

Spatial Variability of Metals in Surface Water and Sediment in the Kolo Creek and Geochemical Factors That Influence Their Interactions

By

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Abstract

Heavy metals have been used as indicator of pollution because of their high toxicity to human and aquatic life. They are commonly known as environmental pollutants particularly since their occurrence not only originate from natural factors such as the weathering of soils and rocks, but also anthropogenic input such as industrial waste, agricultural and mining activities. Metal Ions are inorganic elements that are either essential nutrient to living organisms at micro (trace) levels or very toxic and poisonous in relatively higher concentration. They are biologically non degradable and easily assimilated and bio-accumulated in the protoplasm of aquatic organisms. In the Niger Delta region, research projects have been carried out on some of the important Rivers, Creeks, Streams and lakes, and it has been observed that most of the water quality is gradually deteriorating due to unmanned crude oil explorations and exploitations, industrial discharge. This study therefore assessed the spatial variability of heavy metals concentration of the surface water and sediment of the Kolo Creek area of Nigeria by means of Geo-Accumulation Index (Lgeo) and Pollution Load Index (PLI). Kolo Creek is an area that is exposed to oil exploration activities, water disposal and receives effluents from industrial activities including artisanal refineries and a gas flaring station yet serving as a major water source for drinking, bathing, fishing, washing and recreation. The study reveals that Iron concentrations in this study were above the recommended permissible limits of 0.3mg/L by the Standard Organisation of Nigeria (2007) and WHO (2011). This is an indication of highly contaminated surface water to extremely contaminated sediment in the Kolo Creek area. This study can be considered the first attempt to evaluate the heavy metals pollution in sediments and surface water of Kolo Creek using Geo-Accumulation Index (Lgeos) and Pollution Load Index (PLI) to determine toxicity levels.

Key Words: Kolo Creek; Geo-accumulation index; heavy metals; environmental pollutants pollution load index;

1.0 Introduction

Metal Ions like Copper (Cu), Zinc (Zn), Cobalt (Co), Manganese (Mn), Nickel (Ni) and Iron are inorganic elements that are either essential nutrient to living organisms at micro (trace) levels or very toxic and poisonous in relatively higher concentration. They are biologically

non degradable and easily assimilated and bio-accumulated in the protoplasm of aquatic organisms. However, metals like Lead (Pb); Cadmium (Cd); Mercury (Hg); Chromium (Cr) and Arsenic (As) are very toxic to living organism even at low concentrations and are listed as global contaminants and most hazardous inorganic of the EPA Hazardous Substance Priority list which have detrimental effect on the health of people and ecology (UNEP, 2008).

Heavy metals (elements with an atomic density greater than 6g/cm^3) have been used as indicator of pollution because of their high toxicity to human and aquatic life (Olele, Falodun & Wangboji, 2013). They are not regarded as natural trace components of the aquatic environment but also commonly known as environmental pollutants particularly the receiving inputs from anthropogenic activities. However, their occurrence not only originate from natural factors such as the weathering of soils and rocks, but also anthropogenic input such as industrial waste, agricultural and mining activities (Angaye & Mieiyepe, 2015; Budu, Ononugbo & Avwiri (2018).

Heavy metals discharged either through direct discharge or surface run-offs into the environment rapidly associate with particulates and ultimately settles in bottom sediments of water bodies (Inengite, Oforka & Osuji, 2010; Izah, Chakrabarty & Srivastav, 2016). In their discharged into the environment, they tend to distribute between the aqueous phase and the suspended sediment during their transportation and assimilate in sediment with the organic matter, Fe/Mn oxides, Sulphide and clay thus forming several reactive components, which are harmful to their environment (Wan, Ahmed & Mohamed, 2012); hence regarding sediment as the potential reservoir for metals that plays an important role in absorption of dissolved heavy metals. Heavy metals also undergo numerous changes in their specification due to dissolution, precipitation, sorption and complications phenomena when discharged into water bodies (Moore & Behnam, 2011; Seiyaboh, Inyang & Izah, 2016).

According to Inengite, Oforka and Osuji (2010), the accumulation of metals from the overlying water to the sediment depends on a number of external environmental factors such as pH, electrical conductivity and the available surface area for adsorption caused by the variation in grain size distribution. Like sand, the particulate size of sediment is in different categories including loose sand, clay, silt and other soil particles found in water (Ogamba, Ebere & Izah, 2017). Surface water has sediment and play a vital role for the aquatic ecosystem particularly the benthic organisms like shelled fish reside in the sediment especially in the brackish and marine ecosystem (Aghoghovwia, Oyelese & Ohimain, 2015; Seiyaboh, Inyang & Izah, 2016; Seiyaboh, Izah & Oweibi 2017b). As sediment affects water quality irrespective of the type of sediment (Suspended and deposited), so also change in water quality arising from anthropogenic activities such as water transportation, dredging, waste deposition and natural effects resulting from runoff following precipitation also affect the sediment quality, hence the need for continuous assessment into the presence of toxic

metals due to their environmental persistence, bioavailability and toxicity to aquatic organisms and the ability to be incorporated into food chains.

In the Niger Delta region, research projects have been carried out on some of the important Rivers, Creeks, Streams and lakes, and it has been observed that most of the water quality is gradually deteriorating due to unmanned crude oil explorations and exploitations, discharge of industrial and domestic waste, and urbanisation; posing high risk to water resources used.

This study therefore assessed the spatial variability of heavy metals concentration of the surface water and sediment of the Kolo Creek by means of Geo-accumulation Index (L_{geo}) and Pollution Load Index (PLI); an area that is exposed to oil exploration activities, water disposal and receives effluents from industrial activities including makeshift refinery and a gas flaring station yet serving as a major water source for drinking, bathing, fishing, washing and recreation. In this study, the following heavy metals were considered: Pb, Fe, Cd, Mn, Hg, Cu and Ni. Ni and Cd were considered based on the fact that they are the substantial metals in crude oil and gross indices of the biodegraded oil; Pb, Fe, Hg and Cu were considered mainly due to their association in piping system and corrosion inhibition as well as an anti-knocking agent in automobile engines. This study can be considered the first attempt to evaluate the heavy metals pollution in sediments and surface water of Kolo Creek using Geo-accumulation Index (L_{geo}) and Pollution Load Index (PLI) to determine toxicity levels.

2. Materials and Methods

2.1 Study Area

Kolo Creek lies within latitude $04^{\circ}24'26.893''$ and $04^{\circ}59'05.094''$ North and longitude $06^{\circ}14'59.190''$ and $06^{\circ}20'47.701''$ East. The full length of the Kolo Creek is 85km, covering a total area of about 1,625 square kilometers (NEDECO, 1961; Eli, 2012). Kolo Creek is located at the central part of the Niger Delta and transverses about twenty-one (21) communities including Okarki; Otegue II, Ibelebiri, Oruma/Yibama, Otuasega, Imiringi, Emeyal 1 and 2, Kolo 1, 2 and 3, Otuegila, Otakeme, Otuabagi, Ewoma/Otuabi, Otuogidi, Ogbia Town, Otuabo/Abobiri, Ekpenkiri, Akakumama, and Bukiri (Eli, 2012; Gobo, Amangabara and Etiga, 2013) (Fig. 2.1).

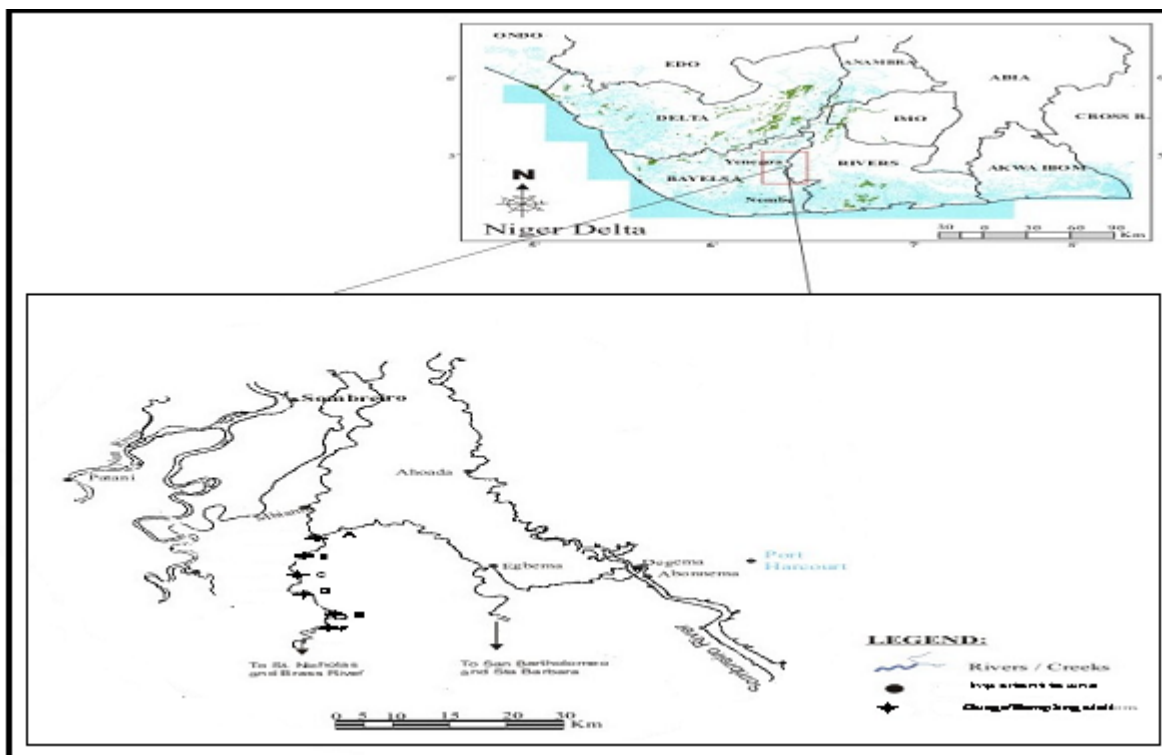


Fig 2.1 The Kolo Creek: Niger Delta
Source: Eli, 2012

2.2 Water and Sediment Sampling and Preservation

Water samples and sediment samples were collected monthly between March - July, 2018. Plastic containers for metals analysis were washed with hot soapy water and rinse (Aghoghovwia, Oyelese & Ohimain, 2015). They were soaked for 4 hours in HNO_3 to prevent adsorption of metals into walls of the bottle, then rinsed thoroughly with de-ionised water. The bottles were air-dried and stored until time for sample collection. Water samples along the Kolo Creek within the eight (8) purposive sampling sites (A-H) (table 2.1) were collected in triplicate in 2litre (HDPE) capacity plastic bottles with screw caps at 35cm depth, labelled and stored in 4°C ice cool box before taken to the Chemistry Laboratory of the Federal University, Otuoke, Bayelsa State for analysis. Sediment Samples were collected from the waterbed with aid of stainless steel Eckman Grab into plastic bag (Udoidiong, Oribhabor, Munam & Bernard, 2013). The top 30.0cm of each grab sample were stored in clean dark polyether bag for metal analysis. The samples were transferred into 4°C icebox to halt biological and chemical transformation in the sample. They were air-dried at room temperature and preserved for further analysis (Seiyaboh, Izah & Oweibi, 2017).

Table 1 Sampled Station, Absolute Location and Activities

Stations	Location	Activities
A (Okarki)	4 ⁰ 59 ^I 05.094 ^{II} 6 ⁰ 25 ^I 47.701 ^{II}	Source of Kolo Creek
B (Ibelebiri)	4 ⁰ 57 ^I 47.232 ^{II} 6 ⁰ 24 ^I 51.732 ^{II}	Activities like makeshift refineries
C (Otuasega)	4 ⁰ 54 ^I 55.993 ^{II} 6 ⁰ 23 ^I 12.326 ^{II}	3 km away from the makeshift refinery with a rusted dilapidated iron bridge.
D (Kolo Creek Flow Station)	4 ⁰ 53 ^I 42.259 ^{II} 6 ⁰ 22 ^I 43.123 ^{II}	SPDC base and a gas flaring station
E (Imiringi)	4 ⁰ 51 ^I 08.529 ^{II} 6 ⁰ 22 ^I 14.725 ^{II}	Major constructions activities such as bridge constructions
F (Kolo Town)	4 ⁰ 48 ^I 18.612 ^{II} 6 ⁰ 22 ^I 35.954 ^{II}	Mini industrial activities with manual sand quarries
G (Otuabagi)	4 ⁰ 42 ^{II} 35.736 ^{II} 6 ⁰ 21 ^I 51.786 ^{II}	An area with crude oil activities
H (Ogbia Town)	4 ⁰ 41 ^I 26.893 ^{II} 6 ⁰ 18 ^I 59.190 ^{II}	Confluence between the Kolo Creek and Otuoke Creek with a tidal influences

Source: Fieldwork, 2017

2.3 Analysis Technique

Water samples collected from respective locations were not subjected to further treatment. They were aspirated directly in the flames of the Varian Tectron B Atomic Adsorption Spectrophotometer (AAS) (Ehi-Eromosele & Okieki, 2012; Ogamba, Ebere & Izah, 2017). Sediment samples were air dried at 40⁰C after handpicked stick stems and other dirt's; grounded to powder. The powder was passed through 2mm diameter sieve to remove ungrounded materials, after which 2.5g of sediment was taken and 10ml of nitric per Chloric acid mixture in a ratio of 2:1 by volume was added before digestion. It was further heated at 150⁰C until a clear solution was obtained, distilled with 10ml water to digest samples thus preventing formation of complex compound before filtration. The filtrates were diluted with distilled water to 50ml and the samples taken in bottle and stored in refrigerator pending analysis. The Perkin Elmer Analyst 3100 (model) Atomic Absorption Spectrophotometer was used for the analysis of the heavy metals.

2.4 Statistical Analysis

The Geo-accumulation index and pollution load index was further applied on the samples to determine the level of metal concentration in sediment and surface water of the Kolo Creek.

Geo-Accumulation Index (Lgeo): The Lgeo has been widely utilized as a measure of pollution in freshwater sediment while the pollution load index (PLI) represents the number of times by which the heavy metal concentrations in the sediment exceeds the background concentration, given a summative indication of the overall level of heavy metal toxicity in a particular sample (Rabee, Al-Fatlawy; Abdown & Nameer, 2011). The geo-accumulation index (Lgeo) was introduced by Muller in 1979 for determining the extent of metal accumulation in sediments (Muller, 1979). However, in this study the geo-accumulation index and Pollution Load Index was employed to assess the extent of metals concentrations (toxicity) in sediments and surface water of the Kolo Creek in bid to observed the concentration differences following the equation below.

$$\text{Pollution Load Index (PLI)} = \frac{\sqrt[n]{cf_1 \times cf_2 \times cf_3 \dots \dots \dots cf_n}}{1/n} \quad \text{Equ. 1}$$

where: CF= The Contamination factor (Metal concentration / Background values
n = Number of metals study

$$L_{geo} = \log_2 (C_n / 1.5B_n) \quad \text{Equ. 2}$$

where: Cn is the measured concentration of heavy metal in the Kolo Creek, Bn is the Geochemical background value in average shale of element N as presented in table 2 below which is used to quantify the extent and degree of metal pollution (Ong, Menier, Shazili & Kamaruzzaman, 2013). The factor 1.5 is used for the possible variations of the background data due to lithological variation. The obtained value is read on a legend table as follows.

Table 2 Background values of some common heavy metals

Parameters	Fe	Pb	Cd	Mn	HgS	Cu	Ni	Co	Cr	Ti	Al
Background Value	3.59	20	0.3	720	13	32	49	20	97	0.38	6.93

Source: Tomison, Wilson; Haris and Jeffrey (1980)

Table 3 Geo-accumulation (Lgeo) Index Legend Table

Lgeo	Lgeo Class	Explanations
<0	0	Uncontaminated
0-1	1	Uncontaminated to Moderately contaminated
1-2	2	Moderately contaminated
2-3	3	Moderately to strongly contaminated
3-4	4	Strongly contaminated
4-5	5	Strongly to extremely contaminate
>5	6	Extremely contaminated

Source: Muller (1979)

3. Results and Discussions

Table 4 Mean concentrations of Heavy metals in surface water of the Kolo Creek

Element s	A	B	C	D	E	F	G	H	Mean	SON
Fe	68.9	65.2 4	67.8 2	62.1 1	57.4 2	54.9 1	51.3 5	48.3 2	59.52	0.3mg/L
Pb	0.00 1	0.00 9	0.00 2	0.00 6	0.00 4	0.00 2	0.00 4	0.00 1	0.003 6	0.01mg/L
Cd	0.00 0	0.00 2	0.00 1	0.00 2	0.00 1	0.00 0	0.00 2	0.00 1	0.001	0.003mg/ L
Mn	0.00 1	0.09 8	0.06 5	0.06 9	0.04 5	0.02 5	0.05 7	0.04 4	0.051	0.2mg/L
Hg	0.00 0	0.00 1	0.00 0	0.00 1	0.00 1	0.00 0	0.00 1	0.00 0	0.001	0.001mg/ L
Cu	0.49 8	1.39 5	1.06 2	1.24 5	1.14 9	0.65 8	1.14 8	0.94 5	1.013	2.0mg/L
Ni	0.00 4	0.01 4	0.01 2	0.01 3	0.01 2	0.00 5	0.01 2	0.01 0	0.010	0.02mg/L

Source: Fieldwork, 2017

Table 5 Mean Heavy Metals concentration in sediment of the Kolo Creek

Element s	A	B	C	D	E	F	G	H	Mean	WHO
Fe	120.8	153.3	132.1	163.4	150.3	122.1	148.4	119.1	138.67	0.3mg/L
Pb	0.004	0.014	0.005	0.009	0.008	0.004	0.006	0.003	0.007	0.005mg/L
Cd	0.001	0.003	0.002	0.003	0.002	0.001	0.003	0.002	0.002	0.003mg/L
Mn	0.025	0.159	0.145	0.167	0.143	0.089	0.152	0.114	0.124	0.1mg/L
Hg	0.001	0.001	0.001	0.002	0.002	0.001	0.001	0.001	0.001	0.000mg/L
Cu	0.975	1.025	1.043	1.868	1.524	1.098	1.249	1.139	1.240	2.0mg/L
Ni	0.012	0.024	0.015	0.022	0.021	0.014	0.022	0.021	0.019	0.000mg/L

Source: Fieldwork, 2017

Iron concentrations in this study were above the recommended permissible limits of 0.3mg/L by the Standard Organisation of Nigeria (2007) and WHO (2011). The concentration difference between the surface water concentration to sediment concentrations in iron contents accounted for about 40% in this study. The concentration of lead was below recommended permissible limits by SON and WHO, although, its highest concentration were at station B and D which is associated with fossil burning from the flow stations and makeshift refinery including fumes from vehicular traffic that got flushed into the Kolo Creek through runoff in addition to the atmospheric precipitation at this point; similar with the report of Nabizarde, Mahvi, Mardan, Yunesian, (2015). Similarly, the concentration of Cadmium (Cd) was highest at station B and D due to filling operation and bridge construction in this location at the time of sampling. Been that Cd is used in electric batteries and in various electronic components and inorganic fertilizers produced from phosphate ores; it constitutes a major source of diffuse cadmium pollution through floodplain agriculture in the Kolo Creek. The concentration difference between surface water and sediment was about 33%. According to Aghoghovwia, Oyelese and Ohimain (2015), these activities can help release pore solution (rich in heavy metals) in the sediment. Mn also was below permissible limits by SON (2007) and WHO (2011). The concentration difference in surface to sediment was about 42%. Cu and NI were also below permissible limits by SON (2007) and WHO (2011), and the concentration differences of Cu in surface water and sediment account for 10% hile that of Ni accounted for 31%.

Table 6. Pollution Load Index for Surface water and Sediment of the Kolo Creek

Surface Water	Sediment
0.664	1.501

Source: Fieldwork, 2017

Table 6 represents the pollution load index in surface water and sediment of the Kolo Creek, and only 0.664 times in surface water as against 1.501 times toxicity level by which the heavy metal concentrations exceeds the background concentration in the Kolo Creek.

Table 7. Geo-accumulation Index (Lgeo) for Surface Water and Sediment of the Kolo Creek

parameters	Lgeo Values for Surface water	Lgeo Value for Sediment
Iron (Fe)	3.327	7.751
Lead (Pb)	0.0009	0.0145
Cadmium (Cd)	0.043	0.061
Manganese (Mn)	0.000028	0.00027
Mercury (Hg)	0.000026	0.0002
Copper (Cu)	0.0007	0.0048
Nickel (Ni)	0.0028	0.011

Source: Fieldwork, 2018

All the heavy metals had geo-accumulation indices below zero which indicates no pollution except Fe which had geo-accumulation index in the range 3.327 in surface water and 7.751 in sediment. This indicates strongly contaminated surface water to extremely contaminated for sediment of the Kolo Creek. The concentration is more in sediment than in surface water because sediments acts as the ultimate reservoir for the numerous potential chemical and biological contaminants. The highest is in station D. According to Galadima and Garba (2012) iron is known as the second most abundant metals in the earth's crust which has reflected on the result in this study. Although, the metal construction, dilapidated iron bridge and the bride constructions activities across the creek is a suspect contributor of Fe to the creek at this point (Plate 1 and 2), also solid municipal waste as scraped metals are also freely dumped in the Kolo Creek; results similar with formal studies by Inegite, Oforka and Osuji (2010) but far below the report of Aghoghovwia, and Agatari (2012). Comparisons of the heavy metals concentrations and limits according to WHO (2011) (Table 4&5) showed that the heavy metals concentrations where far below the WHO limits except for Fe. The iron concentrations as observed in this study is high enough (above the maximum tolerable daily intake of 0.8kg/day) to caused *Hemosiderosis* (Genetic Disorder), *Hemachromatosis* skin pigmentation and Hepatic Disorders on the health user of water from the Kolo Creek. This indicates that

there is virtually no imminent danger. However, bioaccumulation in the aquatic organisms could be a concern, since the Kolo Creek serve as a means of fishing activities.



Plate1. Rusty and Dilapidated Iron Bridge in the Kolo Creek.



Plate 2. Ongoing Bridge Constructions in the Kolo Creek

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