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Geochemistry and Risk Assessment in Surface Sediments of the Brass River, Bayelsa State, Niger Delta Region, South-South, Nigeria

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ABSTRACT

This paper deals with the physico-chemical parameters and some heavy metals in sediment samples of the Brass River, Bayelsa State, Nigeria. Physico-chemical parameters and heavy metals such as pH, chloride, sulphate, magnesium, potassium, sodium, copper, chromium, zinc, cadmium, lead, manganese, iron and nickel were analyzed. In this present study, all heavy metals investigated showed low concentration of the Brass River. This means that there is a low source of pollution arriving to the Brass River. Potential ecological risk index assessment of heavy metals and comparison with DPR / FEPA standards was employed to infer anthropogenic input from natural input. The heavy metals concentration and potential ecological risk were evaluated systematically using geoaccumulation index (Igeo) and potential ecological risk index (RI). The results showed that the geoaccumulation index placed Brass River under practically unpolluted (Igeo < 0). Furthermore, the potential ecological risk index of both single and multi-element placed the Brass River under the category of low ecological risk (E^i_r < 40).and RI<150) respectively. In general, the ranking of heavy metals in surficial sediment samples of the Brass River in terms of potential ecological risk coefficient (E^i_r) was as follows: Cu > Pb > Ni > Zn. Compared to the heavy metals permissible limit in DPR/FEPA standards copper, chromium, zinc, cadmium, lead, manganese, iron and nickel showed lower concentration, possibly indicating that the origin of these heavy metals is lithogenic.

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1.0 Introduction

Crude oil and natural gas extraction are prominent sources of energy and revenue in the country, however, these activities may have disastrous impacts such as, impair water quality, sediment quality, aquatic organisms, implications on human health etc.

In a coastal environment which play's host to multi-national oil company, subsidiary industries, LNG project, oil export terminal, constant ballasting of medium and small vessels, fishing, and other human activities, it is critical to think that the ecosystem may be at risk, and it needs to be protected from the animosity of contaminants.

Due the significant role in maintaining the tropic status of any water body, sediments are ecologically important components of the aquatic habitats (Singh et al., 1997; Akan et al., 2010) Process such as erosion, weathering and acidification are common natural ways heavy metals enter into the environment (Tajam and Kamal, 2013). Human activities such as industrialization, urbanization, domestic wastes, agricultural, vehicular emissions and factory plants are the main sources of some heavy metals enter and deposited into the environment (Demirak *et al.*,2013; Abdullah *et al.*, 2015). Pollution of heavy metals in aquatic ecosystem is growing at an alarming rate and has become an important global problem (Malik et al., 2010). Increase in population, urbanization, industrialization and agricultural practices have further aggravated the situation (Gupta *et al.*, 2009; Olusola and Festus, 2015).

Coastal environments receive sediment inputs from many different sources, including allochthonous terrestrial materials transported from land, by rivers and groundwater, allochthonous marine materials brought in through tidal action from the open sea (Gon˜ *et al.*, 2003). Physical processes, such as currents, waves, tides, surges, etc., are usually very effective in coastal sedimentary environments (Sagheer, 2013).

In the aquatic environment, heavy metals can accumulate to toxic levels and cause severe effects to organisms and on human health (Gupta *et al.;* 2009). Factors such as climate and hydrology (Caruso and Bishop, 2009), water chemistry (Matache *et al.;* 2009) and biological activity (Van Hattum *et al.*, 1996) control heavy metal deposition and fixation in the sediments, which may act as both sinks and sources of secondary aquatic pollution (Pekey, 2006; Coynel *et al.*, 2007, Nwajei *et al.*,2014).

The present study area and it's environ is an industrial hub of the Niger Delta region, South-South, Nigeria. The aim of this work was (1) to determine the levels of some physico-chemical parameters and heavy metals in sediment of the Brass River, (2) to use two most commonly used pollution indices such as the potential ecological risk index method and geoaccumulation index to ascertain the degree of pollution and (3) carry out comparison analysis with reference

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standards and similar environments to know the extent of deterioration.

2.0 MATERIALS AND METHODS

2.1 STUDY AREA

The Brass River is a natural river geographically located in Bayelsa state, Niger Delta region, Nigeria. Twon-Brass is a community on Brass Island in the Nun River estuary of Southern Bayelsa State, Nigeria, in the Brass Local Government Area. The river lies between the coordinates of latitude 04o 19' 1'' North and longitude 06o 14' 34'' East. Brass River is a distributary and it also flows into the Atlantic Ocean.

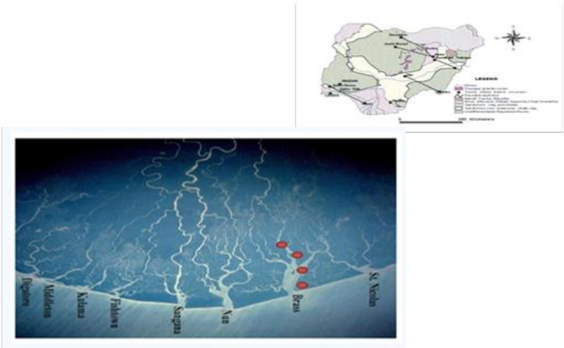

Figure 1. Map of Brass River showing sampling locations.

2.2.1 SAMPLING AND ANALYSIS

Sediment samples were collected using a bottom grab sampler (Hydro-Bios) from four stations: upstream, middle reach, mouth and downstream along the Brass River system. Sediments were then immediately transferred into plastic bags and refrigerated and transported to the laboratory. In order to get a representative sample for each station, several sub-samples were collected and mixed together. At the laboratory, the samples were air-dried, pulverized and sieved through a 2mm mesh to remove dirt and other debris, then stored in closed plastic containers for digestion and analysis. The air-dried, sieved sediment samples were used to perform the following physico-chemical analysis: pH, electrical conductivity, chloride, sulfate, magnesium, potassium and sodium content according to standard techniques (Jackson, 1973 ;Singare *et al.*, 2011).

Furthermore, the dried sediment samples were digested in a mixture of concentrated nitric acid (HNO3), concentrated hydrochloric acid (HCl) and 27.5% hydrogen peroxide (H2O2) according to the standard USEPA method 3050B for the analysis of heavy metals and major ions (USEPA, 1996; Amadi *et al.*, 2012; Leizou *et al.*, 2016). The resulting solutions were subjected to elemental analysis using an atomic absorption spectrometer (ANALYST 400 Perkin-Elmer AAS),in compliance with manufacturer's instructions and specifications.

3.0 RESULTS AND DISCUSSION

Table 1 Summaries the concentrations of physico-chemical parameters and heavy metals in (range, minimum, maximum, mean ± standard deviation) except pH; others are expressed as milligram / Kilogram (mg/Kg) of dried sediments of the Brass River, Bayelsa State, South-South, Nigeria.

The Concentration of pH, Cl-, SO4 2- , Mg, K, and Na in sediment ranged from 2.36-5.29, 2459-12678, 425-8776, 0.03-1.04, 1.63-27.63 and 6.44-125.50 with mean values of 4.03±1.25, 6.85E3±4278.24, 4.93E3±4043.14, 0.68±0.45, 19.37±12.01 and 87.26±54.47 respectively. Vincent-Akpu *et al.*, 2015 reported that the sediments of Bodo Creek, Niger Delta, Nigeria exhibit fluctuating pH values that ranged from 5.7 to 8.0, that is, from acidic to alkaline. pH is a simple parameter but is extremely important, since most of the chemical reactions in aquatic environment are controlled by any change in its value. Anything either highly acidic or alkaline would kill marine life (Singare *et al.*, 2011).

The data in this study suggested low concentration of heavy metals in surface sediments of the Brass River. The concentration (mg/kg) of heavy metals: copper, zinc, iron and lead in sediments ranged from 0.65 – 1.07, 0.11-0.30, 4.93-128.91 and 0.02-0.03 with mean value of 0.83±0.18, 0.21±0.10, 79.49±52.94 and 0.02±0.01 respectively. The highest value for copper (1.07 mg/kg), was recorded in the sediment from downstream and was closely followed by sediment from mouth (0.82 mg/kg). The lowest value was recorded in the sediment from upstream (0.65 mg/kg) (Table 1).

Klassen (1996) grouped metals into four categories: a) major toxic metals with multiple side effects, b) essential metals with potential for toxicity, c) metals related to medical therapy, and d) minor toxic metals. Copper and zinc are essential elements with potential for toxicity and both exhibit an oxidation state of 2+. Copper is widely used in electrical wiring, roofing, various alloys, pigments, cooking utensils, piping and in the chemical industry. Copper is present in amunitions, alloys (brass, bronze) and coatings. Copper compounds are used as or in fungicides, algicides, insecticides and wood preservatives and in electroplating, azo dye manufacture, engraving, lithography, petroleum refining and pyrotechnics. Copper compounds can be added to fertilizers and animal feeds as a nutrient to support plant and animal growth. Copper compounds are also used as food additives (Abbasi et al., 1998; Eaton, 2005; WHO, 2004). In addition, copper salts are used in water supply systems to

Table 1. Summary of physico-chemical parameters and heavy metals in sediment

Variables	Range	Min.	Max.	Sum	Mean	Std Error	Std Dev.	Variance
pH	2.93	2.36	5.29	16.12	4.03	.63	1.25	1.57
Chloride	1.02E4	2459.00	12678.00	2.74E4	6.85E3	2.14E3	4278.24	1.83E7
Sulphate	8351.00	425.00	8776.00	1.97E4	4.91E3	2.02E3	4043.14	1.64E7
Mg	1.01	0.03	1.04	2.73	.68	.23	.45	.21
K	26.00	1.63	27.63	77.48	19.37	6.00	12.01	144.18
Na	119.06	6.44	125.50	349.04	87.26	27.24	54.47	2.97E3
Cu	.42	0.65	1.07	3.30	.83	.09	.18	.03
Zn	.19	0.11	.30	.85	.21	.05	.10	.01
Cr	.00	0.00	.00	.00	.00	.00	.00	.00
Cd	.00	0.00	.00	.00	.001	.00	.00	.00
Pb	.03	0.02	.03	.08	.02	.01	.01	.00
Mn	.58	0.01	.59	1.74	.43	.14	.29	.08
Fe	123.98	4.93	128.91	317.97	79.49	26.47	52.94	2.80E3
Ni	.73	0.07	.09	.89	.22	.17	.34	.12

control biological growths in reservoirs and distribution pipes and it forms a number of complexes in natural waters with inorganic and organic ligands (WHO, 2004). Exposure to excess Cu can cause chronic vascular disease, gastrointestinal problems, hypotension, and Wilson's disease (Patrick et al., 1977; Klassen, 1996; McBride, 1994; EPA, 2009; Zimmerman, 2010).

Zn deficiency is the usual cause of medical problems but excess Zn can cause gastrointestinal problems and hematological systems effects.. Some of the medical effects of Pb are cardiotoxicity, neuropathy, encephalopathy, and kidney, vascular, and reproductive effects (Patrick *et al.*, 1977; Klassen, 1996; McBride, 1994; EPA, 2009; Zimmerman, 2010).

A comparative analysis of copper, zinc, iron and lead levels in the sediment with DPR, 2002; FEPA, 2009 standards and shale values (Turekian and Wedepohl, 1961). revealed that the results obtained in this study were lower(Table 2). These results are in concomitant with those reported by (Vincent-Akpu et al., 2015; Leizou et al., 2015; Horsfall and Spiff, 2005).

The concentration (range, mean ± standard deviation, mg/kg) for manganese and nickel in sediment ranged from 0.01-0.59 and 0.07-0.09 with mean values of 0.43±0.29 and 0.22±0.34 (Table 1), while chromium and cadmium were below detection limit (BDL). The concentration of nickel ranged between 0.07–- 0.09 mg/kg with an average of 0.22 ± 0.34 mg/kg. The highest value for manganese was 0.59 mg/kg (Table 1) was recorded in the sediment from middlestream and upstream, and closely followed by the sediment from downstream (0.56mg/kg). The lowest value was recorded in the sediment from mouth (0.05 mg/kg).

Manganese is essential for plants and animals. Manganese usually enters the food chain through foods such as fruits and vegetables but is also being introduced into the environment as an octane booster in gasoline, replacing Pb in the 1980's(Zimmerman, 2010).. Manganese dioxide and other manganese compounds are used in products such as batteries, glass and fireworks. Potassium permanganate is used as an oxidant for cleaning, bleaching and disinfection purposes. Other manganese compounds are used in fertilizers, varnish and fungicides and as livestock feeding supplements. Manganese can be adsorbed onto soil; the extent of adsorption depends on the organic content and cation exchange capacity of the soil. It can bioaccumulate in lower organisms (e.g., phytoplankton, algae, molluscs and some fish) but not in higher organisms; biomagnification in food chains is not expected to be very significant (Abbasi *et al.*, 1998; Eaton, 2005; WHO, 2004). Common effects of excessive Mn are pneumonitis, epithelial necrosis, mononuclear proliferation, central nervous system and liver disorders, and neuropsychiatric disorder (Patrick *et al.*, 1977; Klassen, 1996; McBride, 1994; EPA, 2009; Zimmerman, 2010). The result obtained in this study for manganese, nickel, chromium and cadmium concentrations agreed with those reported by [Vincent-Akpu *et al.* 2015, Horsfall and Spiff, 2005] from Bodo Creek in Ogoni land and Diobu River in Port Harcourt, which are of the same geographical Niger Delta region with similar sources of contaminants input. As shown in Table 2, the concentration levels of manganese, nickel, chromium and cadmium were also lower when compared to levels in DPR, 2002; FEPA, 2009 and shale values (Turekian and Wedepohl 1961).

3.1 ASSESSMENT OF ECOLOGICAL RISK

The two methods that are frequently and mainly used for quantitative determination of the potentially toxic heavy metals pollution and ecological risk in sediments of aquatic ecosystem are: (1) the geoaccumulation index (Igeo) and (2) the potential ecological risk index (RI). The Geo-accumulation index (Igeo), introduced by Muller (1969) for determining the extent of metal accumulation in sediments, and has been used by various workers in their studies (Ntekim *et al*., 1993; Sagheer**,** 2013; Odat, 2015; Yan g *et al*., 2016; etc). The geoaccumulation index (Igeo) is mathematically expressed as follows:

$$Igeo = log2 \frac{[metal\ content, Cn]sample}{[1.5 * metal\ content, Bn]background} \quad 1$$

Where, Cn is the concentration of element 'n', Bn is the geochemical background value of the metal (n) and1.5 is the background matrix correction factor due to lithogenic effects. The geoaccumulation index (Igeo) scale consists of seven grades (0-6) ranging from practically unpolluted to extremely polluted. Geoaccumulation index (Igeo) categories are listed below in Table 3.

Table 3. Classes for the geo-accumulation index (Igeo)

Class	Value	Soil quality
0	*I*geo <0	practically unpolluted
1	0 < *I*geo <1	unpolluted to moderately polluted
2	1 < *I*geo <2	moderately polluted
3	2 < *I*geo <3	moderately to strongly polluted
4	3 < *I*geo <4	strongly polluted
5	4 < *I*geo <5	strongly to extremely polluted
6	*I*geo > 5	extremely polluted

According to geoaccumulation index (Igeo) scale, the studied heavy metals of the Brass River surficial sediments were placed under the category of practically unpolluted(Igeo < 0). These results are in concomitant with those reported by Sagheer, 2013; Yan g et al., 2016 Leizou *et al.*, 2016).

The potential ecological risk index method introduced by Swedish scholar Hakanson was formulated in line with the characteristics of heavy metal, its behavior and to evaluate the heavy metal contamination from the perspective sedimentology (Jing Li, 2014; Soliman *et al* 2015; Yan g *et*

Table 2. Results of heavy metals of the Study area

METAL	mouth	downstream	middlestream	upstream	DPR/FEPA	SHALE VALUE
Cu	0.82	1.07	0.65	0.76	35/20	45
Zn	0.11	0.29	0.15	0.30	50-300	95
Fe	4.93	128.91	98.81	85.32	20	47200
Pb	BDL	0.30	0.02	0.03	2-20	20
Cd	BDL	BDL	BDL	BDL	0.03-0.3	0.3
Cr	BDL	BDL	BDL	BDL	0.5	90
Mn	0.05	0.56	0.59	0.59	-	850
Ni	BDL	0.07	0.07	0.09	0.8	68

Table 4. E^i_r and RI index categories

Grade	E^i_r a single element	Classification	RI values	RI of the multi-element
1	E^i_r<40	Low ecological risk	RI<150	Low ecological risk
2	40<E^i_r≤80	Moderate ecological risk	150<RI<300	Moderate ecological risk
3	80<E^i_r≤160	Appreciable ecological risk	300<RI<600	High ecological risk
4	160<E^i_r≤320	High ecological risk	RI≥600	Significantly High ecological risk
5	E^i_r<320	Serious ecological risk		

al., 2016). This method is of two categories; first to assess the potential ecological risk coefficient E^i_r of a single element and secondly the potential ecological risk index (RI) of multi-The RI is mathematically expressed in equation 2.

$$\mathbf{RI = \sum_{i=1}^{n} Er = \sum_{i=1}^{n} Tr\ x\ Cf = \sum_{i=1}^{n} Tr\ x\ Cs/Cn} \quad 2$$

where Er is the potential ecological risk coefficient, Tr is the toxic response factor , Cf is the contamination factor , Cs is the measured concentration of heavy metal in surface sediments, and Cn represents the background value of heavy metal. The toxic response factors of the studied heavy metals are as follows: Cu (5), Cr (6), Pb (5), Ni (5), Mn (1), Cd (30) and Zn (1). The potential ecological risk coefficient (Eir) for single element and potential ecological risk(RI) for multi-element interpretation guidelines are shown in (Table 4). Potential ecological risk index method is a powerful and versatile technique for predicting the degree of contamination risk of environmental compartment, especially soils and sediments. The results of ecological risk coefficient (Er) for single element and potential ecological risk index of multi-element (RI) of the investigated heavy metals in the sediments samples suggested low ecological risk for single and multi-element.

Brass River is unpolluted with respect to Cd, Cr, Cu, Zn, Fe, Mn, Ni and Pb in surface sediment, fall under class 1 (Eir<40) indicating Low ecological risk. In general, the ranking of heavy metals in surface sediments samples in terms of potential ecological risk coefficient (Er) was as follows: Cu > Pb > Ni > Zn. The results of potential ecological risk index (RI) for multi-element of the investigated heavy metals in all the sampling sites were at low ecological risk level (RI<150). These results are in concomitant with those reported by (Jing Li, 2014; Soliman *et al*., 2015; Yan g *et al*., 2016).

3.2 CONCLUSION

Potential ecological risk method is a powerful and versatile technique for predicting the quantitative determination of hazardous heavy metals pollution and their potential ecological risk in sediments of a river system. In this study, all heavy metals investigated are relatively stable under normal conditions and suggested low concentration of Cu, Zn, Fe, Pb, Mn and Ni, while Cr and Cd were below detection limit. This means that there is a low source of heavy metals pollution arriving to the Brass River system. The two most commonly used pollution indices geoaccumulation index and potential ecological risk index placed Brass River surficial sediments under the category of practically unpolluted (Igeo ≤ 0) and Low ecological risk (Eir<40). The order of potential ecological risk coefficient (Eir) of heavy metals in sediments of the Brass River follows the order: Cu > Pb > Ni > Zn. The potential ecological risk index RI of multi-element confirmed that all the sampling sites were at low ecological risk level (RI<150). Consequently, the study recommended protection of the biodiversity and aesthetic value of the Brass River, to achieve this, allochthonous inputs should be devoid of harmful chemicals.

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