Distribution of Heavy Metals in Sediments and Surface Water of Crude Oil Impacted Area in the Niger Delta, Nigeria

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Abstract. Characteristic levels of Cd, Cu, Cr, Ni, Pb, Mn and Zn in surface water and sediments from an oil impacted area in the Abalagada-Aboh catchments in the Niger Delta were studied. Except for Pb, the concentrations of dissolved or heavy metals in the surface water were below the limits of detection. However, mean concentrations of lead in the surface water exceeded WHO limit for drinking water; whereas, the concentrations of heavy metals in the natural and agricultural soils sediments were found within limits. The significant enrichment in the levels of heavy metals was due to oil spillage and related anthropogenic activities. The enrichment factor for heavy metal in the sediment follow the order Cd > Ni > Zn > Pb > Cr > Mn > Cu. The Mehlich III extractable metals in the sediment ranged from 62.0-78.3% for Cd, 1.3-11.4% for Cr, 6-18.0% for Cu, 14.0-51.3% for Pb, 12.0-20% for Ni, 8.0-17.5% for Mn and 26.3-45.0% for Zn. The Mehlich III extractable metals follow the order: Cd > Zn > Pb > Mn > Ni > Cu > Cr which does not tally with the order of enrichment factor indicating that heavy metal enrichment of sediment does not necessary implies lability and bioavailability of the elements in the sediment matrix. Overall metal availability indicates contamination potential risk of cadmium, lead and zinc in the Abalagada-Aboh catchment.

Keywords: heavy metals, bioavailability, enrichment factor, oil spillage, sediments, Niger Delta

Introduction

Waterways are of particular significance to the geochemical cycling of toxic and potentially toxic metals. Most of the toxic metals become associated with the solid phase at the bottom of the waterway. Although a complex equilibrium exists which support low level metals in the overlying surface water, sediment serves as an effective sink for these metals because a number of metal immobilization reactions are supported by the physical, chemical and biological properties of the sediments. In many waterways, particularly near waste outfalls, large quantities of heavy metals and biostimulants accumulate in sediments that may be toxic at high levels (Khalid *et al.*, 1978).

In this scenario, heavy metals have a great ecological significance due to their toxicity and bioaccumulation. These elements, contrary to most pollutants, are not biodegradable and undergo ecological cycling in which natural waters are the main pathway (Chakrapani and Subramanian, 1993; Nurberg, 1984). River sediments, by precipitation, adsorption and chelation process provide the major sink for heavy metals in the aquatic environment.

Ndiokwere (1984) used neutron activation analysis and atomic absorption spectrometry techniques for the determination of As, Au, Cd, Hg, Ni, Pb, Sr and Zn in sediments and algae from the river Niger and the Nigerian Atlantic coastal waters.

The measured concentrations of As, Cd, Hg and Sb were higher in the sediments from the coastal waters than sediments from the river Niger which contained Mn, Pb and Zn in high concentration. Other studies in the area (Kakulu and Osibanjo, 1992; 1988) revealed elevated levels of Pb, Cr, Ni and Zn in the Port-Harcourt and Warri sediments which suggested that effluent from petroleum refineries located in these areas have contributed significantly to the heavy metal pollution of respective aquatic system.

The distribution of heavy metal content in the bottom sediment of lake Illawarra, show that elevated concentrations of trace metals particularly, zinc was linked to the ash concentration. The highest concentrations of total metals (up to 10 times the locally defined background) were recorded in Griffin Bay, adjacent to the Port Kembla industrial complex. Other sites exhibited only slight metal enrichment near surface, typically 1.4 to 2 times the background (Chenhall *et al.,* 1994). The purpose of this study was to determine the characteristic levels and the bioavailable fraction of metals in sediment as well as the soluble metal content in the surface water from crude oil impacted area in the Niger Delta, toprovide information on contamination and the associated ecological risks.

Geographic features of the area. Abalagada-Aboh catchment, the area under study, is located in northern part of the Niger Delta, south central Nigeria and within Ndokwa east

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local government area of delta state. The study area lies within the coordinates 454400-464000 E and 181750-183000 N. It is marked with natural deposit of levee. The principal relief feature of the area are generally low lying but galloping terrain, dominated by the flood plains that are seasonally inundated with flood from the river Niger and the two creeks (Ozara and Eko) forms its drainage system. This area is characterized by crisscrossing of oil pipelines and multiple oil wells. Apart from farming and fishing, the major activities in this area are oil and gas exploration and exploitation.

Communities in these areas depend solely on the swamps and creek as their source of drinking water. On the 11th of October, 2003, there was an accidental spill from KW15 and 16 oil wells covering a large expanse of land and water bodies in this area. The spillage was accompanied by the fire out break which lasted for 30 days.

Materials and Methods

Sample collection and analysis. Water and sediments were collected from 9 sites in the water bodies adjoining the oil wells which had received various degrees of impact. The baseline (backgrounds levels) recorded before drilling and operation of the oil wells was taken as the control. Water samples were collected manually into polyethylene bottles already cleaned with 10% HNO_3 and rinsed with distilled water and water to be analysed. At each site, three samples were taken at the surface level and three at the mid depth level and mixed. The water samples were filtered, transferred directly into the bottles and acidified to a pH < 2 by adding concentrated nitric acid. The samples were then stored in refrigerator at 4 °C.

The surface sediments were collected by scooping up 10 cm of soft mud at each site with 0.9l wide mouth glass freezer (acid rinsed) jar to remove possible trace metal contamination. The samples were air dried, ground to pass through 22 mm sieve and stored at 4 °C till the analysis. The total metal concentration was measured as HF/aqua regia extract-

able amount. The sample solution was analyzed for Cu, Zn, Pb, Cr, Ni, Cd and Mn, using air-acetylene flame atomic absorption spectrophotometer (Perkin Elmer A3100). The atomic absorption spectrophotometer (AAS) was fitted with D_2 background correction devices and analysis of blanks were also carried out. Bioavailable metals in the sediment were determined by extracting the sediment with Mehlich III solution (0.2M CH_3COOH + 0.25M NH_4NO_3 + 0.015M NH_4F + 0.013M HNO_3 + 0.001M EDTA, pH 2.0) and measuring the concentration using AAS (Mehlich, 1984). Briefly, 2.5 g air-dried sediment was placed in a 50 ml polystyrene centrifuge tube and 25 ml Mehlich III extractant was added. The suspension was shaken for 5 min and filtered through Whatman # 42 filter paper. Concentrations of the extractable metals in the filtrate were analysed using AAS. All samples were analysed in triplicate; the coefficient of variation was less than 5% in all cases.

Heavy metal enrichment factor (EF) for the sediment was derived using the expression (Chenhall *et al.,* 1994; 1992):

$$EF = \frac{\text{Mean concentration of trace metal in the upper 20 cm of sediment}}{\text{Background concentration}}$$

Results and Discussion

Physiochemical and heavy metal characteristics of sediment. The sediments are mostly acidic in nature with mean pH 5.33 (Table 1). In the Niger delta, this near neutral to weakly acidic pH is common to anaerobic soil and sediments (Iwegbue *et al.,* 2006) which decreases upon oxidation and could result in increased mobility and biological availability of certain trace and toxic metals (Gambrell *et al.,* 1983). Percent organic carbon and sulphur are two important factors that control metal availability in the sediment. In anaerobic conditions, metals may be precipitated as sulphide. In oxic or anoxic sediments, metals can be adsorbed onto the organic matter. The organic matter content of the sediments was generally low as compared to the value reported by Horsfall *et al.* (1999) for Okirika

Table 1. Some physicochemical characteristics of the sediments for all sites

Parameters	Mean ± SD	Range	RSD*(%)
PH	5.33 ± 0.91	4.5 - 6.64	17
EC (µS/cm)	82.94 ± 18.55	49.6 - 18.0	22.4
Organic matter %	0.73 ± 0.47	0.26 - 1.76	64.4
Total nitrogen (%)	0.11 ± 0.14	0.02 - 0.44	120.9
Nitrate-nitrogen (mg/kg)	256.40 ± 310.21	42.25 - 995.48	121.0
Total phosphorus (mg/kg)	25.83 ± 14.54	11.46 - 55.92	56.2
Available phosphorus (mg/kg)	9.43 ± 5.31	4.18 - 20.33	56.2

* = relative standard deviation

River system and by Gupta and Pant (1983) for eutrophic lake in Naini Tal (UP, India).

The mean concentration, range and coefficient of variation of heavy metal concentration in the surface water is presented in Table 2. The concentrations of Cu, Zn, Cr and Cd in the surface water were below the limits of detection at all sites, except for Mn and Ni from sampling sites 3 and 4 which were above the detection limits. The concentration of Ni was almost same, 0.18 mg/l, for site 6 and 7. The concentrations of Cu, Zn, Cr, Ni, Cd and Mn were below the permissible limits for both aquatic life and human consumption. In case of lead, the mean concentration 0.46±0.26 mg/l (range 0.20-0.74 mg/l) was observed. The concentrations of Pb in all sites were above the WHO, EU and USEPA guideline and standards for drinking water quality. Lead toxicity may pose a serious problem in this area since local communities depend on these sources of drinking water. Persons drinking such contaminated water consume, on an average, 6.44 mg Pb per week, (based on the average consumption of two litres of water per day). The levels of heavy metals reported in this study were lower than those reported by Olajire and lmeokparia (2000), Mombeshora et al. (1981), Kakulu and Osibanjo (1992), and Martin (1978) for some river systems in Nigeria. The levels of lead recorded in this study were similar to those reported by Watling and Watling (1982). The concentration of heavy metals in water column can be relatively low, but the

concentration in sediments may be elevated. Low discharge of contaminants into water bodies may not harm the water quality criteria, but long term process could result in building of high loads of pollutants in the sedement.

It has been estimated that about 90% of the particulate matter carried by rivers settles in estuarine and coastal areas (Martin and Whitefield, 1983). Once heavy metals are discharged into estuarine and costal waters, they rapidly become associated with particulates and are incorporated in bottom sediment (Hanson et al., 1993). The accumulation of metals from the overlying water to the sediment is dependent on a number of external environmental factors such as pH, Eh, ionic strength, anthropogenic input, the types and concentration of organic and inorganic ligands, and the available surface area for adsorption caused by grain size distribution (Davies et al., 1991). Diagenetic processes in the sediment can change and redistribute these contaminants between the solid and the dissolved phases, but most of the elemental contaminants are immobilized through sedimentation (Hanson et al., 1993). pH of the surface water favours natural mechanism of metal precipitation from the water column. This accounts for low levels of metals observed in the surface waters in the sites under study (Table 2). Table 3 presents the mean concentration, relative standard deviation range and background concentration of heavy metals in the sediments at all sites. Analysis of variance ANOVA (P≤0.05) revealed significant spatial variation in the concentrations of heavy metals. Concentrations of total and Mehlich III extractable metals, at individual sites, are presented in Tables 4 and 5, respectively. Paired t-test (P<0.05) was used to compare differences in the mean levels of heavy metals in the heavy and less impact areas.

The result indicated obvious and significant differences in the concentration of heavy metals at these sites e.g. sites 5,6,7,9 have higher concentrations of heavy metals as compared to other points. Concentrations of heavy metals in the sediments correspond to the levels generally found in natural and unpolluted agricultural soils except for Cd. Cu, Pb, Cr, Ni, and Cd

Table 2. Mean concentration of dissolved metals in overlying surface water in the impact area

Metal (mg/kg)	Mean ± SD	Range	RSD%
Copper	0.001 ± 0.00^a	-	-
Zinc	0.001 ± 0.00	-	-
Lead	0.46 ± 0.20	0.02-0.74	44.7
Chromium	0.001 ± 0.00^a	-	-
Nickel	0.07 ± 0.09^a	<0.002-0.18	134
Cadmium	0.001 ± 0.00^a	-	-
Manganese	0.45 ± 1.28	<0.002-3.65	284

^{a} = mean computed on base half of the detection limit

Table 3. Mean concentration and range of heavy metals in sediment at all sites

Metal (mg/kg)	Mean ± SD	Range	RSD (%)	Background levels
Copper	7.18 ± 13.12	<0.002-40.67	183	9.50
Zinc	22.77 ± 15.33	4.74-47.51	67.4	10.5
Lead	15.82 ± 9.72	0.08-34.60	61.5	10.5
Chromium	17.17 ± 22.92	<0.002-36.65	133.5	13.5
Nickel	20.55 ± 12.47	7.53-46.59	60.6	4.75
Cadmium	0.61 ± 0.48	<0.002-1.66	70.6	<0.02
Manganese	150.62 ± 121.29	42.04-334.95	80.5	150

are significantly correlated (P≥0.05) (Kabata-Pendias and Pendias, 1992). The correlation pattern suggests the source of these elements to be common. Zn showed no correlation with any metal. All these metals showed positive correlation with organic matter content of the sediment which implies that most heavy metals in the sediment may be chelated by organic matter. The concentrations of heavy metals found in this study are lower than levels reported for some river systems in the Niger Delta (Horsfall and Spiff 2005; Horsfall et al., 1999; Kakulu and Osibanjo, 1988) and some African inland water sediments. Ihenyen (2001) reported mean levels of 350 mg/kg, 9.0 mg/kg, 2.0 mg/kg, 6.20 mg/kg, 0.60 mg/kg, 4.0 mg/kg, 5.40 mg/kg for Mn, Zn, Cu, Cr, Cd, Ni and Pb, respectively, for sediments from Benin River estuary. The levels found in this study are higher than the mean levels stated above.

Heavy metal enrichment factor was derived by applying the equation described by Chenhall et al. (1992) for comparison. The results indicate significant enrichment in the heavy metal levels of the sediment due to oil spillage and related anthropogenic activities. The mean enrichment factors (range in parenthesis) were 0.76 (0-4.3), 2.27 (0.45-4.5), 1.51 (0.08-3.3), 1.27 (0.00-2.7), 4.33 (1.58-9.8), 30.5 (0.00-83) and 1.0 (0.28-2.23) for Cu, Zn, Pb, Cr, Ni, Cd and Mg, respectively. Chenhall et al. (1995) reported that in the southern part of Griffin Bay (close to the Port Kembia industrial complex), the enrichment factors, for Zn, Pb and Cu were greater than 5.9, 3.5 and 1.8, respectively. The mean enrichment factors found in this study were lower than those reported by Chenhall et al. (1995). Ni and Cd had enrichment factors significantly higher than any other metals studied. Heavily impacted sites e.g. 5,6,7 and 9 showed enrichment factor higher than at any other site. The Mehlich III method was originally developed to evaluate plant availability of macro and micro-nutrients in soil (Zhang et al., 2003; Reed and Martens, 1996; Mehlich, 1984). Mehlich III extractable metals ranged 62-78% for Cd, 1.3-10.4% for Cr, 6-12% for Cu, 14-51% for Pb, 9- 20% for Ni, 8-17% for Mn and 26.3-45% for Zn. The Mehlich III

Table 4. Total metal concentration in the impacted sediments

Site	Metal concentration (mg/kg)						
	Cd	Pb	C r	C u	N i	M n	Zn
1	0.05 ± 0.00	$4.1\ 8 \pm 0.21$	0.001 ± 0.00^a	0.001 ± 0.00^a	7.53 ± 0.23	42.04 ± 2.10	4.74 ± 0.19
2	0.59 ± 0.03	0.80 ± 0.03	0.78 ± 0.04	1.07 ± 0.05	11.87 ± 0.71	77.50 ± 3.10	18.94 ± 0.57
3	0.001 ± 0.00^a	17.70 ± 0.71	2.64 ± 0.13	0.01 ± 0.00	11.87 ± 0.30	38.86 ± 1.55	9.63 ± 0.48
4	0.59 ± 0.03	17.70 ± 0.53	9.44 ± 0.47	0.14 ± 0.01	20.55 ± 0.62	86.04 ± 2.58	18.22 ± 0.91
5	0.59 ± 0.02	14.32 ± 0.72	$29.23 \pm 1\ .I\ 7$	9.45 ± 0.39	29.23 ± 1.46	285.78 ± 13.15	37.8 ± 2.27
6	0.59 ± 0.02	17.70 ± 0.53	8.82 ± 0.44	4.33 ± 0.17	16.21 ± 0.81	197.77 ± 5.93	47.51 ± 2.85
7	1.66 ± 0.08	34.60 ± 1.73	66.92 ± 4.02	40.63 ± 1.22	46.59 ± 1.86	267.66 ± 11.50	8.85 ± 0.44
8	0.86 ± 0.03	1432 ± 0.72	0.001 ± 0.00^a	0.001 ± 0.00^a	11.37 ± 0.36	27.02 ± 1.08	19.03 ± 0.91
9	0.59 ± 0.03	21.08 ± 1.05	$29.23 \pm 1\ .I7$	8.98 ± 0.45	29.23 ± 1.75	334.95 ± 13.40	$40.1\ 9 \pm 2.01$

Table 5. Mean concentrations of Mehlich Ill extractable metals in the sediments

Site	Metals (mg/kg)						
	Cd	Pb	Cr	Cu	Ni	Mn	Zn
1	0.03 (62.0%)	0.84 (20.0%)	-	-	0.99 (13.0%)	6.51 (15.5%)	1.71 (36.0%)
2	0.37 (63.0%)	0.18 (23.0%)	0.04 (4.7%)	0.06 (6.0%)	1.98 (16.7%)	11.55 (15.0%)	5.68 (30.0%)
3	-	4.83 (27.3%)	0.08 (2.9%)	-	1 .66 (14.0%)	0.29 (8.0%)	2.65 (27.5%)
4	0.39 (65.6%)	2.48 (14.0%)	0.12 (1.3%)	0.03 (1 8.0%)	3.08 (15.0%)	8.95 (10.4%)	6.74 (37.0%)
5	0.37 (62.0%)	2.66 (1 5.3%)	2.57 (8.8%)	0.80 (8.5%)	3.45 (11.8%)	44.01 (15.4%)	15.50 (41.0%)
6	0.45 (76.0%)	9.45 (27.3%)	0.20 (2.3%)	0.58 (13.3%)	1.95 (12.0%)	34.61 (17.5%)	31.38 (45.0%)
7	1.30 (78.3%)	17.75 (51.3%)	7.63 (11.4%)	4.23 (10.5%)	9.32 (20.0%)	30.25 (11.3%)	3.44 (38.9%)
8	0.61 (70.6%)	3.67 (25.6%)	-	-	1.48 (12.5%)	4.05 (15.0%)	5.01 (26.3%)
9	0.44 (75.0%)	5.25 (24.9%)	2.68 (7.3%)	1.37 (15.32)	3.51 (12.0%)	56.94 (17.0%)	12.34 (30.7%)

N.B.: - mean of triplicate analysis relative standard deviation (RSD) % less than 5%; values in parenthesis are percentage fractions of Mehlich III extractable metals of the total metal concentration of the sediments

extractable metal has been interpreted as a sign of relative lability and biological availability of heavy metals in the soils. The results indicate that Cd, Pb, Ni and Zn are relatively labile and bioavailable in the sediment matrix. The proportions of the Mehlich III extractable heavy metals found in this study were higher than the proportion of Mehlich III extractable metals reported for muck sediments from the St Lucie estuary, USA (Zhang *et al.*, 2003). There is significant spatial variation in the concentrations of metals extracted by Mehlich III solution. However, Cd has the highest percentage of Mehlich III extractable metal as compared to any other metal. Heavily impacted sites e.g. 6, 7 and 9 showed appreciable higher concentrations of Mehlich III extractable metals as compared to less impacted sites. This is probably due to the fact that exogenous metals are usually weakly bound to the soil and sediment matrix and therefore are readily released (Abollino *et al.*, 2002; Li *et al.*, 1995). The Mehlich Ill extractable metals follow the order: Cd > Pb > Ni > Mn > Zn > Cu > Cr. which does not agree with the order of enrichment factor, indicating that heavy metal enrichment of the sediment does not necessary implies lability and bioavailability of the metals in the sediments.

Conclusion

Concentrations of heavy metals in the water samples examined were below the detection limits, except for lead having concentration exceeding the WHO limits for drinking water. Lead will pose a problem for communities in the Abalagada-Aboh catchment, since they depend on these water bodies as source of potable water. The concentrations of heavy metals found in the sediments agree with the concentrations found in natural and agricultural soils, except for cadmium. Cadmium and nickel showed higher enrichment factor as compared to any other metal. The enrichment factors of these metals reflect the oil spillage and related anthropogenic activities in the catchment.

The Mehlich Ill extractable metals indicate that cadmium, lead and zinc are the most labile and bioavailable in the sediment. The overall picture of metal availability indicates a potential contamination risk by cadmium, lead and zinc in the catchments. However, the effect of zinc will be minimal since the zinc is required by aquatic flora and fauna.

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