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Research Article

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Quality Assessment of Akinbo River Sediment around Lafarge Cement Wapco, Ewekoro, Nigeria

Adeoye Abiodun Oluwatosin[1], Abdus-Salam Nasiru[1], Ademola Olamide Sodiq[1], Odebiyi and Oluwasegun Samuel[2]

[1]*Department of Chemistry, University of Ilorin, Ilorin, Nigeria.*

[2]*Department of Mechanical Engineering, Kampala International University Correspondingauthor:isnmcim0415@gmail.com Tel no: +2348056478597.*

[*]Corresponding author
Adeoye Abiodun Oluwatosin, 1Department of Chemistry, University of Ilorin, Ilorin, Nigeria, E-mail: isnmcim0415@gmail.com.

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Abstract
A study was conducted to assess the impact of industrial discharge on the quality of sediment obtained from River Akinbo around Lafarge Cement WAPCO, Ewekoro. Four locations were chosen along the water course (River Akinbo) to reflect a consideration of all industrial activities that are capable of changing the quality of sediments. Sediment samples were collected in three monthsbetween (October 2015 - June 2016) at the four sampling points. The physicochemical parameters determined were sediment pH, moisture content, sulphate (mg/l), nitrate (mg/l), phosphate (mg/l) and chloride (mg/L) using standard methods. Sequential Extraction Procedure (SEP) was used to determine the concentration of heavy metals to include (Pb, Cr, Cd, Mn, Ni, Fe) while XRF was used to determine the geo-chemical index of the sediment. Sediment pH is between slightly alkaline, the bioavailability of the metal followed a trend Ni > Cr >Mn> Cd>Pb> Fe with a little interchange at some sampling point. Percentage by weight trend for the XRF were in the order of major metals Al > Fe >Ca> K > Na and in the order of minor metals Mn> Cr > Zn. The concentration of cadmium, chromium and iron were above the permissible limit WHO and FEPA. The high concentration of heavy metals in sediment is most likely as a result of the amount of effluents (dust and waste water) discharged into the river from the factory. To prevent mass extinction of aquatic organisms due to anoxic conditions, proper regulations should be implemented to reduce the organic load the river receives.

Keywords: Geo-chemical index,heavy metals, industrial discharge, physicochemical parametersand sequential Extraction.

Introduction
Globally, man-made pollutants from combustion, construction, mining, agriculture and warfare are increasingly significant in the air. Air pollutants are responsible for vegetation injury and crop yield loses and are also causing increased concern (Bower *et al*., 2011) [1]. Cement factories were established in Nigeria in response to the increased wave of construction after independence and during the oil boom era of the seventies (Oyedele *et al*., 1990) [2]. It has been shown that cement factories constitute one of the worst pollutants in Nigeria today. The major products that Ewekoro Cement factory produces are cement and the raw materials used are limestone, gypsum, red alluvium, clay and water. At Ewekoro Cement factory, the major air pollutant is dust which results from cement processing activities. These activities include the burning of the raw material such as (limestone, gypsum, red alluvium) in the kiln and the burning of coal in the factory area. Cement dust contains heavy metals like chromium, nickel, cobalt, lead and mercury pollutants which are hazardous to the biotic environment with negative impact on vegetation, human health, animal health and ecosystem (Baby *et al*., 2008) [3]. Accumulated dust from cement factory leads to changes in sediment pH and heavy metal accumulated in sediment could affect both the organic and physicochemical characteristics of the sediment. Cement pH value is between slightly acidic to slightly alkaline (Mlitan *et al*., 2013) [4]. Some of the metals associated with cement dust, such as sodium, potassium, zinc, magnesium, manganese, chromium etc needed in major or minor quantities for the growth of soil microorganism could becomes toxic if their concentration exceeds a certain limit (Mlitan *et al*., 2013) [4]. The goal of this study is however, to assess the influence of anthropogenic activities (cement production) on the quality of sediment in river Akinbo. The study is needed due to recommendation from previous work and for the fact that many of the previous work in this area were focused on the effect of cement production on plant and animal, and also there is need for a continuous assessment of the impact of cement production in the study area. Hence, inquiry into the status of soil at the study area is of agricultural, health and economical importance.

Materials and Methods Study Area
The study site is River Akinbo at Akinbo Community in EwekoroOgun state. The river flows through the West African Portland Cement Company (WAPCO). The Ewekoro plant of WAPCO is located in Ewekoro local government area of Ogun State in the south west Nigeria. The local government area is bounded in the North by Abeokuta, in the East by Obafemi - Owode, in the West by Yewa South and in the South by Ado-Odo Ota.

Moreover, Ewekoro cement factory it is on a latitude 5° 50'N and longitude 3° 17 ' E. Also it is approximately 64 kmnorth of Lagos and 42 km south of Abeokuta. Majority of the inhabitants are farmers and the area is largely rural. Most of these farmers engaged in the planting of sugar cane, cassava, maize and vegetable. Cash crops such as cocoa, kolanut and oil palm are also cultivated. These farmers also engaged in the rearing of livestocks like small ruminants, poultry and pigs.

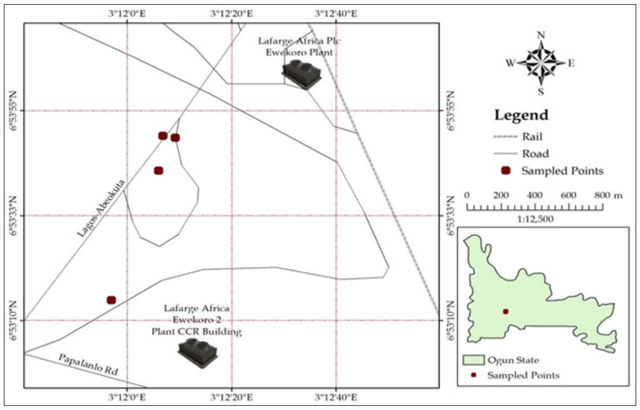

Figure 1: Location of the study area.

Table 1: Water Sampling points for the study

Sampling Code	Latitude	Longitude
A	6°53'49.4"N	3° 12'09.2"E
B	6°53'49.4"N	3° 12'08.2"E
C	6°53'42.4"N	3° 12'06.0"E
D	6°53'14.7"N	3° 11'57.0"E

a. Sediment Samples Collection and Parameters Analysed

Four representative sediments at distances (A, B, C & D) along the river were taken each for the months (October, 2015, February, 2016 and June, 2016) respectively. Sediments were collected using hang auger and stored in sealed polyethylene bag. Sediment samples for moisture content determination were stored in non-corrodible airtight containers between 3°C and 30°C and in an area that prevented direct sunlight contact. The sediment samples were oven dry at 105°C for a minimum period of 48 hrs to remove moisture and gently pulverized using mortar and pestle (Jonathan and Quirine, 2006)[5]. The crushed samples were sieved using a 2 mm sieve into coarse and fine fractions. The sample was stored in a pre-cleaned polyethylene bag. A 5- sequential extraction method was used to examine the mobility of heavy metals in sediments.

b. Procedure for sediment analysis

Physicochemical analysis of sediment was done in accordance to the following methods. Elemental determinations in sediment samples (Funtua II,1999) [6], Sequential Extraction Procedure (SEP)(Tessier *et al*., 1979) [7], determination of nitrate in sediment (Greweling and Peech, 1965) [8], determination of sulphate in sediment (Rabinder *et al*, 2011) [9], determination of phosphate in sediment (Samira *et al*., 2009) [10], chloride determination in sediment by Mohr method, moisture content determination in sediment (Hausenbuiller, 1975) [11] and determination of sediment pH (Davis and Freitas, 1970; Singh *et al*., 1999) [12,13].

c. Statistical Analysis

Descriptive statistics were computed for every physico-chemical parameter for each sediment sampling location. The parameters computed include mean, minimum and maximum values, and standard deviation. Finally, mean values of the parameters obtained form the various sampling locations were compared with the standard of WHO, FEPA and Denmark in order to identity the parameters that are above or below the permissible limit of the above standards.

Results and Discussion

From **Table 2**, the % moisture content ranged from 2.96 to 34.38. Highest moisture content was recorded at point D which is the furthest distance from the factory. The mean % moisture content is 15.08. This value is similar to those reported by (Stanley *et al*.,2014) [14]. From Table 2, highest pH recorded were predominant at point A, the point closest to the factory. A maximum value of 8.6 was recorded which shows that the sediment is slightly alkaline. Similar result was reported by (Stanley *et al*.,2014) [14]. Soil pH is considered to be significantly high due to the fact that the major raw material for cement production which is calcium carbonate is basic in nature when dissolved in water. From Table 2, Soil Chloride ranged from 22 to 48 mg/l, highest value was obtained at point A. This is because some of the raw materials used in the production of cement have chloride as one its component. The major raw material which is calcium carbonate could also have calcium chloride inherent in it. Highest value for phosphate is 32.62 mg/l and this is because marble used in the manufacture of cement contains phosphorus. The intrinsic high value of phosphate obtained might also have other origin apart from cement dust deposited in the area. Soil nitrate analysis showed no significant difference in values across the sampling point but highest value was recorded at point A. (Smyth and Montgomery, 1962) [15] as well as (Jeje and Ekanade, 1988) [16] observed that there could be no major differences between sediment, which are derived from chemically similar rocks under same condition of climate and vegetation. Sediment moisture content, pH, nitrate and phosphate values obtained are similar to values reported by (Salami *et al*., 2002) [17].

Table 2: Sediment physicochemical properties

Points	% Moisture Content	pH	Cl-(mg/l)	PO43 (mg/l)	NO3- (mg/l)	SO42- (mg/l)
A	9.08	8	37.99	26.06	1.34	4826.67
B	7.26	7.6	33.99	23.72	1.21	4458.67
C	5.26	7.9	31.99	22.03	0.23	4000
D	2.96	7.8	30.99	10.59	0.02	3818.67
A	12.84	7.6	39.99	15.89	0.04	8000
B	19.38	7.7	28.99	24.36	0.04	4434.67
C	19.52	7.7	23.99	16.1	0	2893.33
D	34.38	6.9	47.99	32.62	0.01	4320
A	12.5	8.6	35.99	31.14	0.086	6250.67
B	14.64	8.5	29.99	24.15	0.058	5861.33
C	28.48	8.6	34.99	24.79	0.04	5800
D	14.62	8.2	21.99	22.25	0.083	5554.67
Mean	15.08	7.925	33.24	22.808	0.26308	5018.223
STDEV	9.26	0.49	7.03	6.24	0.48	1354.74

Table 3: Percentage concentration level of bioavailable and non-bioavailable fractions of the sediment for the month of October, 2015, February, 2016 and June, 2016.

Point	Fraction	Fe (%)	Pb (%)	Cr (%)	Cd (%)	Mn (%)	Ni (%)
A	Bioavailable	1.72	24	44.37	24.8	33.15	64.17
	Non-bioavailable	98.28	76	55.63	75.2	66.84	35.83
B	Bioavailable	11.83	27.41	14.5	9.41	31.82	75.87
	Non-bioavailable	88.17	72.58	85.5	90.59	68.18	24.13
C	Bioavailable	0.63	58.41	18.13	13	39.29	82.82
	Non-bioavailable	99.37	41.59	81.86	87	60.71	17.18
D	Bioavailable	1.12	12.12	17.09	25.67	54.15	80.27
	Non-bioavailable	98.88	87.88	82.9	74.33	45.84	19.73

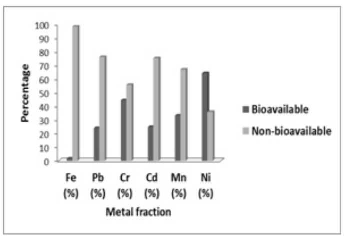

Fig 2. (a) Point A

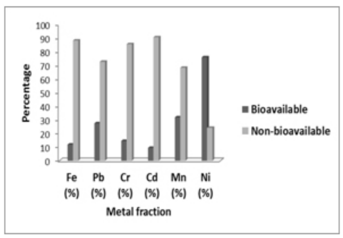

Fig 2. (b) Point B

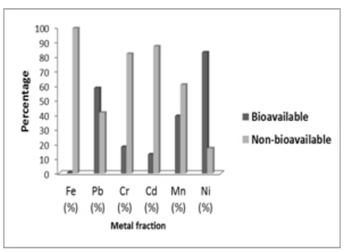

Fig 2. (c) Point C

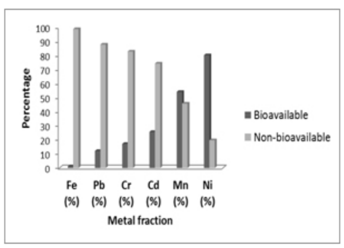

Fig 2. (d) Point D

Figure 2: (a-d) Graph of Percentage bioavailability and non-bioavailability graphs of the heavy metals in the sediments of the various points.

From **Table 3**, the most abundant bioavailable metal at point A on the river is Ni with 64.17 % followed Cr with 44.37 %, Mn with 33.15 %, Cd of 24.80 %, Pb of 24 % and Fe with the least value of 1.72 %. The trend is Ni > Cr >Mn> Cd>Pb> Fe.

From Table 3, the bioavailability of metals in point B follows the trend Ni >Mn>Pb> Cr > Fe > Cd. The result shows that nickel has the highest bioavailability and iron has the lowest bioavaliabilty. From Table 3, the bioavailability of metals in point C follows the trend Ni >Pb>Mn>Cr> Cd > Fe. From Table 3, the bioavailability of metals in point D follows the trend Ni >Mn>Cd> Cr >Pb>Fe. A similar report of environmental impact assessment of Obajana cement PLC on Obajana village reported that the level of exchangeable cations were low. The level of Al, Ni, Cr, Zn and Cu are within values considered normal for sediments. However, the level of Pb (82.8 -207 mg/kg) and Fe (1937.6- 20490.4 mg/kg) was high for a pristine area like Obajana (EIA of OCP/CPP project, 2004). A similar report was given by (Vinod *et al*.,2013) [18]. According to (Adekola *et al*., 2010)[19], he reported that under the anoxic conditions of the bottom of the lake, metals bound to the oxides of Mn or Fe are more thermodynamically unstable and are more easily leached than the metals bound to organics and sulfides. The combined conditions of pH and redox potential required for the release of metals bound to organics and sulfides fraction are not easily attainable. The bioavailable fraction represents the fraction that when the right pH and redox conditions are favourable, the metal ions will be soluble and can be taken up by aquatic plants or ingested by animals.

The total average concentration of Fe at points A, B, C and D are 11561.03 mg/kg, 10160.11 mg/kg, 7208.32mg/kg and 13361.61 mg/kg respectively (Table not shown). These values show that the soil is lateritic in nature and it exhibits a predominant of sand which enabled the soil to act as a seal to leachants of potential pollutants. Similar result was reported by (Ibitoye and Ajibade, 2008). Table 5 shows the list of WHO, FEPA and Denmark permissible limit of heavy metal in soil, no fixed value reported for Fe.Point B recorded the highest value for Pb to be 1.25 mg/kg. This value falls within the permissible limit of the standards of WHO, FEPA and Denmarkwhile point C recorded the highest value for chromium to be 30.33 mg/kg. No fixed value for the metal.Point B recorded the highest value for cadmium to be 45.61 mg/kg, which is far higher than the permissible limit of WHO, FEPA and Denmark.High concentration recorded for manganese and nickel are not good for plant growth since they are metals needed in trace quantity in both plant an animal.

Table 4: Result of elemental analysis of sediment using XRF

COMPOUND	A	B	C	D	AVERAGE
SiO_2	80.15	74.82	72.8	94.07	80.46
Al_2O_3	5.29	7.75	9.84	1.35	6.06
Fe_2O_3	1.71	2.59	5.51	2.69	3.13
CaO	4.62	4.37	1.47	0.46	2.73
MgO	0.23	0.29	0.93	0.04	0.37
SO_3	0.02	0.27	0.04	0.01	0.09
Na_2O	0.4	0.74	-0.07	-0.11	0.24
K_2O	0.86	1.35	0.39	0.06	0.67
TiO_2	0.46	0.44	0.66	0.15	0.43
P_2O_5	0.04	0.04	0.15	0.05	0.07
Mn_2O_3	0.02	0.02	0.02	0.01	0.02
Cr_2O_3	0.01	0.01	0.02	0.01	0.01
SrO	0.01	0.01	0	0	0.01
ZnO	0	0	0.01	0	0.003
Lossonignition	6.12	7.18	9.01	1.79	6.03

Percentage by weight trend for the XRF result is Si > Al > Fe >Ca> K> Ti> Na >Mn> Cr =Sr>ZnWhile SO3> P2O5.). In the order of major metals Al > Fe >Ca> K > Na while in the order of minor metals Mn> Cr > Zn. Similar trend was reported by (Leith and Mead's, 1915)[20] and in the mineralogical and geochemical studies of sandstone in Imobi by (Akintolaet al., 2012) [21].

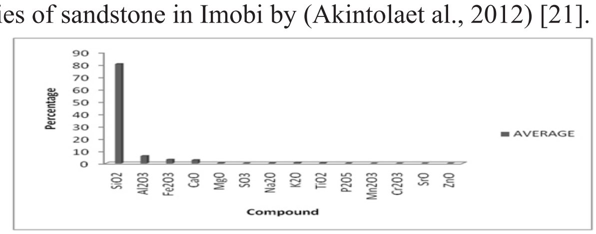

Figure 3: Graph of percentage by weight of each compound.

Table 5: Standard Threshold Limit Values for Heavy Metals in the Soil (ppm). Sources: (Ezigbo, 2011) [22]

Parameters	Stipulated Concentration Denmark (ppm)	Stipulated Concentration WHO(ppm)	Stipulated Concentration FEPA
Cadmium	5	10	03-Jun
Chromium	Not Fixed	Not Fixed	Not Fixed
Lead	40	70	250-500
Iron	Not Fixed	Not Fixed	Not Fixed
Zinc	500	200	300-600

WHO: World Health Organisation FEPA : Federal Environmental Protection Agency

Table 6: Geochemical index of heavy metal in (mg/kg)

Metal	A	B	C	D	Average	Bn	Igeo
Fe	59.36±0.04	51.37±0.13	44.06±0.03	35±0.23	47.45±7.00	280	2666.32
Pb	3.40±0.43	2.18±0.21	1.01±0.04	0.89±0.20	1.87±1.02	100	37.52
Cr	0.56±0.25	0.42±0.23	0.31±0.05	0.15±0.04	0.36±0.15	75	5.41
Cd	0.043± 0.002	0.040± 0.012	0.031± 0.001	0.019± 0.001	0.033± 0.01	1	0.01
Ni	0.86±0.04	0.79±0.01	0.44±0.02	0.34±0.04	0.61±0.22	40	4.89
Mn	0.62±0.02	0.54±0.04	0.33±0.01	0.19±0.05	0.42±0.17	0.97	0.08

Geoaccumulation index was computed according to Abdus-Salam *et al*.,(2013) [23], using the following equation; $I_{geo} = \log_2(Cn/1.5Bn)$. The result from Table 6, showed that the soil was extremely contaminated ($I_{geo} \geq 5$) with Fe, Pb and Cr of 2666.32I_{geo} , 37.52 I_{geo} and 5.41 I_{geo} respectively. The result from Table 6, showed that the soil has 0.01 I_{geo} and 0.08 I_{geo} for cadmium and manganese respectively, a concentration range reported to be between uncontaminated to moderately contaminated ($0 < I_{geo} \leq 1$). Nickel has 4.89 I_{geo} it falls between heavily to extremely contaminated ($4 < I_{geo} \leq 5$)[24].

Conclusion

Sequential extraction of metals from sediment based on the Tessier'sprocedure was used to evaluate soil contamination in the industrial area. The contents of Cr, Fe, Mn, Pb, Zn, Cd in the five fractions (exchangeable, bound to carbonates, bound to iron and manganese oxide, bound to organic matter and residual) were determined. This study has shown that soil composition and physicochemical characteristics strongly influence metal partitioning in soil. Elements are mainly bound to Fe/Mn oxides and are present in the exchangeable fraction in only small percentage. The high concentration of heavy metals in the sediment is most likely as a result of effluents (dust and waste water) discharged into the river from the factory. The sediment is polluted. Consequently, a periodical evaluation of the soil status is necessary in the area

Therefore this study recommends:

- Treatment of effluents and solid waste before final disposal to reduce contaminant load.
- Consistent inquiry in the status of the study area is suggested as necessary for sustainable resources exploitation at the study area;

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