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Quality and Self-purification Capacity Assessment of Sediments Burdened with Heavy Metals from Cement Industry: A Case Study of Onyi River of Nigeria

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Abstract Sediments of the Onyi river are subjected to pollution from cement industry and tend to accumulate heavy metals as it receives effluent from the industry. This study highlights the concentrations of toxic heavy metals, dissolved organic matter contents and particle size distribution of the sediments. These parameters were measured to determine the sediment quality with reference to some international sediment quality standards. In order to investigate the self-purifying capacity of the river, the upstream and downstream sediments were monitored monthly for a year and the waste assimilation capacity was calculated. The levels of Co, Cd, Cr, Cu, Ni, Pb and Zn in downstream sample were above the levels in upstream samples. Of these metals, Cd concentration exceeded the Australia and New Zealand sediment guidelines for the protection of aquatic life. The pollution load indexes of 1.26 (dry season) and 1.31(wet season) were above one (1.0), confirming that the sediments were deteriorated. The contamination factor (CF>1) for all the metals showed moderate degree of contamination. The Igeo values during the dry and wet season indicated moderately contamination of sediment. The sediments of Onyi river revealed purification capacities of 63.0 %(Co), 7.0 %(Cd), 15.7 %(Cr), 77.4 %(Ni), 5.6 %(Pb) and 18.8 %(Zn).

Keywords: *industrial effluents, heavy metals, Onyi River, pollution load index*

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1. Introduction

Sediments in water bodies have been regarded as the main receptacles for various pollutants owing to largely uncontrolled discharges during industrial processes [1,2]. Often times, discharges of untreated and partially treated industrial effluents results to sediment pollution [3]. Toxic metal contamination in the aquatic environment particularly sediment owing to the practice of discharging of industrial waste has been documented in the literature. For instance, coal mining activities in the Sydney basin of Australia were associated with significant environmental impacts of heavy metal contamination. Arsenic, nickel and zinc were the major sediment contaminants in downstream region, and their levels exceeded the Australian and New Zealand Environment and Conservation Council (ANZECC) guideline limits [4]. An urban river in Bangladesh had been associated with water quality problems because of huge amount of untreated industrial wastes that are discharged to it. A considerable amount of heavy metal enriched suspended solids was released from Jalpaiguri district of West Bengal in India to river Korotoa in Bangladesh. As a consequence, heavy metals in water and sediment of the river Korotoa became an issue due to its extreme pollution [5]. The pollution derived from the Magdalene river, most important river in Columbia, was a clear consequence of effluents from multiple sources along its course. One of such sources was industrial discharges and the metal toxicity of river Magdalena was assessed using Caenorhabditis elegans in sediments to show the pervasiveness of discharges. Cadmium and lead were primarily associated with sediment contamination of Magdalena river [6].

In the aquatic environment, sediment has been widely used as environmental indicators for the assessment of metal pollution in the natural water [7]. The performance of metals in the natural water is a function of sediment composition and the water chemistry. During transport heavy metals in substrate, suspended sediment and water may undergo many changes in their speciation [8]. The changes may be due to dissolution, precipitation, sorption and complexation concepts [9,10], which influence the metal behavior and bioavailability. The degree of contamination in a sediment will depend upon the deposition rate of the pollutant from a pollution source, and its subsequent rate of movement through the sediment column. Therefore, assessment of metal contamination of sediment during environmental monitoring should be carried out from the point source to downstream of the water body. The physicochemical properties including heavy metals of the sediment particles can provide a definitive measure of the pollution status of a water body. In rivers contaminated by effluents containing metals, the metals accumulate in sediments. The rivers have the inherent capacity to assimilate the metals and recover to their original quality. However, many rivers have become overburdened with pollutants having potential to distort their self-purification properties. This challenge particularly for developing countries makes Millennium Development Goals for environmental sustainability unrealistic [11].

Onyi river located in Obajana of Nigeria receives discharges of untreated wastes from a cement producing plant. Potentially toxic metals are released due to these discharges, and may adsorb on settling particles, which accumulate in sediments of the river. Previous studies on the pollution status of the Onyi river focused on the occurrence of heavy metal contamination in the water samples, in spite of intense urbanization and industrial activities within the community. The influx of cement effluent was reported to have contributed significant levels of toxic metals to the riverwater. [12]. There is dearth of information on sediment quality of the river in terms of scope and duration for pollution studies. There is no study dedicated thus far on the assessment of self-purification capacity of sediment of Onyi river Hence, it expedient to evaluate sediment quality of the river for toxic metal concentrations and its capacity to assimilate these contaminants in order to ascertain the potential impact of the effluent on the river ecosystem. Therefore, the objectives of this study was to assess the extent of contamination of Onyi river sediment and to establish seasonal variability in toxic metals accumulation in the sediments. The data obtained was subsequently employed to investigate the self-purification capacity of the river sediments.

2. Materials and Methods

2.1. Description of Sampling Area and Study Design

The Onyi river is located in Obajana community of Nigeria on latitude 7.916 °N and longitude 6.433 °E. The river receives discharges of effluents from a cement plant, owing to its proximity to the river (Figure 1). The cement plant in Obajana is the largest cement company in Africa. There are steep sided valleys around the river back and Fulani migrant settlements at downstream location. The river water is largely depended upon by the communities for irrigation bathing and drinking by their cattle. In mapping out some selected portions along the river and effluent channel, the whole length of the river was divided into four zones using discharge point as the basis for apportionment. The dam location, upstream zone, discharge point, and downstream location were the zones. The sampling points selected along these zones were: Four sampling points at the upstream location [U1(50m), U2(100m), U3(150m) and U4(200m)]; One sampling point at the discharge point [JP(0m)]; Three sampling points at 15m apart along the effluent channel [E1 to E3]; Five sampling points at varied distances downstream [D1(200m), D2(400m), D3(600m), D4(800m) and D5(1000m)].

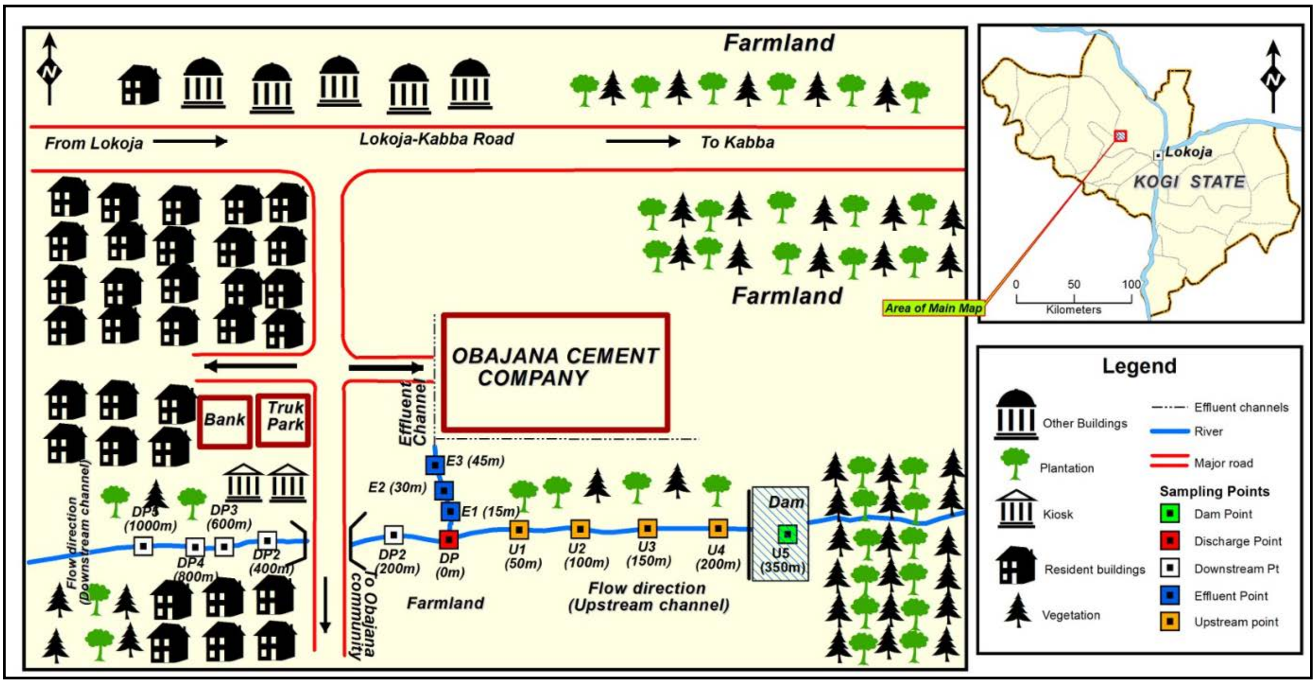

Figure 1. Selected area of Onyi river at Obajana showing sampling points [12]

2.2. Sampling and Chemical Analysis of Samples

Surface sediment samples were collected monthly for a year at each sampling point at a depth of 0-15cm. Samples collected were stored in clean polythene bags and air dried in the laboratory. Stones and dirt were removed by hand picking, and the samples were crushed using porcelain mortar and pestle. The sediments were sieved using a 2mm mesh sieve and stored in polythene bags for analysis. The laboratory analyses were carried out following the standard methods. A known weights of air-dried sediment samples were extracted with aqua regia, a mixture of HNO_3 and HCl (1:3, v/v). The extract was then filtered into a 25 ml volumetric flask and made up to the mark with distilled water. A sample blank was prepared following the same procedure. Analysis of a spiked sample was carried out to determined method efficiency. The digested sediment samples were analyzed for Cd, Co, Cr, Cu, Ni, Pb and Zn using a Bulk Scientific (model 200A) flame atomic absorption spectrophotometer.

Particle size analysis was determined using hydrometer method after digestion of organic matter with 30 % H_2O_2 and dispersion with 5 % sodium hexametaphosphate (Gee and Bauder 1986). Organic carbon was determined according to the Walkly and Black method. Organic matter was evaluated through organic carbon measurement whose content was multiplied by a factor (Nelson and Sommers 1996). In determining organic carbon, organic matter was initially oxidised with an excess amount of acid dichromate solution. This was followed by titration of excess dichromate with standard ferrous sulphate solution.

2.3. Data Treatment and Metal Accumulation Assessment

Analysis of variance (ANOVA) was performed on metal concentrations. The means of metal concentrations were compared using Turkeys Studentized Range and Waller-Ducan tests. The degree of heavy metal contamination and toxicity in sediment were assessed using different indexes.

2.4. Geoaccumulation Index (*Igeo*)

Geoaccumulation index prescribed by [13] as shown in Eq. (1) was employed to quantify the extent of toxic metal contamination associated with the sediment. In the equation, $[C_{metal}]_{sediment}$ is the concentration of metals investigated in surface sediment and $[C_{metal}]_{background}$ is the geochemical background concentration of the metal. The constant 1.5 is introduced as a background matrix correction factor due to lithogenic influences on the sediment.

$$\text{Igeo} = \log_2\left(\frac{[C_{metal}]_{sediment}}{1.5[C_{metal}]_{background}}\right) \quad (1)$$

Sediment is practically uncontaminated if Igeo≤0, uncontaminated to moderately contaminated if 0≤Igeo≤1, moderately contamisnated if 1≤Igeo≤2, moderately to heavily contaminated if 2≤Igeo≤3, heavily contaminated if 3≤Igeo≤4, heavily to extremely contaminated if 4≤Igeo≤5 and extremely contaminated if 5≤Igeo.

2.5. Sediment Pollution Index (SPI)

Sediment pollution index was introduced to assess sediment quality with respect to heavy metal concentration given proper consideration to the relative metal toxicity. This index is regarded as a linear sum of the metal enrichment factor with respect to the account of metal toxicity weights [14,15]. The metal toxicity weights are dependent on the relative toxicity of different metals. The SPI can be evaluated using the Eq. (2), where CF and W are the contamination factor and toxicity weight for each metal respectively. The contamination factor (CF) is defined as the ratio of each metal concentration in the downstream sediment to the background metal concentration in upstream sediment. A toxicity weight 1 was given to Zn, Co and Cr; 2 to Cu and Ni; 5 to Pb; and 300 to Cd [16].

$$\text{SPI} = \frac{\sum(CF_{metal} X W_{metal})}{\sum W_{metal}}. \quad (2)$$

The contamination factor (CF) is classified into four categories for monitoring the pollution of each metal over time [17]. The categories are low degree (CF<1), moderate degree (1≤CF≤3), considerable degree (3≤CF≤6) and very high degree (CF≤6) of contamination of sediment with each toxic metal.

Another useful tool in assessing the ecotoxicology of heavy metal contamination in the sediments is the sediment quality guidelines (SQGs). Sediment quality guidelines are indicative of concentration limits of contaminants in sediment below which adverse effects were not likely to occur and above which the effects were likely to occur [4]. Two SQGs identified by [18] are the effect range-low (ERLs) and the effect range-median (ERM). The National Oceanic and Atmosphere Administration (NOAA) named the indicative of concentrations below which adverse effects rarely occur as the “Effect Range-Low (ERL)”. Concentrations below the ERL values were rarely associated with adverse effects, and were rarely observed. The representative of concentrations above which the adverse effects frequently occur was named the “Effects Range-Median (ERM)” [19]. The ANZECC guidelines provides equation (3) to evaluate the threshold value that can trigger an adverse effect. The ERM values of 9.6, 370, 270, 51.6, 218, and 410 are respectively provided by NOAA for Cd, Cr, Cu, Ni, Pb and Zn [19].

$$\text{Effective range median mean quotient (ERMQ)} = \frac{\sum_{i=1}^{n} M_i / ERM_i}{n} \quad (3)$$

Where Mi is the concentration of metal i in sediment and ERMi earlier defined as the effect range-median is equally regarded as the lower Sediment Quality Guidelines Value (SQGV) for each metal. The SQGV is derived based on the adverse effect of the metal on inhabitants [19]. The derived ERMQ value is intended to provide basis for predicting sediment toxicity with which the sediment can constitute adverse effect on sediment-dwelling organisms [20]. The ERMQ value of <0.1, 0.11 to 0.5, 0.51 to 1.5 and >0.1 are respectively indicative of the sediment sample being 12, 30, 46, and 74 % toxic to sediment-dwelling organisms in aquatic environments.

3. Results and Discussion

3.1. Sediment Quality Characteristics

The pH values of upstream and downstream sediment ranged respectively from 7.3 to 8.3 and 7.7 to 8.4, indicating a weakly alkaline environment. Sediments at the discharge point showed a slightly higher pH value than that of downstream sediment by 3.7 % (Table 1). An increase in the pH of downstream sediment above the background pH value of sediment could be attributed to the effluent discharges from the cement producing plant.

The earth crust consists of 95 % igneous rocks and 5 % sedimentary rocks. Of the latter about 80 % are shales, 15 % sandstones and 5 % limestone. The basement complex, younger granites and sedimentary basins are the three litho-petrological components that form the geology of Nigeria [21]. The sedimentary basins containing sediment that is full of cretaceous to tertiary ages occur throughout Nigeria. The cement plants in the country are located near these sedimentary basins where limestone and marble deposits are found and exploited. Therefore, the deposition of the Onyi river sediment must have been facilitated by a number of inorganics, organic and biological processes. Most limestone are acted upon by aquatic organisms such as oysters and corals to make shell or bones. The shell and bones settle to the river bed and accumulate as sediment once the organisms die. Sediments specifically consist of mixture of clay, silt, sand, organic matter, and various minerals. This study revealed that the sediment particles of the Onyi river were predominantly fine-grained sand. The order of proportion of sediment texture in the river was sand >> clay > silt, which was similar to the trend observed in sediments of Alaro and Olosun rivers of Nigeria that received discharges of industrial effluents [22,23]. The sand compositions ranged from 93.3-96.4 % and 86.8-96.8 % respectively for upstream and downstream locations. The distributions of sediment grain size upstream were 1.0±0.9 %, 3.2±1.2 % and 95.3±1.5 % respectively for the proportion of silt, clay and sand. The corresponding proportions downstream were 3.8±2.9 %, 3.5±0.7 % and 92.8±2.6 % (Table 1). The order of proportion of sediment grains suggests that the settling velocity for sand grain is much greater than for silt and clay particles. In view of this order sand settles out of the river water faster than clay and silt when perturbed.

The total organic matter (TOM) contents for the upstream locations ranged from 0.4 % to 4.2 %, while the downstream locations ranged from 2.2 % to 8.5 %. The TOM contents of the downstream sediments were slightly higher than the levels in the upstream sediments. The TOM content (3.3±1.6 %) of sediment at the discharge point was higher than TOM proportion (2.3±1.1 %) in upstream sediment (Table 1). Organic matter, whose content is often determined indirectly as organic carbon, possesses high affinity for divalent metals together with precipitation of heavy metals in high pH medium (Davies, 1984). The sediments at the discharge point exhibited high concentrations of heavy metals when compared with the upstream sediments (Table 1). The input raw materials play significant role for the influx of certain levels of heavy metals into cement production and subsequently to Onyi river via effluent discharges. Upon the discharges of effluent into the Onyi river, the heavy metal concentrations in the downstream sediment were compared with the guideline quality values so as to adjudge the sediment of the river for contamination.

The concentrations of Co, Cd, Cr, Cu, Ni, Pb and Zn in the sediments collected at the discharge point varied considerably, ranging from 4.56 to 29.0, 0.75 to 5.0, 12.0 to 42.0, 1.1 to 14.5, 2.5 to 16.3, 24.4 to 52.0 and 27.0 to 79.0 µg/g. The average concentrations of the metals at the discharge point were above the background metal concentrations in the sediments (Table 1). Mean concentrations of 9.5±3.1, 3.0±0.2, 17.8±3.3, 6.2±1.4, 9.5±1.6, 33.9±3.7, and 34.0±4.8 µg/g was observed in the downstream sediments with considerable varying ranges of concentrations for Co, Cd, Cr, Ni, Pb and Zn respectively. Of these metals, cadmium concentration was observed to have exceeded the sediment quality guideline for the protection of aquatic life [24]. Lead concentration was about the guideline limits (Table 1). The range of lead concentrations (15.0-48.0 µg/g) in downstream sediments revealed that some downstream locations had higher lead concentrations than the allowable limit of 35.0 µg/g set by Canadian sediment quality guideline. As shown in Table 2, the average concentrations of heavy metals in sediment were in the order of Zn≈Pb>Cr>Co>Ni>Cu>Cd. The correlations among some pairs of metals as shown in Table 3 were significant, signifying that such metals shared a common source of pollution. Table 2 shows the comparison of metal concentrations in sediment of Onyi river with those from other countries. The comparison of lead concentration in downstream sediment with that of previous studies shows that the concentration was higher than the levels measured in other countries except Tigris river in Turkey [25]. The levels of metals in upstream sediments of Onyi river were lower than those reported for Tigris river in Turkey. In addition to natural source, the concentration of lead obtained in this study was probably contributed from anthropogenic source particularly discharges from the cement plant. The concentrations of metals observed, with the exception of copper, in sediments from the Onyi river were much higher than those of Chenab river in Pakistan (Table 2). The levels of metals reported for the sediment of Chenab river were 7.95 µg/g (Co), 1.67 µg/g (Cd), 18.1 µg/g (Pb) and 33.7 µg/g (Zn) [26]. Chromium (17.8±3.3 µg/g) and copper (6.2±1.4 µg/g) concentrations in the Onyi river sediment were low compared with those of Dakar coast in Senegal [16] and Cauvery river in India [27]. The river sediments of Cox and Nepean rivers were reported to be highly affected by increased concentrations of Co, Cr, Cu, Ni, Pb and Zn from industrial and coal mining activities in the Sydney basin of Australia [4]. Considering downstream areas of these rivers, the metals concentrations for in sediments of Coxs river were found to be substantially higher, while those of Nepean river were much lower than those of the Onyi river sediments.

Table 1. Sediments quality of Onyi River and comparison with the sediment quality standards

Parameter	Upstream		Discharge point		Downstream		Canada (Environment, 2002)	Australia & New Zealand (ANZECC, 2000)	CF	% RC
	Mean± SD	Range	Mean± SD	Range	Mean± SD	Range				
pH	7.7±0.3	7.3-8.3	8.4±0.4	7.6-9.0	8.1±0.2	7.7-8.4	-	-		
TOC (%)	1.3±0.6	0.2-2.4	1.9±1.0	0.8-3.7	2.3±1.1	1.2-4.9	-	-		
TOM (%)	2.3±1.1	0.4-4.2	3.3±1.6	1.3-6.3	4.0±1.8	2.2-8.5	-	-		
Sand (%)	95.3±1.5	93.3-96.4	96.7±0.8	95.2-97.4	92.8±2.6	86.8-96.8	-	-		
Clay (%)	3.2±1.2	1.5-5.6	2.7±0.7	1.5-4.2	3.5±0.7	2.0-4.5	-	-		
Silt (%)	1.0±0.9	0.1-3.0	0.64±0.52	0.04-1.8	3.8±2.9	0.4-10.2	-	-		
Co (µg/g)	8.4 ±1.4	4.7-16.0	15.6±8.1	4.56-29.0	9.5±3.1	3.47-14.0	-	-	1.1	63.0
Cd(µg/g)	2.8 ±0.1	0.38-4.0	3.4±1.1	0.75-5.0	3.0±0.2	1.7-11.0	0.6	1.5	1.1	7.0
Cr (µg/g)	18.3±3.1	9.3-46.0	20.8±7.7	12.0-42.0	17.8±3.3	13.0-29.0	37.3	-	0.9	15.7
Cu (µg/g)	3.9±1.0	1.7-11.0	7.6±4.1	1.1-14.5	6.2±1.4	0.33-15.0	35.7	65	1.6	79.9
Ni (µg/g)	7.2±1.9	3.88-23.0	9.6±4.8	2.5-16.3	9.5±1.6	3.75-16	-	-	0.9	77.4
Pb (µg/g)	31.7±1.6	13.0-50.0	34.5±8.2	24.4-52.0	33.9±3.7	15.0-48.0	35	50	1.1	5.6
Zn (µg/g)	25.3±1.8	19.0-44.0	44.4±15	27.0-79.0	34.0±4.8	20.0-58.0	123	200	1.3	18.8

CF= Contamination Factor; Recovery Capacity, RC= $(C_o-C_1)/C_o$ x 100 (C_o is the level of the parameter at the furthest-downstream sampling point and C_1 is the corresponding average level upstream where there is no pollution).

Table 2. Physicochemical characteristics of Onyi sediments with qualities of sediments from other rivers

	TOC (%)	Silt (%)	Sand (%)	Co (µg/g)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Ni (µg/g)	Pb (µg/g)	Zn (µg/g)	Reference
Onyi River (downstream)	2.3±1.1	3.8±2.9	92.8±2.6	9.5±3.1	3.0±0.2	17.8±3.3	6.2±1.4	9.5±1.6	33.9±3.7	34.0±4.8	This study
Chenab river, Pakistan				7.95	1.67	-	8.16	-	18.1	33.7	[26]
Tigris river, Turkey				516	7.9	-	2860	-	66	1061	[25]
Dakar coast, Senegal				1.85	0.36	61.9	24.8	3.58	16.0	2.1	[16]
Cauvery river, India				2.7-5.5	ND-0.1	13.9-34.4	5.6-30.4	6.4-17.4	1.7-12.4	5.4-53.6	[27]
Coxs river, Australia	3.4	14.6	85.0	180	-	10.0	17.0	210	24.0	650	[4]
Nepean river, Australia	0.96	2.3	99.7	5.0	-	7.0	5.0	5.0	6.0	20.0	[4]
Alaro river, Nigeria	3.2±0.5	4.6±1.4	89.8±3.3	9.6±1.6	0.47±0.03	5.78±0.47	7.36±0.61	7.74±0.97	7.76±0.80	19.5±4.6	[23]
Olosun river, Nigeria	3.2±0.8	4.2±2.2	92.6±3.6	4.4±1.3	0.35±0.04	16.1±5.2	9.8±1.7	10.1±0.2	5.6±2.5	112±10	[22]

Table 3. Pearson correlation coefficients for the pairs of metals in sediment of Onyi River

	Co	Cd	Cr	Cu	Ni	Pb	Zn
Co	1						
Cd	0.540*	1					
Cr	0.684**	0.136	1				
Cu	0.494	0.230	0.625*	1			
Ni	0.535*	0.127	0.904**	0.739**	1		
Pb	0.651*	0.616*	0.416	0.476	0.385	1	
Zn	0.640*	0.792**	0.143	0.296	0.104	0.704**	1

*correlation is significant at the 0.05 level. **correlation is significant at the 0.01 level.

3.2. Assessment of Metal Pollution of Sediment

The pollution load indexes (PLI) of heavy metals in sediments obtained for dry and wet seasons are shown in Figure 2. The figure revealed that PLI values ranged from 1.01 to 1.50 for dry season and 1.01 to 1.96 for wet season. The annual PLI of 1.26 and 1.31 for dry and wet seasons respectively confirmed that the sediment of Onyi river was polluted. The contamination factors (CF) of Zn, Cu, Co, Pb and Cd as revealed in Figure 3 were major contributors to high PLI values obtained. The contamination factors for all the metals showed moderate degree of contamination (CF>1) particularly for wet season. Overall, the annual CF for all metals followed the decreasing order of Cu>Co>Cd≈Zn>Ni>Pb>Cr (Figure 3).

The average geo-accumulation index (I_{geo}) values for heavy metals are illustrated by Figure 4. The ranges of I_{geo} for Co, Cd, Cr, Cu, Ni, Pb and Zn were 0.71-2.45, 0.77-4.87, 0.43-2.04, 0.11-3.57, 0.86-2.57, 0.62-1.38 and 0.98-1.81, respectively (Figure 4). The decreasing order of I_{geo} values for metals was Cu>Co>Cd>Zn>Ni>Pb>Cr, similar to that of the contamination factors for all metals.

The I_{geo} values for all metals ($1 \leq I_{geo} \leq 1$) for dry and wet seasons indicate moderately contamination of sediment. Among the metals, copper has the highest geoaccumulation index (Figure 5) due to the highest concentration in downstream sediments than the level in background sample.

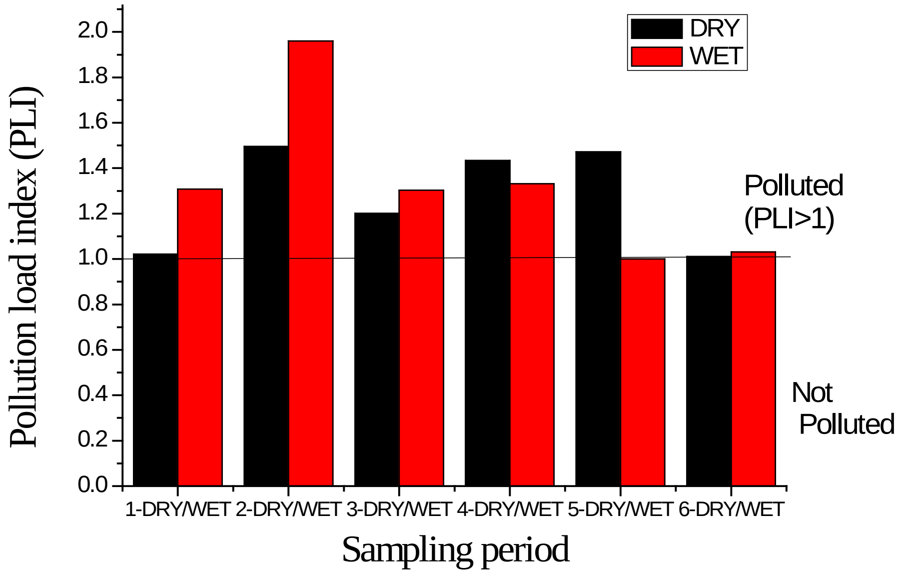

Figure 2. Pollution load index values of heavy metals in sediments for dry and wet seasons

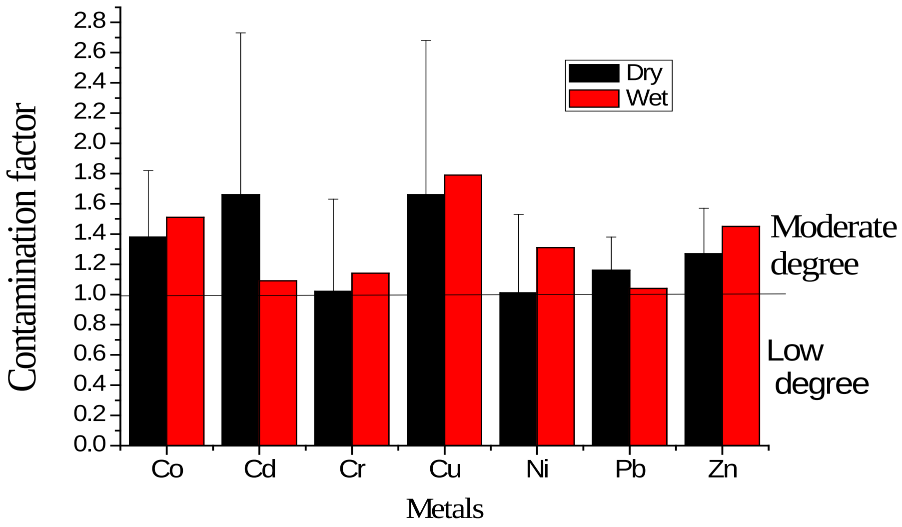

Figure 3. Contamination factors of heavy metals in sediments for dry and wet seasons

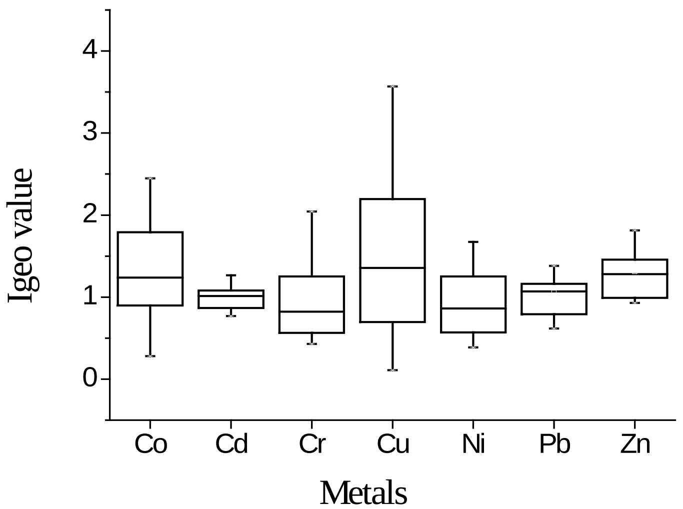

Figure 4. Box chart illustrating average values of geoaccumulation index of heavy metals in sediments

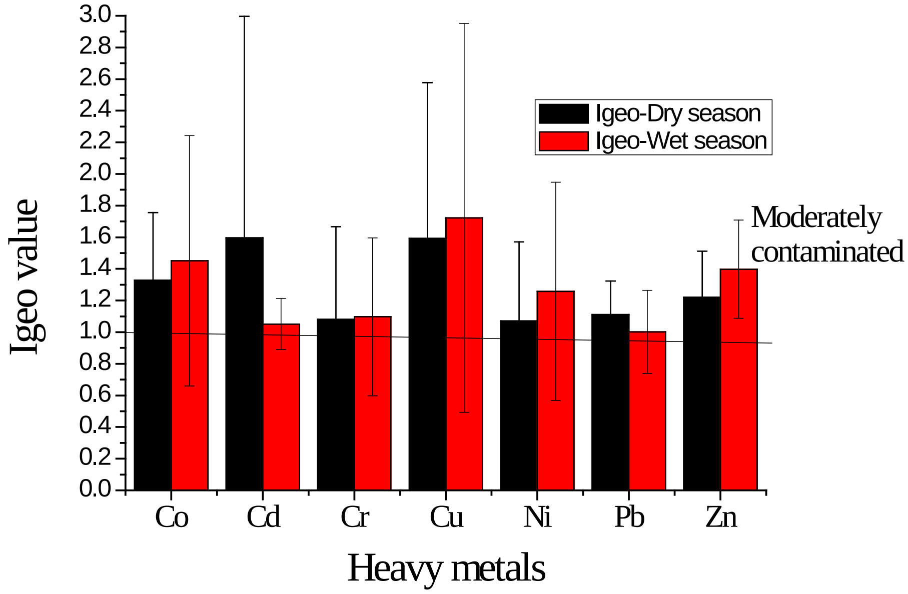

Figure 5. Seasonal variations of geoaccumulation index of heavy metals in sediments

3.3. Pollution Potential Assessment Using Sediment Quality Guidelines

The concentrations of Cd, Cr, Cu, Ni, Pb and Zn in downstream sediments were 3.0±0.2, 17.8±3.3, 6.2±1.4, 9.5±1.6, 33.9±3.7 and 34.0±4.8 µg/g, respectively (Table 2). With ERM values of 9.6, 370, 270, 51.6, 218 and 410 correspondingly assigned to each metal [28], the result of the evaluation of ERMO quotient as indicated in Eq. 3 is 0.344. This is an indication that the sediments have 30% predictive ability to be toxic to sediment-dwelling organisms in Onyi river.

3.4. Assessment of Self-purification of Sediment

Accumulation of heavy metals in the bottom river sediments is germane in waste assimilation of aquatic environment. Heavy metal polluted rivers possess capacity to rid themselves some levels of pollution by means of natural and certain processes. The natural process by which a river system assimilates anthropogenic contaminants to maintain its pristine condition despite the introduction of contaminants is referred to as self-purification of the river, and it often results in remarkable decrease in contaminants concentrations. Sediment, being part of the natural aquatic environment, plays a pivotal role in removing contaminants such as heavy metals from water. This could be achieved through a variety of physical, chemical and biological processes. Heavy metals do not degrade in water but are found primarily in sediments by deposition [29]. The average metals concentrations in the Onyi river downstream were found to be less compared to the levels at the discharge point. The Onyi river revealed purification capacities of 63.0, 7.0, 15.7, 79.9, 77.4, 5.6, 18.8 % for Co, Cd, Cr, Cu, Ni, Pb and Zn respectively by the decrease in metals concentrations in the bottom sediments (Table 1). The reduction in metals concentrations downstream could have resulted from the suspension of sediments, which enabled the metals redistribute themselves among different components of aquatic ecosystems. The suspension was attributed to higher flow disturbance in the Onyi river caused by inflow of industrial effluent to the river. The mobility of heavy metals within the aquatic system is usually dependent on their forms of occurrence in the solid substrates and the pore solution of the bottom sediment. Owing to industrial pollution, sediments of Reconquista river basin of Argentina were reported to accumulate heavy metals. The mobility of metals that occurred within the sediments could be attributed to biocatalysed redox reaction of sulphur compounds that occurred within the sediment [30]. Sulphur in cement kiln is derived from pyrite and marcasite (FeS_2) and there is likelihood that sediments of Onyi river contain reduced sulphur species traceable to local reducing conditions in the kiln or lack of intimate contact between the flue gases and kiln feed [31]. The supposed reduced sulphides could be oxidized by sulphide-oxidizing bacteria such as *Acidithiobacillus ferroxidants* and *Acidithiobacillus thiooxidants*. Following the oxidation process, heavy metals from contaminated sediments could be released into surface water by re-suspension. This process which tend to maintain heavy metals in a low available state illustrates self-purification capacity of sediments [30]. The release of heavy metals from pore solution is one of the major ways of exchange between the bottom sediments and water [32].

4. Conclusion

The downstream sediments of the Onyi river were enriched with Co, Cd, Cr, Cu, Ni, Pb and Zn from cement producing effluent discharges. This enrichment was supported by the pollution load and geo-accumulation indexes, which revealed that the sediments were considerably polluted particularly with Cd. The health challenge that the release of these potentially toxic metals pose to aquatic ecosystem is a concern in developing country like Nigeria. Therefore, future research should address toxicological impact of Cd in particular on available aquatic organisms. The exchangeable metal fraction of the sediment, which needs to be known for the evaluation of availability is equally required for quantification in the future research.

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