, mainly driven by anthropogenic inputs from the catchments of the study locations, showed negative ORP values which was indicative of high microbial activities. Increasing Fe concentration and presence of other micronutrients suggest that inputs of minerogenic matter will continue to be a major composite in the sustenance of eutrophication in the waters.

Keywords: *Iron; Eutrophication; Microbial Activities; Micronutrients.*

Introduction

Eutrophication of coastal surface waters is one of the most extensively studied contemporary marine and estuarine pollution problems. The control of eutrophication is predicated on a good knowledge of the dynamics of the phenomenon and ability to carry out comparisons between similar sites and thereby, assess the trends in each of these areas (Karydis, 2009). Coastal waters are a very dynamic environment since they are influenced by both terrestrial inputs, natural and anthropogenic, as well as from inshore – offshore water exchanges, weather conditions and wind – driven water movements (Abayomi *et al.*, 2011). These influences, sometimes result in unbalanced ecosystems, thus instigating unsustainable condition such as eutrophication, an alteration in the ecological functioning of aquatic ecosystems due to excessive growth of primary producers stirred by high nutrient inputs. Nutrients and organic matter could accumulate in an aquatic ecosystem through the contiguous activities of human such as artisanal sand dredging and uncontrolled discharge of sewage/waste in the water system, and through natural phenomenon like agricultural run-offs and atmospheric depositions (Oladosu *et al*., 2016).

The physicochemical properties of water and sediment often stimulate the dynamics of primary producers present in the aquatic environment (Kusler, 2003). The growth of these primary producers, such as algae, is influenced by supply of nutrients, light, temperature, water flow, turbidity, zooplankton grazing and toxic substances from catchments of the receiving water (Olayinka *et al*., 2016). The availability of nutrients through biogeochemical pathways can also depend on alterations in the phytoplankton community structure, growth of excessive algal biomass and possible toxic algal blooms. When the accumulated organic matter exceeds a system's carrying capacity, then hypoxia could occur with attendant decline in fisheries and shell fisheries yields, poor water quality and ecosystems deterioration (Cognetti, 2001). The aquatic ecosystem also thrives on the presence of micronutrients, which are trace elements required in small quantities but can be considered 'essential' for planktons and directly required for normal healthy growth, development, and biodiversity of flora and fauna (Alloway, 2012). Thus, essential trace elements are referred to as micronutrients and many of the micronutrients are potentially toxic metals (PTMs) which could come from both natural and anthropogenic sources (Liesje *et al.,* 2007). Micronutrients such as iron (Fe), manganese (Mn), selenium (Se), Zinc (Zn), Silicon (Si) as well as several potentially toxic metals (PTMs) have been found to play a significant role in the biogeochemical cycle of surface waters (Alloway, 2012).

While increase of organic matters to an ecosystem, mostly lead to increases in phosphorus and nitrogen inputs, has been generally known to modulate the effects of eutrophication of the marine ecosystem (Paerl *et al*., 2014; Malone and Newton 2020), elements such as iron (Fe) has been found as an important element with a significant role in the biogeochemical cycle of major elements (Ekström *et al*., 2016). Iron has been found very essential for the metabolism of plants and animals due to its very important functions and interactions with several essential elements (Alloway, 2012), hence, iron is usually not considered a PTM but a key element which often plays a decisive role in the biogeochemical cycling of marine ecosystem (Sarkkola *et al.,* 2013). Iron occurs in the minerals as heamatite (Fe_2O_3), magnetite (Fe_3O_4), pyrite (FeS_2) Geothite ($FeO(OH)$) and taconite amongst others (Mahmut, 2023). Two (2) oxidative states are possible for iron in aquatic environment – the oxidized form Fe^{3+} (ferric ion) and reduced form Fe^{2+} (ferrous ion). Ferric ion is insoluble and forms a number of oxides and hydroxides which settles at the sediments surface in the presence of excess oxygen (Nicholas *et al*., 2021).

Organic peatland, forest and minerogenic sediments yield significant level of iron in surface water. This is evident in the relationship of iron and organic matter (Maranger *et al.,* 2006). The interaction of organic matter with iron maintains the suspension of Fe^{3+} in oxic and circumneutral waters (Sarkkola *et al.,* 2013) while Fe^{2+}dominate species in the anoxic waters hence, the oxidation state is sensitive to changes in redox potential (Ekström *et al*., 2016). When dissolved oxygen has been consumed as terminal electron acceptors for microbial oxidation of organic matter, ferric ion may undergo chemical and microbial reduction. Ferrous ion on the other hand is soluble and circulates back into the water column. Ferric ion (Fe^{3+}) dominates oxic and circumneutral waters while ferrous ion (Fe^{2+}) is the dominating species in anoxic waters as a result of microbial iron and its redox potential, hence, the level of iron in surface water is driven by redox dynamics (Ekström *et al.,* 2016). Iron and organic matter show significant correlation in eutrophication of surface water. Some researchers have suggested that Fe plays an important role in the control of cyanobacteria blooms which are symptoms of eutrophication (Molot *et al*., 2014). Iron is an important catalytic component for many enzymatic and electron transport systems (Kalff, 2002) hence, this study aims to assess the spatial variation of Fe and its increasing concentration in the eutrophication dynamics of Lagos coastal water in relation to the physicochemical conditions of the water and observed indicators of the eutrophic states of the sampled locations.

Methods

Study Area and Sampling

This study was conducted along a part of the Lagos lagoon with particular attention to watersheds discharging water into the system. The Lagos Lagoon system is the largest in the West African coast with series of estuaries—located between longitude 3°23’ and 3°40’ E and latitude 6°27’ and 6°48’ N. It is a brackish coastal lagoon with a shallow expanse of water (0.3–3 m deep), 50 km long and 3–13 km wide which is separated from the Atlantic Ocean by a narrow strip of barrier bar complex (Alo *et al.,* 2014). The lagoon forms part of an intricate system of water ways dominated by a widespread of estuaries, creeks and a deltaic complex of swamps and salt tolerant mangrove forests (Oyebisi *et al*., 2013). Parts of the lagoon have riparian vegetation and their catchment hosts settlements of artisanal fishermen. The lagoon system is open and experiences environmental gradients linked to rainfall patterns as well as various anthropogenic activities due to increasing urbanization (Akagha *et al.,* 2020). Twenty (20) water samples were collected for five (5) months between November 2019 and March 2020 from both top and bottom layer. Each point was geo-referenced and activities around the sampling points are shown in Table 1.

Table1. Description of the Study Area

Code	Location	GPS	Description of Site
S1	Makoko	N 06.46532° E 003.38129°	Coastal settlement; anthropogenic activities; fishing hub; fishing and recreational activities
S2	Iddo	N 06.47377° E 003.38679°	Coastal settlement; anthropogenic activities; fishing hub; dump site; mechanic workshop
S3	Ijora	N 06.46535° E 003.37191°	Anthropogenic activities; urban settlement; shipping activities; Gas plant; Refineries
S4	Abule Eledun	N 06.52247° E 003.40185°	Coastal settlement; water in-let; dump site; presence of hyacinth
S5	Oworonsoki	N 06.54716° E 003.40927°	Local sand mining, coastal settlement, highly anthropogenic activities, fishing
S6	Odo Iyalaro	N 06.56361° E 003.40420°	Dredging activities, dark coloured water, coastal settlement, foul odour
S7	Ogun River	N 06.56764° E 003.41132°	Surrounded with vegetation and water hyacinth
S8	Majidun	N 06.60430° E 003.47010°	Urban settlement and presence of hyacinth
S9	Egbin Power Plant	N 06.55645° E 003.61232°	Powerline, presence of hyacinth and dredging activities.
S10	Itokin	N 06.62098° E 003.80854°	Major inlet, fishing and surrounded by plant vegetation

Water samples from the top and bottom layers of the study area were collected in prewashed 2 L high-density polyethylene (HDPE) bottles. Top layer samples were collected just below the water level while bottom layer was collected at a depth of about 2 m at each sampling point using a Conbar ep^{R} water sampler. Water samples were stored in an ice chest from the field to the laboratory and kept at 4°C prior to each laboratory analysis.

Experimental Procedure

The physicochemical parameters pH, Dissolved Oxygen (DO), Oxidation-Reduction Potential (ORP), Total Dissolved Solids (TDS), Turbidity and Salinity were carried out in-situ using a calibrated Horiba U-52 multi parameter instrument. Concentration of iron (Fe) in the water samples were determined by the principle of phenanthroline method adopted from APHA (2023) using PG Instrument, T80 UV/VIS spectrophotometer at 510nm. All analyses were conducted using analytical grade reagents and double distilled water. Stock solutions used for working standards were prepared daily. All necessary QA/QC were carried out to ensure the reliability of the data obtained.

Results and Discussion

The pH values of the catchment area were in the range 7.11 ± 0.11 - 7.96 ± 0.26 and 7.07 ± 0.69 - 8.00 ± 0.06 for both top and bottom layers of the water system while the DO values were 7.54 ± 0.84

- 15.76 ± 2.92 and 7.99 ± 0.21 – 16.33 ± 2.52 (Figure 1a and 1b). The pH was observed to be in the neutral range and within the recommended limit of 6.0 – 9.0 of the Nigerian Federal Ministry of Environment (FMEnv, 1991) for water with aquatic life, while the DO values indicated that it is suitable and conducive for the survival of aquatic lives, nevertheless some locations within the study area which are exposed to effluent discharge and evidently higher expanse of macrophyte presence had lower DO levels. Location S7 for the top layer and S3 at the bottom layer (Figure 1b) showed lower DO compared to other stations possibly, due to the level of hypoxia in the catchment area although, still in the acceptable range of > 6.8 by the FMEnv (1991). The relatively satisfactory DO concentration could largely due to the constant tidal movement of the water and continuous intrusion of the well oxygenated Atlantic Ocean water (Alo *et al.,* 2014). The top layer of the catchment area showed an average of 12.09 ± 3.26 mg L^{-1} while the bottom layer was 11.90 ± 1.90 mg L^{-1}. Although, the bottom layer was slightly lower, which could possibly be due to a level of biological aerobic breakdown of organic matter at the bottom layer, however, both layers showed a similar variation within the catchment area (Figure 1b) which could be as a result of higher exposure of the top layer to the atmospheric oxygen. The high DO, could suggest possibility of higher oxidation of pollutants as well as providing sufficient oxygen to aerobic microorganisms.

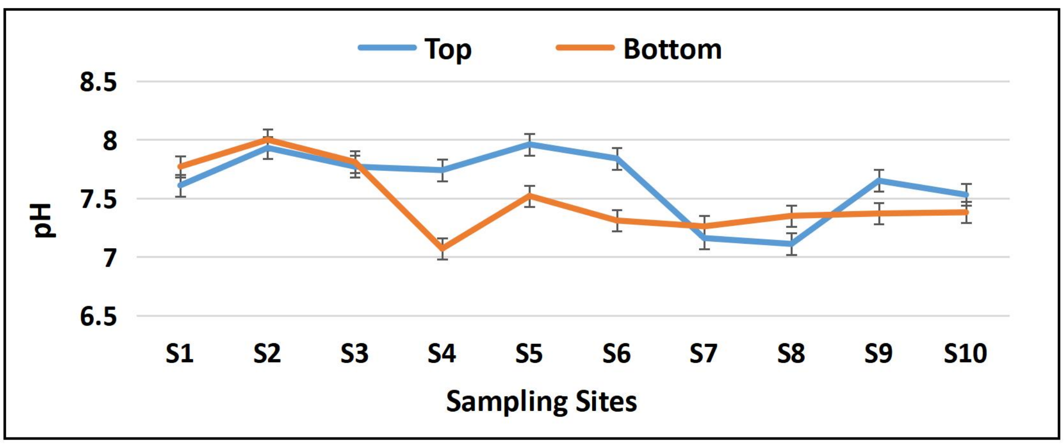

Figure 1a: pH Levels in the Top and Bottom layers of the Catchment

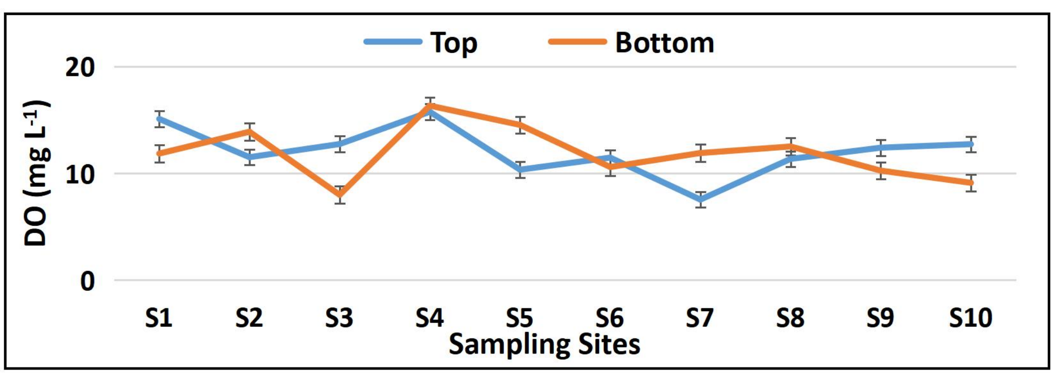

Figure 1b: DO Levels in the Top and Bottom layers of the Catchment

Figure 2 (a, b and c) showed the turbidity, TDS and salinity levels of the catchment area respectively. Turbidity level ranged from 14.67 ± 10.52 to 107.67 ± 8.20 NTU for the top layer and 18.80 ± 2.42 to 131.00 ± 45.15 NTU at the bottom layer (Figure 2a). Locations S4, S6 and S7 showed higher level of turbidity compared to other locations, which could be the consequence of the relatively high level of suspended particulate at these locations, owing to uncontrolled artisanal sand mining activities and upwelling of bottom detritus as a result of active water transportation around the catchment area. Location S3 and its corridor was observed to have lower turbidity possibly due to its proximity and exposure to Atlantic Ocean water incursion and possible dilution.

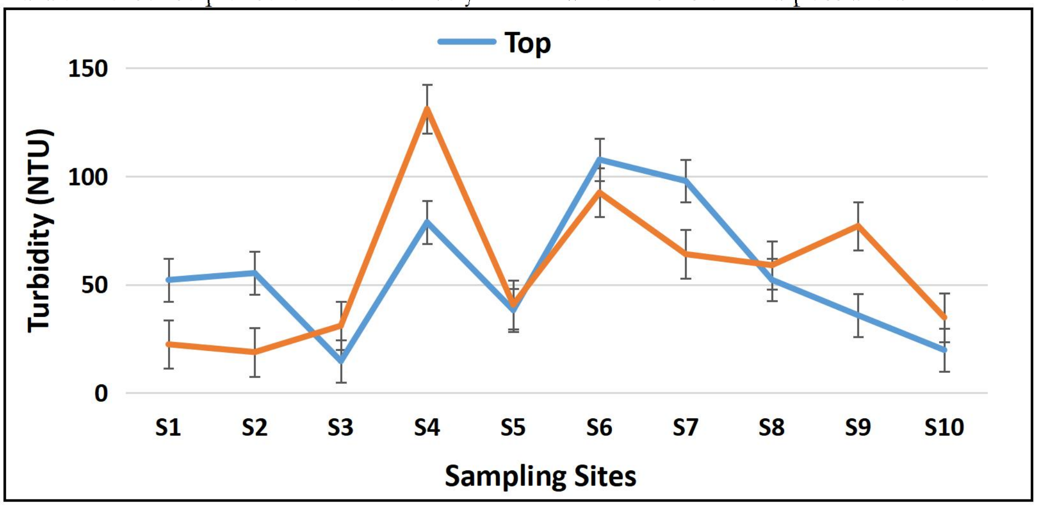

Figure 2a: Turbidity Levels in the Top and Bottom Layers of the Catchment

TDS values were in the range of 0.19 ± 0.16 – 21.63 ± 1.84 g L^{-1} and 0.25 ± 0.10 – 22.47 ± 2.10 g L^{-1} for both top and bottom layers respectively (Figure 2b). TDS references the level of inorganic solutes present in the water system. The major ions are usually cations of calcium, magnesium, sodium, and potassium, and anions of carbonate, hydrogen carbonate, chloride, sulfate, and nitrate (Islam *et al.*, 2017). Although TDS may not be regarded as a major water pollutant, however, it has been identified as an indicator of water quality. Coastal water degradation by parameters such as TDS is caused by climate change, urban development, and contamination caused by rapid and uncontrolled environmental changes such as drought, wastewater discharges, and agricultural runoffs resulting in adverse impacts such as the proliferation of harmful blue-green algae, accelerated eutrophication, and extreme turbidity among others which have implications on the sustainability of the limited water resources (Adjovu *et al.*, 2023). TDS and salinity levels are much-related concepts as the most dissolved solids typically consist of inorganic ions, which are the components of salts (Ferdous *et al.,* 2019). Salinity affects water density and the higher the dissolved salt concentration, the higher the density of water (EPA, 2014). Salinity values were in the range of 0.15 ± 0.11 – 22.34 ± 1.84 ppt and 0.19 ± 0.08 - 24.46 ± 4.72 ppt (Figure 2c) for both top and bottom layers respectively. Locations S1 – S3 for both top and bottom layer showed higher values compared to other locations owing to the closeness of the saline nature of the Atlantic Ocean (Echebiri *et al.,* 2023), while Location S10 was lowest for both top and bottom layer. Location S10 is an estuarine catchment which receives riverine water and discharges it into the eastern part of the Lagoon system. Salinity intrusion in water bodies occurs when salts get dissolved in the water bodies thereby inhibiting the growth of biomass and macrophyte (Thomas *et al*., 2023). It has the tendency of threatening the metabolic processes of aquatic organisms (Nguyen *et al*., 2020) and affects the natural environment, causing economic loss due to the devastating effect on agricultural productivity and food safety (Adjovu *et al*., 2023).

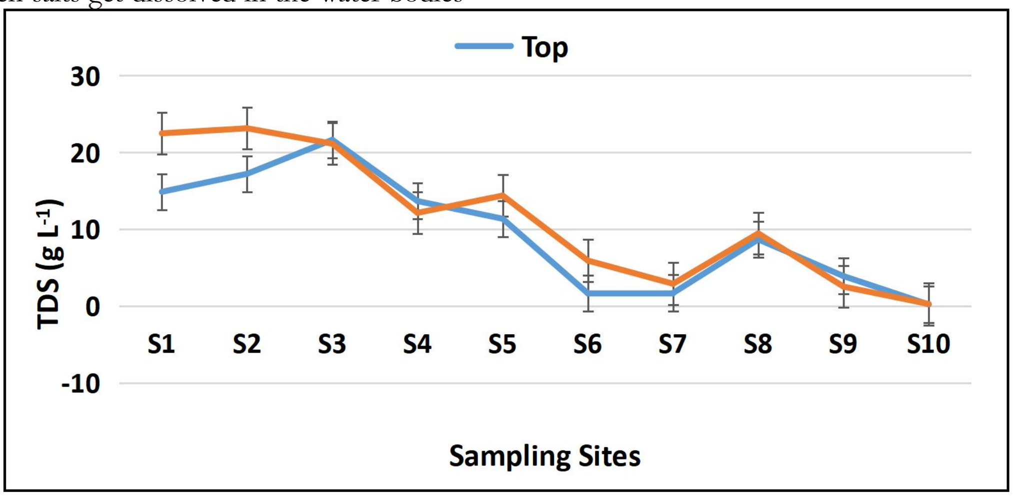

Figure 2b: TDS Levels in the Top and Bottom Layers of the Catchment

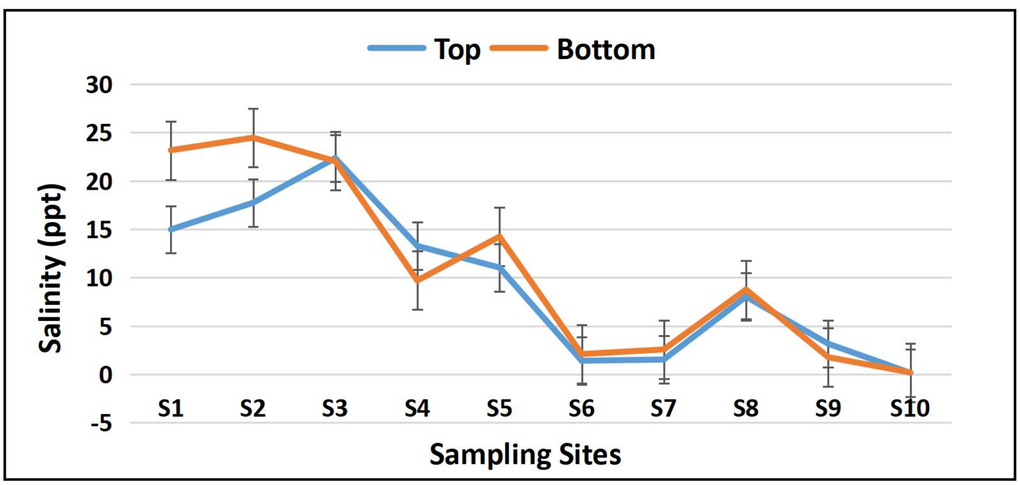

Figure 2c: Salinity Levels in the Top and Bottom Layers of the Catchment

ORP is one of the pointers of redox-sensitive chemical processes in the overlying water – sediments interface. Its determination is important in coastal water system containing relatively high concentration of redox-active species, such as salts of iron and manganese with strong oxidizing (chlorine) and reducing (sulphate) agents influenced by anthropogenic pressure of the catchment area which are key pathways in the degradation of organic matter (Teal *et al.,* 2009;

Lenstra *et al.,* 2021; Echebiri *et al.,* 2023). ORP depends on the amount of dissolved oxygen that is in the water, as well as the number of other elements that function similarly to oxygen (Yingzhi *et al.,* 2010). ORP values in the study locations were in the range of -71.20 ± 44.97 – 99.71 ± 63.39 mV and -24.4 ± 38.40 – 103.42 ± 64.56 mV for both top and bottom layers respectively (Figure 3a). The water system was observed to have low ORP values as shown in Figure 3a. Generally, healthy coastal waters should have ORP value in the range of 200 – 500 mV (Datastream Initiative, 2021). Low ORP is indicative of reducing tendencies of the water system, suggesting a degree of pollution (Datastream Initiative, 2021) as observed in the catchment area especially at Locations S6 and S7 in spite of the tolerable dissolved oxygen concentration. The degree of pollution may be a consequence of untreated domestic and industrial effluents being discharged from adjoining rivers to the Lagoon. This is also reported by SØndergaard (2009) who attributed low ORP levels to elevated pollutant concentrations from domestic and industrial effluents in rivers discharging into the coastal waters (Echebiri *et al*., 2023). Low ORP, as observed particularly at S6 and S7 with negative values is an indicator of unsustainable aquatic environment and hypoxia and could threaten the existence of aquatic lives, including benthic organisms. These locations were characterized with foul odour indicative of advance organic matter decomposition and general absence of fishery presence due to the degree of pollution. Fe values were in the range of 0.19 ± 0.02 – 1.00 ± 0.90 mg L^{-1} and 0.25 ± 0.17 – 2.00 ± 0.61 mg L^{-1} for both top and bottom layers at these locations respectively (Figure 3b). At the top layer of the water body, Fe was observed to be lowest at Locations S9 and S10 and highest at S4 while at the bottom layer, Fe was lowest at S9 and highest at S4 (Figure 3b). Although the levels, as observed were generally below the regulatory limit of 1.00 mg L^{-1} for natural waters (FMEnv, 1991) with the exception of S4, however, an increasing concentration of iron was observed with decreasing lower ORP especially at Locations S6 and S7 with exception of S9 possibly due to the large volume of water with sufficient dissolution of atmospheric oxygen within the catchment area.

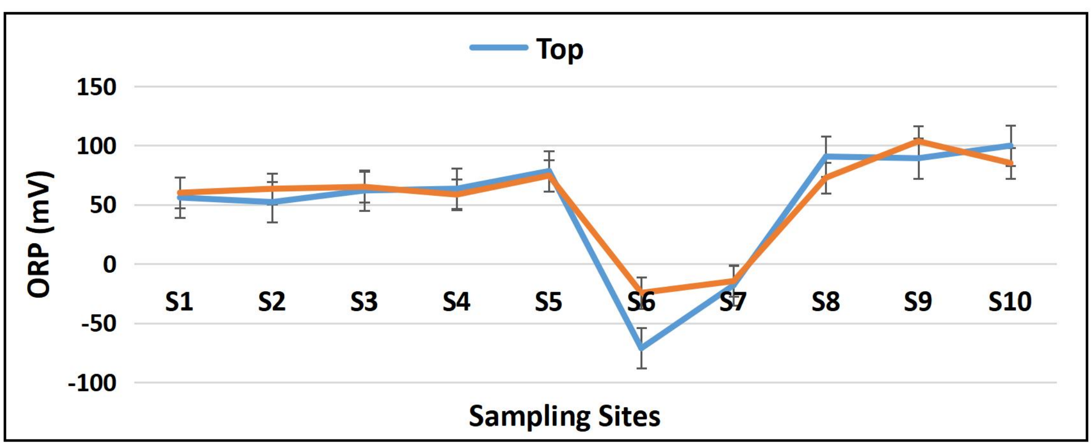

Figure 3a: ORP Levels in the Top and Bottom Layers of the Catchment

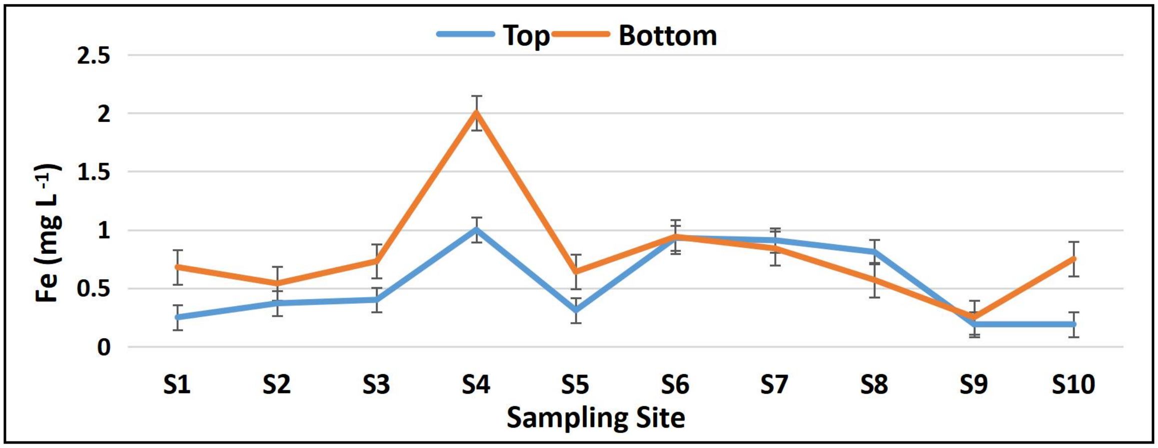

Figure 3b: Fe Levels in the Top and Bottom Layers of the Catchment

Relationship between Physicochemical Parameters and Fe in the Catchment Area

The relationship between the variables of the water parameters for both top and bottom layers of the water system were analyzed using Pearson's correlation coefficients, and the results are as shown in Table 2. TDS showed a strong positive correlation with Salinity ($r = +0.999$, $p < 0.01$) and ($r = +0.990$, $p < 0.01$) for both top and bottom layer. The positive correlation could suggest they are from a common origin with respect to incursion of sea water from the Atlantic Ocean into the lagoon system especially at locations around its corridor. While ORP shows a weak positive correlation with DO ($r = 0.201$, $p < 0.05$) at the top layer and weak negative correlation ($r = -0.203$, $p < 0.05$) at bottom water layer, DO showed a negative correlation with Fe ($r = -0.176$, $p < 0.05$) at the top layer and ($r = 0.399$, $p < 0.05$) at the bottom layer, and ORP shows a relative weak negative correlation with Fe ($r = -0.364$, $p < 0.05$) at the top layer and a strong negative correlation ($r = -0.662$, $p < 0.05$) at the bottom layer. This is indicative of the reducing condition of Fe within the catchment area. Although, the water system was sufficiently oxygenated based on the observed dissolved oxygen (DO) concentrations, however, the low ORP showed a level of reducing condition from Fe^{3+} to Fe^{2+} down the water column with increase in microbial activities as posited by Teal *et al.,* (2009).

Fe biogeochemistry is sensitive to changes in redox potential following its interaction with decomposition of organic matter, and increase in microbial activities. This is consistent with the observation of Snape *et al.* (2004) that Fe and organic matter content can significantly be affected by strong redox effects frequently observed in estuarine and coastal systems. This condition, according to Alo *et al.* (2010) favours the depletion of available oxygen thus, leading to hypoxia especially at Locations farther from the fringes of the Atlantic Ocean water incursion into the Lagoon. The oxidized forms of (Fe^{3+}) are usually found as insoluble oxides in the oxic water layer, while the reduced forms (Fe^{2+}) can be soluble and controls the species within the anoxic water layer (Nealson, 1983; Teal *et al.,* 2009; Sarkkola *et al.,* 2013). Turbidity, which is a degree of light attenuation has a strong positive correlation with

Fe ($r = 0.812$, $p < 0.01$) at the top layer and ($r = 0.345$, $p < 0.05$) at the bottom layer possibly due to the particulate suspensions of oxidized Fe in form of Fe^{3+} at the surface level. While TDS is positively correlated with salinity and negatively correlated with turbidity, pH was observed to be positively correlated with TDS and salinity, and negatively correlated with turbidity (Hussein, 2019).

Table 2: Water Parameter Using Pearson's Correlation Coefficient

Top Layer							
	pH	DO	TDS	Salinity	Turbidity	Iron	ORP
pH	1						
DO	0.329	1					
TDS	0.419	0.418	1				
Salinity	0.426	0.406	0.999(**)	1			
Turbidity	-0.157	-0.266	-0.358	-0.360	1		
Iron	-0.334	-0.176	-0.181	-0.190	0.812(**)	1	
ORP	-0.056	0.201	-0.372	-0.386	-0.520	-0.364	1
Bottom Layer							
	pH	DO	TDS	Salinity	Turbidity	Iron	ORP
pH	1						
DO	-0.208	1					
TDS	0.779(**)	0.240	1				
Salinity	0.831(**)	0.189	0.990(**)	1			
Turbidity	-0.913(**)	0.227	-0.623	-0.706(*)	1		
Iron	-0.388	0.399	0.078	0	0.345	1	
ORP	0.055	-0.203	-0.191	-0.128	-0.091	-0.662(*)	1

** Correlation is significant at the 0.01 level (2-tailed)
* Correlation is significant at the 0.05 level (2-tailed)

Conclusion

The study has highlighted the implication of spatial Fe concentration in relation to the physico-chemical conditions of the Lagos lagoon. The causes of increase in Fe concentration within the monitored catchment areas of the Lagoon are more indefinable but strongly linked to increased anthropogenic indicators at these Locations, and perhaps increased oxidation-reduction activity accompanying the decomposition of excess organic matter from eutrophic biomass. Oxidation-reduction potential in the water system indicated the variation of Fe within the water column in spite of the availability of dissolved oxygen during the study. The results showed that Fe has a negative relationship with ORP due to the pollution status of the studied catchment Locations. The wanton input of particulate and soluble nutrients into the Lagos Lagoon is evidenced by the proliferation of increased organic matter biomass such as water hyacinth over the Lagoon surface and water-column hypoxia. Although, the study of eutrophication has majorly been based on macro elements such as phosphorus and nitrogen inputs into the lagoon systems, however, more attention needs to be paid to the role of micronutrients in the ecological and biogeochemical cycles of the coastal system.

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