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AN ASSESSMENT OF HEAVY METALS CONTAMINATION IN SURFACE SEDIMENTS OF THE NIGER DELTA, NIGERIA

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ABSTRACT

The concentrations, source and contamination status of heavy metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb and Cd) in surface sediments of rivers and canals in the oil producing area of the Niger Delta were investigated. The average concentrations of individual metals ranged from 0.09 to 19.0 ug/g and 0.11 to 24.2 ug/g in rivers and canals sediment samples respectively. All the metals studied have very low Enrichment factor (EF) which indicated a natural origin. An assessment using a set of widely cited sediments guidelines indicated that the levels of heavy metals concentrations in Niger delta sediments do not pose any serious adverse risk to the ecosystem and human health. The concentration of metals in the samples were comparable to those of aquatic systems classified as uncontaminated from other regions of the world.

Keyword: Rivers, canals, ecosystem, enrichment factor, human health.

INTRODUCTION

Globally, heavy metal accumulation in the aquatic environment is of great concern because of their toxicity to the ecosystem and man. Metals such as Cu and Zn are generally regarded as essential trace metals because of their valuable role in metabolic activities in organisms. However, metals like Cd, Pb, Ni and Hg exhibit extreme toxicity even at trace levels (Merian, 1991). Sediments represent the most important sink of heavy metals in aquatic environments because more than 90% of heavy metals load in marine sediments is bound to suspended particulate matter or sediments (Daskalakes and O'Connor, 1995; Calmano *et al*., 1993). Heavy metals accumulate in the sediments through complex physical and chemical adsorption mechanisms depending on the nature of the sediment matrix and the properties of the adsorbed compounds (Ankley *et al*., 1992; Leivouri, 1998). These metals could enter the aquatic environment through natural source which involves weathering of minerals and soils or from anthropogenic source (Daskalakes and O'Connor 1995; Merian, 1991; Komarek and Zeman, 2004). Weathering associated with the release of heavy metals is of environmental importance because they can serve as either natural contamination sources or soil nutrient input. The concentrations of natural metals in estuarine sediments depend on the geology of the area (Windom *et al*., 1989). Anthropogenic inputs are mainly from domestic sewage, industrial effluent, traffic emissions or from mining and refining operations (Merian, 1991; Kabala and Singh, 2001). The sediments serve as metal pool that can release metals into the overlying water through bioturbation and dredging, causing potential adverse health effects of human life and ecosystem (Daskalakis and O'Connor 1995; Argese *et al*., 1997; Fatoki and Mathabatha, 2001, Kishe and Machiwa, 2003; McCready *et al*., 2006). Marine organisms or biota can uptake heavy metal, which in turns increases the potential of some metals entering into the food chain (Chen *et al*., 2007).

The Niger Delta is one of the major oil producing regions of the world and covers an area of about 75,000 km^2. The region is also home to major oil refineries and many other manufacturing industries. Petroleum exploration activities and oil spillage have been reported to be sources of heavy metals contamination in sediments in some oil producing areas (Newbury, 1979; Patin, 1999). Petroleum contains in addition to the main hydrocarbons, some heavy metals such as Ni, Fe, V, Cu, Mn, Pb and Cd. Heavy metals are also found as components of most drilling fluids that are commonly discharged into the marine environment by oil companies (Conklin *et al*., 1983; Kennicut II *et al*., 1996; Gray *et al*., 1999). The assessment of heavy metals contamination in the Niger delta region is very important because of claims of environmental pollution resulting from oil exploration activities by the inhabitant. Sediment contamination due to various exploration and exploitation activities and industrial effluent discharge in the area is inevitable. Therefore, the present study was conducted to determine the concentration, source(s) and the extent of heavy metals contamination in surface sediments of some rivers and canals in the Niger delta.

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MATERIALS AND METHODS

Sample collection

Fourteen sediment samples were collected from rivers (Bakkasi, Calabar, Greak Kwa and Qua Ibo) and canals (Ogini, Olomoro and Ughelli) in some parts of the Niger Delta (Fig. 1) at depths ranging from 0-20 cm. The sediments were collected using a hand trowel in shallow water and metallic bucket grab sampler in deep water. Representative samples were prepared by mixing five to eight sub-samples from an area of approximately 4 m^2. The samples were transported to the laboratory in pre-cleaned polyethylene bags and stored in a Freezer at -20°C prior to analysis.

Metal analysis

The samples were oven dried at 65°C for at least 24 hrs and pulverized into a fine texture (<µm 65) using an agate mortar and pestle. About 1 g dry weight sediment sample was digested with 10 mL acid mixture of $HNO_3/HClO_4$ (2:1). Digestion was carried out for 2hr on the Tecator digestion block set at 250°C. The digest was allowed to cool and filtered into 25 ml volumetric flask, and made up to mark with distilled water. Metal concentrations in the digested sediment samples were determined using a Buck Scientific Atomic Absorption Spectrophotometer (Model: 210VGP). Quantification of the metals was based upon calibration curves of standard solutions of metals. Blanks were included in each batch of analysis and calibration standards were regularly performed to evaluate the accuracy of the analytical method.

Enrichment factor

The enrichment factor (EF) is an index used to evaluate the anthropogenic contributions in sediments (Aloupi and Angelidis, 2001; Chisholm-Brause and Conrad, 2004). The EF of the heavy metals in the sediment samples was calculated using the following equation:

$$EF = (Me/Fe)_{\text{sample}} / (Me/Fe)_{\text{average shale value}}$$

where $(Me/Fe)_{\text{sample}}$ and $/(Me/Fe)_{\text{average crust value}}$ represent the metal concentration (µg/g dw) in relation to Fe levels (% dw) in the sediments samples and average crust value (Taylor 1964), respectively.

Statistical analysis

Data analysis was performed using SPSS software (version 11.0). Pearson's correlation coefficient matrix was used to test the relationship between trace metals concentrations in the sediments.

RESULTS AND DISCUSSION

Metals concentrations

The overall average concentrations of the metals ranged from 0.09 (Cd) to 19.0 (Mn) ug/g and 0.11 (Co) to 24.2 (Mn) ug/g in rivers and canals sediment samples, respectively (Table 1). The concentration of Mn was higher compared to other metals in all the samples (Fig. 2). The predominance of Mn compared to other heavy metals in surface sediments from aquatic environment has been reported by other workers (Leivuori, 1998; Mora *et al*., 2004). The sediments from canals showed slightly higher concentrations of metals compared to samples from rivers, probably due to differences in dilution rate at the locations (Fig. 2). None of the metals are enriched compared to the average crustal abundance (Taylor, 1964). The average concentrations of all the metals in the sediments were below the effective range low (ERL) and effect ranges medium (ERM) sediment quality guideline (Table 1). The ERL represents the concentration of chemical in sediments below which toxic effects are rarely observed among sensitive species while the ERM represents the chemical level above which effects frequently occur in aquatic organisms (Long *et al*., 1995).

The heavy metal concentrations in the sediments were also lower than the minimal values recommended by the UK Ministry of Agriculture, Fisheries and Food Action levels (MAFF), the US Environment Protection Agency threshold levels of sediment contaminated with heavy metals (EPA) (Table 1). These observations showed that trace metal concentrations in the sediments do not pose any adverse effects on the ecosystem and human health.

Enrichment Factor (EF)

The extent of metal contamination in the sediment samples was assessed using the enrichment factor (EF). EF is a good tool to differentiate between anthropogenic and natural source of metals in sediments (Selvaraj *et al*., 2004; Vald'es *et al*., 2005). EF values were interpreted as suggested by Birth (2003) where EF < 1 indicates no enrichment; < 3 is minor; 3-5 is moderate; 5-10 is moderately severe; 10-25 is severe; 25-50 is very severe; and > 50 is extremely severe. Table 2 shows the EF values of the metals in the sediments with respect to crust averages (Taylor, 1964). The EF values for all the metals are generally < 1 suggesting non contribution from anthropogenic source and depletion in relation to the Earth's crust average. All the metals have EF values lower than 0.5, with the exception of Cd which has values > 0.5 at some locations. EF values lower than 0.5 have been suggested to reflect mobilization and the loss of the metals relative to Fe, or an indication of overestimation of the reference metal contents (Zhang, 1995).

Correlation matrix

Pearson's correlation coefficient matrix among Mn, Fe, Zn, Cu, Ni, Cd, Co, Cr, and Pb concentrations in the sediments are presented in table 3. The correlation matrix showed that the metals do not correlate with each other, except in some few cases. A significant correlation is obvious between Zn and Cu (r = 0.861), Cd and Co (r

=0.633), Cd and Pb (r = 0.657). A highly significant correlation between elements indicates their common origin.

Table 1. Metal concentration (ug/g) in surface sediments of Niger Delta Rivers and canals.

Site	Cr	Mn	Fe (%)	Co	Ni	Cu	Zn	Pb	Cd
Rivers									
Bakkasi	0.43	15.9	10.4	0.65	0.38	4.55	5.85	0.29	0.05
Calabar	0.49	21.6	4.12	0.05	0.33	3.60	5.95	0.26	0.12
Great Kwa	0.55	18.7	5.14	0.09	0.36	2.00	3.05	0.27	0.09
Qua Iboe	0.36	19.8	4.47	0.05	0.23	4.06	4.61	0.28	0.09
Overall average	0.46	19.0	6.03	0.21	0.33	3.55	4.87	0.28	0.09
Standard Deviation	0.08	2.07	2.94	0.29	0.07	1.11	1.35	0.01	0.03
Canals									
Oginni	0.51	28.7	5.75	0.14	0.42	3.41	4.81	0.33	0.19
Olomoro	0.49	21.1	7.43	0.10	0.44	5.03	6.46	0.48	0.16
Ughelli	0.43	22.8	6.28	0.09	0.32	3.82	5.21	0.32	0.07
Overall average	0.48	24.2	6.49	0.11	0.39	4.09	5.49	0.38	0.14
Standard Deviation	0.04	4.00	0.86	0.03	0.06	0.84	0.86	0.09	0.06
ERL	81	-	-	-	150	34	150	46.7	1.2
ERM	370	-	-	-	51.6	270	410	218	9.6
MAFF	100	-	-	-	2	40	200	40	2
EPA	25	-	-	-	31	136	760	132	31
ACA[a]	100	950	5.63	25	75	55	70	12.5	0.2

ACA[a] = Average Crustal Abundance

Table 2. Enrichment Factor (EF) of metals in surface sediments of Niger Delta.

Site	Cr	Mn	Co	Ni	Cu	Zn	Pb	Cd
Rivers								
Bakkasi	0.002	0.009	0.014	0.003	0.045	0.045	0.013	0.135
Calabar	0.007	0.031	0.003	0.006	0.089	0.116	0.028	0.820
Great Kwa	0.006	0.022	0.004	0.005	0.040	0.048	0.024	0.493
Qua Iboe	0.004	0.026	0.008	0.004	0.093	0.083	0.021	0.567
Canals								
Oginni	0.005	0.030	0.005	0.005	0.061	0.067	0.026	0.931
Olomoro	0.004	0.017	0.003	0.004	0.069	0.070	0.029	0.607
Ughelli	0.004	0.022	0.008	0.004	0.062	0.067	0.023	0.314

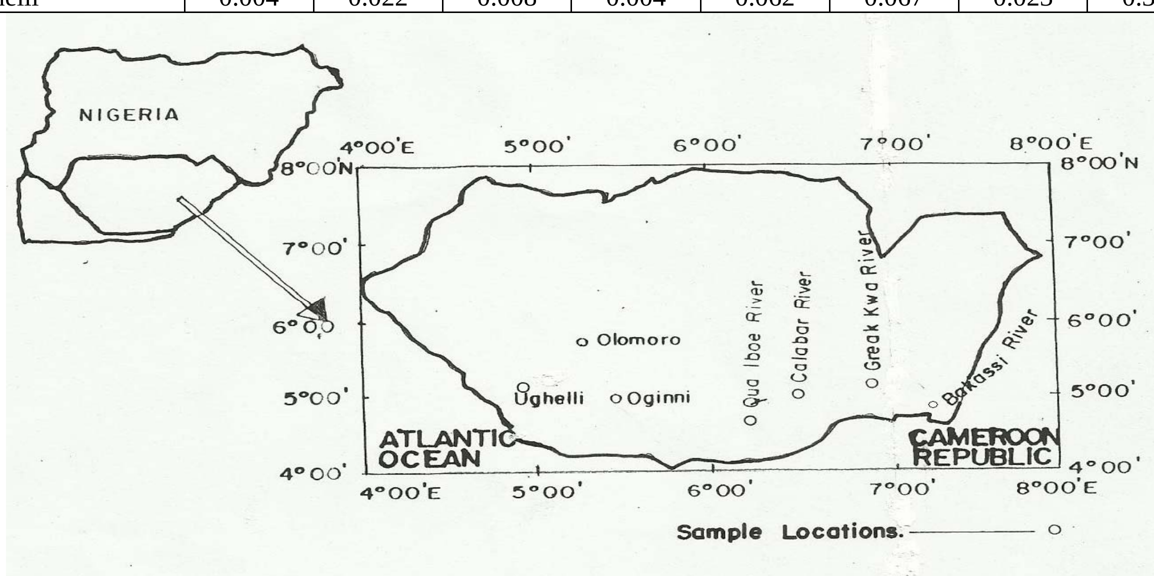

Fig. 1. The map of the study area showing sampling locations, the inset maps show the location of the study area (top left) in Nigeria.

Table 3. Correlation matrices of metal levels in surface sediments of Niger Delta.

-	Mn	Fe	Zn	Cu	Ni	Cd	Co	Cr	Pb
Mn	1.000	-	-	-	-	-	-	-	-
Fe	-0.020	1.000	-	-	-	-	-	-	-
Zn	0.174	0.392	1.000	-	-	-	-	-	-
Cu	0.045	0.495	**0.861**	1.000	-	-	-	-	-
Ni	0.094	-0.034	0.312	0.321	1.000	-	-	-	-
Cd	0.106	0.228	0.146	0.014	0.123	1.000	-	-	-
Co	0.156	0.569	0.073	0.073	-0.059	**0.633**	1.000	-	-
Cr	0.087	-0.030	-0.191	-0.200	0.570	0.558	0.168	1.000	-
Pb	0.328	0.328	0.506	0.535	0.394	**0.657**	0.456	0.388	1.000

Table 4. Metal concentrations in surface sediments of Niger delta and from different regions of the world.

References	Location	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb	Cd	Classification
This study	Niger Delta										
	Rivers	0.46	19.0	6.03	0.21	0.33	3.55	4.87	0.28	0.09	uncont.
	Canals	0.48	24.2	6.49	0.11	0.39	4.09	5.49	0.38	0.14	uncont.
Leivuori (1998)	Bothanian Bay	73	8960	6.2	-	48	52	212	79	0.94	cont.
	Bothanian Sea	80	3550	6.0	-	53	36	190	42	0.37	cont
	Gulf of Finland	85	5070	4.5	-	42	43	175	50	1.07	cont.
Mora *et al.* (2004)	Azerbaijan	85.3	832	3.71	14.9	50.1	31.9	83.2	19.6	0.14	cont.
	Iran	85.2	815	3.55	15.9	51.6	34.7	85.3	18.0	0.16	cont
	Kazakhstan	31.4	196	0.67	3.0	10.4	6.4	11.1	5.75	0.05	uncont.
	Russia	32.0	200	0.55	3.8	14.0	8.3	17.1	4.19	0.06	uncont
Acevedo-Figueroa *et al.* (2006)	Puerto Rico										
	San Jose Lagoon	-	-	3.9	-	-	105	531	219	1.8	cont.
	Joyuda Lagoon	-	-	4.9	-	-	22	52	7.6	0.10	uncont.

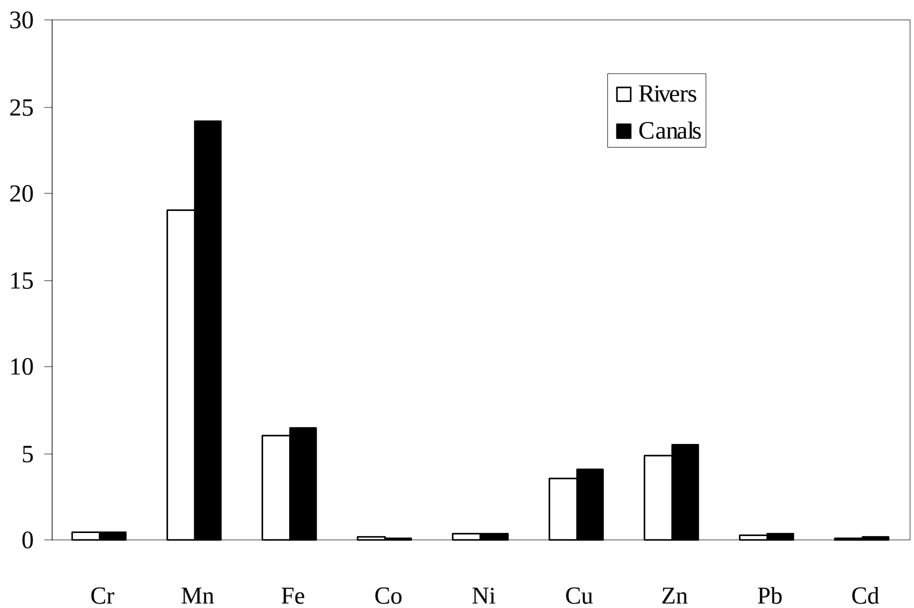

Fig. 2. Average concentrations of heavy metals in surface sediments of rivers and canals of the Niger Delta.

Comparison with other studies

Metal concentrations in sediments from the Niger Delta were compared to other studies performed in other area of the world (Table 4). Generally, metal concentrations in sediments from Niger Delta were comparable with uncontaminated sediments and in many cases lower. Therefore, the Niger delta sediments can be classified as uncontaminated.

CONCLUSION

The concentrations, possible source and pollution status of heavy metals were investigated in surface sediment samples from rivers and canals in the Niger delta. The metal concentrations in the samples are generally very low and do not exceed the effective range low (ERL) and effect range medium (ERM) sediment quality guidelines. The low EF observed in all the samples indicated that metals in the sediments were of natural origin. The sediments were classified as uncontaminated and do not pose any serious adverse effect to the ecosystem and human health.

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