

# ATMOSPHERIC CORROSION OF MILD STEEL IN THE NIGER DELTA REGION OF NIGERIA. PART 1: CHARACTERIZATION OF THE CALABAR, CROSS RIVER STATE ENVIRONMENT

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## ABSTRACT

The atmospheric corrosion of Calabar, Cross River State environment has been investigated for 12 months using weight loss technique. The extent of pollution of the environment was also determined via measurements of the precipitation and air quality parameters. Apart from the suspended particulate matter (SPM) ( $113\text{-}630 \mu\text{g}/\text{m}^3$ ) and  $\text{NO}_2$  ( $> 0.06$  ppm) values, other measured atmospheric parameters ( $\text{CO} < 9.2$  ppm,  $\text{NH}_3 < 4.3$  ppm and  $\text{SO}_2 < 0.380$  ppm) and precipitation parameters (pH  $> 5.0$ , conductivity  $< 60 \mu\text{Scm}^{-1}$ , TDS  $< 41.48$  mg/l, TSS  $< 0.05$  mg/l,  $\text{NO}_3^- < 3.00$  mg/l,  $\text{SO}_4^{2-} < 1.00$  mg/l and  $\text{NH}_4^+ < 1.00$  mg/l) indicate that the environment has received little or no detrimental influence by human activities. The average corrosion rates for all the stations studied were below  $35 \mu\text{m}/\text{yr}$ , and are due principally to natural phenomenon (high rainfall, humidity and temperature).

**KEYWORDS:** Mild steel, Atmospheric corrosion, Calabar, Nigeria

## INTRODUCTION

Atmospheric corrosion refers to the corrosive action that occurs on the surface of a metal in contact with an atmospheric environment. It is a complex process involving a large number of interacting and constantly varying factors, such as meteorological factors (including temperature, wind speed, rainfall and relative humidity), air pollutants, metallurgical factors (including metal type, microstructure and morphology), distance from the sea etc. (Jones, 1996; Feliu *et al.*, 1999; Dunn *et al.*, 2000; Townsend, 2001; Chen *et al.*, 2004; Zhang *et al.*, 2004). The combined effect of these factors may results in significant variations in corrosion rates.

The cost of atmospheric corrosion include damage to structures such as buildings and bridges, transport vehicles such as automobiles,

aircrafts and ships, historical monuments and electronic systems such as in the power grid and communications hardware (Matthes *et al.*, 2004). Household equipments and other metallic hardwares do not escape the scourge of this wide spread problem. It is estimated that about 20 % of the failures of aircraft electronics are thought to be due to atmospheric corrosion related causes (Chen *et al.*, 2004).

Atmospheric corrosion has become a major subject of research for decades now and there is substantial knowledge today about atmospheric corrosion and the processes involved. However, most available field exposure data have been obtained in regions with temperate climate (Tidblad *et al.*, 2005). The relative performance of metals changes with locations (Abdul-Wahab *et al.*, 2004; Chen *et al.*, 2004), therefore, the available quantitative relationships between the

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environment and corrosion cannot necessarily be directly transferred to Nigeria.

In the Niger Delta region of Nigeria emissions resulting from the activities of the oil and gas industries and high rise in road unworthy vehicles as well as other environmentally unsafe activities are increasing and may increase dramatically in the near future if the conventional development path is followed. This is bound to increase the corrosivity of our atmospheric environment and consequently aggravate its detrimental effects on structures.

This study is therefore aimed at assessing the extent of atmospheric pollution using precipitation quality and air quality parameters and the impart of these parameters on the corrosion of mild steel exposed to the atmosphere in Calabar Municipality, South – Eastern Nigeria, being a part of the Niger Delta region of Nigeria.

### 1.1 Description of study area

#### Niger Delta

The Niger Delta of Nigeria extends from the Benin River in the west of the Bonny River in the East of the country inland (Figure 1). It is situated a few kilometres from the village Aboh at a point where the Niger forks into the Nun and Forcados Rivers. It is a low-lying region riddled with an intricate system of nature water channels through which the Niger finds its way into the sea (Uwah, 2002). The Niger Delta occupies an area of 75,000 km<sup>2</sup> which is approximately 10 % of Nigeria's total land space (Ekweozor, 1997). The area is very rich in oil and gas reserves and thus attracts extensive human activities including oil and gas exploration and exploitation.

#### Calabar

Calabar lies roughly between latitude 4° and 7° North of the Equator and between longitude 8° and 9°30' East of Greenwich. The area is bordered in the East west of South by Cross

River. It expands from the coast to about 150 km inland and much of the area is under the influence of the sea.

The climate of Calabar Municipality is characterized by seasonal north-south movement of a zone of discontinuity which separates the continental air masses; that is, the wet and dry continental air masses. Wet continental air mass brings about wet season which lasts from April to October while the dry continental air mass brings about dry season which extends from December to February. November and March are transitional months (Offiong and Edet, 1996).

Calabar is an urban site and is subjected to normal precipitation patterns typical of urban contaminants. Two major rivers cross the municipality: the Great Kwa and the Cross Rivers (Figure 1). The area is sandwiched between Akpabuyo and Odukpani Local Government Areas. Although Calabar is in the Niger Delta region of Nigeria, there is no flow station and no gas flaring in the area. The only presence of Oil Company in the city is the NNPC tank farm at Ekorinim. However, increase in the number of road unworthy vehicles and the associated traffic jams and other environmentally unsafe activities in the city has led to an increased emission of gaseous pollutants in the city (Etiuma *et al.*, 2006).

### Experimental

#### Weight loss determination

The mild sheet used in the present work was obtained from Ejison Resources (Nigeria) Ltd., Onitsha, Nigeria with the composition presented in Table 1. Mild steel specimens of size 15 x 15 cm and thickness 0.8 mm were used. Before weight loss measurements, all test mild steel samples were polished using emery paper up to 800 grits. They were degreased in absolute ethanol, dried in acetone and weighed. All chemicals used were Analar grade.

**Table 1:** Chemical composition of the mild steel used

Element	C	Si	Mn	S	P	Ni	Cr	Mo	Cu
Composition (%)	0.19	0.26	0.64	0.05	0.06	0.09	0.08	0.02	0.27

Six coupons were exposed at four different locations in Calabar City for a total of twelve months. The locations were University of Calabar (UNICAL), West African Peoples' Institute (WAPI), Egerton/Johnstone (EGERTON) and

Uwanshe by Mount Zion (UWANSE) as indicated in the map (Figure 1). The coupons were exposed facing south at an angle of 30° to the ground. All coupons were uniformly prepared and exposed on the same day (June, 2005).

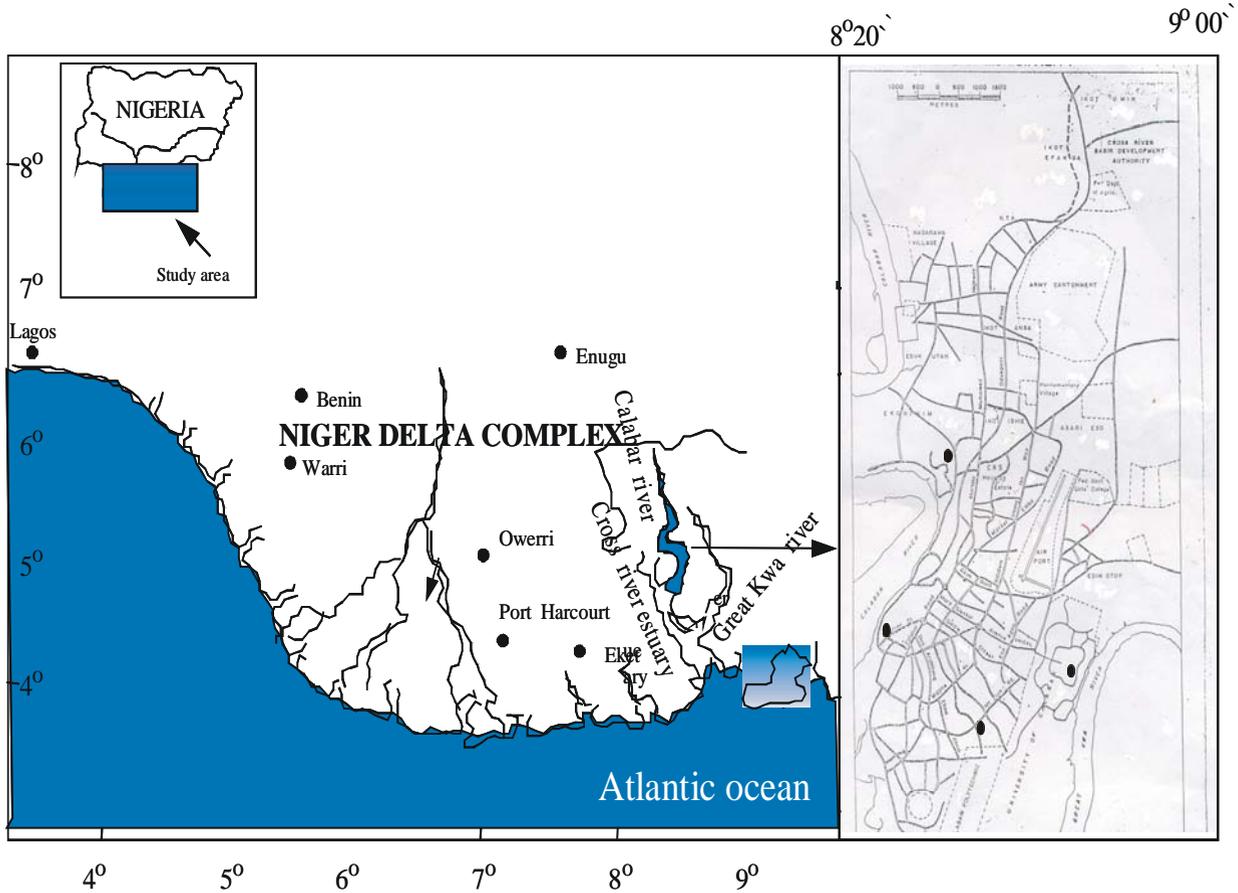


Figure 1: Map of the Niger Delta region of Nigeria showing the study area

After six months of exposure, the coupons were removed and cleaned. The corrosion products were removed by scrubbing the metal surface with a soft brush using a boiling solution of 20% NaOH/200 g/l zinc powder. After removal of the rust, the coupons were degreased and rinsed with ethanol, dried (with acetone), weighed to determine their weight losses and replaced in the test rack for another six month exposure.

From the weight losses, the corrosion rates (CR) were calculated using equation 1 (Jones, 1996):

$$CR = \frac{87600(WL)}{\rho AT} \quad 1$$

where (WL) is weight loss in g,  $\rho$  is the density of iron in g/cm<sup>2</sup>, A is surface area of the coupon in cm<sup>2</sup> and T is time of exposure in hours.

**Precipitation analysis**

Rain water samples were collected monthly from June 2005 to December, 2006. Samples were collected as direct rain water in plastic bottles, mounted on the platforms in an open space free from any interfering matter that could contaminate the rainwater. A week prior to the day of collection of samples, the plastic bottles were carefully rinsed with de-ionized water.

Samples were analysed using the methods described by World Meteorological Organisation (WMO) operations manual for sampling and analysis techniques for chemical constituents in air and precipitation. The pH was determined with the aid of Mettler Toledo MP 220 pH Meter and the conductivity with HANNA H18733 conductivity meter. The nutrients; nitrate ( $\text{NO}_3^-$ ), sulphate ( $\text{SO}_4^{2-}$ ), and ammonium ( $\text{NH}_4^+$ ) ions concentrations were determined using HACH 3000 DREL UV spectrophotometer.

### Atmospheric quality assessment

For the atmospheric assessments, suspended particulate matter (SPM), carbon monoxide (CO), sulphur dioxide ( $\text{SO}_2$ ), ammonia ( $\text{NH}_3$ ) and nitrogen dioxide ( $\text{NO}_2$ ) gasses were determined. High volume air sampler (General Metal Works and Staplex samplers) with a constant flow rate ranging from 1.1 to 1.7  $\text{m}^3/\text{min}$ . was used for measuring the suspended particulate matter (SPM) within 6 hour duration. Ambient air was drawn through a Gelman quartz micro fibre filters (20 x 25 cm) of known weight which had been annealed for 8 hours at 500°C to remove potential background contaminants. After the 6 hours collection period, the sample filter was collected. Re-weighing of the filter after sampling under controlled condition gave a direct measurement of particulate matter. The concentration of the particulate was determined by dividing the mass of the SPM by the volume of air sampled. The CROWCON GASMAN portable CO,  $\text{SO}_2$ ,  $\text{NH}_3$  and  $\text{NO}_2$  monitors were used for measuring the values of CO,  $\text{SO}_2$ ,  $\text{NH}_3$  and  $\text{NO}_2$  gasses, respectively, in the atmosphere during the period of study.

### Meteorological data

Meteorological data were collected from the Metrological Unit of the Margaret Ekpo International Airport, Calabar.

## RESULTS AND DISCUSSION

### Atmospheric quality parameters

#### Carbon monoxide

Carbon monoxide (CO) results from incomplete combustion of natural gas, diesel or gasoline in traffic engines, non-transportation fuel combustion, industrial processes, bush burning and some indoor sources such as leaking gas stove (Han and Naeher, 2006). High concentrations of CO generally occur in areas with heavy traffic intensity and congestion (Han

and Naeher, 2006). The average CO concentrations obtained from UNICAL and Ekorinim during the period of study are as shown in Figure 2(a). For both studied area, CO concentration varies from June, 2005 to July, 2006 with levels falling between 5.4 – 7.7 ppm for UNICAL and 7.5 – 9.2 ppm for Ekorinim. The difference is probably due to the relatively heavy traffic in Ekorinin area. However, the levels obtained falls below the guidelines of ambient air pollutants establish by WHO (2001) (which is 26 ppm at averaging time of 1 hour and 8.7 ppm at averaging time of 8 hours) and thus may not make any significant contribution to metallic corrosion.

### Nitrogen compounds

The average concentration of nitrogen dioxide ( $\text{NO}_2$ ) in UNICAL was between 0.260 to 0.329 ppm and Ekorinim 0.200 to 0.521 ppm (see Figure 2(b)) and falls within data already published for Calabar metropolis but quite high when compared with the limits set by the Nigerian Federal Ministry of Environment for  $\text{NO}_2$  which is 0.06 ppm (Etiuma *et al.*, 2006). This is most likely due to high traffic density and stationery fuel combustion process emissions from running of generators and domestic purposes like cooking (Etiuma *et al.*, 2006) and burning of bushes.

The average values of ammonia ( $\text{NH}_3$ ) in the atmospheres at the studied locations are between 1.000 and 4.300 ppm for UNICAL and 0.869 and 3.900 ppm for Ekorinim as depicted in Figure 2 (c).  $\text{NH}_3$  sources in the atmosphere are animal waste, ammonification of humus followed by emission from soils, loss of  $\text{NH}_3$ -based fertilizers from soils, and industrial emission. The values of  $\text{NH}_3$  are quite below the FEPA (1991) maximum limit and may not make any significant contribution to the metallic corrosion of mild steel.

### Sulphur dioxide

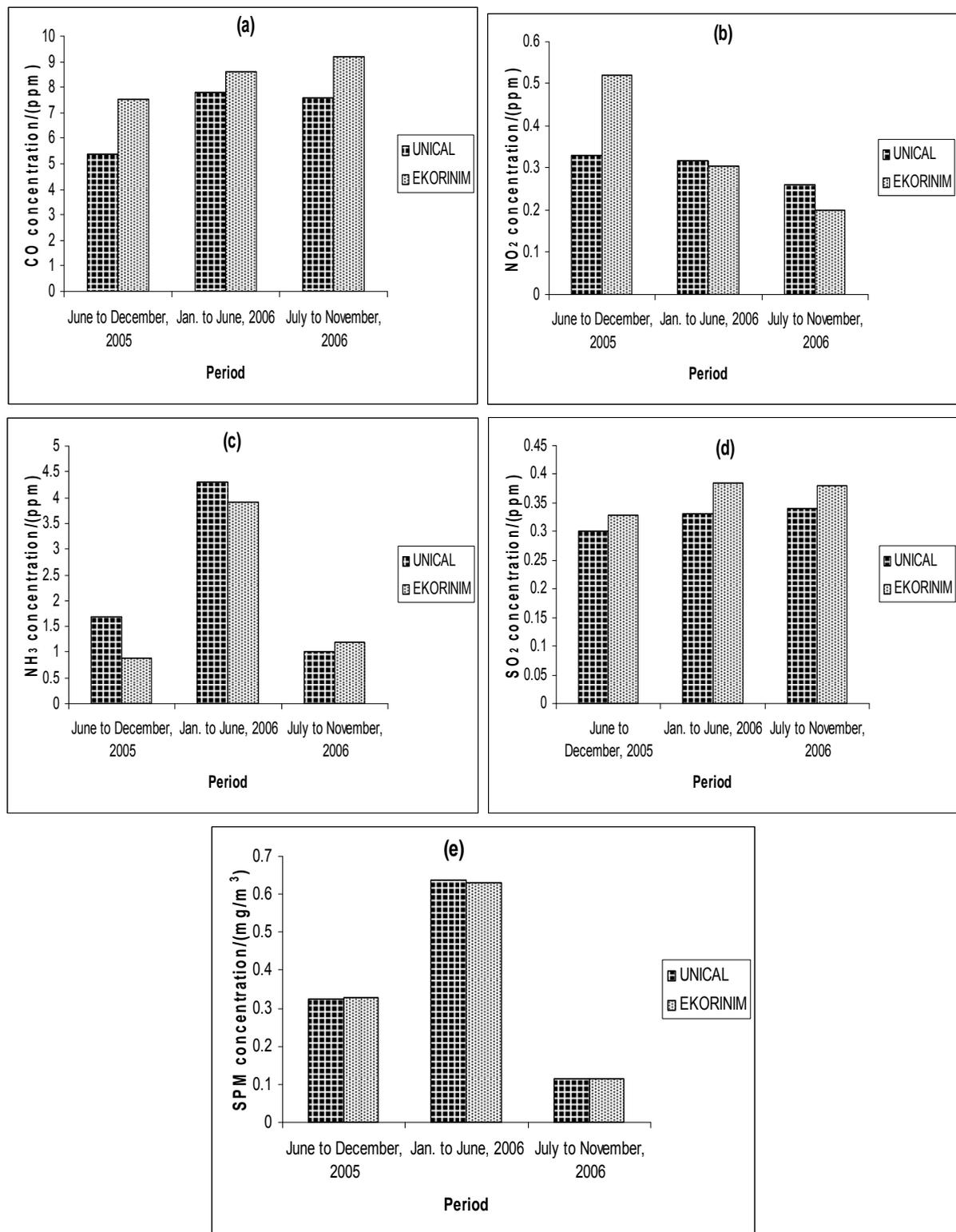
The average values of sulphur dioxide ( $\text{SO}_2$ ) obtained in UNICAL was between 0.301 to 0.340 ppm and between 0.329 to 0.380 ppm for Ekorinim as shown in Figure 2 (d). The sources of atmospheric sulphur compounds in the atmosphere are biological decay, combustion of fossil fuels and organic matter, and sea spray (Seinfeld, 1986). The sources of  $\text{SO}_2$  in this area are probably due to traffic density and stationery fuel combustion process emissions from running of generators and domestic purposes like

cooking. The values obtained were less than 0.5 ppm and may result only in a weak attack on metal surfaces (Oesch and Faller, 1997).

#### **Suspended particulate matter**

Airborne particulate matter refers to particles or droplets of various sizes, physical characteristics and chemical compositions present in the air (Han and Naeher, 2006). Their anthropogenic sources include but are not restricted to traffic, industries, commerce and domestic heating and cooking (Han and Naeher, 2006). In highly industrialized countries, more than 50 % of the total emissions of particulate matter in the urban areas are from traffic generated emissions (Laden *et al.*, 2000; Wrobel *et al.*, 2000; Han and

Naeher, 2006). Data obtained from Calabar City show that the average SPM are similar for both UNICAL and Ekorinim as shown in Figure 2 (e). However, the values vary from season to season. The highest being between January to June, 2006 ( $630 \mu\text{g}/\text{m}^3$  for Ekorinim and  $636 \mu\text{g}/\text{m}^3$  for UNICAL) which is the peak of the dry season which is associated with dust. Other values obtained are 329 and  $325 \mu\text{g}/\text{m}^3$  for Ekorinim and UNICAL, and  $113 \mu\text{g}/\text{m}^3$  and  $115 \mu\text{g}/\text{m}^3$  for Ekorinim and UNICAL in the months of June to December, 2005 and July to November, 2006, respectively. Apart from the July to November, 2006 values, the average SPM values were above FEPA (1991) limit of  $250 \mu\text{g}/\text{m}^3$ .



**Figure 2:** Average atmospheric concentrations of (a) CO, (b) NO<sub>2</sub>, (c) NH<sub>3</sub>, (d) SO<sub>2</sub> and (e) SPM in UNICAL and EKORINIM (near WAPI) in Calabar from June to November

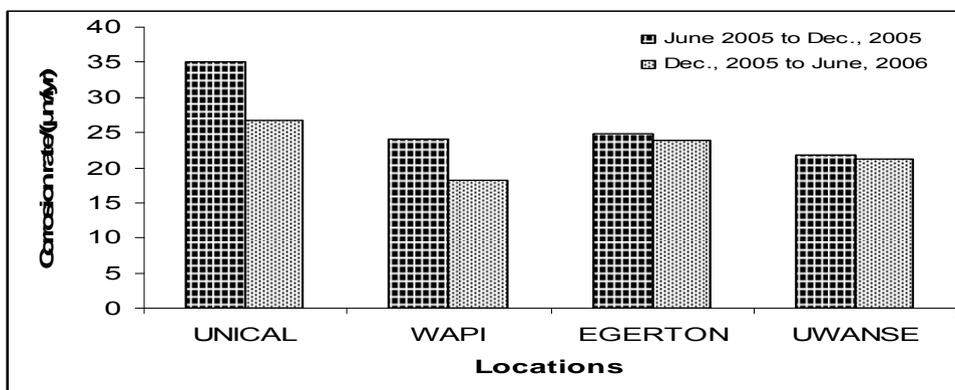


Figure 3: Average corrosion rate for mild steel exposed in Calabar from June 2005 to June 2006

### Precipitation parameters

The precipitation parameters measured during the period of this study is as shown in Table 2 and are as discussed below:

#### pH

The pH values for the studied locations fell between 5.03 and 6.39 and thus it may be said that the environment has received little influence by man with respect to the acidification of the environment. Rain of pH greater than 5.6 (WAPI) is assumed not to have been influenced by man, or if it has, it has sufficient buffering capacity so that acidification does not occur (Seinfeld, 1986). Rain with pH between 5.0 and 5.6 (UNICAL, EGERTON and UWANSE) may have been influenced by man but not to an extent exceeding that of natural background sulphur species (Seinfeld, 1986). It is therefore, reasonable to say that the rain water does not fall into acid rain category ( $\text{pH} < 5.0$ ) during the period of investigation.

### Conductivity, TDS and TSS

The conductivity of the water samples was within the freshwater limits of 10 to 1000  $\mu\text{Scm}^{-1}$ . Excess of 1000  $\mu\text{Scm}^{-1}$  is an indication of pollution (Chapman and Kimstach, 1996). Total dissolved solids (TDS) were observed to be between 7.74 and 24.22 mg/l from June to December 2005 to about 29.31 - 41.48 mg/l from January to December 2006. These values fall within the WHO maximum allowable concentrations for drinking water. The total suspended solids (TSS) are all below 0.05 mg/l which falls below the WHO maximum allowable concentrations for drinking water.

### Nutrients

The average nitrates values for the studied locations fall within 2.02 to 3.00 mg/l from June to December, 2005, 1.17 to 2.5 mg/l from January

to December, 2006 and 1.36 to 2.40 mg/l from July to August, 2006. There are three major pathways by which nitrate can be incorporated into precipitation: nucleation scavenging of nitrate-containing aerosols in cloud rain, absorption of gaseous nitric acid by cloud aerosols in cloud formation and below-cloud scavenging of nitrate-containing aerosols by rain (Seinfeld, 1986). Concentrations of the nitrate values obtained indicate that the environment has not been influenced by human activities and falls within the WHO recommended values (Chapman and Kimstach, 1996). Though, the  $\text{NO}_2$  contents in the different locations were high, it is assumed here not to have contributed significantly to the nitrate level since the aqueous-phase formation of nitrate from NO and  $\text{NO}_2$  is too slow to be of atmospheric importance (Seinfeld, 1986).

The ammonium values obtained were all less than 1.00 mg/l. Since there are no industrial emissions in these areas, the sources of ammonium in the rain water may be assumed to be principally due to the absorption of ammonia in the air by rain water.

The average sulphate values are as shown in Table 2 and falls within the values 0.26 to 0.59 mg/l from June to December, 2005, 0.03 to 0.04 mg/l from January to December, 2006 and 0.05 to 0.10 mg/l from July to August, 2006. Like in nitrates, the major ways by which sulphate can be incorporated into precipitation are nucleation scavenging of sulphate-containing aerosol particles in cloud formation, aqueous-phase formation of sulphate from absorbed  $\text{SO}_2$  in cloud droplets, and below-cloud scavenging of aerosol sulphate by rain (Seinfeld, 1986). Values obtained were below 1.00 mg/l also indicating little or no influence on the sulphate content by human activities.

Table 2: Average physiochemical measurements from rain water in Calabar

Parameters	June to December, 2005				July to August, 2006				January to December, 2006			
	UNICAL	WAPI	EGERTON	UWANSE	UNICAL	WAPI	EGERTON	UWANSE	UNICAL	WAPI	EGERTON	UWANSE
pH	5.45	6.1	5.52	5.2	5.03	6.39	5.8	5.29	5.27	6.01	5.78	5.57
Cond./ $\mu\text{S}/\text{cm}$	8.12	19.87	6.38	8.76	30.63	34.68	32.58	29.23	44.16	62.23	43.93	48.9
TDS/(mg/l)	9.52	24.22	7.74	11.42	18.82	21.3	20.01	17.93	29.38	41.48	29.31	32.49
TSS/(mg/l)	0.0181	0.0141	0.081	0.0145	0.001	0.00055	0.00012	0.0011	0.00167	0.0245	0.00179	0.00198
$\text{NO}_3^-$ /(mg/l)	2.02	2.64	3	2.79	1.36	1.85	2.4	2.14	1.17	1.2	1.32	2.5
$\text{NH}_4^+$ /(mg/l)	0.57	0.89	0.37	0.59	0.05	0.05	0.06	0.05	0.17	0.14	0.2	0.18
$\text{SO}_4^{2-}$ /(mg/l)	0.59	0.37	0.26	0.3	0.1	0.05	0.08	0.09	0.04	0.03	0.04	0.04

### Corrosion

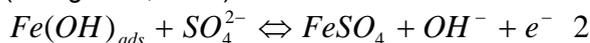
From the meteorological data shown in Table 3, the average relative humidity of the environment at the observed periods were above 75 % and thus assumed to form more than five monolayer

of water on the surface of the metal (Phipps and Rice, 1979; Leygraf and Graedel, 2000; Chen *et al.*, 2004), a condition which favours the formation of thin film of corrosive electrolyte on the metal surface.

**Table 3:** Average meteorological data for Calabar from June to December 2006

Parameters	Periods		
	June to Dec., 2005	Jan. to June, 2006	July to Dec., 2006
Maximum temperature/(°C)	29.2	31.42	29.48
Total rainfall/(mm)	406.03	173.77	259.02
Relative humidity/(%)	89.14	85.33	87.17

From Figure 2, it is observed that the corrosion rate during the period June to December, 2005 was higher than those from December 2005 to June 2006 for all the locations studied. From the meteorological data collected, average total rainfall from June to December, 2005 was more than twice that from January to June, 2006, and relative humidity was higher in the 2005 periods than in the 2006 periods and thus may be responsible for the higher corrosion rates. Comparing the corrosion rates of the locations, UNICAL stations were observed to have the highest corrosion rate. A closer look at the average physiochemical measurements from rain water in Calabar (Table 2) shows that the sulphate content in UNICAL is more than those in the other stations and may be responsible for the higher corrosion rate in UNICAL. Sulphate ions in thin electrolyte layer interferes with the formation of an intermediate species ( $Fe(OH)_{ads}$ ) in the iron corrosion reaction according to the process (Wang *et al.*, 1996):



This interference leads to acceleration in corrosion rates. However, the corrosion rates for all the stations fall within the excellent relative corrosion resistance range (Jones, 1996) and thus the atmosphere can be considered not to be corrosive to mild steel.

### CONCLUSIONS

The measured atmospheric and precipitation parameters indicate that Calabar, Cross River State, Nigeria environment has received little or no detrimental influence by human activities and thus can be used as a control environment for atmospheric studies.

The corrosion rates of mild steel in Calabar fall within the excellent relative corrosion resistance range ( $< 35 \mu\text{m/yr}$ ) and thus the atmosphere can be considered not to be corrosive to mild steel.

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