Analysis of heavy metals in sediment in selected Nigerian deep offshore.

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Abstract
The concentrations of heavy metals in sediments in some selected deep offshore locations in Nigeria including Cadmium (Cu), Chromium (Cr), Copper (Cu), Nickel (Ni), Lead (Pb), Barium (Ba), Zinc, (Zn) and Iron (Fe) havebeen determined. The concentrations of heavy metals at 30 different sampling points werestudied using ATI Atomic Absorption Spectrophotometer. The sampling was done in two seasons, dry and wet and compared with the National Oceanic and Atmospheric Administration limit. The dry season sediment sample result showed the highest concentration of Cd,Cr, Cu, Ni,Pb, Ba, Zn and Fe as1.82mg/kg, 3.39mg/kg,8.41mg/kg,26.0mg/kg,23.53mg/kg, 0.90mg/kg, 0.90mg/kg, and 12.43respectively. The concentrations of the heavy metals during the wet season were 1.00mg/kg, 3.41mg/kg 8.55mg/kg, 20.40mg/kg,12.45mg/kg, 0.86mg/kg, 22.30mg/kg, and 920.40mg/kg, respectively.The dry season results implies that the Cd and Ni are above the Threshold effect concentration, Cr, Cu, and Pb are below the lowest effect level. While for the wet season the Cd is within the Threshold effect concentration, Ni is above the Threshold effect concentration, Cr, Cu and Pb concentrations are below the lowest effect level.

Key word: Heavy metals, deep offshore, pollutants, sediment, environment.

1. Introduction
Heavy metals in surface water and sediment are pollutants that impact on the aquatic environment. This can result to bioaccumulation at toxicity level that differs with each particular trace metal. These metals including cadmium (Cd), Nickel (Ni), Copper (Cu), Chromium (Cr), Zinc (Zn), Manganese (Mn), Lead (Pb) and Iron (Fe), due to their direct grievous effect on man and aquatic system poses' serious concern and have attractednoticeable research interest and stakeholders concerns[1]. These metals arising from industrial and other anthropogenic activities when discharged into coastal waters, oceans, estuaries and noticed in level that are highly toxic or poisonous with its overall effect on the food chain and its bioaccumulation nature. Less is known of the uptake of these metals by ingestion with food or from close contact with contaminated sediments [2].

In deep offshore facilities and other water bodies where oil and gas is explored, produced, processed, stored, or loaded out, waste are discharged with some effect on the receiving water body characteristics and the sediment constituent. The Nigerian oil and Gas industry activities have been on the increase with both offshore and onshore production facilities having enormous growth in crude oil and natural gas production with proven oil reserves estimated at about 37.2bn bbl as at the end of 2010 and 5.29 trillion cubic metres of natural gas reserve [3]. Nigerian's production facilities that are in deep and ultra-deep water off the Niger delta which is know as the bright of Biafra recorded a total Fifteen (15) offshore FPSO listed as at 2004 either as currently production, under repair or under fabrication. The number of FPSO increased to about thirty (30) in 2016 [3]. The multination companies that operate these offshore production facilities include; The Shell Nigeria Exploration and Production Company (SNEPCo) and Shell Petroleum Development Company (SPDC), Total Upstream, Nigeria Agip Exploration (NAE), YinkaFolawiyo, Nigeria Petroleum Development Company (NPDC), Mobil Producing, Esso E & P, Chevron, Texaco Star Deep, Elf Petroleum, Amni International, Addax, Conoco, Conoco/Philips, Trafigura and Tuskar Resources.

These facilities generate waste which has its handling and monitoring of compliance to regulatory level highly difficult to access. Nigerian agencies for the monitoringof effluent discharge limits for the oil and gas firm and their facility includes the Department of Petroleum Resources (DPR) and Federal Ministry of Environment (FMEnv). Empowered by the Federal Environment Protection Agency Decree 58 of 1988, and is statutory responsibility for overall protection of the Environment the agencies state up guideline including[5];

1. No industry shall release toxic substances into the air, water and land of the Nigerian Environment beyond permissible limits.
2. It is mandatory for all industries to have industrial pollution effluent monitoring facilities within their own set up. Preferably, they should have on-site pollution control unit or assigned to a consultant/contractor charged with the responsibilities of environmental consultancy services.

Deep offshore facilities produce waste that has negative effect to the marine ecosystem. These waste in the form of pollutants results to various environmental impact to the marine life especially the once from anthropogenic sources. Heavy metals are a major part of offshore facility anthropogenic discharge is of great concern because it is persistent and high toxic when present in the marine ecosystem[1].Sediment is at the bed of oceans and other water bodies are the last receptacle contaminants including concentration of the heavy metals that are released to the surface water or even in the air [6] as shown in the Figure 1. with adsorption and desorption processes also taking place in the sediment.

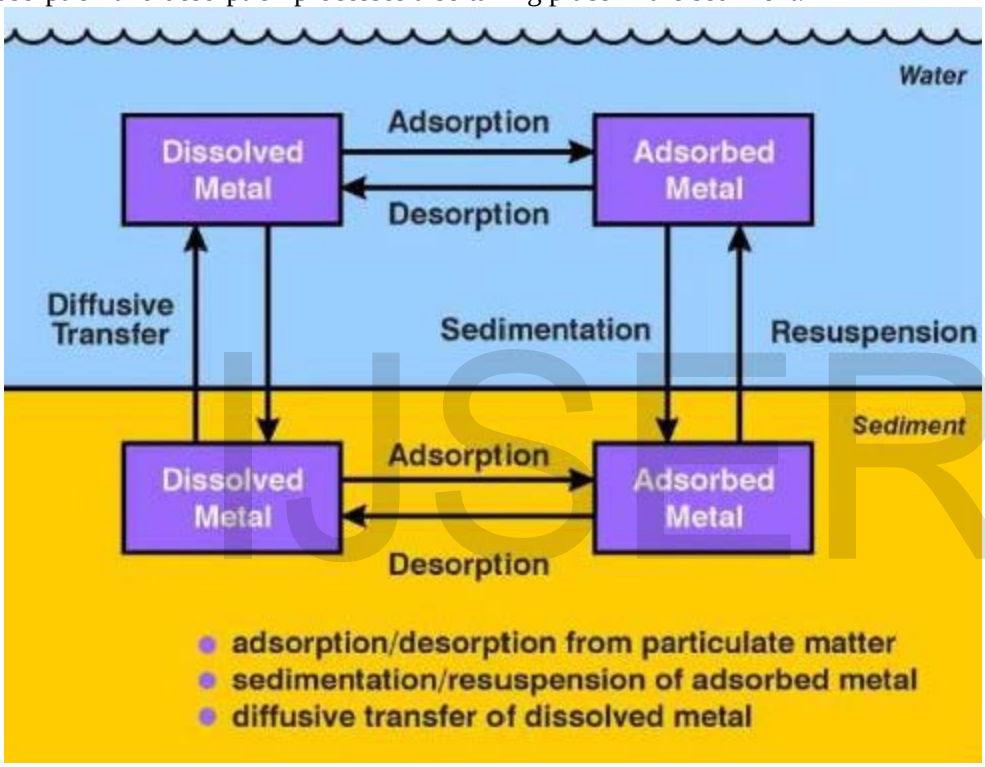

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Figure 1: Movement of metals between water and sediment [1].

Some amount of heavy metal some heavy metals including; copper, chromium and iron are required in small quantity for metabolism in human and animals, while others that are classified as non-essentials like lead and cadmium are toxic to biological systems even in trace amount[5].

Pollutant in air water and sediment can find their way into the biota and it is required that agencies monitor the discharge from facilities into the ecosystem to insure compliance.Monitoring compliance on the effluent discharge of oil and gas firm to ensure the preservation of ecosystem and forestall pollution is low mainly due to resource available to regulators.National Oceanic and Atmospheric Administration (NOOA) classifies pollutants intofour categories [6]; Lowest effect level (LEL), Threshold effect concentration (TEC) and Probable effect concentration(PEC) and Severe effect level (SEL). These levels respectively for Cd, Cr, Cu, Ni, and Pd (in mg/kg dry weight) are LEL(0.60, 26.0, 16.0, 16.0 and 31.0), TEC (0.99, 43.4, 31.6, 22.7 and 35.8), PEC (4.90, 111.0, 149.0, 48.6 and 128.0) and SEL (100.0, 110.0, 110.0, 75.0 and 250.0).
Thisresearch is aimed at the analysis of heavy metal concentrationsin thirty (30) different points in deep offshore coast of Nigeria and to classify them according to the NOOA sediment quality guideline.

The result is expected to show the level of heavy metal concentration around deep offshore of the Niger delta coast within the area of study have noticeable level these heavy metals in in the two distinct season, the dry season that is predominate from the months of November to March and the wet season from April to October.

2. Methodology

Sediment was collected from deep offshore Nigeria using grab (Figure 2A) and the geo-reference was done to help for the two season sampling from 30 different sampling points.

Figure 2:Sampling grab deployment (A) and collected sediment (B)

The offshore sediment sampling was achieved using sea going vessels for the dry and wet season sampling respectively. A GPS was used to get coordinates for geo-referencing of sampling points for the different sampling locations recorded.

The sediment samples (Figure 2B) on collection were transferred directly into a sample container and then sieved through a 1.0mm mesh size sieve. The resulting residue was then transferred into a plastic container, preserved and stored for laboratory characterization.The second set of samples were homogenized and sub-sampled into recommended containers and stored for transfer to the laboratory for analysis. Standard sediment handling and storage protocol were employed.

Heavy metal content of water samples was determined using ATI Atomic Absorption Spectrophotometer, Model 939. AAS measurement of heavy metal content sediment samples was done following the procedures indicated below.

Cd, Zn, Cu, Fe, Cr, Ni and Pb: APHA 3111B (20th edition)
Ba: ASTM D3651

$$\text{Metal concentration of water sample (mg/l)} = \frac{C \times Y}{X} \quad (1)$$

Where C=Concentration of metal from calibration curve (mg/l)
Y=Final volume made-up (ml)
X=Sample volume (ml)

Hg is determine d using APHA 3112B 20ed test method

$$\text{Hg concentration, } (\mu g/l) = \frac{A \times B}{D} \quad (2)$$

Where A = concentration of mercury in sample, µg/l as determined by AAS (Instrument Reading)
B = concentration of mercury found in blank, µg/l.
D = Volume of sample in litres

3. Results

The result of the 8 different heavy metals sampled at 30 different points are recorded in tables 1 and 2.

Table 1: Sampling points and Variation in Heavy metals concentration for the Wet season

S/N	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Ba (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Zn (mg/kg)
1	1.31	1.62	1.14	0.58	100.10	9.80	9.55	10.30
2	1.22	2.40	2.20	0.65	20.80	10.22	10.30	11.45
3	1.20	2.76	3.16	0.77	80.60	12.40	12.44	10.25
4	1.30	1.69	4.35	0.70	450.80	10.40	10.82	11.20
5	1.25	1.73	1.20	0.60	720.30	6.20	8.40	9.10
6	1.00	2.26	8.55	0.84	650.60	7.00	20.40	12.20
7	1.42	1.10	2.00	0.70	295.80	9.10	12.22	10.40
8	1.22	1.80	1.38	0.60	300.30	6.50	9.80	10.10
9	1.31	2.32	2.00	0.68	20.90	11.30	10.44	9.40
10	1.23	1.00	1.10	0.30	6.44	4.90	6.40	6.56
11	1.30	1.52	1.35	0.65	9.02	11.22	10.30	9.44
12	1.33	3.41	1.12	0.77	10.01	10.00	14.50	10.20
13	1.35	1.68	1.41	0.86	180.90	8.20	9.44	8.00
14	1.46	2.20	0.88	0.60	66.36	10.40	10.20	7.40
15	1.38	2.60	2.00	0.80	35.21	11.82	15.60	14.10
16	1.78	2.41	3.40	0.77	100.22	10.60	13.56	11.64
17	1.20	1.68	1.55	0.85	420.00	10.44	12.38	13.20
18	1.41	1.42	3.45	0.82	620.30	12.45	15.68	12.66
19	1.35	1.00	1.82	0.80	500.25	11.40	12.00	11.60
20	1.46	1.46	2.00	0.70	460.54	11.70	10.66	11.60
21	1.38	1.35	2.38	0.82	675.00	8.44	12.44	13.34
22	1.14	1.60	1.40	0.80	420.10	9.00	10.65	10.22
23	1.20	1.10	3.52	0.80	920.40	9.60	16.20	14.25
24	1.15	0.98	2.20	0.64	490.25	8.30	11.44	11.30

25	1.20	0.88	2.70	0.62	439.60	8.50	11.00	11.31
26	1.35	0.76	3.88	0.78	440.40	10.30	13.24	12.46
27	1.32	1.04	4.10	0.66	780.22	9.80	17.22	11.43
28	1.04	1.68	1.50	0.64	411.22	5.40	5.64	22.30
29	1.31	1.45	0.56	0.80	428.60	6.20	12.33	10.44
30	1.46	1.22	1.22	0.71	520.32	9.80	11.20	12.40

Table 2: Sampling points and Variation in Heavy metals concentration for the Dry season

S/N	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Ba (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Zn (mg/kg)
1	1.05	1.84	1.19	0.61	9.65	10.78	10.29	0.61
2	1.11	2.52	2.19	0.67	10.45	12.67	11.38	0.67
3	1.16	2.78	3.18	0.74	12.43	12.83	12.53	0.74
4	1.28	1.79	4.33	0.72	11.43	10.79	12.30	0.72
5	1.27	1.83	1.11	0.53	6.18	8.00	9.04	0.53
6	0.99	2.44	8.41	0.86	6.55	23.53	14.70	0.86
7	1.38	1.06	2.03	0.63	9.14	12.42	10.72	0.63
8	1.22	1.76	1.41	0.55	6.68	8.60	9.32	0.55
9	1.37	2.27	1.94	0.74	11.40	10.63	12.60	0.74
10	1.19	0.96	0.89	0.20	4.87	4.26	3.47	0.20
11	1.28	1.49	1.63	0.67	11.12	11.36	11.45	0.67
12	1.28	3.39	1.13	0.66	9.88	15.48	11.24	0.66
13	1.37	1.67	1.26	0.47	7.90	8.24	8.01	0.47
14	1.49	2.21	0.74	0.45	10.06	9.89	7.67	0.45
15	1.44	2.58	2.91	0.90	11.99	14.89	15.30	0.90
16	1.82	2.35	3.99	0.75	10.59	14.05	12.74	0.75
17	1.32	1.66	1.99	0.78	10.33	14.40	13.25	0.78
18	1.39	1.40	3.60	0.81	12.43	16.85	13.74	0.81
19	1.33	0.97	1.92	0.70	11.34	12.20	11.88	0.70
20	1.38	1.25	2.05	0.66	11.60	12.92	11.23	0.66
21	1.32	1.15	2.59	0.78	6.27	13.98	13.25	0.78
22	1.06	1.57	1.41	0.60	8.80	13.09	10.18	0.60
23	1.26	0.97	3.51	0.83	11.03	17.19	14.03	0.83
24	1.13	0.79	2.14	0.66	8.65	13.92	11.21	0.66

25	1.20	1.00	2.68	0.66	8.65	11.05	11.19	0.66
26	1.34	0.93	4.41	0.80	11.18	15.64	13.65	0.80
27	1.25	1.12	4.15	0.82	10.33	18.02	13.94	0.82
28	0.85	1.84	0.75	0.53	5.95	4.56	26.08	0.53
29	1.20	1.59	0.46	0.75	5.88	13.52	12.18	0.75
30	1.45	1.16	1.71	0.73	10.58	12.01	12.42	0.73

A bar chart of the result of the analysis of the sediment samples from the 30 different sampling points are shown in Figure 2 and Figure 3.

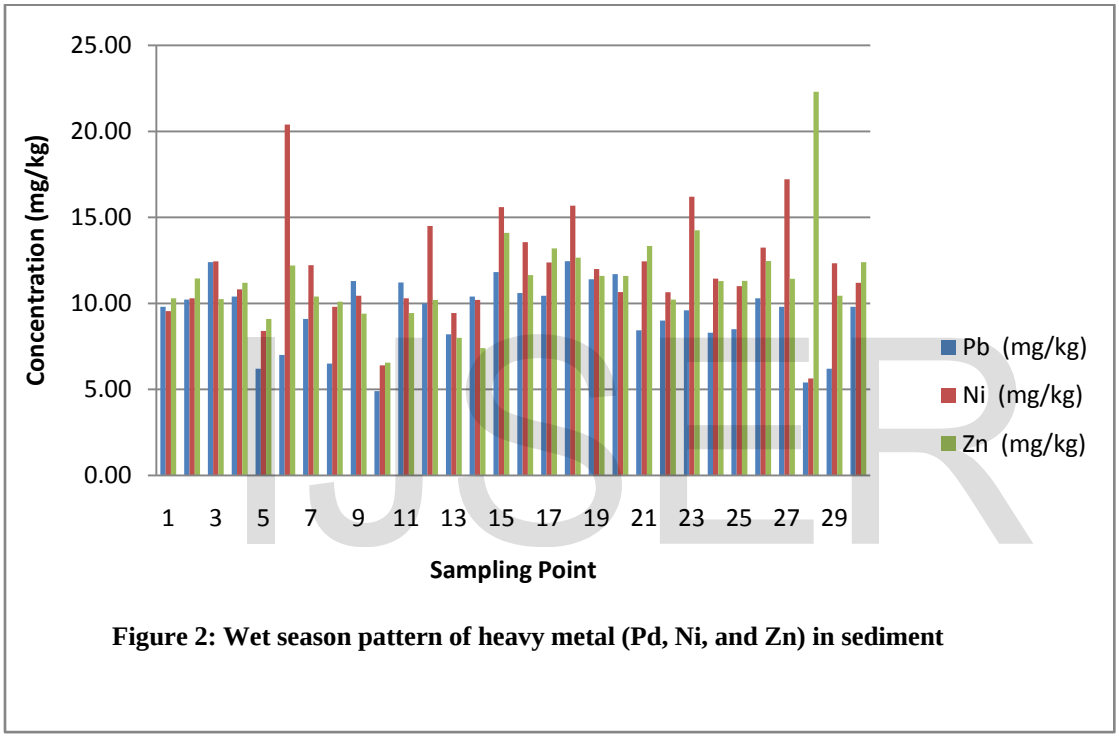

Figure 2: Wet season pattern of heavy metal (Pd, Ni, and Zn) in sediment

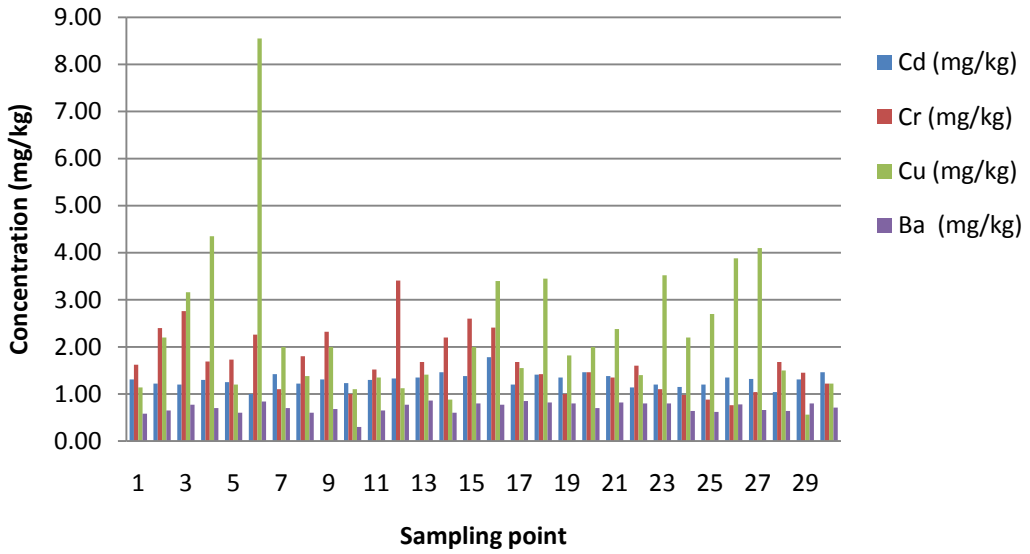

Figure 3: Wet season of pattern of heavy metal (Cd, Cr, Cu and Ba) in sediment

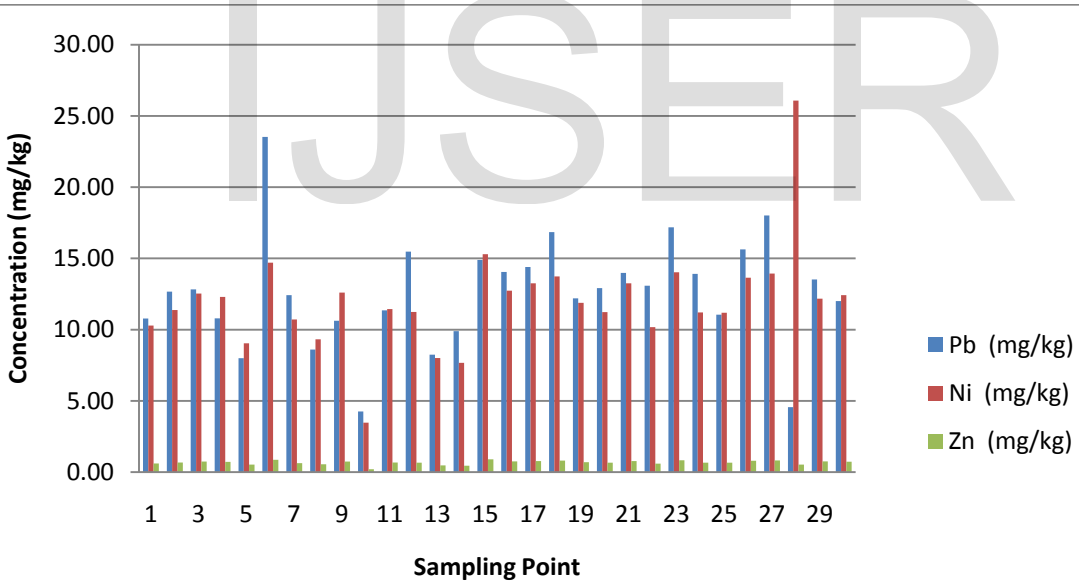

Figure 5: Dry season pattern of heavy metal(Pd, Ni, and Zn) in sediment

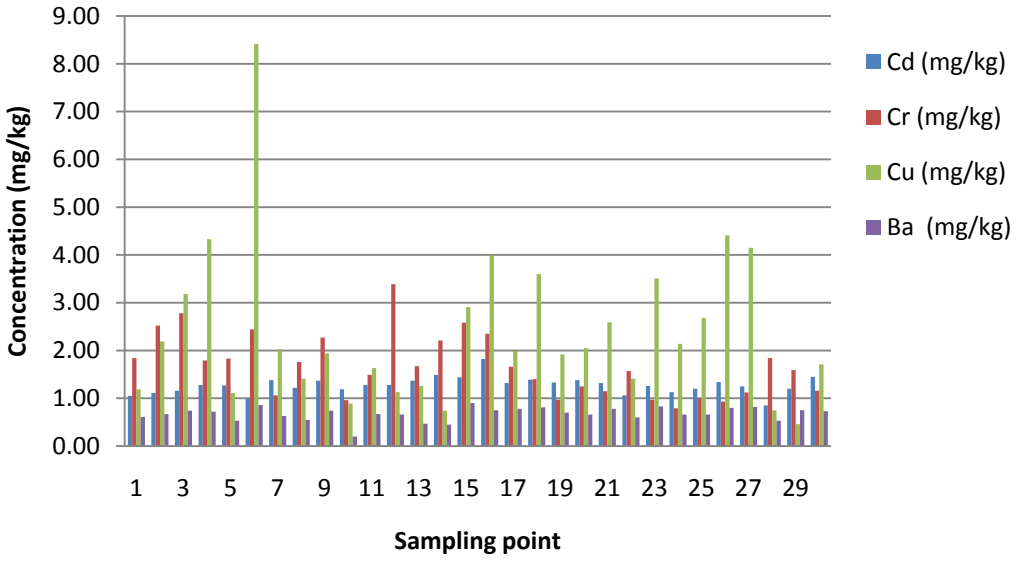

Figure 6: Dry season pattern of heavy metal (Cd, Cr, Cu and Ba) in sediment

Heavy Metals in concentration in the Sediment

The sedimentsamples collected from the 30 different sampling points showed varying concentration of the heavy metalsin dry season and wet season. The amounts of heavy metals observed in terms of Lowest (L), highest (H), and the mean (M) value recorded. Dry season; Cd: 0.85 - 1.82 in mg/kg dry weight; Cr: 0.79 - 3.39 in mg/kg dry weight; Cu: 0.46 - 8.41 in mg/kg dry weight; Ni: 3.47 - 26.0 in mg/kg dry weight; Pb: 4.25- 23.53 in mg/kg dry weight; Ba: 0.20 - 0.90 in mg/kg dry weight; Fe: 4.87, - 12.43 in mg/kg dry weight; Zn: 0.20 - 0.90. Wet season Cd: 1.00 - 1.78 in mg/kg dry weight; Cr: 0.76 - 3.41 in mg/kg dry weight; Cu: 0.56 - 8.55 in mg/kg dry weight; Ni: 5.64 - 20.40 in mg/kg dry weight; Pb: 4.90 - 12.45 in mg/kg dry weight; Ba: 0.30 - 0.86 in mg/kg dry weight; Fe: 6.44- 920.40 in mg/kg dry weight; Zn: 6.56 - 22.30.

The concentrations of heavy metals in the sediment under study were within the localand international monitoring/ regulatory organization.

In ranking the result of the sediment heavy metal concentration, in the National Oceanic and Atmospheric Administration the dry season sediment sample result showed the highest concentration of Cadmium (Cd) in the sample, 1.82 mg/kg is above the Threshold effect concentration, 0.99mg/kg, but below the Probable effect concentration of 4.90 mg/kg. The highest concentration of Chromium (Cr) in the sample, 3.39 mg/kg is below the lowest effect level, 26.0mg/kg. The highest concentration of Copper (Cu) in the sample, 8.41mg/kg is below the lowest effect level, 16.0mg/kg. The highest concentration of Nickel (Ni) in the sample, 26.0mg/kg is above the Threshold effect concentration, 22.7mg/kg, but below the Probable effect concentration of 48.6 mg/kg. The highest concentration of Lead (Pd) in the sample, 23.53mg/kg is below the lowest effect level, 31.0mg/kg.

The wet season sediment sample result showed the highest concentration of Cadmium (Cd) in the sample, 1.00 mg/kg which is almost the same value with Threshold effect concentration of 0.99mg/kg, but far below the Probable effect concentration of 4.90 mg/kg. The highest concentration of Chromium (Cr) in the sample, 3.41mg/kg is below the lowest effect level, 26.0mg/kg. The highest concentration of Copper (Cu) in the sample, 8.55mg/kg is below the lowest effect level, 16.0mg/kg. The highest concentration of Nickel (Ni) in the sample, 20.4mg/kg is below the Threshold effect concentration, 22.7mg/kg, but above the lowest effect level of 16.0 mg/kg. The highest concentration of Lead (Pd) in the sample, 12.45mg/kg is below the lowest effect level, 31.0mg/kg. The results are within the concentrations shown in other studies [1][5].

4. Conclusion

The Nigerian deep offshore water has a great level of activities including oil and gas exploration activities. The waste discharged from the operations finally end in the sediment of the water system adding among other things heavy metals to the sediment. Thisresearch has carried out analysis on heavy metal concentrations including Cadmium (Cu), Chromium (Cr), Copper (Cu), Nickel (Ni), Lead (Pb), Barium (Ba), Zinc, (Zn) and Iron (Fe) in thirty (30) different points in deep offshore coast of Nigeria in two seasons (wet and dry). The level of the heavy metals where compare with an international standard, theNational Oceanic and Atmospheric Administration(NOOA) sediment quality guideline.

The resultsshow that the concentration of most heavy metal are within the lowest effect level in both season except Cd and Ni that are above the threshold effect concentration in the dry season and only Cd that is above the threshold limit in the wet season.

It is recommended that continuous monitoring of the sediment and also to review the interaction between the heavy metal in the surface water and sediment in the area.

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