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Full Length Research Paper

The role of sulphur dioxide and gas flare particulates on the corrosion of galvanized iron roof sheets in south-south region of Nigeria

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The failure of galvanized iron roofs is one of the problems suspected to be associated with environmental pollution in the south- south region of Nigeria often called Niger Delta. In this study, two parameters, sulphur dioxide and particulate matters linked to gas flaring were examined in an outdoor exposure test to determine their relative contributions to the corrosion impact. The experiment involved the exposure of specimen of galvanized iron sheets to the atmosphere for twelve months while readings of the two parameters were taken periodically. The mass loss of each of the specimens was determined at the end of the experiment. The obtained data were subjected to statistical treatment and the examination of the output of the descriptive statistics, multiple regression and Pearson product moment correlation analyses reveal that sulphur dioxide (SO_2) did not significantly contribute to the problem while aerosol did. When the pollutants were regressed separately, their results showed that sulphur dioxide had an R^2 value of 0.389 and significant F change of 0.030 ($p<0.05$), and aerosol, an R^2 value of 0.660 and significant F change of 0.001 ($p<0.05$); however, in combination, the two parameters were shown to be more significant in a combined regression analysis ($R^2 = 0.70$) ($p<0.05$). Thus, their combined influence in the promotion of corrosion is higher than their separate impacts suggesting synergism. The study confirmed that gas flaring contributed significantly to the corrosion of galvanized iron roofs in the region.

Key words: Atmospheric corrosion, gas flaring, sulphur dioxide, particulate matter.

INTRODUCTION

Nigeria's South-South Region (Niger Delta) has been at the fore of international attention in recent time. Most of the discussions have been on oil spill and the associated ecological impact on the rich ecosystem of the mangrove environment. Now, world attention driven more by the threatening global warming has shifted to air pollution in the Delta perceived to be a major contributor to the planetary atmospheric carbon dioxide imbalance. Nigeria flares about 50,000 m^3 (1.8 million cubic feet) of associated gas daily coming out of over 123 onshore and offshore flare points (Ekpoh and Obia, 2010; Uyigue and Agho, 2007). The major by-product of this combustion is carbon dioxide, mostly because of the poor (incomplete) combustion at the flare chambers (Egbuna, 1987; Obia, 2008). Scientists have pointed that the excess CO_2 exuded to the atmosphere is exacerbating the climate change effect. Climate change is global and attracts global attention, however, the local effect of this pollution is hardly mentioned and thus limited studies are done in this direction in the region. Indeed, for quite sometimes now, the residents of close communities to gas flare points in the Niger Delta have been vocal on the effect this pollution has on the health of the citizens as well as their metallic (galvanized iron) roofs (Obia, 2009; Uyigue

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and Agho, 2007). Health problems often associated with gas flaring include asthma and such respiratory illnesses as chronic bronchitis, coughing and wheezing, difficulty in breathing; sometimes leading to such complications as impotency, blindness and premature death (USEPA, 2007, Palmer, 2009; Ekpoh and Obia, 2010). The communities' position especially as it relates to galvanized iron roof corrosion had always been countered by the simple argument that Nigeria's crude oil is low in sulphur content and would not produce sulphur dioxide in a volume that could be detrimental to materials (Inyang, 2001; Obia, 2008). In the industrialized economies, sulphur dioxide is the major industrial exhaust that degrades building materials. As plausible as this scientific fact may appear to be, the local residents still insist that roof corrosion is a recent phenomenon noticeable only after the gas flares began some five decades ago when oil extraction started in the region. These contradictory positions necessitate a scientific investigation to ascertain: 1) whether the gas, sulphur dioxide plays a significant role in the rust of galvanized roofs in the region either in isolation or in synergy with other pollutants; 2) whether hydrocarbon particulates (aerosols) that are exuded as a result of the incomplete combustion significantly contribute to the menace, either in isolation or in combination with SO_2. The choice of these two parameters associated with flaring is instructive; sulphur dioxide is often a product of industrial exhaust in an oil facility because of the presence of sulphur in the hydrocarbon fuel and the incomplete combustion in the flare chambers would likely lead to the abundant release of particulates of multi-compound nature into the atmosphere of the area.

The complexity of atmospheric chemistry as well as the diverse nature of air-borne pollutants makes prediction of atmospheric corrosion difficult. Thus, it is difficult to pinpoint a particular pollutant responsible for such effect. More so, some of the variables could be acting in synergy to promote corrosion. Therefore, scientific literature often base predictions on direct measurement of observed corrosion rates and correlating them to the various atmospheric parameters (Syed, 2006). The approach adopted in examining the problem in this study involved the atmospheric exposure of this metallic material in the outdoor environment of this region for a period of one year. The outdoor exposure test is one sure way of determining the behaviour of the studied object under natural atmospheric conditions. There are however, other accelerated chamber tests where synthetic environments are created and experiments exposed to extreme conditions for the corrosion mechanism involved. The chamber test approach is aimed at reducing the experimental time the outdoor exposure test would consume. It is a controlled experimental approach where the parameters could be varied under different artificially created environments. The outdoor experiment mimics the actual (life) situation the material would naturally be exposed and thus is a more predictive and reliable test.

MATERIALS AND METHODS

Study sites

South-South geopolitical region of Nigeria, otherwise called Niger Delta, where the study was undertaken, encompasses the states of Edo, Delta, Bayelsa, Rivers, Akwa Ibom and Cross River. It is wide ecological zone covering an area of about 2,000 km^2 of mangrove/fresh water swamps, lowland rainforest and coastal barrier islands bordering Atlantic Ocean to the south and close to the Equator at the Gulf of Guinea. The Delta is considered to be one of the richest wetlands in the world (Idris, 2010; Wikipedia, 2010). The southern tip of the zone is a network of creeks harbouring a myriad of oil mines, oil flow stations and gas flare chambers (Figure 1). Virtually the whole area is seated on a geologically rich hydrocarbon base hence, the high oil and gas exploration and exploitation activities in the region. Much of the crude is mixed with associated gas that is often flared or vented after oil extraction. Three sites were chosen for this experiment. Two of the sites, Ibeno and Ebocha were within zones of extreme gas flaring activities while the control site was Abamba, a forested area in Cross River State with no industrial activities and no vehicular traffic flow (Table 1 for site classification). Ibeno is Mobil Producing Unlimited onshore station where gas is flared ceaselessly all-year round. It is a seaside facility situated at latitude 04°23′N and longitude 07°45.16′E at the Bight of Bonny in the Gulf of Guinea. Ibeno is a village in Akwa Ibom State of Nigeria. Ebocha, the second site is in Rivers state and could be found at latitude 05°35′N and longitude 06° 41' E, and is home to the National Agip Oil Company crude oil tank farm where flaring is also a 24-h activity. Ebocha has the additional problem of being surrounded by flares from such adjoining communities as Egbema and Oguta in Imo states, all within a radius of about 20 km. The third site, Abamba is taken as the control station in this experiment because of its unique location. It is not less than 200 km away from the nearest flare station and not less than 150 km away from the sea. It is geographically located at latitude 05° 35′ N and longitude 08°08′E in an isolated area in the rain forest.

The region as a whole is found within the humid tropical equatorial zone with mean yearly temperature of about 27°, relative humidity in excess of 80% and a high rainfall range of 3000 to 4000 mm.

Experimental procedure

In the experiment, specimens of the local commercial galvanized iron roofing sheets were exposed for one year and monitored for corrosion wear while concentrations of industrial air-borne particulates (aerosols) and sulphur dioxide were recorded monthly. The sample specimens (100 × 150 mm each) were cut from a 1-mm thick corrugated sheet of the metal. This small size of the coupons is often preferred in atmospheric exposure test because of ease of manipulation and greater reliability of measurement [ISO 9226 (Tidblad et al., 2007; Natesana et al., 2008)]. The specimens were cleaned in the laboratory by chemical means in accordance with ISO 8407 (Lien et al., 2007; Acevedo-Hurtado et al., 2007). The specimen pieces were first washed in ethanol solution, cleaned with number 120- abrasive paper and then degreased by scrubbing with bleach – free scouring powder (Chotimongkol et al., 1999; Ekpoh and Obia, 2010). The cleaning action was to present a uniform surface by removing any extraneous particles especially

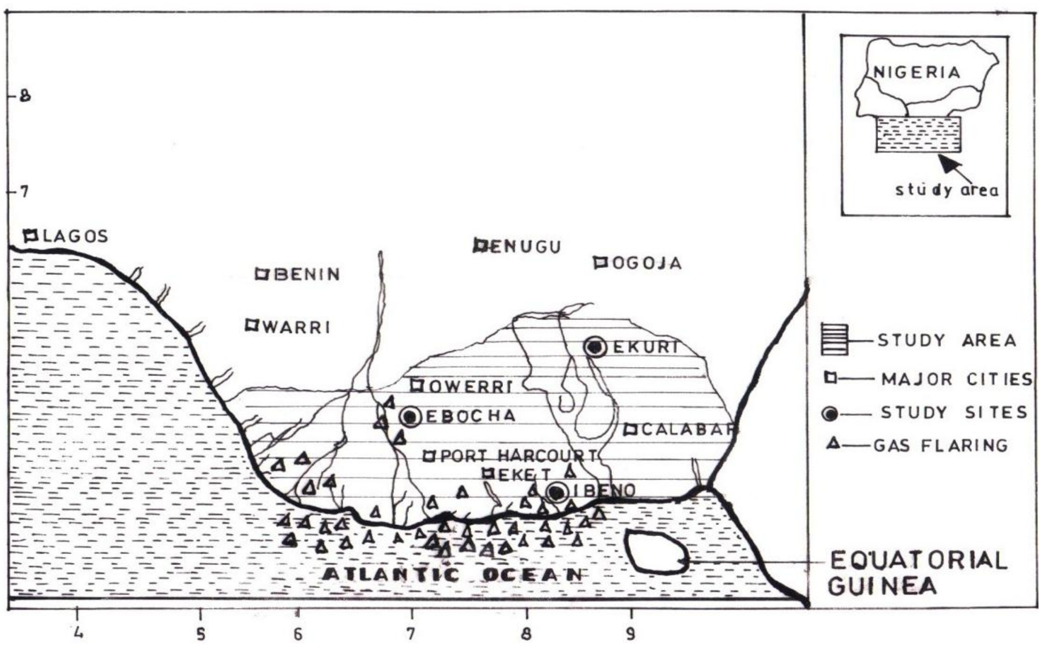

Figure 1. Map of South-South (Niger Delta) showing the area and the study sites.

Table 1. Sites classification.

Sites	Environment	Location	Unique characteristics
'A' QIT, Ibeno	Marine/industrial.	04° 32′ N/07°55′ E	A seaside oil facility with flare points that burn all-year round.
'B' NAOC Ebocha	Industrial.	05° 28′N/05° 41′ E	Rural village with gas flare points that burn all-year round.
'C' Abamba village	Non-marine/rural.	05°35′ N/08°08′ E	An open field at the village of Abamba in the forest.

NAOC source: Author's field records.

metallic debris that could promote corrosion. It is a generally accepted procedure in the scientific community to pre-clean galvanized iron coupons before atmospheric exposure test (Syed, 2007; Lien et al., 2007). After exposure, the specimens were cleaned and re-weighed. The sample specimens, each properly labeled were suspended on a wooden rack with plastic strings tied to nails fixed unto the rack frame and the assembly inclined at an angle of 22° to the surface. Each rack stationed in an open field away from trees and buildings was elevated 1.2 m above the earth surface to avoid corrosive dirt in rain splashes from the surrounding ground. The chosen slope is the average gradient of roofs in the locality (Obia, 2009; Ekpoh and Obia, 2010). The samples on each rack were in quadruplicates to ensure greater reliability of result. The difference between a sample mass before and after exposure represents its mass loss and the mean of the replicates' mass losses in a rack represents the mass loss in that station. There were a total of twelve stations across the three sites, four per site and stationed within 400 m radius.

The pollutants were monitored with high sensitive equipment. Sulphur dioxide was monitored with an environmental monitoring station manufactured by ELE International of United Kingdom mounted with sensor for the gas. The aerosol was monitored with an AMSA595OIS intrinsically safe air-borne particulate monitor manufactured by CASELLA Limited of United Kingdom with a range of 0-200 µg. Mass loss was determined by an analytical electronic weighing balance (WA) manufactured by Adam Equipment of United Kingdom with a range of 0 to 21.0 mg designed to measure light objects in the laboratory and used where high degree of precision is required. The pollutant sampling was done between 0600 and 1200 h every fortnight and the monthly/annual mean determined.

Statistical treatment

The relationship between mass loss and distance from pollution sources as well as that between pollutant concentration and distance were graphically analyzed. The other statistical data analyses were done with the aid of SPSS 2007 statistical software package. The analyses involved the determination of descriptive statistics (the means, standard deviations and coefficients of variation). Others included multiple regression analysis to determine the significance of these parameters in the corrosion effect and Pearson product moment correlation analysis to determine their relative strengths. The relative impact of corrosion at each of the three sites were determined by performing analysis of variance (ANOVA) to determine the mean mass loss differences among them and a further post hoc test to determine the significance of the impact at each of the sites.

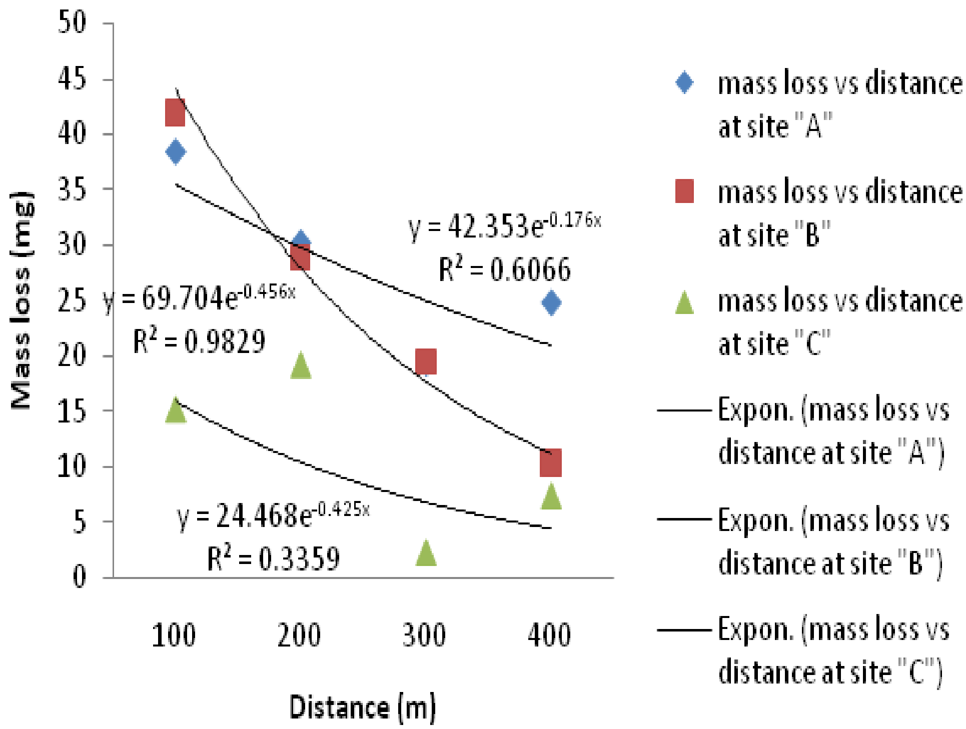

Figure 2. Graph of mass loss against distance at sites "A", "B" and "C".

RESULTS

Mass loss

Table 1 show the mean annual readings of the parameters captured in the experiment (mass loss, sulphur dioxide and aerosol concentration) as well as the descriptive statistics indicating their grand means, standard deviations and coefficients of variation. The relationship between mass loss and distance of specimen racks from pollution source is shown Figure 2. The coefficients of determination (R^2) of 0.61 and 0.98 for sites A (Ibeno) and B (Ebocha) suggest high dependence of mass loss on distance from pollution source. These sites harbour gas flare chambers. The dependence is negatively correlated indicating that the farther the sample was from the pollution source, the less the effect. Site C indicates relatively low dependence of mass loss on distance with an R^2 value of 0.34 only.

Sulphur dioxide and aerosol concentration

The relationship between sulphur dioxide and distance is shown in Figure 3 and that between aerosol and distance is shown in Figure 4. From Figure 3, it could be seen that there was a high dependence of sulphur dioxide concentration on distance from pollution source with R^2 values of 0.83 and 0.65 for A and B respectively. Similar relationship is established between aerosol concentration and distance with R^2 values of 0.89 and 0.57 for A and B. Again this dependence shows a decreasing relationship suggesting that the farther a station was, the less the concentration of the pollutants (sulphur dioxide and aerosol). Site C shows negligible dependence of the two pollutants on distance from pollution sources.

Combined effect

The highest mean mass loss as seen in Table 1 was recorded at QIT, Ibeno (28.23 mg) and the least was at Abamba (13.18 mg). Mean sulphur dioxide was highest at NAOC, Ebocha (0.53 ppm). Similarly, the highest aerosol concentration (16.49 µg/m^3) was recorded at Ebocha. Sulphur dioxide also recorded the greatest coefficient of variation (59.78%) followed closely by mass loss (55.77%) while aerosol indicated only 32.86% (Table 2). The multiple regression output shows a significant change value of 0.005 ($p<0.05$) and coefficient of determination of R^2 of 0.69. The partial correlation coefficients showed aerosol as having a higher figure of 0.702 as against a figure of 0.298 for sulphur dioxide. When the pollutants were regressed separately, their results showed that sulphur dioxide had an R^2 value of 0.389 and significant F change of 0.030 ($p<0.05$) and aerosol had an R^2 value of 0.660 and significant F change of 0.001 ($p<0.05$). The result of analysis of

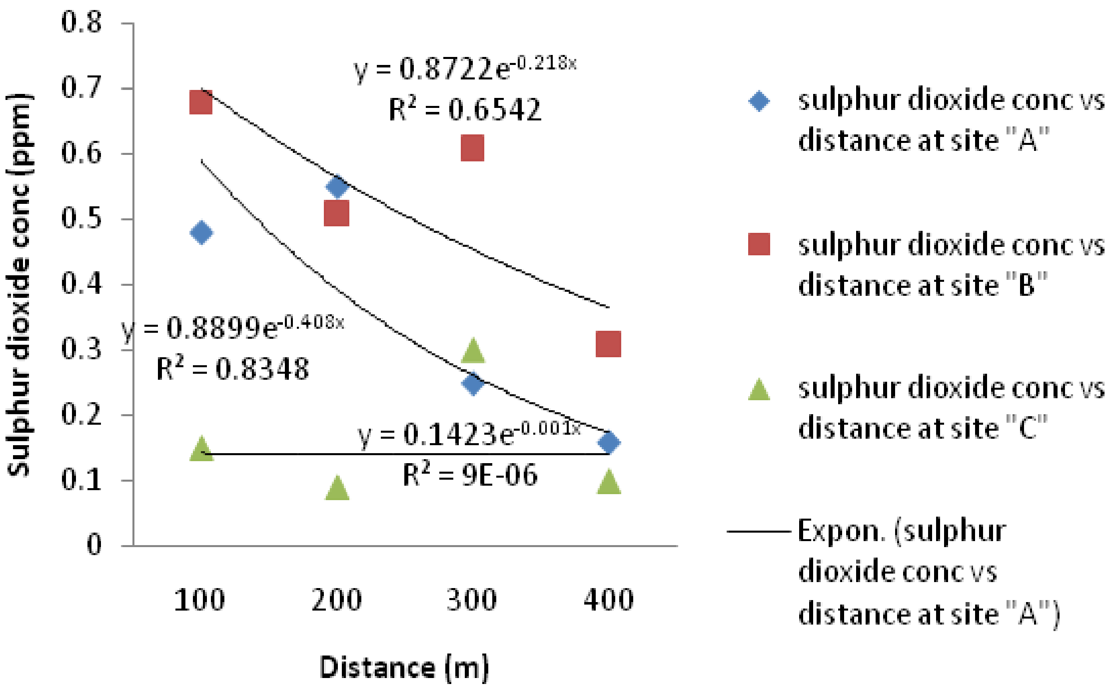

Figure 3. Graph of sulphur dioxide concentration against distance at sites “A”, “B” and “C”.

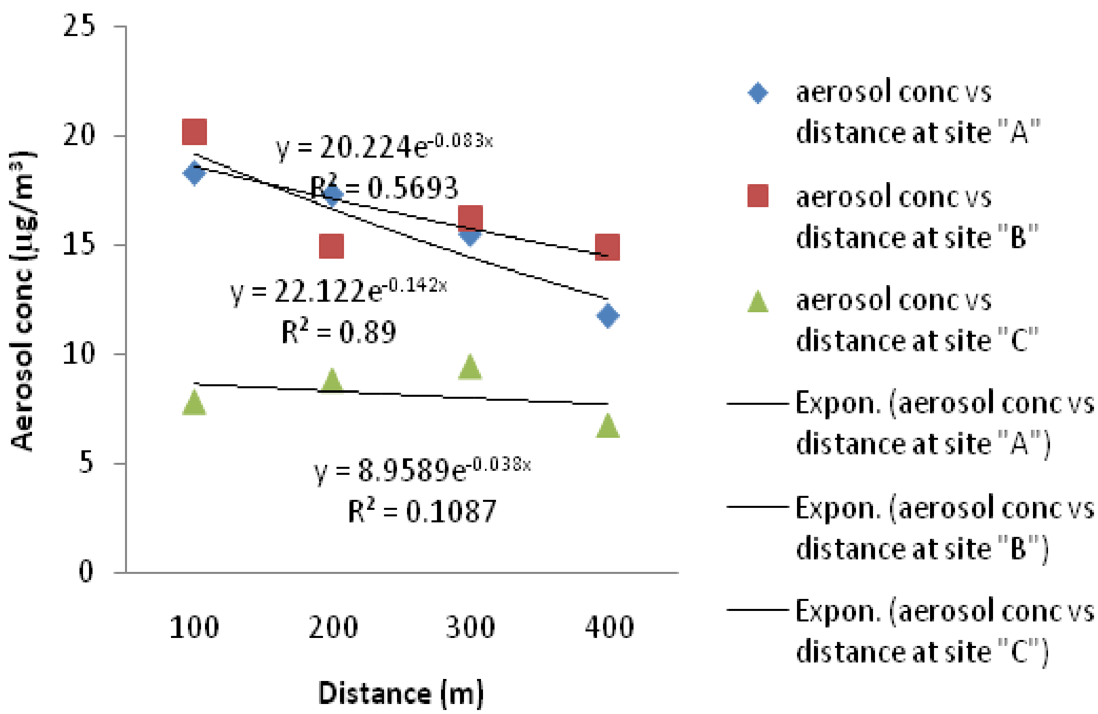

Figure 4. Graph of aerosol concentration against distance at sites “A”, “B” and “C”.

variance indicates that there was a significant difference ($p<0.05$) in mass loss between two of the sites while the other pairs failed the test. A Post Hoc Test (LSD) shows that there is a significant mean mass difference of 17.165 mg between ‘B’ (Ibeno) and ‘C’ (Abamba). However, there is no significance between sites ‘M’ (Ebocha) and

Table 2. Mean readings of mass losses and corresponding concentrations of sulphur dioxide (SO_2) and aerosols (particulates) across the stations.

Site (m)	Station	Distance from flare points	Mean mass (mg)	Mean SO_2 (Ppm)	Aerosol (µg/m^3)
"A"	S_1	100	38.38	0.25	17.30
QIT	S_2	200	30.20	0.55	15.50
Ibeno	S_3	300	19.55	0.48	11.80
Eket	S_4	400	24.80	0.16	18.27
Mean			28.23	0.36	15.72
"B"	S_5	100	41.90	0.68	20.17
NAOC	S_6	200	28.92	0.61	14.95
Ebocha	S_7	300	19.50	0.51	16.20
	S_8	400	10.45	0.31	14.87
Mean			25.19	0.53	16.55
"C"	S_9	100	19.23	0.15	9.47
Abamba	S_{10}	200	15.24	0.30	8.82
Village	S_{11}	300	7.46	0.09	7.82
	S_{12}	400	2.34	0.10	6.72
Mean			13.18	0.16	9.07
Grand Mean			21.50	0.35	13.49
Std. Dev			11.99	0.21	4.43
CV			55.77%	59.78%	32.86%

'C' (Abamba) with mean difference of 14.125 mg, and 'B' (Ibeno) and 'A' (Ebocha) with mean of 3.04 mg.

Empirical model equations

Figure 2 shows the dependence of corrosion (mass loss) on distance from gas flare sources. Similarly, Figures 3 and 4 shows the dependence of the concentrations of the pollutants (sulphur dioxide and aerosol) on distance. These dependences follow an exponential relationship of the form:

$$\gamma = A\exp(-cx) \quad (1)$$

DISCUSSION

In industrial zones, sulphur dioxide in high concentration is considered a major source of corrosion. However, the concentration of the gas in the atmosphere of the Niger Delta is low and hence often thought to be of little or no effect. Also, gas flaring in the region is considered to be below accepted industrial standard. The incomplete combustion in the flare chambers yields particulate matter of various chemical compositions. In this study, we examine the effect of this gas when acting alone and when in combination with particulate matter associated with gas flaring.

Mass loss and distance

Graphically (Figure 2), mass loss (corrosion) is shown to have negative correlation with distance. There is a decreasing mass loss with distance from the gas flare stations. Thus, the further a station is from the source of pollution the less the effect. At a distance of 2 km for instance, the effect should be negligible, however, the high concentration of gas flare chambers within the region creates distance overlap leading to a wider and even distribution of the effect. The poor correlation (R^2 = 0.34) between mass loss and distance at site C, Abamba is due to the absence of a strong pollution source as seen in Ibeno (site A) and Ebocha (site B) with flare points.

Pollutants and distance

As seen from the graph in Figure 3, the concentration of sulphur dioxide also shows a negative correlation with distance from pollution source. The sudden surges in concentration at some points at the three sites could be attributed to the local microclimatic variability such as wind and pressure. Similarly, Figure 4 shows the dependency of particulate matter (aerosol) concentrations on distance. There is a decrease in the concentration of aerosol as distance increases. Thus the farther away a point is from gas flare station the less polluted it is. Abamba with no gas flare station shows no dependence of pollution on distance.

The combined effect on mass loss

We used multiple regression analysis to examine the relative and combined influences of aerosol (particulate matter) and sulphur dioxide in the atmospheric corrosion of the galvanized iron specimens and found that the concentrations of the parameters are significant ($p<0.05$). When the pollutants were regressed separately, their results showed that sulphur dioxide had an R^2 value of 0.389 and significant F change of 0.030 ($p<0.05$), and aerosol had an R^2 value of 0.660 and significant F change of 0.001 ($p<0.05$). However, in combination, the two parameters are shown to be more significant in a combined regression analysis ($R^2 = 0.708$) ($p<0.05$). The coefficient of determination, R^2 of 0.708 suggests that about 70.8% of the corrosion of galvanized iron roofs could be attributed to these factors; thus, their combined influence in the promotion of corrosion is higher than their separate impacts suggesting synergism. The partial correlation figures of 0.298 for sulphur dioxide and 0.702 for aerosol show the relative contributions of these variables to the impact. The concentration of aerosol could be due to the poor combustion at the flare exhaust chambers that result in the release of admixture of various compounds of acidic origins – carbonaceous soot and hydrocarbon particulates. The high temperature within the chambers (1870 to 3000°C) also yields nitrous oxides particulates leading to the formation of nitric acid (atmospheric nitrogen oxidizes at 1200°C) (Odu, 1994). The result of the ANOVA and the subsequent Post Hoc (LSD) tests suggests that mass loss indicated significant mean difference between Ibeno and Abamba (17.165 mg). The significant mean difference between Ebocha and Abamba is 14.125. This result also shows that Ibeno received the greatest impact followed by Ebocha.

The least impacted site was Abamba, the control station in the experiment. The reason is because Abamba was relatively free from such anthropogenic pollution as noticed in the two industrial sites of Ebocha and Ibeno.

Conclusion

In this study, we have shown that though the individual influences of sulphur dioxide and aerosol concentration may be significant, their combined effect is more severe. Also, the damage equations suggest exponential dependence of corrosion on distance from pollution source. It is obvious therefore that gas flaring that yields these pollutants is mostly responsible for galvanized iron roof corrosion in the region. We therefore suggest a discontinuation of gas flaring in the region as the best solution to the elimination of this menace.

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