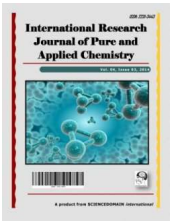

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Fractionation Status and Uptake Potentials of Trace Metals in Water Bodies within Niger Delta Region, Nigeria

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Authors' contributions

This work was carried out in collaboration between both authors. Author GAE designed the study. Author HSE collated the results and produced the first draft. Both authors read and accepted the final manuscript for publication.

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ABSTRACT

Surface sediments were collected from Itu, Qua Iboe, Imo, Atabong and Iko Rivers within Niger Delta, Nigeria and assessed for their trace metals contents. Sediments were also obtained from Ekpene Ukpa River where there is no major anthropogenic source of contaminants as Control. These sediments were treated analytical and analyzed using atomic absorption spectroscopy for total trace metals and their species. Results indicated that, total cadmium, manganese and iron were above their acceptable limits while total copper, nickel, lead and zinc were lower than their recommended limits. However, total concentrations of all the trace metals in sediments studied were higher than that in Control indicating anthropogenic inputs of these metals in studied rivers. Speciation studies revealed that Cd existed mostly in acid extractable fraction, Mn, Cu, Ni and Fe in residual fraction while Pb and Zn existed mostly in reducible fraction. Cd showed highest risk potential while Fe was the least risky element. Strong positive correlation existed among the trace metals in studied sediments. Qua Iboe River was the most polluted river whereas, Itu was the least contaminated river studied. It was revealed that apart from Fe, other trace metals were mostly from

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anthropogenic sources. Periodic assessment of these studied water bodies is recommended since the mobilisable proportions of all the metals were higher than immobilisable fractions.

Keywords: Niger Delta; BCR speciation; bioavailability factor; trace metals; pollution load index.

1. INTRODUCTION

Surface water bodies within the Niger Delta region of Nigeria have been heavily contaminated with harmful substances by the activities of oil and oil-related industries. The deplorable state of surface water bodies within the region could be physically noticed by their turbid nature caused by high solid contents. Unfortunately, most of the residents depend solely on these water bodies for their drinking, domestic use, irrigation and as good sources of edible aquatic organisms such as fish, crayfish, oyster etc. Studies have shown that crude oil and associated activities have resulted in the accumulation of metals in water and aquatic organisms in the Niger Delta region of the country [1]. Thus, these people are constantly exposed to these toxic substances which may have contributed significantly to the high prevalence of waterborne diseases such as cholera, diarrhea, dysentery, hepatitis etc among them [2,3]. Sediments in these aquatic ecosystems also absorb these contaminants especially metals and discharge them later into these environments thereby acting as both carrier and sources of contaminants in these water bodies [4,5]. According to Loizidou et al. [6] contamination of sediments with metals is a serious environmental problem as aquatic organisms may accumulate these metals in their organs to toxic levels and transfer same into human body through consumption, causing serious health hazards [7-11]. Reports have shown that sediments in aquatic ecosystems within urban areas commonly contain high levels of contaminants [12,13]. The occurrences of enhanced concentrations of trace metals especially in sediments may be an indication of human-induces perturbations rather than natural enrichment through geological weathering [14-16]. The tendency of aquatic environment to contain high levels of toxic metals is high since it receives waste materials from both natural and anthropogenic sources such as industrial, municipal discharges, atmospheric depositions, and runoff from agricultural and urban areas [17-23]. Previous studies within Niger Delta region of Nigeria have shown that, surface water bodies within the area accumulate high levels of toxic substances including metals [24-30]. Ekiye and Zejiao [31] reported that industrial effluent is one of the major sources of surface water pollution in Nigeria as less than 10% of industries in Nigeria treat their effluents before discharging them into the surrounding rivers. This coupled with incessant oil spill in Niger Delta region area have led to high load of metals in most water bodies within the zone [32,33]. Between 1997 and 2001 in the Niger Delta region of Nigeria, 2,097 oil spill incidents were recorded [34]. Studies have also revealed that Nigerian crude oil contain high level of metals and toxicity from oil pollution can lead to respiratory illness, kidney disease, neurological diseases etc in human [35,36]. Intensive environmental monitoring and assessment have been undertaken within the Niger Delta area to ascertain the quality however, these were done basically on total metal determination. Thus, health risk hazards and pollution status of these metals in sediments assessed may not have been established. This work was undertaken to identify the metal species, sources, bioavailability and hazardous potentials of trace metals in studied sediments. Metal speciation in environmental medium is the key for understnading their potential risk, mobility and bioavailability [29]. Thus, this study will indicate a comprehensive assessment of the trace metals and studied rivers regarding their pollution status.

2. MATERIALS AND METHODS

2.1 Study Area

Akwa Ibom State is one of the coastal states in the Niger Delta region within the South-South part of the country of Nigeria. It lies between latitudes 4° 32! and 5° 33! North and longitudes 7° 25! and 8° 25! East. The State has two (2) distinct seasons, the dry and wet. Dry season lasts between November and March while the wet season starts from April to October. This research was conducted during the dry season of the area. In this research work, surface sediments were obtained from the following rivers: Itu River (5°39! N and 8°20! E); Atabong (4°38! N and 7°55!E), Iko (4°30!N and 7°45!E); Qua Iboe River (4°27!N and 8°07!E) and Imo

River (4° 30!N and 7° 45!E). Control samples were also obtained from Ekpene Ukpa River (4° 47! N and 7° 50! E). Ekpene Ukpa River may not have been seriously affected by human activities as experienced by other studied rivers and is more than 25 kilometers away from the area with intensive oil activities.

2.1.1 Sample collection and treatment

This study was conducted between the months of October and December, 2015 and sampling was obtained once a month. At each location, three (3) sub-samples and one (1) composite sample were collected for one month. Thus, fifteen (15) sub-samples and five (5) composite samples were obtained for the three months [37]. Surface sediment and Control were collected from their respective locations using grab methods as reported by Ugwu et al. [38]. Surface sediments were chosen as this layer controls the exchange of metals between sediments and water [39,40]. These samples and Control were immediately placed into polyethylene bottles previously washed with 10% v/v HCl acid and rinsed with distilled water before transporting them to the laboratory. These samples and Control were air-dried for 72 hours, disaggregated and sieved through a 2mm plastic sieve to remove large debris, gravels and other unwanted materials. Sediment samples were digested by adding 10ml of with aqua regia to 1g of each sieved sample on a hot plate following the methods of Mendham et al. [41].

2.1.2 Optimized BCR sequential extraction procedures

Sequential extraction of trace metals in sediments was done using optimized BCR procedures as described by Rauret et al. [42]. Fraction 1: Acid extractable (weak acid extractable, exchangeable and carbonate bound fraction): To 1 g of homogenized sediment sample, 40 ml of 0.11M acetic acid (CH_3COOH) solution was added. The mixture shaken with a mechanical shaker at room temperature for 16h and extract separated by centrifugation at 3000 rpm for 20mins collected and stored in polyethylene bottles. Fraction 2: Reducible (Metal fraction bound to Fe-Mn oxides and hydroxides): 40 ml of 0.50 M hydroxylammonium chloride ($NH_2OH.HCl$) solution was added to the residue from step 1 above, shaken for 16 h at room temperature and centrifuged as in step 1 to separate the supernatant from the residue. Fraction 3: Oxidisable (Metal fraction bound to sulphide and organic matters): Residue from step 2 was treated with 10 ml 8.8 M hydrogen peroxide (H_2O_2) and allowed to digest for 1 h. The mixture was evaporated to dryness and 50 ml of 11M ammonium acetate ($CHCOONH_4$) added, shaken for 16h at room temperature and centrifuged to separate the extract from residue. Fraction 4: Residual (Metal fraction bound to crystalline silicates in soil): To the residue from step 3, a mixture of 5ml Conc. trioxonitric acid (HNO_3) and 15ml Conc. hydrochloric acid (HCl) was added and placed on hot plate for 2h. The mixture was cooled and filtered through Whatman No. 50 filter paper into a volumetric flask for analysis.

Percentage recovery was determined using equation

$$\%\text{Recovery} = \frac{\sum n\ Sequential\ Extraction\ \ Procedure}{Single\ Digestion\ with\ Strong\ Acids} \times 100 \quad (1)$$

Where n is the concentration of a particular metal and the single digestion with strong acids used for digestion of residual fraction [43]. Bioavailability factor (BF) of metals in sediments was determined using the equation

$$BF = \frac{F1}{F1+F2+F3+F4} \times 100 \quad (2)$$

Where F_1 = acid extractable fraction, F_2 = reducible fraction, F_3 = oxidisable fraction and F_4 = residual fraction in modified BCR speciation procedures. The relationship among trace metals analyzed for in sediments was identified using Pearson Coefficient (a two-tailed test) in Microsoft Excel 2007 as described by Bentum et al. [44]. Contamination factor (CF) was obtained using

$$CF = \frac{\text{Metal concentration in sediment}}{\text{Background value of metal}} \quad (3)$$

CF is classified into seven (7) categories namely: 0 = none; 1 = none to medium; 2 = moderate; 3 = moderately to strong; 4 = strongly polluted; 5 = strongly to very strong and 6 = very strong. The background values of metals used were as reported by Barciela-Alonso et al. [45]; Nasr et al. [46] and Taylor & Mclennan [47]. The level of site to site contamination of sediments by trace metals was assessed using degree of contamination (C_{deg}) which is given by equation 4

$$C_{deg} = \sum C_f^i \quad (4)$$

where $\sum C_f^i$ is the sum of the contamination factors for all the elements at a particular site. Degree of contamination is categorized as $C_{deg} < 8$ = low degree of contamination, $8 < C_{deg} < 16$ = moderate degree of contamination, $16 < C_{deg} < 32$ = considerable degree of contamination and $32 < C_{deg} =$ very high degree of contamination [48]. Pollution load index (PLI) of trace metals was computed using the equation

$$PLI = (CF_1 \times CF_2 \times CF_3 \ldots \times CF_n)^{1/n} \quad (5)$$

Where n represents the number of metals analyzed (n= 7 in this case) and CF is the contamination factor of individual metal. PLI value of zero (0) = perfection of the site, 1 is only baseline levels of pollutants are present while PLI > 1 shows progressive deterioration of the site [49]. Enrichment factor of trace metals in sediments was determined using equation 6 below:

$$EF = (Cm/CFe)\ sample\ /\ (Cm/CFe)\ control \quad (6)$$

where (Cm/CFe) sample is the ratio of metal concentration (Cm) to that of Fe (CFe) in the sediment sample and (Cm/CFe) control is the ratio of metal concentration to that of Fe in the Control [50]. Iron was chosen as a reference metal because of its relative abundance in the studied area and is the most widely used metal as normaliser [51]. Geoaccumulation index (Igeo) was evaluated using

$$Igeo = \log2[Cn/1.5Bn] \quad (7)$$

where Cn is the metal concentration in sediment, Bn is the background value of individual metal and 1.5 is a constant which takes care of possible variations of the background values due to lithologic variations in sediment. Igeo consists of seven (7) classes: Igeo < 0 = practically unpolluted; Igeo > 0 – 1 = unpolluted to moderately polluted; Igeo > 1 – 2 = moderately polluted; Igeo > 2 -3 = moderately polluted and Igeo > 5 = very strongly polluted [48,52]. Pollution intensity (I_{poll}) was evaluated using equation 8 below

$$I_{poll} = \log_2 (Bc/Lp) \quad (8)$$

where I_{poll} is the pollution intensity, Bc is the bulk concentration and Lp the lithogenous portion from results of sequential extraction procedures [53]. The experimental results were analyzed statistically using Microsoft Excel 2007 and SPSS software (version 20.0 for Windows).

3. RESULTS AND DISCUSSION

Results obtained for the analysis of trace metals in sediments from studied rivers are indicated in Tables 1 – 7. Table 1 shows results for the total concentrations of trace metals in sediments from studied rivers and Control. Results for speciation, percentage recovery and bioavailability factor of trace metals in sediments from studied rivers and Control are indicated in Table 2. Correlation coefficients of trace metals in sediments are given in Table 3. Table 4 shows results for contamination factor, degree of contamination and pollution load index of trace metals in sediments. Table 5 indicates results for enrichment factor of trace metals in sediments studied. Geo-accumulation index of trace metals in sediments are shown in Table 6. Results for contamination class of each trace metal in sediments are shown in Table 7.

Table 1. Mean concentrations (µg/g) of trace metals in sediment

Location	Cd	Mn	Cu	Ni	Pb	Zn	Fe
Itu River	2.70	39.60	17.46	17.08	12.43	73.48	83.17
Qua Iboe River	8.80	67.85	19.34	23.68	36.65	84.42	91.63
Imo River Ikot Abasi	8.16	54.58	23.58	18.74	17.53	62.04	72.74
Atabong River	4.76	43.74	14.90	11.31	21.57	51.16	52.32
Iko River	7.09	56.10	17.11	15.05	25.46	57.08	66.36
Min	2.70	39.60	14.90	11.31	12.43	51.16	52.32
Max	8.80	67.85	23.58	23.68	36.65	84.42	91.63
Mean	6.30	52.37	18.48	17.17	22.73	65.64	73.24
Median	7.09	54.58	17.46	17.08	21.57	62.04	72.74
SD	2.53	11.14	3.26	4.57	9.16	13.32	15.18
Control	1.24	10.15	1.73	1.03	1.58	13.91	24.13

SD = Standard Deviation

Table 2. Results for speciation of trace metals in sediments from studied rivers and Control, percentage composition and percentage recovery

Metal	Aex (F1)	% Comp.	Red (F2)	% Comp.	Ox (F3)	% Comp.	Res (F4)	% Comp.	Sum fraction	Sum Total	% Rec.	BF
Cd	10.66	34.96	8.91	29.22	6.57	21.55	4.35	14.27	30.49	31.51	97	35
Mn	52.53	22.61	49.27	21.20	59.54	25.62	71.02	30.57	232.36	261.87	89	23
Cu	14.65	16.84	19.53	22.45	10.94	12.57	41.89	48.14	87.01	92.39	94	17
Ni	15.78	19.17	20.85	25.33	12.82	15.57	32.87	39.93	82.32	85.86	96	19
Pb	24.80	22.54	37.67	34.23	19.82	18.01	27.76	25.22	110.05	113.64	97	23
Zn	68.85	21.50	121.71	38.00	55.94	17.46	73.80	23.04	320.30	328.18	98	22
Fe	59.67	16.62	92.93	25.89	72.75	20.27	133.60	37.22	358.95	366.22	98	17
Control												
Cd	0.45	38.13	0.28	23.73	0.24	20.34	0.21	17.80	1.18	1.24	95	38
Mn	2.25	23.49	2.54	17.01	3.16	26.51	1.63	32.99	9.58	10.15	94	24
Cu	0.26	16.25	0.45	28.12	0.22	13.75	0.67	41.88	1.60	1.73	93	16
Ni	0.16	16.16	0.21	21.22	0.19	19.19	0.43	43.43	0.99	1.03	96	16
Pb	0.38	24.52	0.74	47.74	0.18	11.61	0.25	16.13	1.55	1.58	98	25
Zn	2.52	18.93	5.64	42.37	2.05	15.41	3.10	23.29	13.31	13.91	96	19
Fe	2.56	11.07	5.85	25.31	5.14	22.23	9.57	41.39	23.12	24.13	96	11

Aex = Acid Extractable fraction; Red = Reducible fraction; Ox = Oxidisable fraction; Res = Residual fraction; % Comp. = Percentage composition; % Rec. = Percentage recovery and BF = Bioavailability factor

3.1 Total Metal Concentration in Sediment

Results for total metals in sediments from the different rivers studied are shown in Table 1. Results as indicated in the Table show that, total cadmium concentrations vary from 2.70 µg/g to 8.80 µg/g. The highest concentration of Cd was recorded in samples from Qua Iboe River while the lowest concentration was reported in sediments from Itu River. Thus, the intensive industrial and commercial activities existing in Ibeno due to the presence of oil Company in the area could have introduced considerable amounts of Cd into the host environment. The range of Cd obtained in this study is higher than 0.01 – 0.69 µg/g reported in sediments from Orogodo River, Nigeria by Puyate et al. [54]. However, this range is lower than 7.34 – 19.34 µg/g obtained in sediments from River Ngada, Nigeria by Akan et al. [55]. This range is also higher than those reported in sediments by Ephraim and Ajayi [25]; Topçuoğlu et al. [56]; Etim and Adie [26]; Osakwe et al. [37]; Coban et al. [57] and Charkhabi et al. [58]. The mean concentration ± SD of total cadmium (6.30±2.53 µg/g) obtained in the studied rivers is higher than 1.24 µg/g recorded in samples from Ekpene Ukpa River (Control). Consequently, this signified the presence of anthropogenic sources of cadmium into these rivers studied. This mean is also higher than 6.0 µg/g recommended for unpolluted water sediment by WHO [59]. Hence, concentrations of Cd in sediments from most of the studied rivers especially Qua Ibo, Imo and Iko might have reached the nuisance level as a consequence of industrial activities in and around these aquatic ecosystems. This may impact negatively on these rivers as elevated cadmium has some negative implications on growth rate and embryonic development of aquatic organisms [60]. In human, cadmium accumulates in the intestine, liver and kidney [59]. The distribution of total cadmium in studied rivers skewed to the left as the median is higher than mean (Table 1).

The distribution of total manganese in sediments from the different rivers studied varied between 39.60 µg/g in samples from Itu River and 67.85 µg/g recorded in samples from Qua Iboe River (Table 1). This range is lower than 280.23 – 400.26µg/g reported in sediments from Khor- Al-Zubair River, Iraq by Sultan et al. [61] but higher than 20.94 – 48.43 mg/kg obtained by Egwaikhide et al. [62] in sediments from River Kaduna, Nigeria. The obtained manganese range is also higher than those reported in sediments by Imiuwa et al. [63] but, lower than those reported by Kumar et al. [64]; Akan et al. [55]; Ekwere and Elueze [24]; Ergüil et al. [65]; Balkis et al. [66,67]; Butu and Iguisi [68]. Nevertheless, the mean concentration ± SD of total Mn (52.37±11.14 µg/g) obtained is higher than 10.15 µg/g recorded in the Control indicating artificial addition of the metal in these areas. Furthermore, the mean is higher than 30.0 µg/g stipulated limit for Mn in un-polluted sediment thus, manganese concentrations in rivers studied may pose some negative environmental and health problems to the aquatic organisms. It can bio-accumulate in lower aquatic organisms such as phytoplankton, algae, mollusks and some fish though not in higher organisms and bio-magnification in food chain may not be significant [59,69]. Concentrations of total Mn in studied rivers skewed to the left (negatively skewed) with a higher median than mean.

Concentrations of total copper obtained in this study varied from 14.90 µg/g in samples from Atabong River and 23.58 µg/g recorded in sediments from Imo River (Table 1). This range is higher than 36.00 – 50.00 µg/g of total copper reported in sediments from Calabar River, Nigeria but lower than 26.32 -89.00 µg/g obtained by Akan et al. [55] in surface sediments from River Ngada, Nigeria. The obtained range is also lower than those reported in sediments by Ekwere and Elueze [24]; Omozokpia et al. [70]; Ergüil et al. [65]; Topçuoğlu et al. [71]; Yücesoy and Ergin [72] but higher than ranges obtained by Puyate et al. [54]; Ideriah et al. [73] and Uwah et al. [30]. The mean concentration ± SD of Cu (18.48±3.26 µg/g) obtained in sediments studied is higher than 1.73µg/g recorded in samples from Ekpene Ukpa River (Control) indicating availability of anthropogenic sources of copper in these rivers. However, the mean is lower than 25.0µg/g recommended limit for copper in un-polluted sediment by WHO [59]. Thus, concentrations of copper in studied rivers may not be considered as a pollutant rather it could be useful for the functioning of enzymes, formation hemoglobin and haemocyanin in bloods of vertebrates and shellfish respectively [74,75]. Nevertheless, the high concentrations of copper in sediments from Imo River calls for concern as this can lead to improper functioning of olfactory response, cardiovascular and nervous systems which may eventually reduce the population of fish in this ecosystem [76-78]. This high concentration of copper in Imo River may be attributed to the intensive activities in and

around the area and the direct contact of the river with Atlantic Ocean. Accordingly, the anthropogenic source of Cu to this aquatic environment and other studied rivers should be monitored and controlled. Timely and proper monitoring of these water bodies should also be encouraged to forestall bioaccumulation of copper and its attendant's negative implications of copper toxicity. The distribution of total copper within studied rivers was positively skewed as the mean is higher than median (Table 1).

Concentrations of total nickel as shown in Table 1 range from 11.31 µg/g in samples from Atabong River to 23.68 µg/g reported in Qua Iboe River. This range is higher than 1.74 – 5.18 mg/kg reported in sediments from Qua Iboe River by Moses et al. [27] but lower than 30.60 – 69.35 µg/g obtained by Kumar et al. [64] in sediments from Cochin Estuary, Southwest coast of India. Range of nickel obtained in this study is higher than those reported by Coban et al. [57]; Osakwe et al. [37]; Etim and Adie [26] and Uwah et al. [30] but lower than ranges recorded by Balkis [67]; Akan et al. [55]; Ephraim and Ajayi [25] and Sultana et al. [79]. The mean concentration ± SD of total Ni obtained in this study (17.17±4.57 µg/g) is higher than 1.03 µg/g recorded in sediments from Control site. Thus, indicating existence of anthropogenic sources of the metal in rivers studied. The mean obtained is lower than 20.00 µg/g recommended limit for Ni in unpolluted sediment by WHO [59]. Consequently, Ni may not be regarded as a pollutant in the studied rivers except in Qua Iboe River. The level of total Ni in sediments from Qua Iboe River could cause behavioural changes such as surfacing, rapid mouth and opercular movements, convulsions in fish [80]. It can also lead to blood hypoxia, decrease concentration of glycogen in muscle and liver, increase in lactic acid and glycogen in blood and eventually death of fish [81,82]. This should be effectively monitored and controlled to forestall problems associated with Ni toxicity along the food chain. The distribution of total nickel in sediments from studied rivers was symmetrical as the mean is similar in value with the median (Table 1).

Levels of total lead in sediments from studied rivers varied between 12.43 µg/g in samples from Itu River and 36.65 µg/g in Qua Iboe River samples. The high levels of lead recorded in samples from Qua Iboe River may be attributed to severe oil activities in the area [28]. This range is higher than 25.63–28.63 µg/g obtained in sediments from gulf of Chabahar Oman sea by Bazzi [83] but lower than 54.33-71.12 µg/g reported in sediments from River Ngada, Nigeria. The obtained range is also lower than those reported by Sultan et al. [61]; Yücesoy and Ergin [72]; Barakat et al. [40]. However, ranges of lead recorded in sediments by Uwah et al. [30]; Puyate et al. [54]; Moses et al. [27] and Ekwere and Elueze [24] are lower than the range of Pb reported in this study. The mean lead concentration ± SD (22.73±9.16 µg/g) is lower than 40.00 µg/g recommended limit in unpolluted sediment by [84]. Thus, lead may not be considered as a pollutant within the studied rivers though periodic assessment is encouraged to forestall bioaccumulation and the associated negative effects. Nevertheless, lead concentrations in sediments from Qua Iboe River were very high possibly due to oil activities within the area and should be controlled to avoid the negative effects of Pb toxicity on aquatic organisms as indicated by [74,85-87]. The mean concentration of total lead in sediments from Control site (1.58 µg/g) is twenty times less than that recorded for studied rivers. Consequently, human activities within and around these studied rivers could have resulted in elevated level of Pb in these aquatic ecosystems. Thus, these anthropogenic sources should be identified, effectively monitored and controlled to avoid the negative effects associated with lead toxicity in food chain as indicated by Wright and Welbourn [75] and WHO [87]. Concentrations of total lead within the studied rivers followed a positively skewed distribution as the mean is higher than median (Table 1).

Results obtained revealed that concentrations of total zinc varied between 51.16 µg/g in samples from Atabong River and 84.42 µg/g for Qua Iboe River sediments (Table 1). The high level of zinc in sediments from Qua Iboe River may be attributed to the intensive commercial and industrial activities within the area. This range is lower than 101.3 – 455.69 µg/g reported in sediments from Cochin Estuary Southwest coast of India by Kumar et al. [64] but higher than 0.02 – 1.67 µg/g recorded for sediments from Orogodo River, Nigeria by Puyate et al. [54]. Concentrations of total zinc obtained in this study are also lower than those reported by Balkis [67]; Ergül et al. [65]; Adekola and Eletta [88]; Akan et al. [55] and Omozokpia et al. [70]. Though, the obtained concentrations are higher than those recorded in sediments by Bazzi [83]; Uwah et al. [30]; Sutan et al. [61] and Moses et al. [27]. The mean concentration ± SD of Zn obtained in this work (65.64±13.32 µg/g) is much higher than the

mean zinc concentration reported in sediments from Control (13.91 µg/g). This is an indicative of anthropogenic addition of zinc to the studied rivers. However, the obtained mean for studied rivers is lower than 123.00 µg/g recommended standard for zinc in unpolluted sediment by WHO [59]. Thus, the studied aquatic ecosystems may be considered unpolluted with zinc though effective monitoring and control of these anthropogenic sources is recommended to forestall its bioaccumulation and associated implications reported by Forth et al. [89]; Beyer et al. [90]; Robinette [91] and Dawson et al. [92]. The concentrations of zinc within studied rivers followed a positively skewed distribution as indicated by the higher mean than median in Table 1.

Concentrations of total iron in sediments studied ranged from 52.32 µg/g in Atabong River to 91.63µg/g in sediments from Qua Iboe River. The elevated levels of iron in sediments from Qua Iboe River may be attributed to the intensive commercial and industrial activities within and around this aquatic environment. Iron recorded the highest mean concentration among trace metals determined, this is similar to the result reported by Ibrahim et al. [93] in sediments. The obtained range of Fe is lower than 1558.38 – 3059.97 mg/kg reported in sediments from Imo River, Nigeria by Osakwe et al. [29] but higher than 1.14 – 44.63 mg/kg recorded for Qua Iboe River sediments by Uwah et al. [30]. The range of Fe obtained in this study is also lower than those reported by Barakat et al. [40]; Tesfamariam et al. [94]; Adekola and Eletta [88]; Omozokpia et al. [70]; Butu and Aguisi [68] and Sultan et al. [61]. However, this range is higher than ranges of iron in sediments obtained by Akan et al. [55]; Puyate et al. [54]; Moses et al. [27] and Topçuoğlu et al. [56]. Mean concentration ± SD of total iron in sediments from studied rivers (73.24±15.18 µg/g) is higher than the mean level of Fe in Control (24.13 µg/g). This is an indicative of additional source of iron in the studied rivers which may probably be due to human activities within and around these aquatic ecosystems. Nevertheless, the obtained mean is higher than 30.00 µg/g stipulated for unpolluted sediment by WHO [59]. Although, iron is known as an essential element for aquatic plants and animals, excess of it can have negative effects within the environment [95–99]. Accordingly, concentrations of Fe in all the studied rivers may be considered as pollutant and could lead to change in physiology and ecology of aquatic plants, damage to gill tissues and anemia in fish [100-102]. Iron concentrations in sediments within the studied rivers followed a normal distribution as the mean is equal in value to the median (Table 1).

3.1.1 Metal speciation in sediment

Cadmium existed principally in acid extractable fraction in sediments from both the studied rivers and Control. Results for the speciation of trace metals in sediments from studied rivers revealed that, cadmium in the acid extractable fraction comprised 34.96% of the total fractions while in the Control samples acid extractable fraction recorded 38.13% of the total fractions. This is similar to the existence of Cd in sediments from Imo River mainly in carbonate bound fraction reported by Osakwe et al. [29]. However, this observation is different from that of Zerbe et al. [103] who reported that cadmium existed predominantly in oxidisable fraction in sediments from Goreckie Lake, Poland. Consequently, majority of Cd in studied rivers were from the activities of human (anthropogenic source) within these areas [104–105]. Results obtained have also shown that, cadmium may pose serious hazard in these aquatic ecosystems and along the food chain since it is readily available for living cells. The order for existence of Cd in the different fractions in sediments from both studied rivers and Control as indicated in Table 2 is Aex > Red > Ox > Res. The readily available nature of Cd in sediments from studied rivers is confirmed by the existence of 85.73% of the metal in mobilisable fractions and 14.27% in immobilisable fraction.

Results of speciation studies revealed that manganese occurred predominantly in residual fraction in both studied sediments and Control with percentage compositions of 30.57 and 32.99 respectively. This is in agreement with result obtained by Eletta and Adekola [106] in sediments from Asa River Ilorin, Nigeria but dissimilar with the predominant existence of Mn in sediments from Aiba reservoir Iwo, Nigeria in acid extractable fraction reported by Olutona et al. [107]. Consequently, manganese concentrations were mostly from natural source and in inert and unavailable form for biological systems [108]. Manganese may not pose immediate threat to both the aquatic life and food chain though periodic assessment should be encouraged as a greater proportion of the metal (69.43%) is in mobilisable fractions. Thus, it may be released into these water bodies at any favourable thermodynamic conditions eventually

causing bioaccumulation, toxicity and associated environmental implications. As shown in Table 2, concentrations of Mn in the different fractions in both sediments from studied rivers and Control are in the order: Res > Ox > Aex > Red (Table 2).

Results in Table 2 show that copper existed chiefly in residual fraction in sediments from both studied rivers and Control. The studied sediments recorded 48.14% for residual fraction of the total fractions while residual fraction comprised 41.88% of the total fractions in the Control. This finding is consistent with that of Osakwe et al. [29] for sediments from Imo River, Nigeria but different from that obtained by Segarra and co-workers who reported principal occurrence of copper in oxidisable fraction in sediments from Vigo Ria, Finisterre Cape Spain [109]. Accordingly, copper concentrations in these rivers may have been mainly from natural source and the metal is not readily available for living organisms since metals in residual form are inert and detrital in nature [110]. Though, the proportion of Cu in mobilisable fraction (51.86%) is relatively higher than the immobilisable fraction so future assessment of these aquatic ecosystems should be done to avoid Cu toxicity and its attendant's effects. The distribution of copper in different fractions in sediments from both studied rivers and Control followed the order: Res > Red > Aex > Ox.

Concentrations of nickel in sediments from rivers studied and Control existed principally in residual fraction with percentage compositions of 39.93 and 43.43 respectively. This is consistent with the findings by Martin et al. [111] in sediments from Ortigas River, Spain but different from the predominant existence of Ni in sediments from Okrika River, Nigeria in oxidisable fraction reported by Horsfall Jr. et al. [112]. Accordingly, nickel may not be readily available in these aquatic ecosystems studied. However, a greater proportion (60.07%) of nickel is available in the mobilisable fractions which could be made available if the conditions are more acidic or reducing [113-114]. Thus, the bioavailability of nickel in these river systems should be closely monitored to avoid bioaccumulation and associated implications in both these water bodies and food chain. Distribution of Ni in the different fractions in sediments from studied sediments and Control as indicated in Table 2 are in the order: Res > Red > Aex > Ox and Res > Red > Ox > Aex respectively.

Concentrations of lead in sediments from studied rivers and Control existed chiefly in oxides and hydroxides of Fe and Mn (reducible) form with compositions of 34.23% and 47.74% respectively. This is similar to the results obtained in sediments from Okrika River, Nigeria by Horsfall Jr et al. [112] but different from the findings by Osakwe et al. [29] who recorded highest fraction of Pb in sediments from Imo River in residual phase. The existence of Pb mostly in the reducible fraction is an indicative of anthropogenic inputs [115-116]. Reducible lead comprised 34.23% of the total Pb fractions while the fraction bound to organic matter and sulphide (Oxidisable) was the least fraction (18.01%). The high accumulation of lead in reducible fraction may be attributed to iron and manganese oxides being good adsorbent for the metal [117-118]. This study has shown that concentrations of lead in the rivers investigated should be examined since the mobilisable fractions recorded much higher proportion (74.78%) than the immobilisable fraction (25.22%). Distribution of lead in sediments from rivers studied in the different fractions in Table 2 follows the order: Red > Res > Aex > Ox however, a different order (Red > Aex > Res > Ox) is shown in the Control site.

Zinc in sediments from both the studied rivers and Control site occurred mostly in the reducible form which could easily be released into the water bodies if the condition is more acidic [114]. The reducible fraction of zinc recorded 38.00% of the total fraction in sediments from studied rivers and 42.37% in Control. This observation is consistent with that reported by Turki [119] in sediments from Al Shabab lagoon, Saudi Arabia but in disagreement with the predominant existence of zinc in acid extractable fraction reported in sediments from Imo River, Nigeria by Osakwe et al. [29]. This finding has shown that, most concentrations of zinc in sediments from studied rivers may have been contributed from anthropogenic sources. The predominant occurrence of zinc in oxides of Fe and Mn may be attributed to the high stability constants of Zn oxides. The distribution of zinc in different fractions in sediments from both studied rivers and Control followed the order: Red > Res > Aex > Ox. The mobilisable zinc proportion in studied rivers (76.96%) is much higher than the immobilisable phase (23.04%). Thus, the bioavailability of zinc should be closely examined and anthropogenic sources controlled to avoid bioaccumulation and the attendants effects.

Iron concentrations in sediments from both the studied rivers and Control existed mainly in the residual fraction. This fraction constituted 37.22% and 41.39% in sediments from studied rivers and Control respectively. This is in agreement with the findings by Eletta and Adekola [107] in sediments from Asa River, Nigeria but different from the existence of iron mainly in oxidisable in sediments from Challawa River, Nigeria reported by Funtua et al. [120]. Iron in this fraction cannot be easily released into these water bodies. The existence of iron mostly in residual fraction is an indication of natural inputs of the metals into these rivers [121]. However, since a higher proportion of Fe is in the mobilisable fraction (58.61%), its bioavailability should properly assess to forestall environmental hazards associated with Fe toxicity in these aquatic ecosystems and food chain. Speciation of iron in sediments from both the studied rivers and Control as indicated in Table 2 is in the order: Res > Red > Ox > Aex.

3.1.2 Bioavailability of trace metals in sediments from studied rivers and control

Results obtained in Table 2 indicate that, cadmium exhibited the highest bioavailability in sediments from both studied rivers and Control. This may be attributed to its existence in readily available fraction (acid extractable). Consequently, this study has revealed the high mobility and toxicity potentials of cadmium in areas studied. Whereas, iron exhibited the least bioavailability potential at both studied rivers and Control indicating the low mobility and toxicity of the element in studied rivers. Generally, the bioavailability, mobility and toxicity of trace metals in sediments from studied rivers followed the order: Cd > Mn = Pb > Zn > Ni > Cu = Fe. However, the trend in Control indicated an order: Cd > Pb > Mn > Zn > Cu = Ni > Fe.

3.1.3 Relationship of trace metals in sediment

Results in Table 3 indicate strong positive correlation among metals analyzed for in sediments. Results obtained indicated that at 99% confidence limit, significant positive correlation existed between the following pairs of metals in sediments studied: Cd/Mn; Cd/Pb; Mn/Cu; Mn/Ni; Mn/Pb; Mn/Zn; Mn/Fe; Cu/Ni; Cu/Zn; Cu/Fe; Ni/Zn; Ni/Fe and Zn/Fe (r values are in Table 3). This study also revealed that at 98% confidence limit, strong positive correlations existed for Cd/Cu; Cd/Ni and Ni/Pb with r values of 0.793; 0.799 and 0.799 respectively. At 95% confidence limit, lead indicated strong positive correlation with zinc and iron with r values of 0.765 and 0.713 respectively. Significant positive relationship existed for Cd/Zn; Cd/Fe and Cu/Pb at 90% confidence limit with r values 0.661; 0.665 and 0.659 correspondingly. The general result has shown that trace metals in sediments from rivers studied exhibited strong positive associations. Thus, an increment in the concentration of one metal can affect the level of the other positively though depending on the nature of their association. This strong positive correlation among trace metals in sediments studied is an indicative of similar chemical properties and common source in these aquatic ecosystems studied [112,122].

3.1.4 Pollution status of trace metals in sediment

Results obtained for contamination factor of trace metals in sediments from studied rivers are shown in Table 4. Results obtained revealed that Mn, Cu, Ni and Zn were in the low contamination class with mean CF values of 0.09, 0.74, 0.86 and 0.94 respectively. Cadmium exhibited considerable degree of contamination with mean CF value of 21.01 while lead and iron with respective mean CF values of 1.14 and1.61 showed moderate degree of contamination. The contamination factor of trace metals followed the order Cd > Fe > Pb > Zn > Ni > Cu > Mn. This demonstrates that cadmium was the most risky element while manganese was the least risky element in aquatic ecosystems investigated. A range of 14.11 – 36.44 was reported for the degree of contamination (Cdeg) in sediments from rivers studied with Itu River indicating the lowest degree of contamination while Qua Iboe River showed the highest degree of contamination. Accordingly, Itu River indicated moderate degree of contamination while Imo, Atabong and Iko Rivers displayed considerable degree of contamination, Qua Iboe River showed very high degree of contamination. Pollution load index (PLI) values recorded for studied rivers ranged between 0.05 and 1.86 for Itu and Qua Iboe Rivers respectively. The PLI results revealed that Qua Iboe River was at a deplorable state while most of these metal contaminants were at their baseline levels pollution in other rivers studied [49]. Results of PLI corroborated the devastating state of Qua Iboe River with respect to metal contamination as indicated by Cdeg.

Enrichment factor (EF) was employed to identify the source of trace metals into these

aquatic ecosystems. Results obtained in Table 5 show that enrichment factors of cadmium range between 0.65 – 2.24 with a mean value of 1.75. EF value lower than or equal to 1.00 in sediment originated predominantly from geologic processes. This study as shown in Table 5 indicate that, apart from Itu River with EF value of Cd less than 1.00, the EF values of the other studied rivers originated from anthropogenic source. Ranges of EF values recorded for all the other trace metals except iron at all the aquatic environments studied revealed anthropogenic inputs of these metals.

Results of geo-accumulation index for trace metals in sediments from studied rivers as shown in Table 6 indicate that, Cd is in class 4, Mn, Cu, Ni, Pb and Zn belong to class zero while Fe is in class 1. Consequently, cadmium severely polluted sediments from studied rivers, manganese, copper, nickel, lead and zinc may not have polluted these sediments while iron slightly polluted the studied sediments.

Table 3. Pearson correlation coefficient among trace metals in soil

	Cd	Mn	Cu	Ni	Pb	Zn	Fe
Cd	**1.000**	0.928	0.793	0.799	0.851	0.661	0.665
Mn		**1.000**	0.882	0.927	0.928	0.868	0.846
Cu			**1.000**	0.912	0.659	0.860	0.859
Ni				**1.000**	0.799	0.973	0.975
Pb					**1.000**	0.765	0.713
Zn						**1.000**	0.989
Fe							**1.000**

Red is significant at P ≤ 0.10; brown at P ≤ 0.05; blue at P ≤ 0.02 and green at P ≤ 0.01

Table 4. Contamination factor (CF), degree of contamination (Cdeg) and pollution load index (PLI) of trace metals in sediments

Location	Cd	Mn	Cu	Ni	Pb	Zn	Fe	Cdeg	PLI
Itu River	9.00	0.07	0.70	0.85	0.62	1.05	1.82	14.11	0.06
Qua Iboe River	29.33	0.11	0.77	1.18	1.83	1.21	2.01	36.44	1.86
Imo River	27.20	0.09	0.94	0.94	0.88	0.89	1.60	32.54	0.39
Atabong River	15.87	0.07	0.60	0.57	1.08	0.73	1.15	20.07	0.05
Iko River	23.63	0.09	0.68	0.75	1.27	0.82	1.46	28.70	0.24
Mean	21.01	0.09	0.74	0.86	1.14	0.94	1.61	26.37	0.52

Table 5. Enrichment factor (EF) of trace metals in sediments from studied rivers

Location	Cd	Mn	Cu	Ni	Pb	Zn	Fe
Itu River	0.65	1.13	2.92	4.78	2.26	1.52	1.00
Qua Iboe River	1.92	1.76	2.93	6.01	6.06	1.59	1.00
Imo River Ikot Abasi	2.24	1.79	4.50	5.99	3.65	1.47	1.00
Atabong River	1.82	1.99	3.96	5.03	6.25	1.69	1.00
Iko River	2.14	2.01	3.58	5.27	5.81	1.48	1.00
Mean	1.75	1.74	3.58	5.42	4.81	1.55	1.00

Table 6. Geoaccumulation index values for trace metals in sediments from studied rivers

Location	Cd	Mn	Cu	Ni	Pb	Zn	Fe
Itu River	2.59	-4.51	-1.10	-0.81	-1.27	-0.52	0.29
Qua Iboe River	4.29	-6.97	-0.96	-0.34	0.29	-0.31	0.43
Imo River Ikot Abasi	4.18	-4.04	-0.67	-0.68	-0.78	-0.76	0.09
Atabong River	3.40	-4.32	-1.33	-1.41	-0.48	-1.04	-0.38
Iko River	3.98	-4.01	-1.13	-0.99	-0.24	-0.88	-0.04
Mean	3.69	-4.77	-1.04	-0.85	-0.50	-0.70	0.08
Igeo class	4	0	0	0	0	0	1
Remarks	SVP	UP	UP	UP	UP	UP	SP

SVP = Severely polluted; UP = Unpolluted and SP = Slightly polluted

Table 7. Contamination classes of trace metals in sediments according to I_{poll} index

Category	Pollution intensity class	Element	I_{poll}	Risk assessment
Extremely polluted	> 5	Cd	2.81	Moderate polluted
Strongly polluted	4 – 5	Mn	1.71	Lowly polluted
High polluted	3 – 4	Cu	1.06	Lowly polluted
Moderately polluted	2 – 3	Ni	1.32	Lowly polluted
Low polluted	1 – 2	Pb	1.99	Lowly polluted
Unpolluted	<0 – 1	Zn	2.12	Moderately polluted
		Fe	1.43	Lowly polluted

3.1.5 Pollution intensity (I_{poll}) and risk assessment of trace metals in sediment

I_{poll} Index proposed by Karbassi et al. [53] for the assessment of metal pollution in aquatic and terrestrial environments was utilized for assessment of metal pollution in sediments from rivers studied. Results for the assessment of metal pollution intensity according to I_{poll} are shown in above Table 7. Results obtained indicated that cadmium and zinc showed moderate level of risk while manganese, copper, nickel, lead and iron indicated low level of risk. Consequently, high levels of cadmium and zinc may be released into these aquatic ecosystems from anthropogenic sources which may eventually results in their toxicities and associated environmental implications.

3.1.6 Quality control of analytical techniques and results obtained

Due to lack of standard reference material (SRM), the analytical techniques used and results obtained were validated using the percentage recovery of trace metals determined. Using equation (1) above, the percentage recovery for each trace metal was recorded. Results obtained are shown in Table 2 and are as follows for metals in studied rivers: Cd (97%); Mn (89%); Cu (94%); Ni (96%); Pb (97%); Zn (98%) and Fe (98%). While the percentage recovery for metals in Control were Cd (95); Mn (94); Cu (93); Ni (96); Pb (98); Zn (96) and Fe (96). These values generally agreed with acceptable ones recommended by Gaithersburg et al. [123] for recoveries of metals.

4. CONCLUSION

Results obtained from this study revealed that, human activities especially by oil industries within the Niger Delta region of Nigeria have greatly affected the quality of surface water bodies within the area. However, most of these trace metals existed in inert and unavailable form thus, reducing their toxicity potentials. Nevertheless, since the mobilisable fractions of these metals are higher than the immobilisable phase adequate monitoring of anthropogenic sources of these metals should be done. Levels of cadmium in sediments from the studied rivers exhibited very high degree of risk. Considering the dependent of the people of Niger Delta on water resources, aquatic organisms should be properly assessed to ascertain their suitability or otherwise for human consumption.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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