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# Microbial corrosion of steel coupons in a freshwater habitat in the Niger Delta

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Microbial corrosion of stainless, mild and carbon steel coupons in a semi static freshwater habitat was carried out monthly for a period of one year. Corrosion rate was determined by weight loss. Carbon steel had corrosion rate of 44 g/year, mild steel 27 g/year, stainless steel 0.64 g/year. Ecological quality parameters of the river water for rainy season decreased from April to October, respectively in the following trend; total dissolved solids (23 to 2.31) mg/l, total suspended solids (40 to 12) mg/l, total organic carbon (78.24 to 4.33) mg/l, conductivity (43 to 4.73) µs/cm, salinity (31 to 3.10) mg/l, oil and grease (34.23 to 1.67) mg/l, Chloride (52.11 to 1.05) mg/l, Sulphate (33.14 to 1.15) mg/l, Sulphite (8.11 to 10.14) mg/l, pH(6.4 to 6.0), temperature (27 to 25°C), biochemical oxygen demand (64.13 to 1.34) mg/l. That of dry season (November to March) respectively showed this trend. Total dissolved solids (3.14 to 52.11) mg/l, total suspended solids (9 to 40) mg/l, total organic carbon (5.10 to 10.24) mg/l, conductivity (6.29 to 104) µs/cm, salinity (5.11 to 87.33) mg/l, oil and grease (2.14 to 1.82) mg/l, Chloride (1.02 to 2.11) mg/l, Sulphate (0.17 to 4.95) mg/l, Sulphite (11.10 to 16.23) mg/l, pH (6.1 to 6.0), Temperature (25 to 26°C), biochemical oxygen demand (1.53 to 7.31) mg/l. Weight loss of stainless, mild and carbon steel for rainy season (April to October) respectively, and showed the following trend (0 to 0.030), (0.695 to 1.568), and (1.000 to 2.316) g, while the dry season (November to March) respectively showed the following trend (0.044 to 0.111), (1.586 to 5.771) and (2.325 to 9.131) g. Corrosion rate of stainless, mild and carbon steel for rainy season (April to October) respectively showed the following trend (0 to 0.004), (0.695 to 0.244) and (1.000 to 0.331) g/month while the dry season (November to March) showed the following trend respectively (0.006 to 0.009), (0.198 to 0.481), and (0.291 to 0.761) g/month. The use of stainless steel, if not already in use should be encouraged as a material for pipelines, flowlines and bulklines in the Nigerian Petroleum industry. Integrity checks on these surface facilities should be increased in the dry season.

Key words: Freshwater, ecological quality parameters, corrosion rate, weight loss.

# INTRODUCTION

Biocorrosion of steel materials is gaining tremendous importance in the petroleum sector of Nigeria's economy. It has been associated with the rupture/failure of pipelines used in transporting petroleum and its products from oil and gas fields, flow stations tank farms, depots and terminals in Nigeria. Unfortunately most of this corrosion has been reported as just corrosion or physicochemically induced corrosion. This is because of the limited knowledge in the Nigerian Petroleum industry that corrosion is mainly physicochemically induced. There is however a dearth of information on biocorrosion in the Petroleum Industry in Nigeria. Biocorrosion is microbially mediated. Bacteria such as sulphate reducing bacteria, iron oxidizing bacteria and sulphur oxidizing bacteria have been implicated in anaerobic and aerobic biocorrosion respectively. Internationally, biocorrosion causes billions of dollars in damage every year (Bitton and John, 2007). According to Gerald and Stams (2008), microbial corrosion of steel results in huge financial losses that amount to more than 100 million US dollar per annum in the USA alone.

According to ICEM (2011), it was told that Pakistan has

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been incurring an annual loss of RS 250 to 300 billion (about 3 billion US dollars) on account of infrastructure, industries and house hold corrosion, which does not include the damage to environment and loss of production due to unscheduled breakdown. Corrosion effects on different equipment or materials in different aspects of food processing and packaging are common (Ashassi-Sorkhabi, 2009). Smith and Hashemi (2006) reported that the materials used for most equipment in the manufacturing sector are mild steel because of its strength, ductility and weld-ability but it is prone to corrosion. In the freshwater habitats, microorganisms such as sulphate reducing bacteria, Iron bacteria and sulphur bacteria have been implicated in corrosion (Pitonzo et al., 2007; Lee and Newman, 2005).

In the freshwater habitat, organic pollutants such as biochemical oxygen demand (BOD), oil and grease, inorganic anionic pollutants including chloride, salinity, sulphate, sulphite and associated factors like temperature, pH, conductivity, total organic carbon, total dissolved solids and total suspended solids all affect microbial corrosion of steel products. Due to its economic importance, microbial corrosion of metals in freshwater has been studied for a long time (Dinh et al., 2004).

Badmos and Ajimotokan, (2009) demonstrated that low pH encouraged corrosion but higher pH reduced corrosion rates. The work of Birnin-Yauri and Garba (2006), demonstrated that low concentration of chloride ions caused corrosion of steel used for reinforcement. According to Jaganathan et al. 13% Cr is required for stable passivity of a Fe-Cr alloy in acidic and neutral solutions not containing inhibitors. Hamilton (2003) has demonstrated microbial influenced corrosion as a model system to study metal microbe interaction.

In this study, the river water from Ndoni River which is a fresh water habitat located in the Niger Delta was used for the test. The study was aimed at determining the corrosion rate of the different test metal types (stainless steel, mild steel and carbon steel) buried in the freshwater environment. In addition the study was to determine appropriate steel type that will be resistant to microbial corrosion in freshwater habitats which will be recommended for use as pipeline materials in the Petroleum Industry in Nigeria. Finally, the study was aimed at determining the effect of seasonal variations on corrosion rates. This was geared towards determining which season should witness more integrity checks as a mitigative action for pipeline failure/rupture.

## MATERIALS AND METHODS

## Area of study

The Ndoni River (Figure 15) is situated in the coastal environment of the Niger Delta in Rivers State, Nigeria. It is a fresh water site and 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 harmattan. The edges of the river are covered with typical rainforest vegetation and the soil is loamy in nature.

## Industrial activities along the river

The main industrial activity in this area is dredging and sand wining (coded AML). Sand wining is a process where sand and water mixtures flow via dredger pipes as dredging goes on and the sand is preserved for other uses. The repair of marine boats also occurs 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<sup>th</sup> of every month between 10.00 and 12.00 a.m from April 2010 to March 2011. Water samples were collected with 100 ml sterile bottle. Samples for biochemical oxygen demand (BOD) determination were collected with 250 ml (BOD) bottles. For other chemical analysis, samples were collected with 500 ml glass bottles that had been sterilized at 121°C and 15 psi for 15 min. All samples were analyzed immediately on reaching the laboratory.

#### Chemical reagents

All chemical reagents employed in this study were products of Aldrich chemical co, Milwauke, 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, mild steel and carbon steel were 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 (Shangai analytical instrument Co). Oil and grease content was estimated using the method of Odu et al. (1988). 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 420 nm 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 lodometric 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, and total suspended solids by gravimetric method (APHA, 2000).

## 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 (10, 1 and 0.1 ml) 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. Winograsky medium composition was used to enumerate iron bacterial, distilled water 1000 ml, NH<sub>4</sub>NO<sub>3</sub> 0.5 g/l, NaNO<sub>3</sub> 0.5 g/l, K<sub>2</sub>HPO<sub>4</sub> 0.5 g/l, MgSO<sub>4</sub>.7H<sub>2</sub>O 0.5 g/l, CaCl<sub>2</sub>.6H<sub>2</sub>O 0.2 g/l, Ferric ammonium citrate 10 g/l, Agar 15 g/l.

The sterile medium was poured in sterile Petri dish in duplicate and inoculated with dilution of scrapings from the metal coupons using spread plate method and incubated for 48 h at room temperature. Different selective media was used to enumerate the different sulphur bacteria. Rodina medium for *Thiosulphate* bacteria, distilled water 1000 ml, K<sub>2</sub>HPO<sub>4</sub> 3.0 g/l, MgCl<sub>2</sub>.6H<sub>2</sub>O 0.5 g/l, CaCl<sub>2</sub>.6H<sub>2</sub>O 0.2 g/l, pH 9.0, Agar 20 g/l, Na<sub>2</sub>SO<sub>4</sub> 10 g. Larsen's medium for colourless sulphur bacteria, distilled water 1000 ml, K<sub>2</sub>HPO<sub>4</sub> 0.2 g/l, NH<sub>4</sub>Cl 0.1 g/l, MgCl<sub>2</sub>.6H<sub>2</sub>O 0.1 g/l, KH<sub>2</sub>PO<sub>4</sub> 3.0 g/l, Na<sub>2</sub>S 0.06 g/l, Agar 20 g/l. Vanniel medium for purple sulphur bacteria, distilled water 1000 ml, NH<sub>4</sub>Cl 1.0 g/l, K<sub>2</sub>HPO<sub>4</sub> 0.5 g/l, MgCl<sub>2</sub> 0.2 g/l, Agar 20 g/l, NaHCO<sub>3</sub> 0.5 g/l. All the sterile media were poured into sterile Petri dishes in triplicate and inoculated with dilutions from metal coupon scrapings using spread plate method and incubated for 48 h at room temperature.

# Statistical analyses

Correlation analyses and student t-test from Microsoft 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 (Finney, 1978).

# RESULTS

Results in Table 1 shows the bacterial count of microorganisms isolated in the freshwater habitat from April 2010 to March 2011. The sulphate reducing bacteria increased from April to June (7 to 14) MPN index per 100 ml before decreasing from July to November (7 to <2) MPN index per 100 ml and increased again from December to March (2 to 21) MPN index per 100 ml. The iron bacteria increased from April to May (261 to 278) 10<sup>3</sup> cfu/ml and decreased from June to October (270 to 65) 10<sup>3</sup> cfu/ml before increasing again from November to March (71 to 321) 10<sup>3</sup> cfu/ml. Sulphur bacteria decreased from June to October (121 to 19) 10<sup>3</sup> cfu/ml and increased again from July to October (121 to 19) 10<sup>3</sup> cfu/ml and increased again from November to March (22 to 201) 10<sup>3</sup> cfu/ml.

Table 2 shows the chemical composition of the various metal coupons namely (stainless, mild and carbon steel). Figure 1 is the graphical representation of weight loss against time of various metal coupons used in this study. There 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. 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. Graphically, Figures 2, 3, 4, and 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. 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).

The ecological quality parameters represented graphically in Figures 6, 7, 8, and 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 March.

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). 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). The results of temperature, sulphate, sulphite and biochemical oxygen demand are represented graphically in Figures 10, 11, 12, and 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 increased 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. The correlation values in weight loss and

Month	Sulphate reducing bacteria MPN index per 100 ml	Iron bacteria 10 <sup>3</sup> cfu/ml	Sulphur bacteria 10 <sup>3</sup> cfu/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 1. Population of microorganisms isolated in the freshwater habitat.

 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	0.03 maximum
Manganese	0.45-0.65	0.45-0.65	2.0 maximum
Phosphorus	-	-	0.04 maximum
Sulphur	-	-	0.03 maximum
Chromium	-	-	16-18
Nickel	-	-	10-14
Silicon	0.25-0.60	0.25-0.60	1.0 maximum
Molybdenium	-	-	2-3
Copper	0.60	0.60	-

Lynch (1989).

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).

# DISCUSSION

Table 1 shows that organisms isolated were sulphur reducing bacteria, iron bacteria and sulphur bacteria. These organisms play a role in corrosion by inducing oxygen gradient which accelerates corrosion in two ways by acting as a depolarizer to form ferrous ions and oxidizing ferrous ions ( $Fe^{2+}$ ) to ferric ions ( $Fe^{3+}$ ). The latter reactions takes place in pH values higher than 4. A

species of sulphur reducing bacteria, *Desulfovibriode sulfuricans* isolated in this study directly removes corrosion product such as hydrogen formed at the cathode, this enhances biocorrosion because it causes depolarization thereby sustaining corrosion current (Battersby et al., 1985). *D. sulfuricans* produces hydrogen sulphide which causes hydrogen blistering and embrittlement in metals and structural fittings (Raloff, 1985).  $H_2SO_4$  from *Thiobacillus ferroxidans* causes dissolution of metals from ores and alloys and also maintain pH levels favourable for Iron bacteria to corrode metals. Similar observations were made by Beech (2004) and Battersby et al. (1985).

The composition of metal coupons in Table 2 shows that stainless steel has alloying elements such as Chromium (16 to 18%), Nickel (10 to 14%) gave stainless steel lots of protection against corrosion because these elements are less reactive and occur in the lower part of the electrochemical series unlike the mild steel and carbon steel which does not have the alloying elements. The composition of mild steel and carbon steel namely

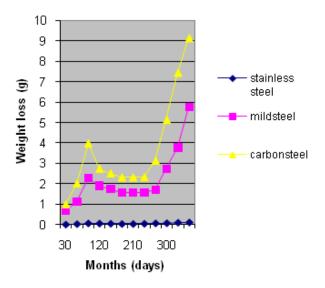


Figure 1. Weight loss against time.

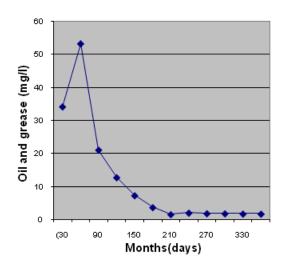


Figure 2. Oil and grease against time.

Manganese, Phosphorous, Copper, Carbon, Silicon are more reactive and hence easily corroded with a lot of weight loss. Similar observation has been made by Jaganathan et al. (2011). They showed that classically 13% Chromium is required for stable passivity of a Fe-Cr alloy in acidic and neutral solutions not containing inhibitors. 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%).

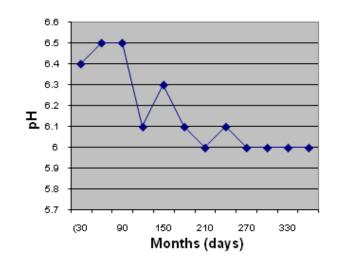


Figure 3. pH against time.

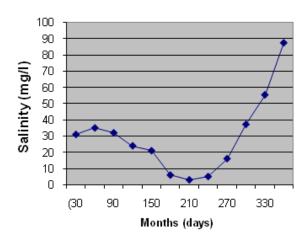


Figure 4. Salinity against time.

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.

The distribution of the ecological quality parameters shows that total dissolved solids, conductivity, salinity,

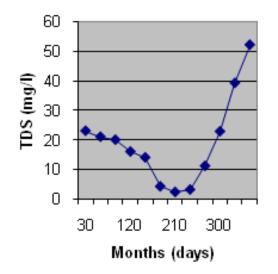


Figure 5. Conductivity against time.

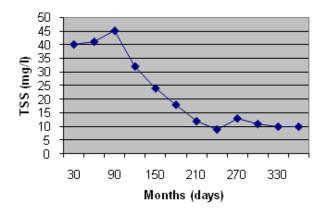


Figure 6. Chloride against time.

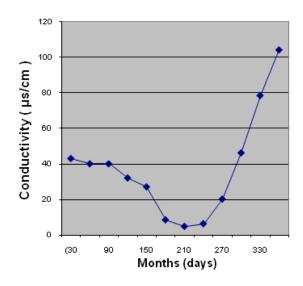


Figure 7. TDS against time.

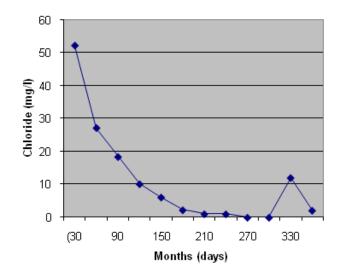


Figure 8. TSS against time.

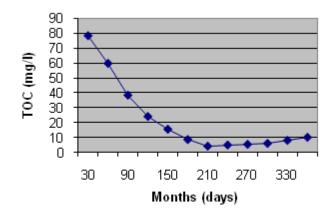


Figure 9. TOC against time.

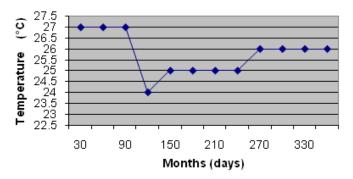


Figure 10. Temperature against time.

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

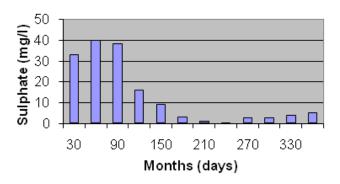


Figure 11. Sulphate against time.

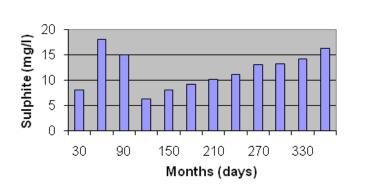


Figure 12. Sulphite against time.

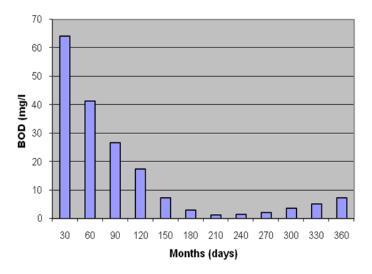


Figure 13. Biochemical oxygen demand against time.

dry season. All these could be attributed to commercial and domestic effluent discharges, run-offs and erosion in the freshwater habitats at different times thereby increasing or decreasing the ecological quality parameters at different seasonal variations. This agrees with the study of Grupa et al. (2008). They showed that

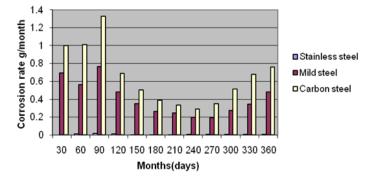


Figure 14. Corrosion rate against time.

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.

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 to 9.06), (7.26 to 1.23) (1.32 to 1.55). Copper increased from April to May (0.61 to 0.81) and decreased from June to August (0.82 to 0.06) after which it was not detected again. Sodium and zinc increased from April to May and decreased from June to September in the manner respectively (1.13 to 1.19, 2.01 to 2.15), (1.16 to 0.09, 2.07 to 0.30). After which they were not detected again. Potassium decreased throughout from April to October (2.26 to 0.03) after which it was not detected again. Calcium decreased from April to May (0.84 to 0.83) and increased in June to (9.83) and decreased from July to September (0.71 to 0.22) after which it was not detected again.

# 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 freshwater habitat. The corrosion rates were higher in the dry season than in the rainy season. The results show that the use of stainless steel for pipelines in freshwater environments should be promoted in the Nigerian 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 serve as a mitigative action against microbial mediated corrosion in brackish water environments. The frequency of integrity checks should be increased especially during the dry season, since rates of microbial induced corrosion are higher during the dry season than

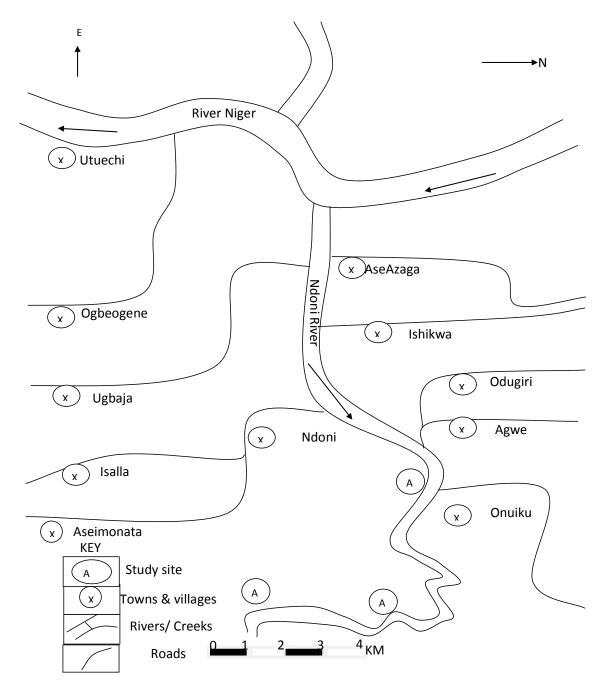


Figure 15. A map showing the sampling site the Ndoni River.

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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