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RESEARCH ARTICLE

COMPARATIVE STUDY OF SEASONAL VARIATIONS IN BIO-CORROSION OF STEEL COUPONS IN NEW CALABAR RIVER AND NDONI RIVER AQUATIC SYSTEMS OF THE NIGER DELTA

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ABSTRACT

Corrosion rate of stainless, mild and carbon steel coupons in New Calabar River and Ndoni River was monitored monthly for a period of one year. Corrosion rate was determined by weight loss. Carbon steel had corrosion rate of 72g/yr, mild steel 39g/yr, stainless steel 1.3g/yr in New Calabar River while carbon steel had corrosion rate of 44g/yr, mild steel 27g/yr, stainless steel 0.64g/yr in Ndoni River. Micro-organisms isolated include Sulphur reducing bacteria, Iron bacteria and Sulphur bacteria. In New Calabar River weight loss of stainless, mild and carbon steel showed these trend for rainy season (April-October) respectively; (0-0.112)g, (1.864-2.139)g (2.113-4.230)g. The dry season (November-March) showed these trend respectively; (0.117-0.141)g, (2.147-8.001)g, (4.272-15.171)g. In fresh water weight loss of stainless, mild and carbon steel for rainy season (April-October) respectively showed the following trend (0-0.030)g, (0.695-1.568)g, (1.000-2.316)g, while the dry season (November-March) respectively showed these trend (0.044-0.111)g, (1.586-5.771)g, (2.325-9.131)g. In New Calabar River corrosion rate of stainless, mild and carbon steel showed these trend for rainy season (April-October) respectively; (0-0.016)g/month, (1.864-0.306)g/month, (2.113-0.604)g/month. The trend for dry season (November-March) respectively was (0.014-0.012)g/month, (0.268-0.667)g/month, (0.534-1.264)g/month. In Ndoni River, the corrosion rate of stainless, mild and carbon steel for rainy season (April-October) respectively showed these trend (0-0.004)g/month, (0.695-0.244)g/month, (1.000-0.331)g/month while the dry season (November-March) respectively showed these trend (0.006-0.009)g/month, (0.198-0.481)g/month, (0.291-0.761)g/month. Total Dissolved Solids, Total Suspended Solids, Total Organic Carbon, Biochemical Oxygen Demand, Conductivity, Salinity, Oil and Grease, Chloride, Sulphate Sulphite, Temperature, pH were monitored for rainy season and dry season in both New Calabar River and Ndoni River. The study was able to show that corrosion rate was higher in New Calabar River than Ndoni River in same steel types comparatively especially in the dry seasons. Stainless steel if not yet in use should be encouraged in pipeline work in oil industries and other related works since it is less bio- corrosive in both New Calabar River and Ndoni River. Lots of emphasis should be laid on microbial influenced corrosion since it has proved to be a menace in corrosion.

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INTRODUCTION

Corrosion in general is the destruction or deterioration of materials because of the reaction of material with its environment surrounding it (Fontana, 2005). The tendency for a material to corrode is normally determined by measuring its rate of corrosion and comparing it with the corrosion rates of other materials in the same environment. In the oil industries, estimating the rate of corrosion provides valuable input to several aspects of pipeline threat to safe operations. Among these threats is external corrosion of buried steel pipelines. The detection of corrosion provides pipeline operators with information regarding the areas vulnerable to eventual failure, however it is the rate of corrosion that will influence how quickly those flaws can grow to critical size and cause failure (Armend, 2009). Corrosion whether physiochemical (aerobic) or microbial (aerobic and anaerobic) has been a menace to activities in the upstream and downstream sector of the petroleum industry in Nigeria (Odokuma and Williams, 2010). In Nigeria pipeline rupture/failure has resulted in the spilling of crude oil into terrestrial and aquatic habitats. These habitats are of immense importance to indigenous biota and human's dependent on the resources (aquatic, terrestrial and biological) in these habitats. The contamination/pollution of these environmentally sensitive habitats (especially brackish and fresh water wetlands) has generated a lot of national and international discourse. In Nigeria there is a dearth of information on the cost of microbial induced corrosion to the petroleum industry. Corrosion in Nigeria seems to be largely

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attributable to physicochemical processes. However, the environmental factors (high oxygen levels whether dissolved or free, low pH, high redox potentials, high populations of sulphate reducing and oxidizing bacteria) that mediate aerobic and anaerobic microbially induced corrosion abound in the Niger Delta where pipelines (flowlines, pipelines, bulklines, trunklines etc) conveying petroleum or its products crisscross the length and breadth of the area. Rupture of these pipelines is more apparent along the pipeline Right of Ways (RoW). There is no doubt that measures to control corrosion (such cathodic protection and applications of various inert coatings) of metals that are the constituents of these pipelines are undertaken by upstream and downstream operators in the Nigerian Petroleum industry.

However, the frequency of integrity checks on these pipelines needs to be increased such that areas of stress and weaknesses could be detected on time to avoid rupture/ failure of these pipelines. Wang *et al* (2004) reported that rate of microbial corrosion has been a problem to industries such as petroleum, transportation, construction and water co operations. This has led to loss of billions of dollars worldwide in diverse processes (Bitton and John, 2007). According to ICEM (2011), Pakistan has been losing about 3 billion dollars to microbial corrosion on account of infrastructure, industries and household corrosion which does not include the damage to environment and loss of production due to unscheduled breakdown. It has been noted by Ashassi-Sorkhabi (2009) that there was an increase in the rate of microbial corrosion on different materials used in processing and packaging in the food industry. Smith and Hashemi (2006) reported that they was an increase in corrosion rate of most of the steel equipment used by manufacturing industries. Pitonzo *et al* (2004), Lee and Newman (2005) noted that sulphate reducing bacteria, iron bacteria and sulphur bacteria have been implicated to cause corrosion in brackish and fresh water ecosystems.

Ecological quality parameters which may either be organic or inorganic provide a conducive environment for corrosion. Organic parameters such as Biochemical Oxygen Demand (BOD), oil and grease provide organic carbon for heterotrophic microorganisms that act in corporation with the main culprit organisms. Inorganic chloride, salinity, sulphate, sulphite and associated factors like Temperature, pH, conductivity, total organic carbon, total dissolved solids and total suspended solids all contribute to microbial corrosion of steel products. Birnin-Yauri and Garba (2006) reported that low concentrations of chloride ions caused corrosion of steel used for reinforcement. Badmos and Ajimotokan (2009) noted that low pH encouraged corrosion rate while higher pH reduced corrosion rate. Some authors have investigated the effect of flow on corrosion rate of metals and alloys such as nickel-aluminum-bronze (Kear *et al* 2004, Whartman *et al* 2005), stainless steel (Rybalka *et al* 2006, Sidorin *et al* 2005), Cu-Ni alloys (Maciel and Agostinho 2000, Martinez and Metilcos-Hukovic 2006, Kear *et al* 2007) and carbon steel (Luis *et al* 2007) in different corrosive solutions. Musa *et al* (2011) determined the corrosion rate of mild steel in 2.5ml H_2So_4 at 30^0c for different flow velocities using Tafel technique. The Ndoni River and the New Calabar River both freshwater and brackish water respectively located in the Niger Delta was employed for this study. The study was aimed at comparing the corrosion rate of the different steel types (stainless steel, mild steel and carbon steel) buried in both fresh water and brackish water environment in-situ.

MATERIALS AND METHODS

Area of study: The New Calabar River is situated in a low energy coastal environment of the Niger Delta within Rivers State of Nigeria. The water is brackish influenced by the marine influx associated with tidal cycle. The river is subjected to frequent precipitation throughout the long rainy season of March to October. The dry season starts in November and terminates in February or March. The rainy season is interrupted by a short dry spell in August called the August break. The edges of the river is covered with green vegetations and some mangrove trees. The Ndoni River is situated in the coastal environment of the Niger Delta in Rivers state Nigeria. It is a freshwater site influenced by River Niger influx. The river has a long rainy season from March to October. The dry season is very short, beginning in November and ending in March of the following year referred to as the harm tan. The edges of the river are covered with lush green vegetation and mangrove trees.

Industrial activities along the rivers: Some industrial activities are present in both the New Calabar River and Ndoni River environment. In New Calabar River, one of them coded (A.S.L) an oil services company its activities include building and repair of oil pipelines. Another company coded (I.D) specialize in food packaging. Other minor industrial activities along the river include various lumbering industries, fish ponds and two markets. In Ndoni River the main industrial activity in this area is dredging and sand wining (coded A.M.L). The repairs of marine boats also occur here. Other minor industrial activities along the river include the lumbering, fish farming and a market situated by the river.

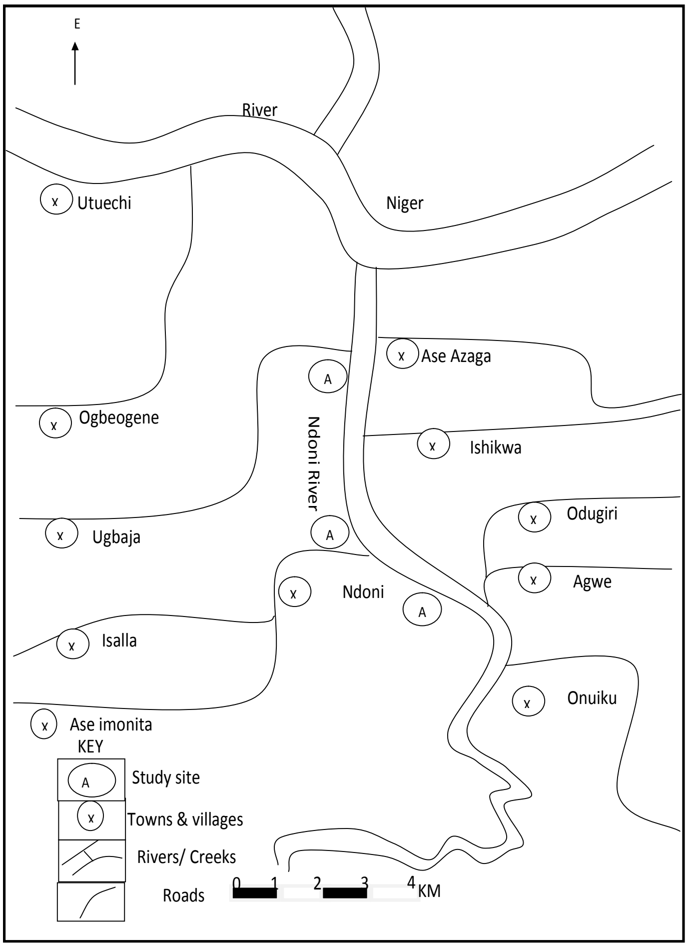
Water sample analyses: Surface water samples were collected on the 15^{th} of every month between 10.00 and 12.00a.m from April 2010 to March 2011 at low tide. Water samples were collected with 100m/1 sterile bottle. Samples for Biochemical Oxygen Demand (BOD) determination were collected with 250m/1 (BOD) bottles. For other chemical analysis, samples were collected with 500m/1 glass bottles that had been sterilized at 121^0C and 15psi for 15 minutes. All samples were analyzed immediately on reaching the laboratory.

Chemical reagents: All chemical reagents employed in this study were products of Aldrich chemical co, Milwaukee, USA, BDG Chemicals, Poole, England and Sigma chemical company, St Louis Missouri, USA.

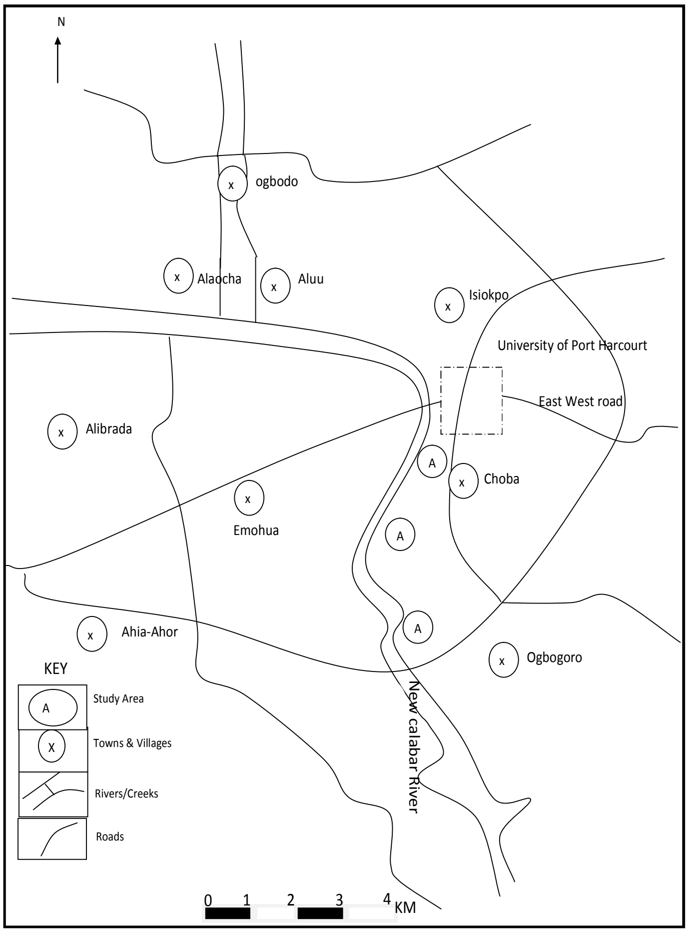
Metal coupons: The steel materials used for this study namely stainless steel ASTM A316L, mild steel ASTM A283 and carbon steel ASTM A36 was obtained from Nigeria Agip Oil Company (NAOC) and TOTAL FINA ELF Nigeria limited.

Ecological quality parameters

The following parameters were determined namely Biochemical Oxygen Demand, Oil and Grease, pH, Temperature, Salinity, Conductivity, Total Dissolved solids, Total Suspended Solids, Total Organic Carbon, Chloride, Sulphate, Sulphite and Heavy metals: Ni, V, Cr, Fe, Na, Ca, K, Zn, Cu. The heavy metals were determined using model AA320 atomic absorption spectrophotometer (Shanghai analytical instrument Co). Oil and grease content was estimated using the method of Odu *et al*. (1988).



A Map showing the sampling site the new calaber river



A map showing the sampling site the Ndoni River

A 10-ml portion of the water sample was shaken with 10-ml of toluene in a separator funnel. The hydrocarbon grease and oil content was then determined by the absorbance of the extract at 420nm in a spectrophotometer. A standard curve of the absorbance of different known concentration of equal amount of crude oil and grease in the extractant was first drawn after taking reading from the spectrophotometer. Oil and grease concentrations in the water were then calculated after reading the optical density of the extract from the spectrophotometer. The standard curve was used to estimate the oil and grease concentration after multiplying by an appropriate dilution factor. All other parameters such as Sulphate, Sulphite, Total Organic Carbon, Total Suspended Solids, Total Dissolved Solids, Salinity, Chloride, and Biochemical Oxygen Demand were determined employing methods from APHA (2000). Total Dissolved Solids by gravimetric method, Sulphite by Iodometric method, Sulphate by Turbidimetric method, Chloride and Salinity by Argentometric method, Total Organic Carbon by Rapid Oxidation method, Biochemical Oxygen Demand by modified Winkler method, Total Suspended Solids by Gravimetric method.

Microbiological analyses

Postgate broth (1985) was used to enumerate the sulphate reducing bacteria using the conventional five tube most probable number method (MPN). Water samples (10ml, 1ml and 0.1ml) were placed in a series of five tubes with nutrients. After sterilization they were inoculated with dilutions of scrapings from the metal coupons and enumerated after 7 days of incubations in an anaerobic gas jar at room temperature.

Statistical analyses: Correlation analyses and student T-TEST from excel 2010 was employed where value of P< 5% was considered to be significant and P> 5% was considered not significant for T-TEST. +1 (perfect correlation) through 0(no correlation) to -1 (perfect negative correlation) for correlation analyses.

RESULTS

Results in Table 1 are the bacterial count of microorganisms isolated in New Calabar River and Ndoni River habitat from April 2010 to March 2011. In New Calabar River, the sulphate reducing bacteria increased from (11-26) MPN index per 100ml from April to June, decreased from (9-<2) MPN index per 100ml from July to October, and increased again from (2-33) MPN index per 100ml from November to March. Iron bacteria increased from (130 - 221) 10^3Cfu/ml from April to May, decreased from (218 - 21) 10^3Cfu/ml from June to October and increase from (47 - 189) 10^3 Cfu/ml from November to March. Sulphur bacteria increased from (224 - 253) 10^3Cfu/ml from April to June, decreased from (167 - 43) 10^3 Cfu/ml from July to October, increased from (63 - 224)10^3 Cfu/ml from November to March. In Ndoni River, the sulphate reducing bacteria increased from April to June (7-14) MPN index per 100ml before decreasing from July to November (7-<2) MPN index per 100ml and increased again from December to March (2-21) MPN index per 100ml. The iron bacteria increased from April to May (261-278) 10^3 cfu/ml and decreased from June to October (270-65) 10^3cfu/ml before increasing again from November to March (71-321) 10^3 cfu/ml.

BRACKISH WATER

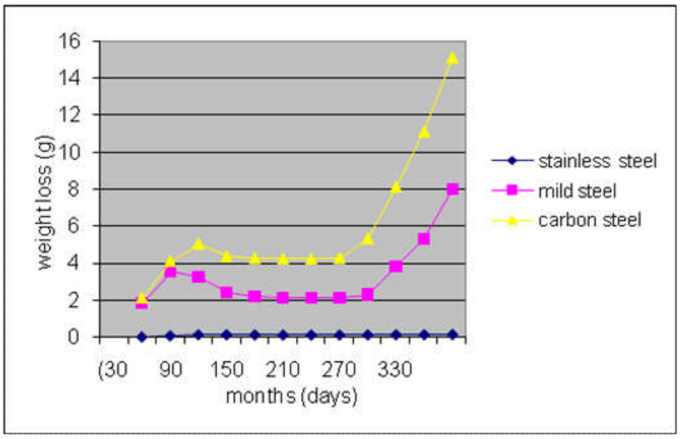


Figure 1. Weight loss against time

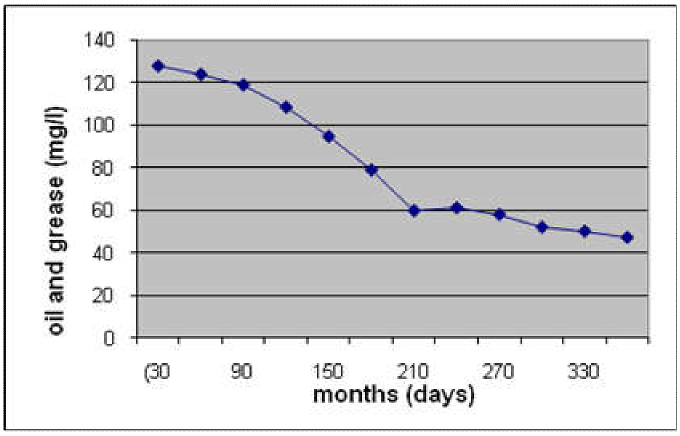


Figure 2. Oil and Grease against time

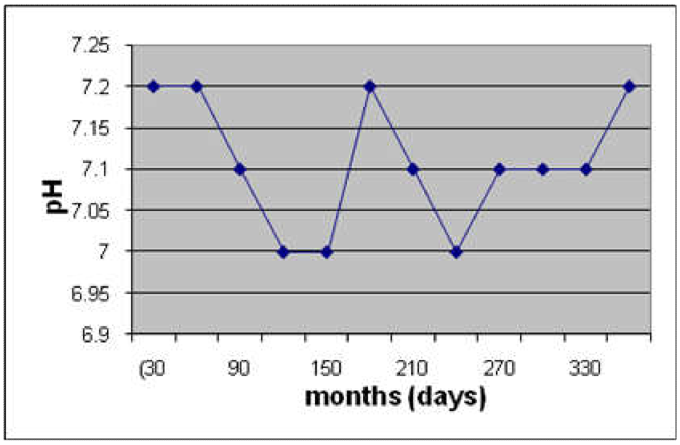


Figure 3. pH against time

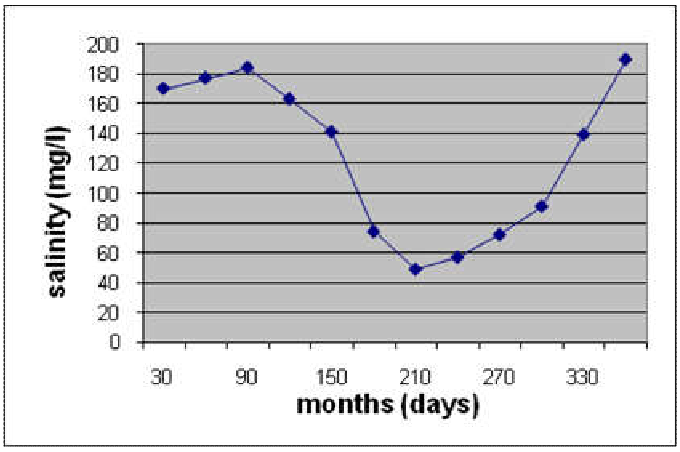


Figure 4. Salinity against time

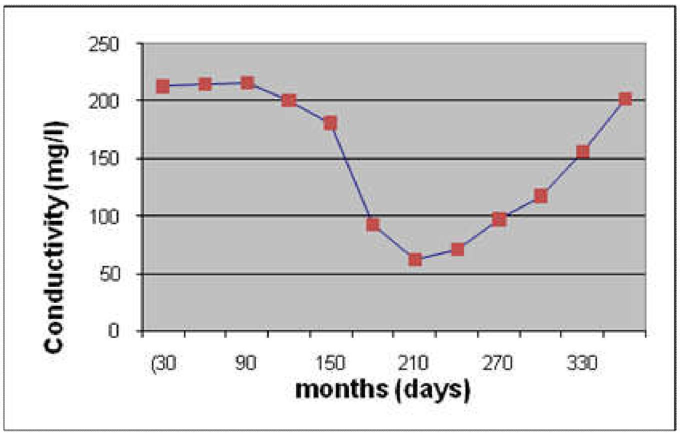


Figure 5. Conductivity against time

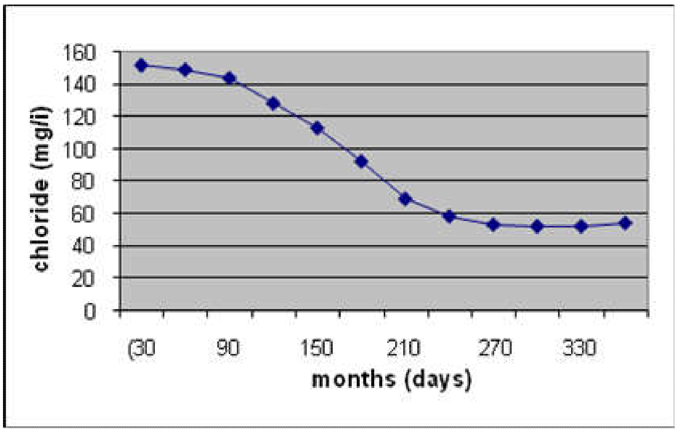


Figure 6. Chloride against time

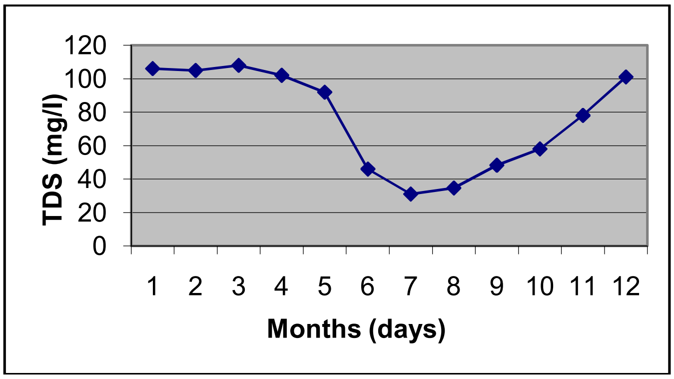


Figure 7. Total Dissolved Solids against time

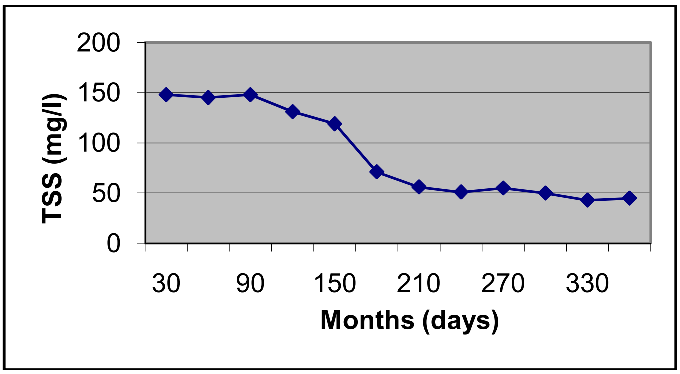


Figure 8. Total Suspended Solids against time

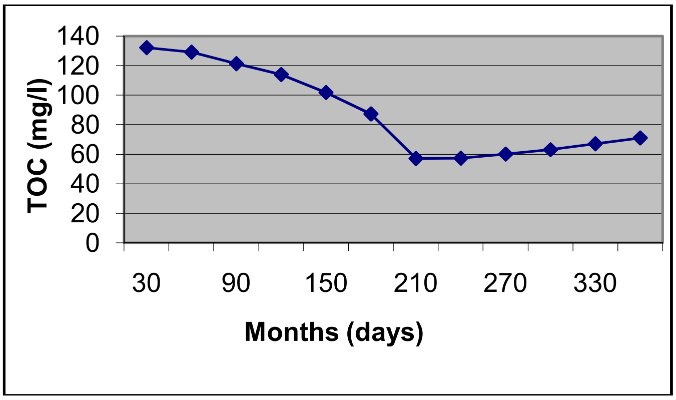


Figure 9. Total Organic Carbon against time

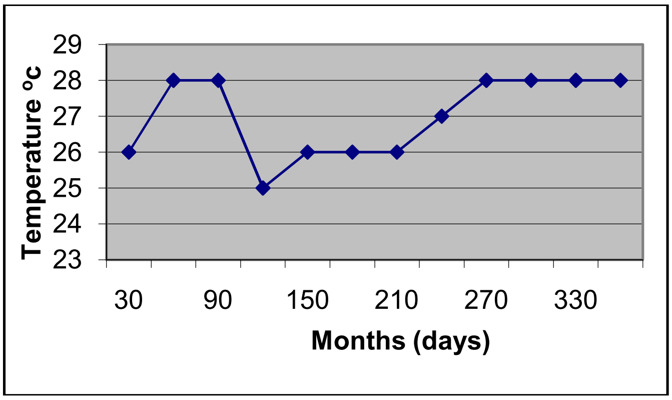


Figure 10. Temperature against time

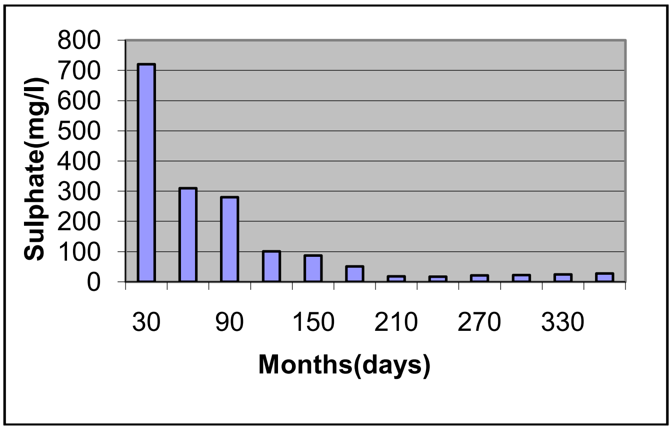


Figure 11. Sulphate against time

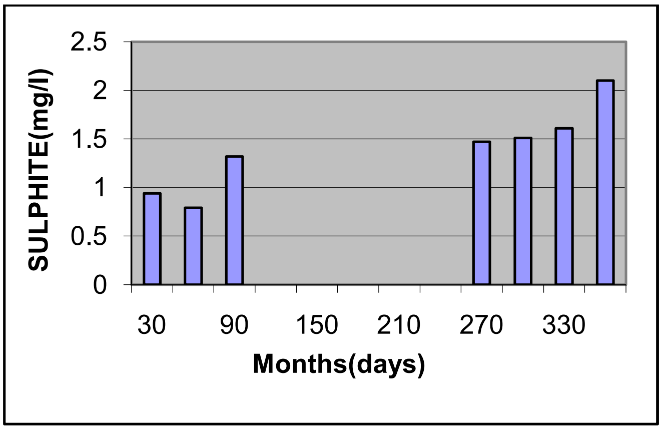


Figure 12. Sulphite against time

Sulphur bacteria decreased from April to May then increased by June and decreased from July to October (121-19) 10^3 cfu/ml and increased again from November to March (22-201) 10^3 cfu/ml. The Chemical composition of the various metal coupons namely stainless, mild and carbon steel used for this study are shown in Table 2. In New Calabar River, graphical representation of weight loss against time of various metal coupons used in the study is shown in Figure 1. There was significance in the weight loss between stainless steel and mild steel, stainless steel and carbon steel, mild steel and carbon steel. P values = (1.95075E-06, 6.86925E-06, 0.014722061) respectively. In New Calabar River, corrosion rate shown graphically in Figure 14 revealed a significance in the corrosion rate between stainless steel and mild steel, stainless steel and carbon steel, mild steel and carbon steel. P values = (0.000184819, 4.34224E-07, 0.048196863) respectively. In New Calabar River Graphically Figures 2, 3, 4 and 5 are the results of Oil and Grease, pH, Salinity and conductivity respectively. Oil and Grease decreased from April to October, increased by November and decreased from December to March. Values for pH were constant between 7.0-7.2 from April to March. Salinity showed an increase from April to June, decreased from July to October, increased from November to March. Conductivity showed the same trend with salinity. In New Calabar River the correlation values in weight loss and corrosion rate between ecological quality parameters and metal coupons namely (Stainless, mild and carbon steel) respectively are weight loss; Oil and Grease r = (- 0.6252, - 0.4199, - 0.6362), pH r = (-0.4534, 0.3511, 0.2078), Salinity r = (- 0.2266, 0.437, 0.2536), Conductivity r = (-0.3021, 0.3361, 0.1236). Corrosion rate; Oil and Grease r = (0.4834, 0.7908, 0.7640), pH r = (- 0.2472, 0.5326, 0.5226), Salinity r = (0.3413, 0.6901, 0.8173), Conductivity r = (0.3615, 0.7313, 0.8400).In New Calabar River, Figures 6, 7, 8 and 9 are the results of ecological quality parameters of Chloride, Total Dissolved Solids, Total Suspended Solids and Total Organic Carbon respectively. Chloride decreased from April to January and increased a little from February to March. Total Dissolved Solids decreased from April to May, increased by June and decreased from July to October and increased from November to March. Total suspended Solids decreased from April to May, increased by June, decreased from July to November, increased by December and decreased from January to March. Total Organic Carbon decreased from April to October, increased from November to March. In New Calabar River, the correlation values in weight loss and corrosion rate between ecological quality parameters and metal coupons namely (Stainless, Mild and Carbon steel) respectively are weight loss; Chloride r = (-0.6022, - 0.3673, - 0.5903), Total Dissolved Solids r = (-0.2871, 0.3319, 0.1247), Total Suspended Solids r = (-0.5497, - 0.3643, -0.5766), Total Organic Carbon r = (- 0.5899, - 0.2154, - 0.4452). Corrosion rate; Chloride r = (0.5006, 0.7914, 0.7762), Total Dissolved Solids r = (0.3636, 0.7133, 0.8249), Total suspended Solids r = (0.5322, 0.7633, 0.7589), Total Organic Carbon r = (0.4550, 0.8316, 0.8417). In New Calabar River graphically, Temperature, Sulphate, Suphite and Biochemical Oxygen Demand are represented in Figures 10, 11, 12 and 13 respectively. Sulphate decreased from April to November, increased from December to March. Suphite followed the same trend as the Suphate. Biochemical Oxygen Demand decreased from April to October and increased from November to March. In New Calabar River, the correlation values in weight loss and corrosion rate between ecological quality parameters and metal coupons namely (Stainless, Mild and Carbon steel) respectively are weight loss;

FRESH WATER

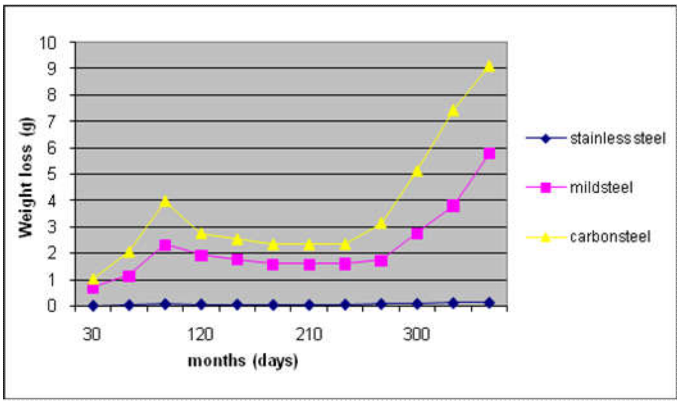


Figure 1. Weight loss against time

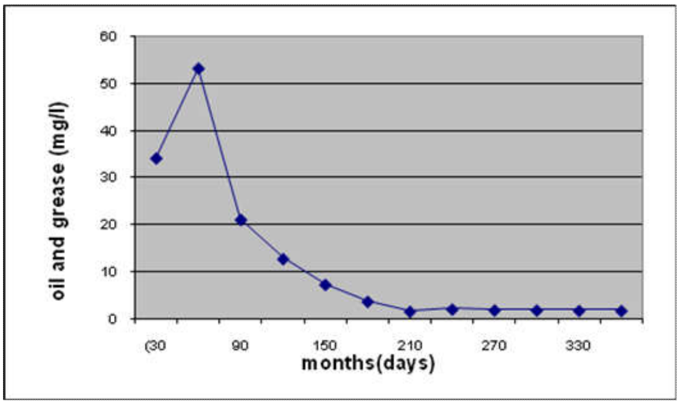


Figure 2. Oil and Grease against time

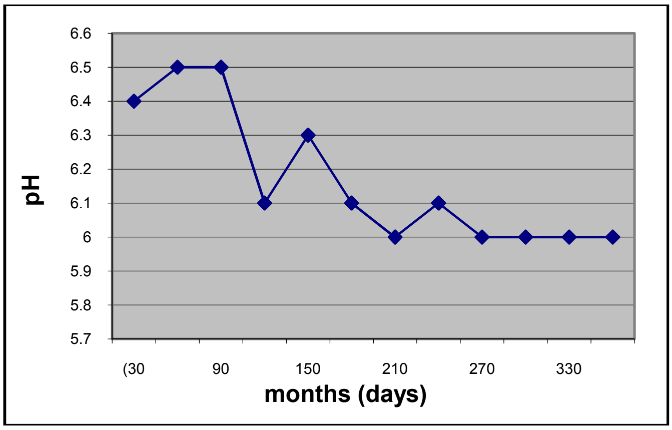


Figure 3. pH against time

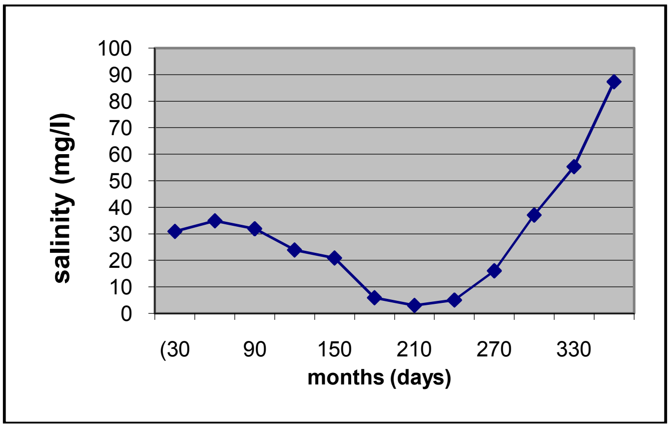


Figure 4. Salinity against time

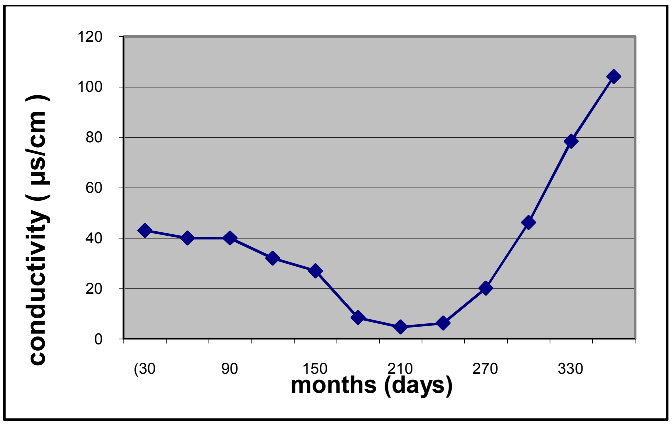


Figure 5. Conductivity against time

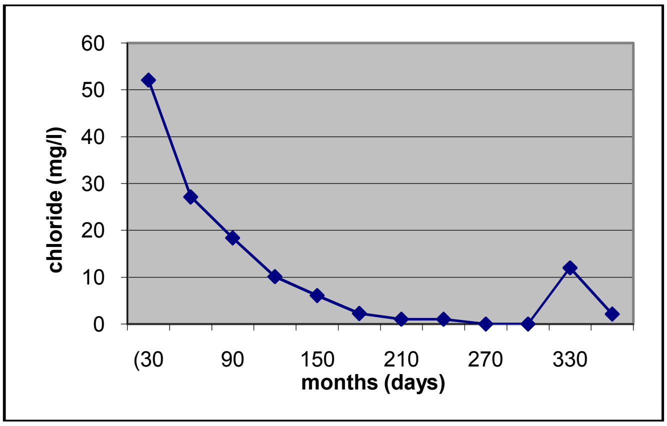


Figure 6. Chloride against time

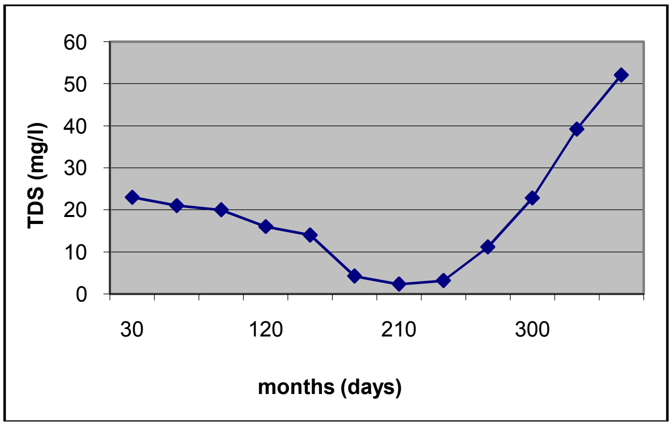


Figure 7. TDS against time

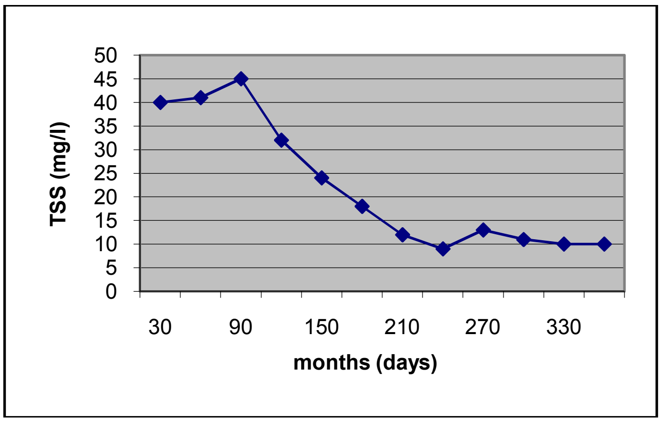


Figure 8. TSS against time

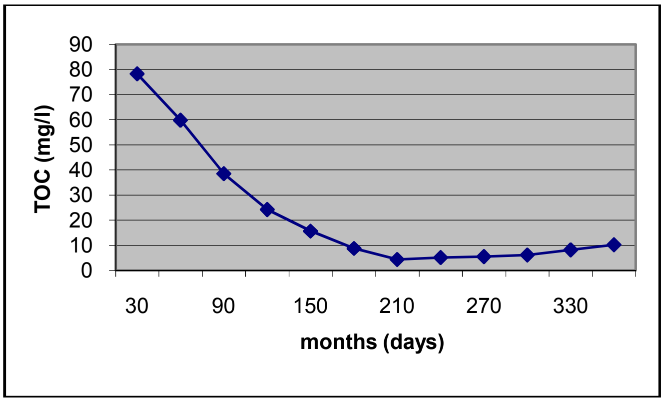


Figure 9. TOC against time

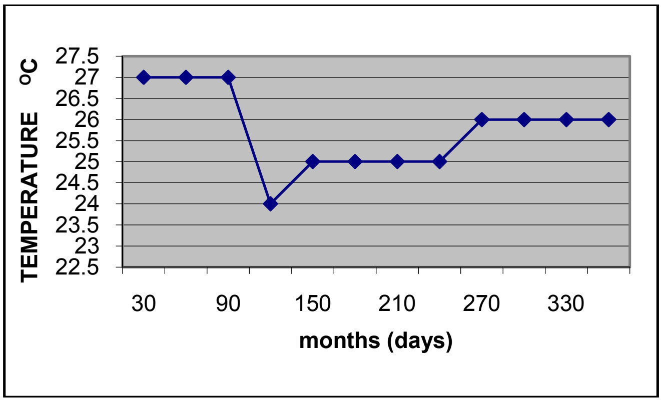


Figure 10. Temperature against time

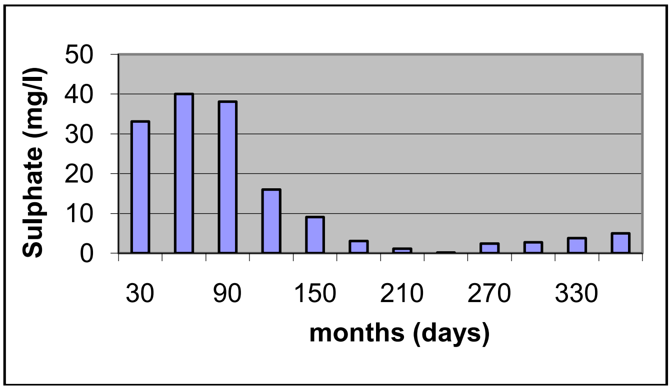


Figure 11. Sulphate against time

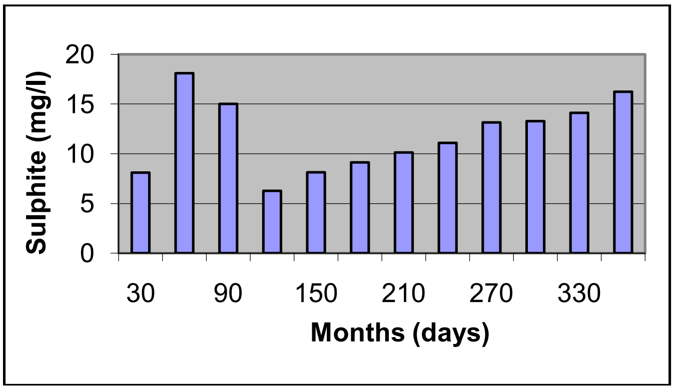


Figure 12. Sulphite against time

Temperature r = (0.2421, 0.5876, 0.5540), Sulphate r = (-0.8990, - 0.2477, - 0.4433), Sulphite r = (0.7755, 0.7810, 0.9086), Biochemical Oxygen Demand r = (-0.5917, - 0.1507, - 0.3843).

Corrosion rate; Temperature r = (0.0687, 0.0274, 0.1397), Sulphate r = (0.9019, - 0.0804, 0.8518), Sulphite r = (-0.7767, - 0.2389, - 0.6676), Biochemical Oxygen Demand r = (0.8586, 0.4287, 0.8786).

From the heavy metals monitored in brackish water Nickel, Vanadium, Chromium and Calcium showed the same trend, they decreased from April to March in this trend respectively (1.15-Nil),(1.04-Nil),(1.22-Nil),(1.77-Nil). Iron increased from April to May (3.23-4.01), decreased from June to November (3.91-0.12), increased from December to January (0.14-0.17), decreased by February (1.13) and increased again by March (1.17). Sodium, Potassium and copper increased from April to May in this trend respectively (2.21-2.26), (3.23-3.27), (2.41-2.48), (1.34-1.38) and decreased from June to March in this trend respectively (2.19-0.62), (3.14-1.21), (2.44-Nil), (1.31-Nil).

In Ndoni River Figure 1 is the graphical representation of weight loss against time of various metal coupons used in this study. They was a significant weight loss between stainless steel versus mild steel, stainless steel versus carbon steel, mild steel versus carbon steel. P=(8.839 E-06, 1.641E-05, 0.041031) respectively. In Ndoni River, the corrosion rate as shown graphically in Figure 14 shows a significance between stainless steel versus mild steel, stainless steel versus carbon steel, mild steel versus carbon steel. P= (1.959E-07, 3.228E-07, 0.016223) respectively. In Ndoni River graphically, Figures 2,3,4,5 is the result of Oil and Grease, pH, Salinity and Conductivity.

Salinity showed an increase between April to May and decreased from November to March. Oil and Grease showed an increase from April to May and decreased from June to October, increased in November and decreased again from December to March. In Ndoni River, the correlation values in weight loss and corrosion rate between ecological quality parameters and metal coupons namely stainless, mild and carbon steel respectively are weight loss; Oil and Grease r=(-0.5504,-0.4446,-0.4224), pH r=(0.2853,0.7797,0.7666), Salinity r=(0.6938.0.8409,0.8459), Conductivity r=(0.6986,0.8309,0.8494)

Corrosion rate; Oil and Grease r= (0.2165, 0.7089, 0.7096), pH r= (0.2853, 0.7797, 0.7666), Salinity r= (0.2583, 0.3889, 0.4553), Conductivity r= (0.2365, 0.3864, 0.4528).

In Ndoni River, the ecological quality parameters represented graphically in Figures 6,7,8,9 are the results of chloride, Total Suspended Solids, Total Organic Carbon respectively. The Chloride decreased from April to January and increased a little from February to March. Total Dissolved Solids decreased from April to October and increased from November to March. Total Suspended Solids increased from April to June, decreased from July to November and increased again from December to March. Total organic Carbon decreased from April to October and increased from November to March. In Ndoni River, the correlation values in weight loss and corrosion rate between ecological quality parameters and metal coupons namely (stainless, mild and carbon steel) respectively are weight loss; chloride r= (-0.5857, -0.4696, -0.4383), Total Dissolved Solids r= (-0.06800, 0.8138, 0.8331), Total Suspended Solids r= (-0.5159, -0.4603, -0.4625), Total Organic Carbon r= (-0.5774, - 0.4250, - 0.4141).

Table 1. Population of various microorganisms isolated in the brackish water habitat

Month	Sulphate reducing bacteria MPN index per 100ml	Iron bacteria 10^3cfu/ml	Sulphur Bacteria 10^3cfu/ml
April	11	130	224
May	17	221	251
June	26	218	253
July	9	149	167
August	5	80	94
September	4	43	68
October	<2	21	43
November	2	47	63
December	7	64	87
January	12	89	118
February	22	115	154
March	33	189	224

Table 1b. Population of microorganisms isolated in the freshwater habitat

Month	Sulphate reducing bacteria MPN index Per 100ml	Iron bacteria 10^3cfu/ml	Sulphur bacteria 10^3cfu/ml
April	7	261	186
May	11	278	180
June	14	270	245
July	7	184	121
August	2	113	87
September	<2	94	38
October	<2	65	19
November	<2	71	22
December	2	92	48
January	6	117	67
February	11	147	92
March	21	231	201

Table 2. Chemical composition of metal coupons

Chemical Element Composition	Carbon Steel	Mild steel	Stainless steel
Carbon	0.008-0.20	0.15-0.25	0.03maximum
Manganese	0.45-0.65	0.45-0.65	2.0maximum
Phosphorus	-	-	0.04maximum
Sulphur	-	-	0.03maximum
Chromium	-	-	16-18
Nickel	-	-	10-14
Silicon	0.25-0.60	0.25-0.60	1.0maximum
Molybdenum	-	-	2-3
Copper	0.60	0.60	-

Corrosion rate; Chloride r= (-0.1032, 0.7571, 0.6621) Total Dissolved Solids r= (0.4070, 0.8610, 0.8193), Total Organic Carbon r= (0.0654, 0.8217, 0.7616).

In Ndoni River, the results of temperature, Sulphate, Sulphite and Biochemical Oxygen Demand are represented graphically in Figures 10, 11, 12, 13 respectively. The temperature decreased a little in the rainy season from April to October but remained constant from December to March. Sulphate decreased from May to November and increased a little from December to March. The sulphite level increase from April to May and decreased from five to increase again from August to March. The Biochemical Oxygen Demand decreased from April to October and increased slightly from November to March. In Ndoni River, the correlation values in weight loss and corrosion rate between ecological quality parameters and metal coupons namely (stainless, mild and carbon steel) are weight loss; temperature r= (-0.04464, 0.0303, 0.1193), Sulphate r= (-0.4228, -0.3398, -0.3206), Sulphite r= (0.4485, 0.4560, 0.5262), Biochemical Oxygen Demand r=(-0.5568, -0.3945, -0.3834).

Corrosion rate; Temperature r= (0.1752, 0.5984, 0.7008), Sulphate r= (0.4348, 0.9004, 0.3784),
Sulphite r= (0.4554, 0.1804, 0.3784),
Biochemical Oxygen Demand r= (0.0255, 0.8166, 0.7473).

In Ndoni River, heavy metals monitored in this study showed that Ni, V, Cr was not detected throughout the study. Iron increased from April to May and decreased from June to October before increasing slightly from November to March respectively (8.13-9.06), (7.26-1.23) (1.32-1.55). Copper increased from April to May (0.61-0.81) and decreased from June to August (0.82-0.06) after which it was not detected again. Sodium and Zinc increased from April to May and decreased from June to September in this manner respectively (1.13-1.19, 2.01-2.15), (1.16-0.09, 2.07-0.30) after which there were not detected again. Potassium decreased throughout from April to October (2.26-0.03) after which it was not detected again. Calcium decreased from April to May (0.84-0.83) and increased in June (9.83) and decreased from July to September (0.71-0.22) after which it was not detected again.

DISCUSSION

The organisms isolated from this study include sulphur reducing bacteria, Iron bacteria and sulphur bacteria as shown in Table 1. Microorganisms including the ones isolated in this study play a role in corrosion by inducing oxygen gradient which accelerates corrosion by acting as a depolarizer to from ferrous ions and oxidizing ferrous ions (Fe^{++}) to ferric ions (Fe^{+++}). The latter reactions takes place in pH values higher than 4 as shown in the pH values in this study. Also organisms depolarize surfaces; specie of sulphur reducing bacteria *Desulfovibrio desulfuricans* which was isolated in this study directly removes corrosion products such as hydrogen formed at the cathode, this enhances biocorrosion because it causes depolarization thereby sustaining corrosion current (Battersby *et al,* 1985). Microorganisms also destroy protective coatings; *Desulfovibrio desulfuricans* produces hydrogen sulphide which causes hydrogen blistering and embrittlement in metals and structural fittings (Raloff, 1985). Tetraoxosulphate VI acid from *Thiobacillus ferroxidans* also isolated from this study causes dissolution of metals from ores and alloys and also maintains pH levels favourable for Iron bacteria to corrode metals. Similar observations were made by Beech, (2004), Battersby *et al.*, (1985) in the study of role of microorganisms in corrosion.

The alloying elements of stainless steel which is chromium and nickel as shown in Table 2 protected the metal coupon from adverse corrosion as shown in this study. This could be attributed to the fact that these alloying elements occur in the lower part of the electrochemical series and are less reactive in nature. The mild steel and carbon steel are made of manganese phosphorous, copper, carbon, silicon which is more reactive in nature hence giving the metal coupons they are made of less protection from corrosion. Similar observations have been made by Jaganathan *et al* (2011). They showed that 13% chromium is required for stable passivity if a Fe-Cr alloy in acidic and neutral solution not containing inhibitors. In New Calabar River, the analyses of corrosion rate and weight loss of stainless steel versus mild steel, stainless steel versus carbon steel, and carbon steel versus mild steel respectively gave a significant difference because their P values were not greater than 5%. Stainless steel versus mild steel and stainless steel versus carbon steel had a higher significance than carbon steel versus mild steel. Their percentage P values are given as follows respectively; weight loss (0%, 0%, 1%), corrosion rate (0%, 0%, 5%). In New Calabar River, the ecological quality parameters monitored showed that Temperature and Sulphite had positive correlation with weight loss in the three metal coupons used for this study namely (stainless, mild and carbon steel). Oil and Grease, Chloride, Total Suspended Solids, Total Organic Carbon, Sulphate and Biochemical Oxygen Demand, had negative correlation with weight loss in the three metal coupons.

In Salinity, Conductivity, Total Dissolved Solids, pH only their stainless steel had negative correlation but their mild and carbon steel all had positive correlation. In New Calabar River, corrosion rate, Oil and Grease, Salinity, Conductivity, Chloride, Total Dissolved Solids, Total Suspended Solids, Total Organic Carbon, Temperature and Biochemical Oxygen Demand all had positive correlation in the three metal coupons used for this study. Only Sulphite had negative correlation in the three metal coupons while Sulphate and pH had negative correlation in their stainless steel and positive correlation in their mild steel and carbon steel respectively. Positive correlation means that ecological quality parameters are directly proportional to weight loss and corrosion rate while negative correlation means that ecological quality parameters are inversely proportional to weight loss and corrosion rate. In New Calabar River, higher values of Total Dissolved Solids, Total Suspended Solids, Total Organic Carbon, Conductivity, Oil and Grease, Chloride, Sulphate and Biochemical Oxygen Demand were recorded in the rainy season while higher values of Temperature, Sulphite, Salinity and pH were recorded in the dry season. This could be attributed to increased nutrient load resulting from inputs from industrial discharges, erosion and surface run-offs, at different times in this study causing the different ecological quality parameters to vary at different seasons. This is in conformity with the study of Gupta *et al* (2008). They showed that ecological quality parameters, nutrients and heavy metals are present in significant amount in all domestic wastes. Krishnan *et al* (2007) in their study showed that pH increase could be attributed to organic pollution, alkaline chemicals, soap and detergents produced due to commercial and residential activities. In Ndoni River statistically the corrosion rate and weight loss of stainless steel versus mild steel, stainless steel versus carbon steel, carbon steel versus mild steel respectively gave a significant difference because their P values were less than 5% even though the level of significance were higher in stainless steel versus mild steel, stainless steel versus carbon steel than in carbon steel versus mild steel. The P value percentages are given as follows respectively; Weight loss (0%, 0%, 4%), Corrosion rate (0%, 0%, 2%).

In Ndoni River, the ecological quality parameters shown in Figures 2 to 13 had positive correlation with corrosion rate in the three metal coupons used for this study, except chloride with negative correlation in stainless steel only. In weight loss, pH, Salinity, Conductivity, Total Dissolved Solids, Sulphite all had positive correlation with the metal coupons. Oil and Grease, Chloride, Total Suspended Solids, Total Organic Carbon, Sulphate, Biochemical Oxygen Demand all had negative correlation with the metal coupons. Temperature had negative correlation with stainless steel but mild steel and carbon steel had positive correlation with temperature. Positive correlation means that ecological quality parameters are directly proportional to weight loss and corrosion rate while negative correlation means that ecological quality parameters are inversely proportional to weight loss and corrosion rate. In Ndoni River the distribution of the ecological quality parameters shows that Total Dissolved Solids, Conductivity, Salinity, Sulphite had higher values in the dry season than the rainy season. Total Suspended Solids, Total Organic Carbon, Oil and Grease, Chloride, Sulphate, Biochemical Oxygen Demand had higher values in rainy season than dry season. All these could be attributed to commercial and domestic effluent discharges, run-offs and erosion in the freshwater habitat at different times thereby increasing or decreasing the ecological quality parameters at different seasonal variations. This agrees with the study of Gupta *et al* (2008). They showed that ecological quality parameters, nutrients and heavy metals are present in significant amount in all domestic wastes. Also Krishnan *et al.,* (2007) stated that pH increase could be attributed to organic pollution, alkaline chemicals, soap and detergents produced due to commercial and residential activities.

Conclusion

The study showed that carbon steel had a higher corrosion rate than mild steel which also had a higher corrosion rate than stainless steel in the New Calabar River habitat than Ndoni River habitat. They were higher corrosion rates in the dry season than the rainy season. The results show that the use of stainless steel for pipelines in brackish water and fresh water environments should be encouraged in Nigeria petroleum industry or at least the composition of stainless steel should be incorporated in the current composition of steel used in the petroleum industry. This will mitigate against microbial mediated corrosion in brackish and fresh water environments. The frequency of integrity checks should be increased especially during the dry season since rates of microbial corrosion are higher during the dry season than rainy season. These results also indicate that emphasis should not just be on physicochemical corrosion. Microbial induced corrosion is a potential cause of pipeline rupture/failure in the petroleum industry in Nigeria.

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