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Environmental aspect of oil and water-based drilling muds and cuttings from Dibi and Ewan off-shore wells in the Niger Delta, Nigeria

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Drilling muds and cuttings derived from Ewan and Dibi off-shore wells in the Niger-Delta petroleum province of Nigeria was studied in order to evaluate their toxicity and possible environmental impacts that may result from their indiscriminate disposal. Oil based drilling wastes (muds and cuttings) were collected at prescribed depths and analyzed for aliphatic hydrocarbon (AH) and polynuclear aromatic hydrocarbon (PAH) using Gas Chromatography Mass Spectrophotometry (GCMS) method. However, both oil based and water-based drilling wastes collected from the same depth were analyzed for metals (iron, copper, zinc, lead, nickel, chromium, manganese, calcium, potassium and magnesium) using Atomic Absorption Spectrophotometry (AAS) method. Results showed that the values of total petroleum hydrocarbon in the two off-shore wells were in the range of 1,004.95 – 2,052.69 mg/kg for the cuttings and 5,759.11 – 6,546.01 mg/kg for the drill mud. It was observed that the concentration ratio of the polynuclear aromatic hydrocarbon to the aliphatic hydrocarbon in the total petroleum hydrocarbon (TPH) is in the ratio of 1:1000 for both the cuttings and drilling muds in both wells. Most of the total petroleum hydrocarbon (TPH), polynuclear aromatic hydrocarbon (PAH) has been found to be relatively lower than the World Health Organization standards. The drill wastes of the Dibi and Ewan off-shore wells also contain high concentration of iron (349.50 mg/kg) calcium (193.72 mg/kg), magnesium (87.50 mg/kg) and potassium (49.31 mg/kg) in that order. It is likely that the drill muds and cuttings wastes will increase the pollution problems in aquatic environment, thereby causing stress for the fish and other aquatic organisms. Therefore, disposal of cuttings and drilling wastes into the offshore environment should be totally discouraged and avoided.

Key words: Drilling muds, cuttings, toxicity, petroleum hydrocarbon,

INTRODUCTION

The only way to confirm the presence of hydrocarbons in an identified promising geological structure is to drill exploratory boreholes or wells. The location of the drill site is dependent upon the characteristics of the underlying geological formations. In an off-shore site, a drilling barge, semi-submersible drilling rig or a drilling ship is used to provide all the functions associated with the drilling activity. The liquid and solid waste associated with

the petroleum hydrocarbon operations include wastes derived from drilling activities, those derived from maintenances of machines and equipment and the wastes derived from life on platform Imevbore (1979). The exploratory wastes generated during the drilling activities include well cuttings, drilling muds, formation water, cement slurry residue, oil cushions e.t.c. Drill cuttings are pieces of the formation being drilled that are returned to the surface with drilling fluid. Solids control equipment separates the cuttings from the drilling fluids so that the drilling fluid can be reused. The cuttings then become a waste stream from the drilling process. A thin coating of

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drilling fluid adheres to the cuttings. Hinwood et al. (1994) and USEPA (1993) observed that cuttings volume depends on the type of fluid used, the depth of the well, and the size of the borehole, and the estimated volume per well range from 130 to 560 m³ per well. Prominent among the composition of the exploratory wastes are the aliphatic hydrocarbons, polynuclear aromatic hydrocarbon (PAH) and heavy metals such as arsenic, cadmium, chromium, lead and mercury (Valkonic, 1978; Darley, 1988; Arscott, 1989). These wastes are diverse in their toxicities and impacts on the biota of the environment (Odiete, 1999).

According to American petroleum institute (API) (1989), both the well cuttings and the drilling fluids constitute about 2% of the total exploratory wastes. It is well known and generally accepted that the drilling muds and cuttings generated during the off-shore drilling activities are dumped into the sea.

Owing to their sizes (that is, 2 – 5 mm) almost all the particles of the cuttings disposed on the sea are deposited below the rig in a thin uniform layer. The disposed well cuttings becomes a problem to the environments – offshore or onshore (Richard, 1993), when they become impregnated with oil during drilling while Reis (1996) believed that many of the additives components in the disposed drilling muds can be toxic to the environment. The oil based drill cuttings and muds according to Darley (1988) have been found to be associated with both saturated (60%) and unsaturated (40%) hydrocarbon which when bioaccumulated in the body of the fish can become carcinogenic on consumption.

This work assesses the concentrations and toxic levels of the total petroleum hydrocarbons and heavy metal constituents of both the drilling cuttings and muds and their possible impacts on the biota components of the off-shore environments where they are indiscriminately disposed during and after drilling activities.

MATERIALS AND METHODS

Location of the study area

Dibi is an offshore well located in the Delta State while Ewan offshore well is sited in the Atlantic Ocean close to the Niger Delta. The two wells are within the southern part of Nigeria. In terms of geographical coordinates Dibi lies within latitude 5° 45' N and 5° 50' N; and longitude 5° 10' E and 5° 15' E while Ewan lies within latitude 5° 45' N and 5° 50' N; and longitude 4° 55' and 5° 00' E.

METHODOLOGY

A total of thirty six (36) oil and water based drilling wastes (i.e. cuttings and muds) from two off-shore wells were used for this study. Twelve (12) of the oil based samples each for cuttings and muds comprising of start samples (at 0-4121 m); final / end samples (at 4121 - 10171 m) and composite samples (4121 – 10171 m) collected from each well were analyzed for both the Aliphatic hydrocarbon (AH) and polynuclear aromatic hydrocarbon (PAH) using Gas Chromatography Mass Spectrophotometry (GCMS) method.

The remaining twenty-four (24) samples both oil based and water-based drilling wastes collected from the same depth were analyzed for metal concentrations in the drilling waste (that is, cuttings and muds) using Atomic Absorption Spectrophotometry (AAS) method.

TPH analysis

10 g of drill mud (or cutting) was weighed into a solvent rinsed beaker. To this was added 50 ml of 50:50 mixtures of acetone and dichloromethane (DCM). The sample was spiked with 1 ml of a surrogate mix (ortho-terphenyl – OTP) and placed in a sonicator for about 15 min at about 20°C. 10 g of anhydrous sodium sulphate was added to the sample and allowed to stand until a clear extract developed. The extract was decanted. The solvent was concentrated, exchanged with HPLC grade hexane and reconcentrated to about 3 ml. The extracted samples was transferred into a Teflon lined screw-cap vial, labeled, corked and transferred to the GC – MS for the TPH analysis. The result was recorded for TPH for drilling muds and cuttings.

PAH analysis

Sample was extracted as done for TPH, and to a 1 m of the extracted samples was added 60 ml of hexane (HPLC grade) in order to first elute the aliphatic hydrocarbon, 75 ml of dichloromethane (DMC) was later added to elute the aromatics. The eluted samples were concentrated and the aromatic was exchanged with hexane before reconcentrating to about 3 ml. The sample was finally transferred into a Teflon lined screw-cap vial, labeled and transferred to the GC – MS for PAH analysis.

Metal analysis

One g of each of the sample type was digested using mixture of perchloric acid, nitric acid and sulphuric acid in the ratio 1:2:2. The prepared solution was analyzed for the elements / metals of interest using atomic absorption spectrometer (AAS). The results obtained were compared with both department of petroleum resources (DPR) guidelines and united state environmental protection agency (USEPA) standard for drilling waste disposal.

RESULTS AND DISCUSSION

Evaluation of total petroleum hydrocarbon (TPH)

Shown in Figures 1 and 2 are the results of the assay analysis carried out on the total hydrocarbon contents of exploration wastes (that is, drill mud and cuttings) from the two off-shore wells in the Niger Delta. The total petroleum hydrocarbon discussed in this study is polynuclear aromatic hydrocarbon (PAH) and aliphatic hydrocarbon (AH).

The obtained values of total petroleum hydrocarbon in the two off-shore wells were in the range of 1,004.95 – 2,052.69 mg/kg for the cuttings and 5,759.11 – 6,546.01 mg/kg for the drill mud. It was observed that the concentration ratio of the polynuclear aromatic hydrocarbon to the aliphatic hydrocarbon in the total petroleum hydrocarbon (TPH) is in the ratio of 1:1000 for both the cuttings and drill muds in both wells.

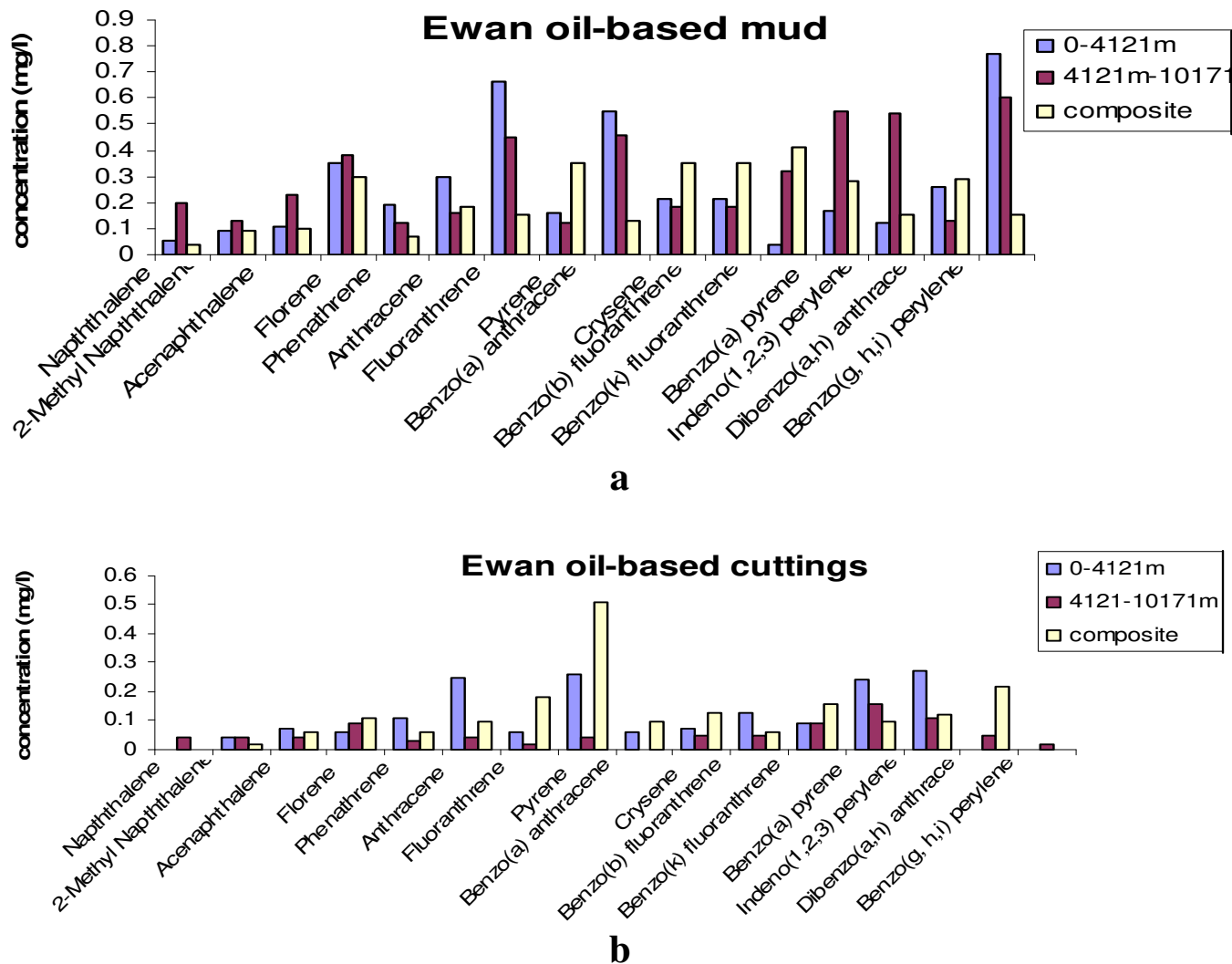


Figure 1. Showing the various PAHs concentrations in Ewan oil well.

The TPH values of the cuttings and drill muds in both off-shore wells are far lower than the values of 50,000 mg/kg recommended by DPR (1991) for allowable oil based drill cuttings and muds in the environment. However, the total petroleum hydrocarbon values obtained in this work are rather too high when compared with USEPA (1993) and WHO (1993) recommendation of "no free seen oil" in the oil based drill cuttings and muds prior to disposal in the environment.

Also, these values are higher than the values of between 600 – 1000 mg/kg, which Harrison (1993) gave as the threshold level of petroleum hydrocarbon in the marine environments. High concentrations of total petroleum hydrocarbons (TPH) in drinking water leave it with the probability of unacceptable taste and odour being detected by consumers. Components of TPH like alkanes have relatively low acute toxicity, but alkanes having carbon numbers in the range of C5–C12 have narcotic properties, particularly following inhalation exposure to

high concentrations. Repeated exposure to high concentrations of n-hexane may lead to irreversible effects on the nervous system. Alkenes exhibit little toxicity other than weak anesthetic properties (TPHCWG, 1997a).

Composition of PAH in drill muds and cuttings from off-shore wells

Also shown in Table 1, is the profile results of the different components of polynuclear aromatic hydrocarbon (PAH) which have been considered by USEPA (1993) as priority pollutants. The values of PAH in the off-shore drill muds and cuttings range from 0.94 – 1.79 mg/kg in cuttings and 4.73 – 4.92 mg/kg in drill muds. According to Odiete (1999), the acute toxicity of PAH in the environment as established by USEPA is 300 µg/l or 0.3 mg/l. Although there is no established for PAH disposal into the marine environment in the DPR guidelines however, the

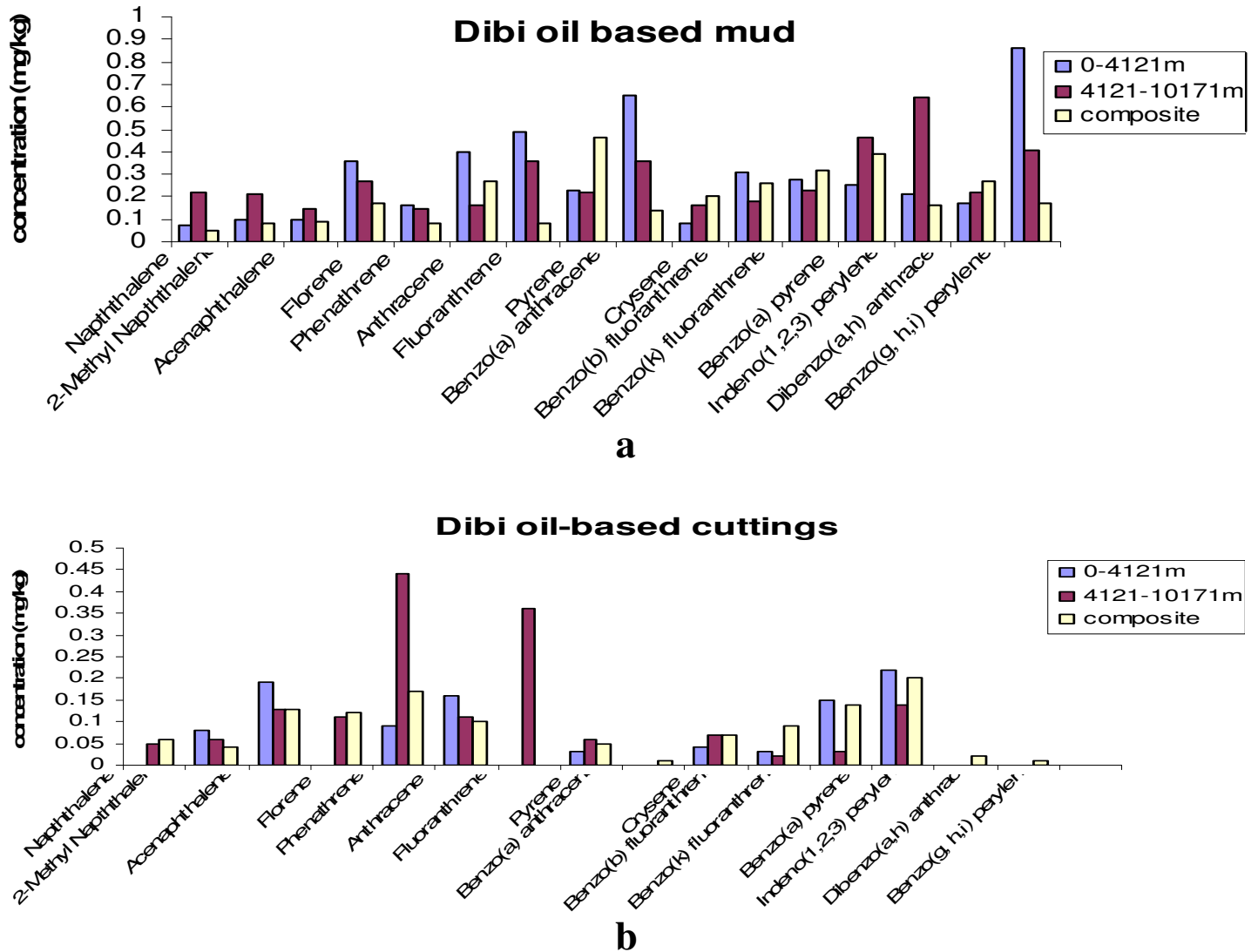


Figure 2. Showing the various PAHs concentrations in Dibi oil well.

values are far higher than this toxicity level and also higher than the Canadian interim standards in soil and water (Wilson and Jones, 1992).

The value of benzo (a) pyrene obtained in this work are far below 10 ppm which was Harrison (1993) stated value. Also, the threshold limits of benzo (a) pyrene, the most important and most bioactive pollutant of the components of PAH, in marine environment. Figures 1 and 2 illustrate the PAHs for both the drill muds and cuttings for the two off-shore wells (Ewan and Dibi wells) for different samples. It can be inferred that initial cuttings have the highest concentration of TPH, followed by the composite cuttings and least for the final cuttings in the two off-shore wells.

This pattern is slightly modified in the case of the drill mud samples where the initial mud have the highest concentration of TPH followed by the final mud and least for the composite mud sample in both wells.

TPHCWG (1998b) stated that most petroleum hydrocarbon mixtures contain very low concentrations of PAHs. The PAHs obtained in this work are relatively low when compared with total hydrocarbon concentration. The major concern regarding PAHs is the potential carcinogenicity of some molecules (IPCS, 1998a). The PAHs constituents classified as probable human carcinogens are Benzo(a)pyrene and benz(a)anthracene while others have shown to induce skin tumours in mice (IPCS, 1998a).

Metals

The results of the analyzed metals in the drill cuttings and muds from Dibi and Ewan off-shore wells are displayed in Figures 3 and 4. The studies of Neff et al. (1988a and 1988b) have shown that heavy metals in drilling fluids do

Table 1. Total petroleum hydrocarbon analysis and polynuclear aromatic hydrocarbon profile for drilling mud and cuttings in Ewan and Dibi oil wells.

Parameters (ppm)	Ewan oil well						Dibi oil well						Standards	
	Oil-based mud			Oil-based cuttings			Oil-based mud			Oil-based cuttings				
	Depth			Depth			Depth			Depth			WHO µg/L	USEPA µg/L
	0-4121 m	4121-10171 m	Composite	0-4121 m	4121-10171 m	Composite	0-4121 m	4121-10171 m	Composite	0-4121 m	4121-10171 m	Composite		
Aliphatics	6381.47	5754.19	5354.97	3584.60	1004.01	2924.68	7270.26	6541.28	4363.85	3894.39	2051.10	3294.58	No guideline	No guideline
PAHs	4.80	4.92	3.41	1.81	0.94	2.06	4.98	4.73	3.47	1.17	1.79	1.41	0.2	0.7
TPH	6386.27	5759.11	5358.38	3586.41	1004.95	2926.74	7275.24	6546.01	4367.32	3895.56	2052.89	3295.98	0.2	0.7
PAH profile														
Naphthalene	0.05	0.20	0.04	0.00	0.04	0.00	0.07	0.22	0.05	0.00	0.05	0.06	No guideline	No guideline
2-Methyl Naphthalene	0.09	0.13	0.09	0.04	0.04	0.02	0.10	0.21	0.08	0.08	0.06	0.04	"	"
Acenaphthalene	0.11	0.23	0.10	0.07	0.04	0.06	0.10	0.15	0.09	0.19	0.13	0.13	"	"
Florene	0.35	0.38	0.30	0.06	0.09	0.11	0.36	0.27	0.17	0.00	0.11	0.12	"	"
Phenathrene	0.19	0.12	0.07	0.11	0.03	0.06	0.16	0.15	0.08	0.09	0.44	0.17	"	"
Anthracene	0.30	0.16	0.18	0.25	0.04	0.10	0.40	0.16	0.27	0.16	0.11	0.10	"	"
Fluoranthrene	0.66	0.45	0.15	0.06	0.02	0.18	0.49	0.36	0.08	0.00	0.36	0.00	"	"
Pyrene	0.16	0.12	0.35	0.26	0.04	0.51	0.23	0.22	0.46	0.03	0.06	0.05	"	"
Benzo(a) anthracene	0.55	0.46	0.13	0.06	0.00	0.10	0.65	0.36	0.14	0.00	0.00	0.01	"	"
Crysene	0.21	0.18	0.35	0.07	0.05	0.13	0.08	0.16	0.20	0.04	0.07	0.07	"	"
Benzo(b) fluoranthrene	0.21	0.18	0.35	0.13	0.05	0.06	0.31	0.18	0.26	0.03	0.02	0.09	"	"
Benzo(k) fluoranthrene	0.04	0.32	0.41	0.09	0.09	0.16	0.28	0.23	0.32	0.15	0.03	0.14	"	"
Benzo(a) pyrene	0.17	0.55	0.28	0.24	0.16	0.10	0.25	0.46	0.39	0.22	0.14	0.20	0.2	0.7
Indeno(1,2,3) perylene	0.12	0.54	0.15	0.27	0.11	0.12	0.21	0.64	0.16	0.00	0.00	0.02	"	"
Dibenzo(a,h) anthrace	0.26	0.13	0.29	0.00	0.05	0.22	0.17	0.22	0.27	0.00	0.00	0.01	"	"
Benzo(g, h,i) perylene	0.77	0.60	0.15	0.00	0.02	0.00	0.86	0.41	0.17	0.00	0.00	0.00	"	"
Total PAH	4.80	4.92	3.41	1.81	0.94	2.06	4.98	4.73	3.47	1.17	1.79	1.41	0.2	0.7

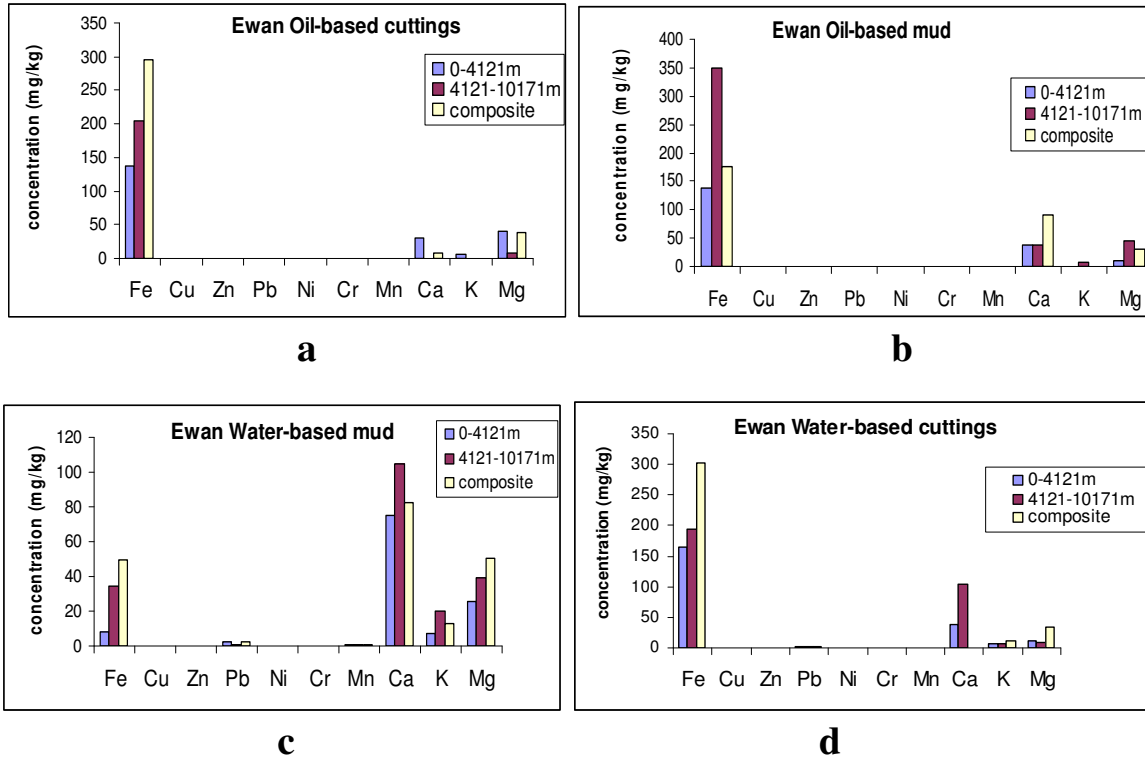


Figure 3. Showing heavy metal concentrations in Ewan oil well.

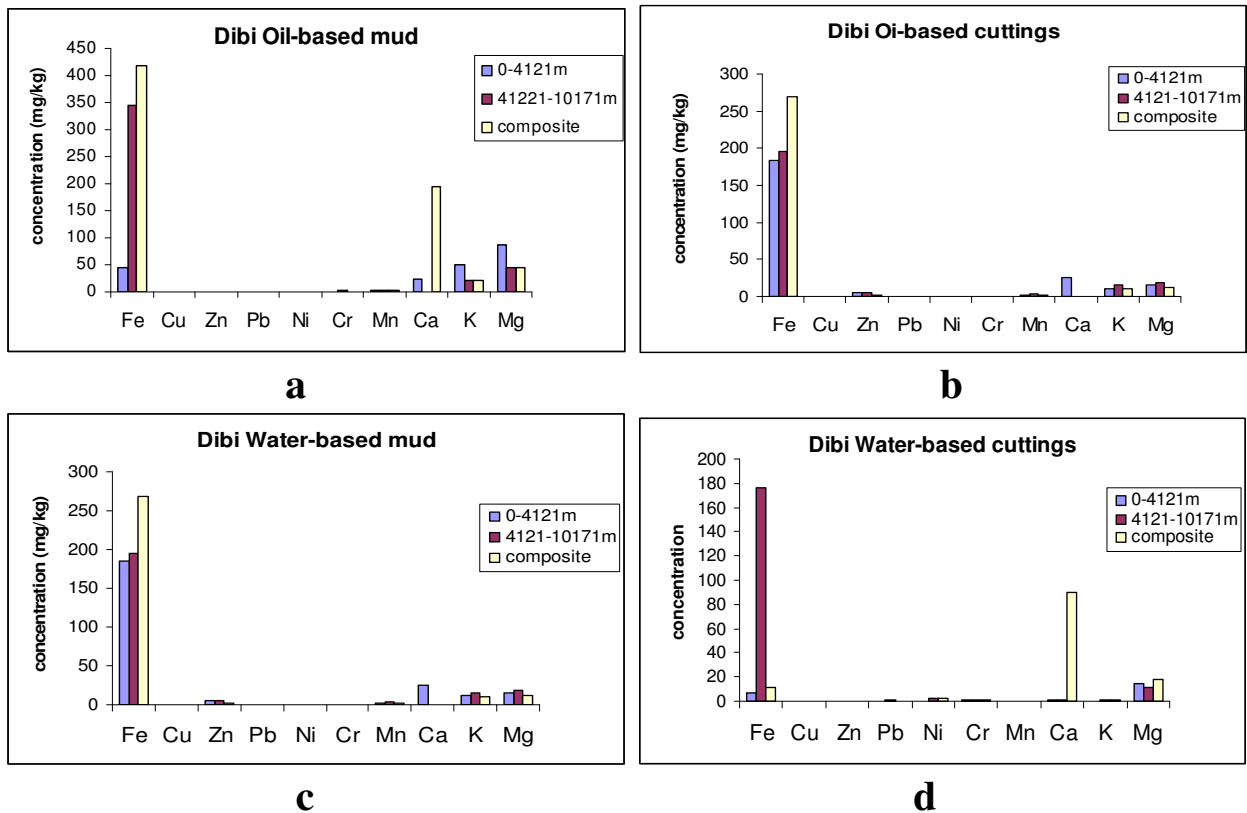


Figure 4. Showing heavy metal concentrations in Dibi oil well.

not biomagnify in marine food webs. Similar results have been found in studies of biomagnifications of heavy metals from sources other than drilling fluids. Kay, (1984); Bascom, (1983); Amiard et al. (1980); Young and Mearns (1979) and Schafer et al. (1982) show that with the exception of organomercury compounds, which are not found in drilling waste discharges, concentrations of most metals in natural marine food webs show either no relation or an inverse relation to trophic level, indicating that food chain biomagnifications of inorganic metals does not occur. The presence of heavy metals in the aquatic ecosystem has far-reaching implications directly to the biota and indirectly on man. In terms of abundance, the drill wastes of the Dibi and Ewan off-shore wells contain high concentration of iron (349.50 mg/kg) (Figure 3b), calcium (193.72 mg/kg) (Figure 4a), magnesium (87.50 mg/kg) (Figure 4a) and potassium (49.31 mg/kg) (Figure 4a). These wastes when released into the ocean will definitely increase the concentration level of these elements in the aquatic body even beyond the threshold level of 10 mg/l recommended for both the calcium and magnesium. Besides, the exceptionally very high values of iron in both the oil based and water based drill cuttings and muds from the wells are of major concern when compared with the WHO (1993) and USEPA (1992) drinking water standard and water quality criteria (1972) for irrigation and fishery. Although these elements are likely to be of nutritional importance to the aquatic animals but the associated metals will also constitute a problems to the aquatic lives even in their very small concentration.

Next in the rank of importance is the abundance of lead in the drill wastes (2.38 mg/kg) (Figure 3d). The water based drill wastes (i.e. cuttings and muds) from Ewan off-shore well contain an appreciable level of lead content than the oil based cuttings and muds. Generally, the lead content of the disposed drill wastes from both off-shore wells are far higher than the recommended 0.005 mg/l by DPR (1991) and the established threshold level of 0.05 mg/l. This will result in increased lead accumulation in the aquatic environment where the drill wastes are disposed. Manganese is relatively very high in oil based drill cuttings and mud from Dibi off-shore well when compared with its water based drill waste counterparts and the entire oil and water based drill waste materials from Ewan wells. The highest value of 3.52 mg/kg recorded for Dibi drill waste has no place for comparison in DPR (1991) guideline for oil drill waste disposal into the Nigerian coastal environment. However, the value is relatively close to the WHO's threshold limit of 0.5 mg/l.

Nickel was completely found absent in both the oil based and water based drill waste materials from Ewan well but appear only in the water based drill cuttings and muds of Dibi well. Concentration of Nickel above 0.10 mg/l in drinking water could result into liver and heart damage as well as skin irritation (Hassingier and Watson, 1998). Contrarily, copper was found present in all the drill wastes from both wells except in the water based drill cuttings and mud from Dibi wells where it was conspi-

cuously recorded nil. Both the values of chromium and zinc have been found less than 1.0 mg/l in all types of drill waste materials from both wells except in oil based drill cuttings of Dibi where Zn concentration was as high as 4.67 mg/l and in water based drill mud of Dibi where chromium level rise up to 1.20 mg/l. The chromium content of the two off-shore drill wastes are above the 0.05 mg/l recommended by WHO (1993) and USEPA (1992) for drinking water and also for fishery by Water Quality Criteria (1972).

The values of zinc in the disposed materials likely to be within the acceptable limit except those of the oil based drill cuttings from Dibi well. Goering et al. (1994) observed that cadmium is one of the most toxic elements with reported carcinogenic effects in humans. It has been found to be toxic to fish and other aquatic organisms (Woodworth and Pascoe, 1982). Lead, has been classified as being potentially hazardous and toxic to most forms of life (USEPA, 1986a). It has been found to be responsible for quite a number of ailments in humans such as chronic neurological disorders especially in fetuses and children.

Hess and Schmid (2002) stated that though Zn has been found to have low toxicity to man, prolonged consumption of large doses can result in some health complications such as fatigue, dizziness, and neutropenia. Zinc could be toxic to some aquatic organisms such as fish (Alabaster and Lloyd, 1980). Nickel-related health effects such as renal, cardiovascular, reproductive, and immunological effects have been reported in animals. Toxicity of Ni to rainbow trout has been reported (Pane et al., 2003). Higher exposure to potassium, K may cause a build up of fluid in the lungs, this can cause death (www.lenntech.com, 2007). Manganese has been reported to cause lung damage in rats via inhalation. Manganese is considered to have moderate acute toxicity based on short-term tests in rats. Other animal tests in which manganese has been given orally have indicated that manganese has low acute oral toxicity (ATSDR, 1997). It has been reported that Copper causes gastrointestinal irritation in man (WHO 1993).

Iron may cause conjunctivitis, choroiditis, and retinitis if it contacts and remains in the tissues. Chronic inhalation of excessive concentrations of iron oxide fumes or dusts may result in development of a benign pneumoconiosis, called siderosis and the use of more than 2.5 grams of calcium per day without a medical necessity can lead to the development of kidney stones and sclerosis of kidneys and blood vessels. (www.lenntech.com, 2007).

CONCLUSIONS AND RECOMMENDATIONS

From this study, it was found that the concentrations of various polynuclear aromatic hydrocarbons analyzed in cuttings from both oil wells are very high. The implication of this is an environmental pollution. Such a discharge into the environment could pose serious environmental

and health hazards. Heavy metals analyses done on these cuttings and mud also revealed that the concentrations in the cuttings are high, which could lead to bioaccumulation in aquatic organisms.

It is therefore recommended that wastes resulting from oil cuttings and drilling muds should be properly treated before it is disposed into the environment by oil exploration companies. Besides, such wastes could be disposed of in secured landfills. Disposal of cuttings and drilling wastes into the offshore environment should be totally discouraged and avoided. There should be guiding rules and regulations for oil companies in order to prevent environmental degradation from oil activities in the Niger Delta. Violation of these rules and regulations by any oil company should be litigated and fine.

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Appendix 1. Metal constituents analysis of drilling muds and cuttings in Ewan and Dibi Offshore Oil Wells

Parameters (ppm)	Oil-based mud			Oil-based cuttings			Water-based mud			Water-Based Cuttings			Standards		
	Depth (m)			Depth (m)			Depth (m)			Depth (m)			WHO (mg/l)	USEPA (mg/l)	
	0 - 4121	4121 - 10171	Composite	0 - 4121	4121 - 10171	Composite	0 - 4121	4121 - 10171	Composite	0 - 4121	4121- 10171	Composite			
Ewan	Fe	138.25	349.50	176.66	138.25	203.73	295.73	7.66	34.54	49.90	165.14	195.02	303.41	0.5-50	0.3
	Cu	0.00	0.05	0.19	0.08	0.22	0.16	0.12	0.17	0.28	0.00	0.24	0.02	2.0	1.3
	Zn	0.55	0.20	0.38	0.00	0.23	0.00	0.25	0.17	0.27	0.52	0.33	0.43	3.0	5.0
	Pb	0.97	0.14	0.27	0.91	0.00	0.20	2.32	1.04	2.06	2.38	1.29	2.19	0.01	0.0
	Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.02
	Cr	0.06	0.02	0.01	0.10	0.32	0.32	0.26	0.13	0.20	0.14	0.13	0.21	0.05	0.1
	Mn	0.88	0.83	0.93	0.63	0.52	0.78	0.62	0.52	0.42	0.15	0.17	0.14	0.5	0.05
	Ca	37.73	37.73	89.73	30.31	0.59	8.02	74.87	104.58	82.30	37.73	104.58	0.59		
	K	0.04	8.18	0.04	5.23	0.04	0.04	7.24	20.18	12.72	6.09	6.45	11.49		
Mg	9.58	45.83	29.17	40.83	8.17	37.67	25.75	39.58	50.42	10.83	8.33	34.33			
Dibi	Fe	44.50	345.66	418.64	184.34	195.10	268.84	19.18	23.02	3.05	6.89	176.66	11.50	0.5-50	0.3
	Cu	0.29	0.24	0.16	0.21	0.28	0.26	0.00	0.02	0.00	0.00	0.00	0.00	2.0	1.3
	Zn	0.19	0.96	0.91	4.67	4.55	2.39	0.55	0.26	0.46	0.29	0.22	0.44	3.0	5.0
	Pb	0.55	0.00	0.00	0.14	0.00	0.00	0.00	2.19	0.00	0.00	1.36	0.06	0.01	0.0
	Ni	0.00	0.00	0.00	0.15	0.00	0.00	0.00	0.20	0.00	0.01	2.25	1.95		0.02
	Cr	0.96	1.82	1.08	0.25	0.47	0.40	0.41	0.95	0.62	1.02	1.00	1.22	0.05	0.1
	Mn	3.45	3.30	3.52	2.22	2.56	1.89	0.30	0.37	0.59	0.15	0.07	0.30	0.5	0.05
	Ca	22.88	0.59	193.72	25.47	0.59	0.59	52.59	30.31	82.31	0.95	0.59	89.73		
	K	49.31	19.99	21.08	10.92	15.16	9.41	0.47	1.19	1.27	0.55	0.98	0.98		
Mg	87.50	45.42	43.75	15.42	18.33	11.25	17.92	9.16	18.75	15.00	10.83	18.30			