

The Role Of Heavy Metals And Polycyclic Aromatic Hydrocarbons In The Degradation Of Emulsion Paintings Of Buildings In Port Harcourt, Nigeria

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ABSTRACT

The Port Harcourt city in the Eastern Niger Delta, Nigeria is home to many industries: oil and gas, manufacturing etc. It is also an environment that experiences heavy rainfall almost throughout the year. And because of industrial activities and other combustion sources, heavy metals and polycyclic aromatic hydrocarbons are common in the air. Thus these chemicals attack/ degrade the emulsion paintings in different buildings. Therefore, it is common to observe green and dark patches on fences and walls of both public and private houses. For purposes of this work, three buildings located in the three campuses of University of Port Harcourt were chosen as the sample sites. Samples were collected from the degraded and undegraded portions of these buildings and analyzed. The heavy metal content of these samples were determined by aspiration using PERKIN ELMER AAS 3100. And these heavy metals were detected: Fe, Na⁺, Cr, Ni, Zn, Ca⁺, Ti, and Cd. The polycyclic aromatic hydrocarbon content of these samples were also determined but with Gas—Mass Spectrometry (GC—FID). It has the ability to identify and quantify all polycyclic aromatic hydrocarbons. These PAHs were detected: acenaphthylene, fluorene, naphthalene, pyrene, and acenaphthene.

KEY—WORDS: Emulsion Paintings, Heavy Metals, Polycyclic Aromatic Hydrocarbons, GC—FID, AAS.

INTRODUCTION

An emulsion paint is water-based and dries by evaporation, while the oil-based paint has a chemical drying agent added to it. (Bentley, et al 1997). However, emulsion

paints contain a lot of additives to impact various properties like foam control, skin control, bacteria growth control, and pigment stability (Turner,1967). Heavy-metals is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4g/cm^3 or 5 times or more greater than water (Hutton and Syman, 1986, 129-150: Battarbee et al,1988,1800-1986: Nriagu and Pacyna,1988 134-139: Nriagu,1989,47-49: Garbarino,et al 1995 140: Hawkes,1997 1374.). These metals are deposited in the environment by both natural and anthropogenic sources especially industrialactivities and automobile exhausts (Hutton and Syman, 1986: Battachee et al 1988: Nriagu, 1989). When ingested into the body, they combine with the body's biomolecules like proteins and enzymes to form stable biotoxic compounds, thereby mutilating their structures and hindering them from the bioreactions of their function (Lenntech,2004).

An environment is defined as the totality of circumstances surrounding an organism or group of organisms especially the combination of external physical conditions that affect and influence the growth, development and survival of organisms (Farlex, 2005). Polycyclic Aromatic Hydrocarbons (PAHs) are chemicals that are often found together in groups of two or more. They are naturally in the environment but they can also be man-made. They are solid and range in appearance from colorless to white or pale yellow. They are created when products like coal, oil, gas, and garbage (ATSDR,1980). PAHs are a concern because they are persistent, they do not burn easily. They can stay in the environment for long periods of time. Individual PAHs vary in behavior, some can turn into vapour in the air very easily and most do not breakdown easily in the water. PAHs can enter the body through breathing contaminated air. Another way this happens is when one eats or drinks food and water contaminated with PAHs. Besides, exposure to PAHs can also occur if the skin contacts PAHs- contaminated soil or products like heavy oils,coal tar, roofing tar or creosote. Creosote is an oily liquid found in coal tar and is used to preserve woods. Once in the body, PAHs target the kidney and liver, and they leave the body through urine and faeces in a matter of days (USEPA, 2001)

METHODOLOGY

- (1) **Analysis of Heavy Metals:** The heavy metal content was investigated using the Atomic Absorption Spectrometry(AAS) method. About 1g of sample was dissolved by using HF/HCL/HCLO₄ in a Teflon crucible. Dissolved sample was transferred into 100ml volumetric flask. The crucible was rinsed several times with deionised water into a volumetric flask after which the solution was taken through the same process to determine the recovery factor which is usually higher than 98%.The levels of heavy metals were determined by aspiration using PERKIN ELMER AAS 3100
- (2) **Analysis of Polycyclic Aromatic Hydrocarbons (PAHs):** The PAHs content was investigated using Gas Chromatography—Mass Spectrometry technique. About 10g of dried sample was thoroughly mixed with anhydrous sodium sulphate and was soxhlet extracted with dichloromethane(200ml) for 6hours. The solvent was concentrated to 5ml in a rotary evaporator under reduced

pressure. About 0.5M potassium hydroxide (100ml) in amethanol was added and the mixture was refluxed for 4hours in a water bath at 80⁰C. After cooling, deionised (20ml) was added and extraction was performed with hexane. The combined organic was dried over anhydrous sodium sulphate (0.5g). The decanted extract was evaporated at 40⁰C in the rotary evaporator under reduced pressure to near dryness, dissolved in isooctane(1ml) for silica clean-up. The glass column (1.2cm 1D) was slurry-packed with silica gel (10g) in dichloromethane and top layer of anhydrous sodium sulphate (0.5g). The column was rinsed with hexane (40ml) before use. The extract was transferred to the column and subsequently eluted with hexane (25ml) and hexane dichloromethane,60 : 40 (30ml) to give fractions enriched in alkanes and PAHs, respectively. The sample was injected into the GC=FID column for analysis.

RESULTS AND DISCUSSION

Atomic Absorption Spectrometry Analysis of Heavy Metals In Lichen

Table1:Mean values of concentrations of heavy metals in degraded sites with their standard deviations (mg/kg)

HEAVY METALS	SITE 1	SITE 2	SITE 3
Titanium	0.97±0.02	0.97±0.02	0.94±0.02
Nickel	10.75±0.16	10.75±0.16	10.56±0.16
Iron	78.35±0.17	78.35±0.17	77.46±0.06
Zinc	4.47±0.20	4.47±0.20	4.48±0.17
Chromium	11.34±0.09	11.34±0.09	11.30±0.02
Calcium	2.70±0.24	2.70±0.24	2.59±0.01
Sodium	35.26±0.25	35.26±0.25	34.97±0.06
Cadmium	0.05±0.02	0.05±0.02	0.02±0.01

Correlation of Degraded Sites

	SITE 1	SITE 2	SITE 3
SITE 1	1		
SITE 2	1	1	
SITE 3	1	1	1

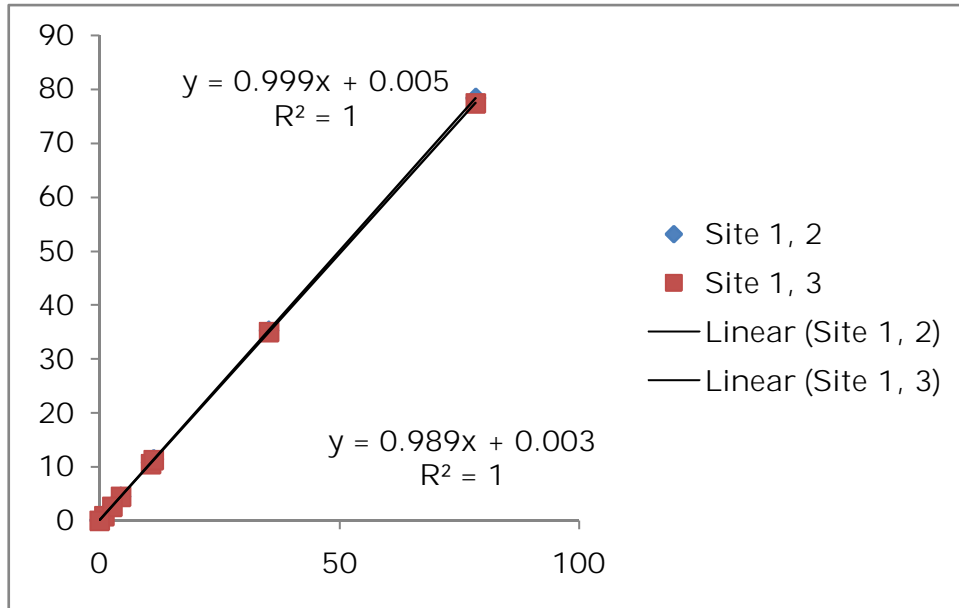


Fig1:Graph of Correlation between Heavy Metal Concentrations in Degraded sites

Table2:Mean values of Concentrations of heavy metals in undegraded sites with their standard deviations (mg/kg).

HEAVY METALS	SITE 1	SITE 2	SITE 3
TITANIUM	0.65±0.04	0.65±0.05	2.71±2.85
NICKEL	6.91±0.61	7.45±0.13	7.41±0.35
IRON	50.34±0.76	54.49±0.41	52.91±0.23
ZINC	2.50±0.44	2.85±0.10	2.42±0.14
CHROMIUM	6.62±0.24	7.45±0.27	6.74±0.23
CALCIUM	1.44±0.21	1.57±0.26	1.43±0.02
SODIUM	34.12±0.51	32.39±0.44	31.59±0.44
CADMIUM	0.02±0.00	0.01±0.00	0.02±0.01

Correlation of Undegraded Sites

	<i>SITE 1</i>	<i>SITE 2</i>	<i>SITE 3</i>
SITE 1	1		
SITE 2	0.997309074	1	
SITE 3	0.996718624	0.999136327	1

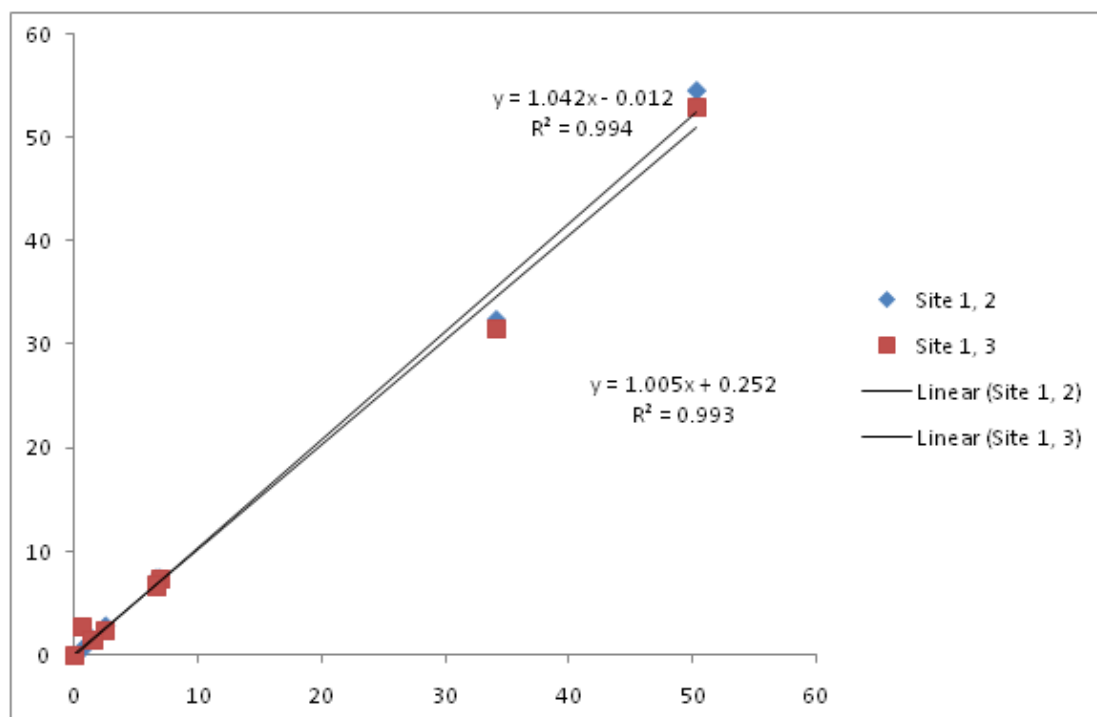


Fig2:Graph of Correlation between Heavy Metal Concentrations in Undegraded sites

DISCUSSION:

The results in tables 1 and 2 indicate the concentrations of heavy metals in both degraded and undegraded sites. It is observed that there is high deposit of iron, sodium, chromium and nickel in both sites, although this is higher in the degraded sites. Perhaps the only reason is that there is no microbe/metal interaction yet in the undegraded sites. But in table 1, there is a microbe/metal interaction and other microbial activities giving rise to degradation. The city of Port Harcourt is home to many oil and gas companies and other production companies. Hence, it experiences a high level of industrial activities. A comparison of results in tables 1 and 2 reveals a higher amount of metal content in the first table than in the second table. This difference in amount of metal content can only be explained by the fact that there is a gradual build up of these heavy metals from the environment. Work by Battarbee, Niragu and others in 1988 and 1989 showed that these metals are released into the environment by both natural and anthropogenic sources, especially industrial activities and automobile exhausts. Gadd, Ehrlich, Macaskie, Beveridge, Brierley and so many others carried out extensive work on the interactions of microbes and metals and made several reports. The uptake of trace metals and their subsequent utilization in enzyme activation occur in all microbes (Wackett et al 1989). Enzymatic microbial detoxification of harmful metals is another type of microbe/metal interaction. In this process, a toxic metal species may be converted to a less toxic or non-toxic entity by

enzymatic oxidation or reduction. The bacterial oxidation of AsO_2 to AsO_4^{3-} by a strain of *Alcaligenes faecalis*, and the reduction of CrO_4^{2-} to Cr(OH)_3 by *P. fluorescens* are examples of such redox reduction (Ehrlich, 1996; Wang and Shen, 1995). Besides, prokaryotic and eukaryotic microbes are capable of accumulating metals by binding them as cations to the cell surface in a passive process (Beveridge and Doyle, 1989, Gadd 1993). These results support our observations that there is usually a gradual build-up of metals from the environment on the painted surface and that they contribute extensively to the degradation of this surface. The results here, $R=1$ and $R^2=1$, for each correlation, show that there is a perfect linear correlation of the concentrations of heavy metals for the three sites in the degraded area. This means that as the concentrations of heavy metals increase in site 1 there is a perfectly corresponding increase of the concentrations of heavy metals in site 2 as well as in site 3. An interesting factor also is that the total variation in the values of the concentrations in all the three sites is predictable by the regression line for both site 1 and site 2 and between site 2 and site 3 as well as between sites 1 and 3. Just as it is in the degraded sites, there is a perfect correlation of metallic concentration in the undegraded sites as well. In this case, 99% of the total fluctuation is also predictable by the regression lines as indicated by the value $R^2=0.99$

Analysis of Polycyclic Aromatic Hydrocarbon in Degraded and Undegraded Sites

Table 3: Mean values of concentrations of PAHs in degraded sites with their standard deviations (mg/kg)

P. A. H.	SITE 1	SITE 2	SITE 3
Anthracene	2.63±0.09	2.53±0.02	2.78±0.08
Fluorene	4.18±0.02	3.83±0.07	4.34±0.12
Pyrene	0.71±0.16	0.65±0.02	0.77±0.05
Acenaphthene	0.71±0.09	0.76±0.04	0.65±0.08
Acenaphthylene	9.03±0.02	8.70±0.01	9.04±0.02
Naphthalene	1.26±0.02	1.15±0.02	1.36±0.04

Correlation of Mean values of concentrations of PAHs in degraded sites

	SITE 1	SITE 2	SITE 3
SITE 1	1		
SITE 2	0.999568097	1	
SITE 3	0.999649548	0.99861795	1

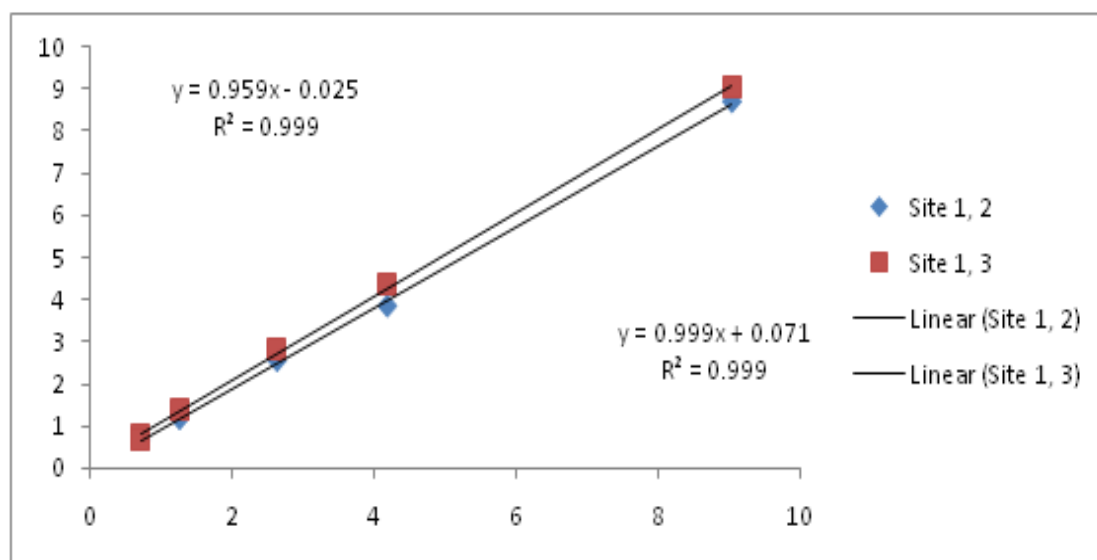


Figure3: Correlation Plot of Mean Values of Concentrations of PAHs in Degraded sites

Table4: Mean Values of Concentrations of PAHs in Undegraded Sites with Their Standard Deviations (mg/kg)

P. A. H.	SITE 1	SITE 2	SITE 3
Anthracene	-----	0.02±0.00	-----
Fluorene	2.60±0.08	2.47±0.17	2.13±0.13
Pyrene	0.47±0.05	1.52±0.08	0.27±0.03
Acenaphthene	0.42±0.07	0.49±0.23	0.28±0.07
Acenaphthylene	0.44±0.13	0.28±0.02	0.16±0.01
Naphthalene	3.71±0.15	2.75±0.13	2.39±0.02

Coefficient of Correlation for Mean Values of Concentrations of PAHs in Undegraded sites

	<i>SITE 1</i>	<i>SITE 2</i>	<i>SITE 3</i>
SITE 1	1		
SITE 2	0.900214	1	
SITE 3	0.9837	0.917094	1

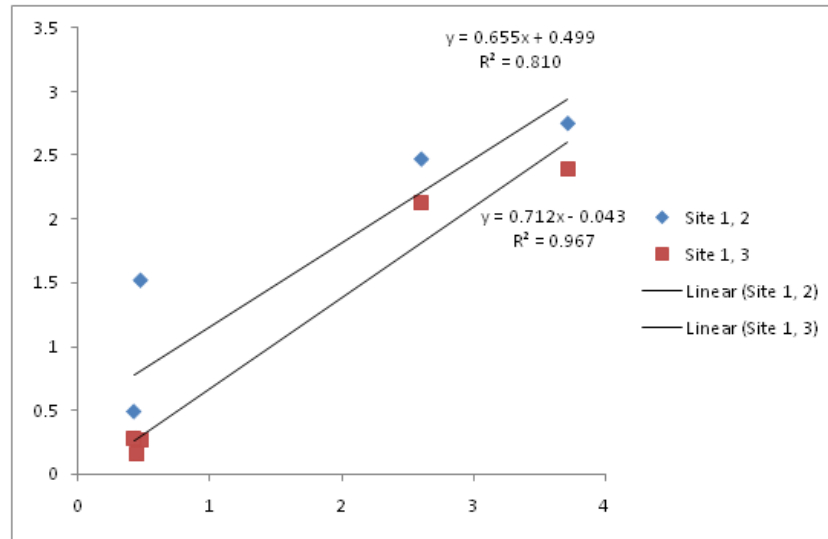


Figure 4: Correlation Plot of Mean Values of Concentrations of PAHs in Undegraded Sites

DISCUSSION:

The results in tables 3 and 4 show the composition of polycyclic aromatic hydrocarbon in both degraded and undegraded sites. It is expected that 48 hours after a surface is painted, the PAHs ought to have evaporated into the air. But the results still show the heavy presence of PAHs, and the PAHs are more abundant in the degraded sites than in the undegraded sites. This implies that there must have been some deposits of these chemicals from the environment. And the fact that they are more in the degraded sites shows that they are contributing to the degradation of the environment. In table 3, anthracene, fluorene and acenaphthylene appear to play a greater role in this respect than the others.

The coefficient of correlation between the concentrations of PAH in all the three degraded sites is almost uniform, indicating an almost perfect correlation which shows that the values of concentration of PAH in the degraded sites increases symmetrically, and the value of coefficient of determination/adjusted correlation $R^2=0.999$ for the relationship between sites 1 and 2 and between sites 2 and 3 shows that both regression lines can explain all of the variations and make predictions at any time. In the undegraded area, sites 1 and 3 have the strongest correlation in terms of concentration of PAH as indicated by the almost perfect value of coefficient of correlation, $R=0.98$, followed by that between sites 2 and 3 ($R=0.917$) and finally that between sites 1 and 2 ($R=0.90$). Nonetheless, all three undegraded sites show very strong correlation in their values of concentration of PAH, meaning that as the concentration of PAH increases in one site it also increases proportionally in the other sites. This report is also supported by the scatter plot and values of R^2 for both series. Series 1 (between sites 1 and 3), with $R^2=0.97$ gives better predictions when compared to Series 2 (Regression line for sites 1 and 2) with $R^2=0.81$ for the total

variations of PAH concentration in the degraded sites.

CONCLUSION

It is obvious from this investigation that the heavy metals and polycyclic aromatic hydrocarbons contribute to the degradation of the emulsion painting. But the heavy metals play a greater role in this respect especially when one considers the microbe/metal interactions in the environment which greatly affect the adhesion of the paint to the wall.

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REFERENCES

1. Bentley,J and Turner,GRA (1997): *“Introduction to Paint Chemistry and Principles of Paint Technology”* Unik ISBN 0412723204.
2. Turner,GRA (1967): *“Introduction to Paint Chemistry”* Chapman Hall ltd, London
3. Hutton,M, Symon,C (1986): “The quantities of cadmium, lead,mercury and arsenic entering entering the UK environment from Human activities SCI Total Environ,57,129-150
4. Battarbee, R; Anderson, N; Appleby, P; Flower,RJ; Fritz,S; Haworth,E; Higgitt,S; Jones,V; Kreiser,A; Munro,MA; Naikanski,J; Okifield,F; Patrick,ST; Richardson,N; Rippey,B; Stevenson,AC;(1988): “Lake Acidification in the United Kingdom.” ENSIS, London.
5. Nriagu,JO; Pacyna,J(1988): “Quantitative Assessment of Worldwide Contamination of Air, Water and Soil by Trace metals, Nature 333 pp134-139.
6. Nriagu,JO(1989): A Global Assessment of Natural Sources of Atmospheric Trace Metals, Nature 338 pp 47-49.
7. Garbarino JR; Hayes,H; Roth,D; Antwelder,R; Brinton,TI; Taylor,H(1995): “Contaminants in the Mississippi River”, U.S. Geological Survey Circular 1133, Virginia, SU.S.A.
8. Hawkes,JS (1997): “Heavy Metals” J. Chem. Educ: 74(11),1374
9. Lenntah: Water Treatment and Air Purification (2004): “Water Treatment” Lenntech, Rotterdamseweg, Netherlands.
10. Farlex Incorporated(2005): Definition Environment, The Free Dictionary, Farlex Inc. Publishing, U.S.A.
11. Agency for Toxic Substances and Disease Registry(1980): ATSDR. Department of Health and Human Services Atlanta.

