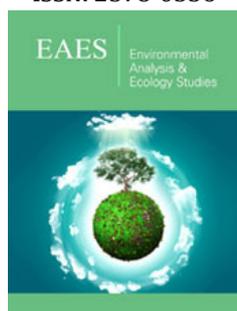


Assessment of Heavy Metal Pollution in Sediments of Silver River, Southern Ijaw, Bayelsa State, Nigeria

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Abstract

The concentrations of heavy metals in sediment of Silver River were determined using atomic absorption spectrophotometer. The result indicated the presence of heavy metals at different concentrations. The concentrations of the heavy metals showed that Fe>Mn>Zn>Cu>Ni>Cr>Pb>Cd>Hg. The mean concentrations of the measured metals in mg/Kg were Cd (2.638±0.900), Pb (6.004±1.368), Cr (6.228±1.752), Ni (6.570±1.102), Cu (8.754±2.386), Zn (15.320±3.486), Fe (219.593±22.641), Mn (54.172±51.645) and Hg (0.006±0.005). All the concentrations of the heavy metals examined when compared with those of average value of heavy metals in shale showed that all the metals were lower than their corresponding world average values except Cd. Contamination factor index analysis of the sediment heavy metals burden showed that the sediment was polluted with Cd, contaminated with Cu, Zn and Cr and uncontaminated with Pb, Fe, Mn and Hg, Ni. Thus, showing that despite the heavy oil discharges from artisanal refining practices, the sediment is yet to be contaminated. The obtained values are yet to implicate anthropogenic input sources of heavy metals into the river. However, frantic effort should be put in place to curb input sources into the river.

Keywords: Sediment; Pollution; Silver river; Heavy metals; Contamination

Introduction

The presence of heavy metals in any environment resulted from natural and anthropogenic causes and are able to accumulate in the sediment strata of rivers, which results in negative environmental consequences for immediate dwellers within the area and the attendant quality of the water [1]. The fact about the toxicity and carcinogenic characteristics of heavy metals and other health effects associated with them has been documented [2]. Heavy metals may not constitute or pose risk to the environment when they are present in quantities that are within natural acceptable values [3]. Heavy metals are found naturally in the earth's crust. Due to disintegration and breakdown of rocks, they are transported from the topsoil through runoffs and deposited at the bottom sediment. Apart the release of heavy metals into the river through natural causes, there exist also the input of heavy metals into the sediment through human activities namely urban growth, mechanization, transportation and energy production [4]. Another aspect of heavy metals distribution within the aquatic environment which is not given adequate consideration is runoffs from storm water. Studies have shown that the rainstorm water traversing the surface of soil carries along its transport path heavy metals that have originated from diversity of normal human activities that is accompanied with wear and tear of material, corrosion, roof run-off and fuel combustion products [5].

In the Niger Delta Region of Nigeria, one of the major routes of pollution is the petroleum and its allied companies. Added to the sophistry of oil production is the present proliferated artisanal refining that has taken over the different waterways of the region. The unapproved production of refined petroleum products is associated with the generation of waste which are discharged into the environment without following laid down rules [6]. The petrochemical and oil industries are the major sources of pollution [7]. The introduction of waste into the aquatic environment without the necessary approach or ways to remove contaminants has the potential to increase the value of heavy metals above the natural value and thus lead to accumulation of heavy metals in sediment and tissues of water dwelling animals [8]. Increased levels of heavy metals in both water and sediment portends danger

to the surrounding environment and have negative transfer effect on human well-being through food channels [9]. The information on the pollution status of any aquatic environment is a function of the contamination or pollution of its sediment, which is the final repository of contaminants or pollutants in any waterbody [10,11]. The retained or accumulated heavy metals in the sediment can be re-suspended back to surface water based on ecological disorders or turbulence that may occur and therefore causing harmful effect on the ecosystem [12]. This study was done to examine the concentrations of heavy metals in sediment of Silver River, an important commercial river for the Southern Ijaw people of Bayelsa State, Niger Delta, Nigeria.

Materials and Methods

Collection of sediment samples

Sediment samples were collected from the surface using plastic trowel and immediately transferred to plastic cellophane bags and then put into ice chest containers. They were transferred to the laboratory immediately. The samples were collected between the Enewari community in the northern axis, through Fonibiri, Opuama and ended at Akamabobou in the southern axis. These are associated with intensive oil spills, local refining operations, sewage disposal, agricultural discharges from runoffs and local industries (Figure 1).

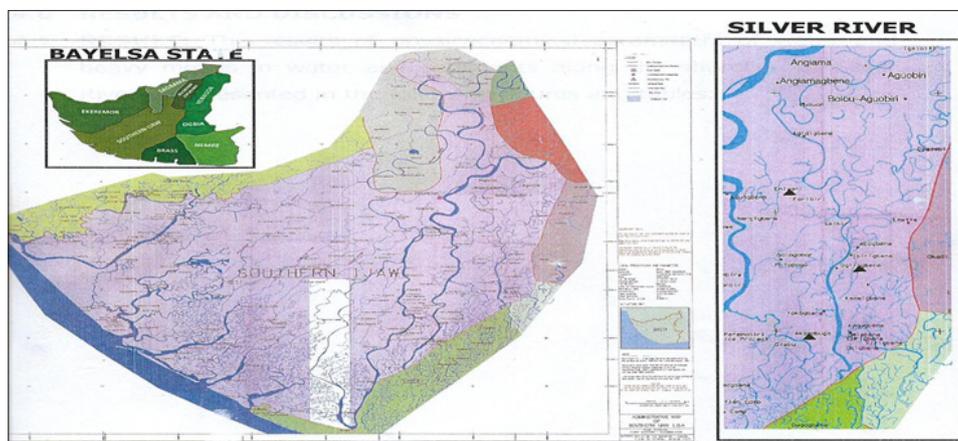


Figure 1: Map of southern ijaw showing silver river.

Preparation of sediment samples

Sediment samples were air dried in the laboratory to constant weight. The dried samples were macerated to fine powder using mortar and pestle. The macerated samples were sieved with a 2mm mesh. Stones and hard objects were removed without being crushed. The samples were then ready for further processing for heavy analysis.

Digestion of sediment samples

Precisely, 3g of the finely pulverized sediment samples were placed in digestion vials to which 20ml of aqua regia mixture (3:1 v/v of HNO_3 and HCl) was added and heated over steam bath to a clear solution. Thereafter, 20ml of deionized water was added and the heating continued for 5 minutes. The mixture was filtered with whatman filter paper in to 50ml sample bottle. The content was made up to 20ml mark and stored in the freezer at 4 °C.

Determination of heavy metals in sediment samples

The concentrations of heavy metals in the sediment samples were done using atomic absorption spectrophotometer. Quality check was done by comparing the values obtained with those of standard reference materials after every ten measurements of the samples.

Determination of Contamination Factor, Pollution Load Index, Contamination Degree and Modified Contamination Degree

The contamination factor of the individual metals in sediment was calculated from the formula adopted from the work by Edori and Kpee (2017) as:

$$CF = C_m / C_b$$

Where CF is the contamination factor, C_m is the concentration of metal measured in sediment and C_b is the background concentration of the metals in sediment. The background values were obtained from the work of Turekian and Wedpohl [13], being the average crustal value of each metal in shale.

Pollution load index was calculated using the formula

$$\text{Pollution Index (PI)} = n\sqrt{(C_{f1} \times C_{f2} \times C_{f3} \times \dots \times C_{fn})}$$

Contamination degree (CD) and modified contamination degree were calculated using the formula of Hakanson (1980)

$$CD = \sum_{i=1}^n C F$$

and the modified contamination degree as

$$mCD = \frac{1}{N} \sum_{i=1}^N CFI$$

The PLI, CD and mCD were then interpreted based on intervals of contamination and pollution provided for each of the assessment

indices (Hakanson, 1980).

Result and Discussion

The concentrations of heavy metals in sediment samples are given in Table 1.

Table 1: Concentrations of heavy metals in sediment samples in the different stations in silver river.

Heavy Metals (mg/L)	Stations			Mean \pm SD	Average Value in Shale
	1	2	3		
Cd	1.694	3.842	2.378	2.638 \pm 0.900	0.3
Pb	4.694	7.891	5.426	6.004 \pm 1.368	85
Cr	4.032	8.321	6.329	6.228 \pm 1.752	90
Ni	5.116	6.81	7.784	6.570 \pm 1.102	68
Cu	6.147	11.913	8.201	8.754 \pm 2.386	45
Zn	10.712	19.142	16.107	15.320 \pm 3.486	95
Fe	189.178	243.469	226.13	219.593 \pm 22.641	47200
Mn	16.017	19.315	127.184	54.172 \pm 51.645	850
Hg	0.0021	0.012	0.003	0.006 \pm 0.005	1.4

Cadmium (Cd)

In the sediment, the values ranged from 1.6942-3.842mg/Kg as against the 0.3mg/Kg, the average value in shale. The values obtained in the sediment samples in the present work were higher than the values observed in sediments of Lake Asejire, Nigeria [14] and those of Wu et al. [15] in two plateau Reservoirs in China. Cd is very vital in the monitoring of aquatic environment; this is due to its toxicity to aquatic flora and fauna. Cd is a known human carcinogen and when it is extensively dispersed in water environment, it has the capacity to bioaccumulate in fishes, aquatic plants, and the sediment. Bottom dwelling species such as crabs, mollusk, crustaceans, and fish accumulate Cd in their tissues at different [16,17].

Lead (Pb)

The concentrations of Pb in the sediment samples were within the range of 4.6941-7.8911mg/Kg. this value is lower than the average value of 85mg/Kg in shale. The observed sediment concentrations of Pb in the present work disagrees with the findings of Shanbehzadeh et al. [18] where Pb concentrations in sediment was found to be in the range of 141 \pm 4.0-270 \pm 0.5mg/L and those of Wu et al. [15] in sediments obtained from Hongfeng and Baihua Reservoirs, Yunnan-Guizhou Plateau in Southwest China, but disagrees with the values observed in both sediment from Ikpoba and Ekpan Rivers in Warri Delta State, Nigeria, impacted with crude oil pollution by Owamah [19]. Pb like Cd is known to be poisonous and carcinogenic in nature. It has not been known to possess any important physiological characteristics in animal or plant system, but rather acts as an inhibitor of many regular systems in humans. Elevated levels of Pb in humans is poisonous and may possibly cause severe disease in animals [20] or a condition known as plumbism [21]. Negative effects of Pb to

marine or freshwater plants and animals namely algae, benthic invertebrates, and embryos and fingerlings of freshwater fish and amphibians comprise loss of sodium, reduction in performance capacity, development difficulties, and irregular growth of algae [22].

Chromium (Cr)

The values of Cr obtained in the sediment ranged from 4.0321-8.321mg/Kg as against 90mg/Kg in world average shale value. Cr values obtained in sediments of the Silver River were lower than those of the Tembi River, Iran as observed by Shanbehzadeh et al. [18]. Cr as a metal is a known low mobile element. This characteristic is very pronounced when there is moderate oxidizing and reducing conditions at pH values that is close to 7. Sources of Cr in both terrestrial and aquatic environment, principally arise from production of steel and other alloys, chrome plating, and pigment production and paint.

Nickel (Ni)

The concentrations of Ni in sediment samples ranged from 5.1163-7.7842mg/Kg, which were lower than the average of 68mg/Kg value in shale. Sediment Ni concentrations in Silver River as observed were lower than the values observed by Decena et al. [23] in urban river in the Philippines, where concentration values were found to be as high as 12.08 to 98.07mg/Kg. Ni is commonly exist bound to organic components of soil or sediment and in acidic or neutral conditions, it becomes readily mobile and available to plants and animals [24]. The sources of Ni in the Silver River might be from wood burning, crude oil combustion, agricultural discharges and domestic effluents and discharges. This observation is in consonance with the observation of Purushothaman and Chakrapani [25] in Ganga River Sediment, India.

Copper (Cu)

The concentrations of Cu in the sediment of the river varied from 6.1474-11.9132mg/Kg respectively. The average value for soil and sediment in shale for Cu is 45mg/Kg. The sediment values of Cu in this river (Silver River) as observed were very low when compared with the values of Cu observed in Mangonbangon River, an urban city in the Philippines, where values ranged from 29.40-217.06mg/Kg [23]. This metal is vital for the appropriate growth of the plants. This is due to the fact that it is part of several enzymes and proteins [24]. Source of Cu in the environment arise from electrical installations, roofing sheets, and manufacturing of alloys, colour pigmentation, household cooking implements, and [26] and the application of fertilizers, growth inducers and pesticides in both plant and animal farms [23].

Zinc (Zn)

Sediment concentrations of Zn in the sampled stations varied from 10.712-19.1419mg/Kg. these values were below the average concentration of Zn in shale, which is 95mg/Kg. Sediment values of Zn from the Silver River is lower than those of [23] in Mangonbangon River in the Philippines, where value range was between 76.83-263.63 mg/Kg and those of Sivakumar et al. [27] in South East Coast of Tamilnadu, India, whose values ranged from 26.8-48.8 mg/Kg. Zn is an indispensable metal for animal and human body metabolism. It is present in food and water as salts or as organic complexes [28]. Fertilizers, sewage The main sources of Zn pollution in the environment are zinc fertilizers, sewage slurry and mining operations. Other sources of Zn in water include runoffs from settlements, drainage or discharges of mine wastes and public sewages discharge systems (Damodharan, 2013). It is difficult to experience Zn poisoning in humans, although rare cases have been reported and it rarely accumulates in human body. Zn activates enzymes, but exceeded levels of Zn affects bone growth, development and functioning of reproductive organs. Its action in water plants is a function of the water hardness, concentration of dissolved oxygen and temperature. Zn is very important in the physiologic and metabolic developments of several plants and animals. Zn toxicity is associated with signs of diarrhea, bloody urine, liver and kidney failure and anemic conditions [29].

Iron (Fe)

The values of Fe observed in the sediment varied from 189.1783-243.469mg/Kg as against the 47200 mg/Kg in the world average value in shale. The values of Fe obtained in the sediment samples from the Silver River in the present research is higher than those of Owamah [19], in sediments of Ijana River, Warri contaminated with spilled petroleum, but lower than those of Sivakumar et al. [27] in Tamilnadu, India. Fe is a known abundant metal in the earth's crust. The chief sources of natural Fe in water system are weathering of rocks, erosion or runoffs and decaying parts of plants, but large quantity or levels of Fe in a river ecosystem resulted from large-scale anthropological activities like urban-industrial discharges of effluents, metropolitan solid waste releases, building of structures, destruction of waste and agro-based activities [26].

Manganese (Mn)

In the sediment samples, the values of Mn ranged from 16.0171-127.184mg/Kg as compared to the average value in shale, which is 850mg/Kg. Sediment concentrations of Mn in the silver River are lower than those of Sivakumar et al. [27] in South East Coast of Tamilnadu, India, Decena et al. [23], in Mangonbangon River in the Philippines, those of Montalvo et al. (2014), in Palizada River, Mexico and those of Kpee et al. [30] in Andoni Rivers, Rivers State, Nigeria. Mn is a crucial metal for both living organisms. Deficiency of Mn in animals can possibly lead to serious skeletal and reproductive defects in higher animal e.g. (*Homo sapiens*) [31]. Mn sources in the environment arise from electronic and electrical constituents or parts and plastics pigments [32], which when carelessly discharged into the environment decays and releases it to the river system [33].

Mercury (Hg)

The concentrations of Hg in the sediment phase of the river varied within the range of 0.0021-0.0121 mg/Kg as against 1.4mg/Kg in world average value in shale. The values of Hg observed in sediments in the present work agrees with the findings of Ogamba et al. [34] in a similar Niger Delta environment, but lower than the values observed in in bottom sediments of the Odra River in parts of Poland and Germany by Boske et al. [35] and those of Medrano et al. [36] in San Juan River, Mexico. Hg sources in water environment can either result from natural or artificial (man-made) causes which may include deposition from the atmosphere, manufacturing developments, quarrying activities and runoffs from agricultural lands. Hg in sediment can as a complex inorganic compound or in elemental form and becomes very poisonous when it exists as methyl mercury [36].

Contamination Factor of Heavy in Sediments of Silver River

The contamination factor of the individual heavy metals in Sediment samples were as follows; Cd varied from 5.647-12.807, Pb varied from 0.054-0.093, Cr was between 0.070-0.448, Ni was between 0.075-0.114, Cu varied between 0.137-0.265, Zn varied between 0.106-0.201, Fe varied between 0.004-0.005, Mn varied from 0.015-0.022 and Hg varied from 0.0008-0.0022. These values when compared to the intervals of contamination and pollution intervals and interpretations as proposed by Lacatusu [37] revealed that the sediment was in the range of severe pollution-very severe pollution with Cd, but uncontaminated with Pb, Fe, Mn and Hg, Ni in station 1 and Cr in stations 2 and 3. The sediment was moderately contaminated with Cr in station 1. The level of contamination of sediment with Cu and Zn varied from very slight contamination slight contamination (Table 2). The pollution load index, contamination degree and modified contamination degree of the heavy metals are given in Table 3. The pollution load index (PLI) obtained from the river varied from 1.231-1.336. All the sediments from the stations examined fall within the range of 1.1-2.0, which is classified in the category of slight pollution with heavy metals. This observation is higher than the observation of PLI by Mortuza

& Al Misned [38] in sediments from Red Sea coast of Jizan, Saudi Arabia, where PLI values were as low as 0.06 and those of Mandeng et al. [39] in sediments collected from two divisions in a river in Abiete-Toko gold region, Southern Cameroon, but either lower, within the range or higher than the values observed in sediments from different stations in two notable streams (Strzyza and Oliwski Streams), which flows into the Baltic Sea, Poland [40].

Table 2: Contamination factor of heavy metals in sediment samples from different stations in silver river.

Heavy Metals	Stations		
	1	2	3
Cd	5.647	12.807	7.927
Pb	0.054	0.093	0.064
Cr	0.448	0.092	0.07
Ni	0.075	0.1	0.114
Cu	0.137	0.265	0.182
Zn	0.106	0.201	0.17
Fe	0.004	0.005	0.005
Mn	0.019	0.022	0.015
Hg	0.002	0.001	0.002

Table 3:

Assessment Indices	Stations		
	1	2	3
PLI	1.231	1.336	1.269
CD	6.483	13.586	8.549
mCD	0.721	1.51	0.95

However, the values of PLI in the present work fall within the range of values observed from sediments collected from the Sanmenxia section of the Yellow River in China [41]. The contamination degree (CD) of the heavy metals obtained from the different stations in the river varied from 6.483-13.586. The value in station 1 fall within the range of $CD < 8$ which can be interpreted as low contamination degree, while those of stations 2 and 3 fall within the range of $8 \leq CD < 16$ which can be classified as moderate contamination degree. The contamination degree for the heavy metals in this work is higher than those of Moslen et al. [42] in sediments of a tidal creek in Niger Delta, Nigeria and either within the range or higher than the values obtained by Fiori et al. [43], in coastal water sediments from the Rio de Janeiro State, Southeastern Brazil. The modified degree of contamination values ranged from 0.721-1.510 in the stations. All the values observed in stations, based on the interpretations of intervals of contamination and pollution as expressed in modified contamination indices fall within the range of $mCd < 1.5$ which is nil to very low degree of contamination and $1.5 \leq mCd < 2$ low degree of contamination. The

values of mCD obtained from this work is lower than the values of mCD observed in sediments of Yellow River Reserve of Zhengzhou, China [41,44].

Conclusion

The present stages of the concentrations of the examined heavy metals in sediment samples in the Silver River were generally lower than established world average values in shale except that of Cd. Despite the fact that the concentrations of the metals were within values that do not presently show stressed sediment environment, except for Cd concentrations, yet the environment require constant monitoring to avert sudden rise in general heavy metal content in the sediment, looking at the present activity that is within the area [45].

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