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HEAVY METALS LEVELS IN SURFACE WATERS AND SEDIMENTS IN AN OILFIELD IN THE NIGER DELTA, NIGERIA

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ABSTRACT

Heavy metal levels in the surface waters and sediments from five sampling stations of the Bukuma oilfield, in the Niger Delta, Nigeria were investigated using the AAS technique after standard procedures of storage and extraction. Mean range (mg/l) in the surface waters varied from Zn (0.19 – 0.64); Pb (ND – 0.60); Cd (ND – 0.07); Cu (ND - 0.20) to Ni (ND – 0.5). Relatively high values (µg/g in dry wt.) were recorded in the sediment samples as follows: Zn (0.18-5.99); Pb (ND – 0.68); Cd (ND -0.48); Cu (ND – 0.83) to Ni (ND – 0.63). The levels of the metals (except Pb) differed significantly ($P<0.05$) between sediment and the surface water. Regression analysis indicated that the sediment load of the metals contributed to the surface water metal loads. Generally elevated metal levels in both media were recorded at the stations with wellheads, implicating oil-related activities as the main source of contamination. All the metal levels except Zn exceeded the Federal Ministry of Environment (FMENV) limits for aquatic life water quality and other related standards. It is therefore suggested that the use of the inter-tidal mudflats of the area for aquaculture and the fermentation of cassava into 'fufu' for human consumption as done by the natives should be discouraged to avoid possible heavy metal poisoning.

KEYWORDS: Heavy metal, Surface water, Sediment, Bukuma oilfield. Niger Delta,

INTRODUCTION

Man's inability to handle the available natural resources sustainably has resulted in the befouling of the once natural environment in recent years. These befouling substances include untreated wastes from processing and manufacturing factories, oil exploration and exploitation activities and agricultural activities among others ultimately gets to the nearest body of waters – streams, rivers and estuaries (Mombeshora, *et al*., 1981). Toxic and hazardous materials from these wastes settle in river water and bottom sediments thereby constituting environmental hazards to the urban and rural population that depend on the water for various purposes. The levels of chemicals including heavy metals are concentrated in the organic matter of the sediment, which influence the adsorption of metallic elements (Goodwin *et al*., 2003).

Beside the risk posed by polluted water, consumption of fish from such waters may even pose greater public health-risk (Friberg *et al*., 1974). Report of the status of aquatic pollution problems in Europe, GESAMP in 1986 identified heavy metals and oil transported through the Mediterranean as major problems in the area (Dethlefsen, 1988). Several workers (Kakulu *et al*, 1988, 1992; Obasohan and Oronsaye, 2000; Agbozu and Ekweozor 2001& 2004; Obire *et al*., 2004) among others have carried out related work in other areas within and outside the Niger Delta area of Nigeria. Some of these studies provided baseline information while others attempted to explain the possible effects of the pollutants to the aquatic ecosystem. But the heavy metal contamination in the surface water and sediments of the Bukuma oilfield and its environs has not been determined.

The study area (Fig. 1) is a brackish tidal water mangrove swamps that represents a reasonable percentage within the oil-producing environment in the Niger Delta area. The economic life of the natives depends majorly on the creeks and mangrove mudflats from where they fetch finfish, shellfish, and wood. Besides, they ferment cassava into 'fufu' (locally made starchy food) from dug out holes on the mud flats of the area. Hence, the need to determine the heavy metal levels in surface water and sediments within the area.

Materials and Method

The area is a mangrove wetland with lots of creeks and creeklets that links up to the lower reaches of the New Calabar River. The creeks are characterised by high seawater inflow and low freshwater input from runoffs of domestic wastewater from adjoining farmlands and forest. Five sampling stations were chosen within the study area as indicated in Fig.1. At the inception of the sampling period, oil sheens were conspicuously seen on the surface waters and sediments of the stations that have crude oil wellheads - C, D, and E.

The oxidised surface layers of sediment, which interact most readily with overlaying water, were collected bimonthly between November 2001 and October 2002. Composite sampling method was employed in the collection of surface water and sediment samples (APHA, 1995). At low tide, sediment samples were scooped out from about a depth of 0.3cm from the surface layer of exposed mudflats along the stations. All collecting bags and scoops were acid washed, rinsed several times with the estuarine water at the collection site before use. The collected samples were packed in well-labeled polyethylene bags and transported to the laboratory for treatment and analysis. The wet sediment samples were air dried for at least four days. Samples and blanks for analysis were prepared by digesting 1.0g dry sediment samples with concentrated nitric acid and perchloric acid (4:1 ratio) on a hot plate. After cooling, the residue were filtered on Whatman No.1 filter papers into 50ml volumetric flasks and made up to the 50ml mark with deionised water which was analysed by Atomic Absorption Spectrophotometry using Buck Scientific 200A. Water samples were collected in clean glass bottles and acidified to a pH < 2 by addition of 2ml concentrated nitric acid per liter of sample.

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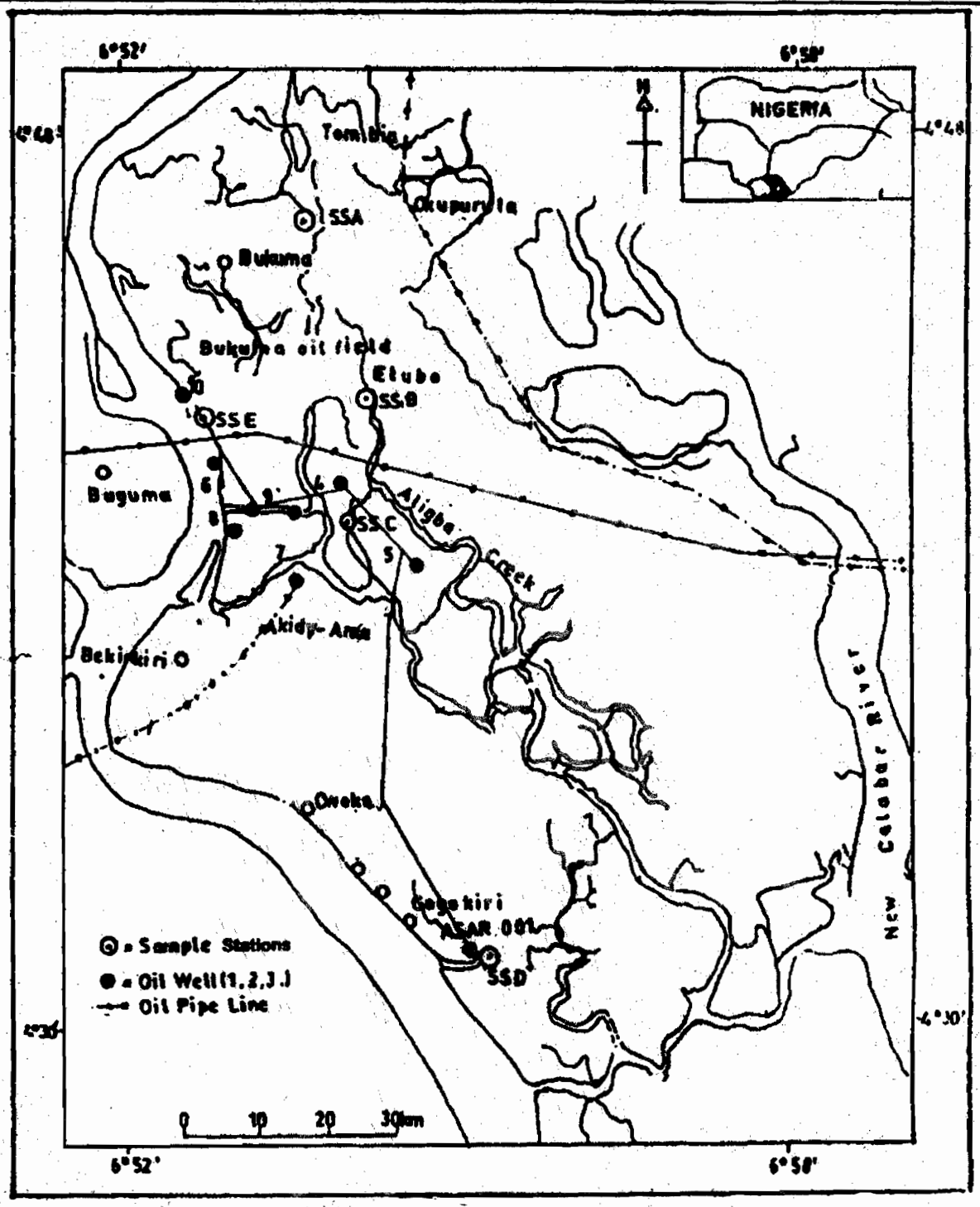

Figure 1 Map of the study area showing sampling stations

This stabilizes the original valence state of the metals. 50ml of each water sample were treated and analysed like the sediment. All quality control measures were duly followed according to the method (APHA, 1995).

Analysis of variance (ANOVA) and correlation coefficients methods were employed to analyse the data by using SPSS version 10, and Data Tools Analysis all in Microsoft Windows 98. The level of significance was set at 95% and 99% respectively.

RESULT AND DISCUSSION

The mean concentrations of the metals in surface water and sediment samples of the study area and a summary of the statistical analysis of the data are as shown in Table 1. Table 2 shows the comparison of the total mean results of this study with other related studies. Generally, the concentrations of the metals in the sediments are higher than those of the water. Apart from lead, all the other metals in the sediment differ significantly ($P<0.05$) from that of the surface water. Copper in surface water and nickel in sediment differed significantly ($P<0.05$). Correlation analysis of the metals between both media gave only significant correlation for Zn ($r = 0.6$: $P<0.01_{0.46}$). From the analysis of variance the order of accumulation of the metals in the sediment was Zn>Pb=Cu=Ni>Cd while that of the surface water is Zn>Pbi>Cu=Ni> Cd.

Zinc: Of all the metals Zn has the highest mean value both in water (0.19 – 0.64; 0.48 ± 0.13mg/l) and sediments (0.18 - 5.85; 3.22 ± 1.40µg/g) all from station E of the study area. These values from station E are significantly ($P<0.05$) different from the other stations (Table 1). The high values recorded for Zn in stations E and C may be as a result of various activities taking place within these stations during the sampling period. These included transportation, surface water runoffs from farms into station E and Oil and gas spillage from a near by oil wellhead in station E and Oily waste water at station C at the inception of the sampling period. The mean values in the two media agree with the findings of Dambo (2000), Agbozu and Ekweozor, (2001, 2004) and others. However, the mean value in the surface water is below the effluent discharge limit of 1.0mg/l limit of FMENV (1991), but the continuous discharge of oily waste containing Zn metal should be discouraged to forestall further increase in the level of the metal in our environment.

Table 1: Mean heavy metal levels analysed in the surface waters and sediments of the study area

Media	Metal	Stations					Total Mean
		A	B	C	D	E	
Surface Water (mg/l) (n = 30)	Zn	0.32 ± 0.08^{c}	0.27 ± 0.09^{bc}	0.41 ± 0.08^{ab}	0.43 ± 0.08^{ba}	0.48 ± 0.13^{a}	0.38 ± 0.16^{A}
	Pb	0.06 ± 0.07^{ab}	0.23 ± 0.07^{ab}	0.22 ± 0.20^{ab}	0.22 ± 0.11^{ab}	0.36 ± 0.17^{a}	0.22 ± 0.09^{B}
	Cd	0.01 ± 0.1^{b}	0.01 ± 0.1^{b}	0.04 ± 0.03^{b}	0.02 ± 0.2^{b}	0.05 ± 0.2^{a}	0.03 ± 0.01^{D}
	Cu	0.05 ± 0.3^{a}	0.06 ± 0.4^{a}	0.09 ± 0.06^{a}	0.11 ± 0.05^{a}	$0.11\ 0.05^{a}$	0.08 ± 0.03^{C}
	Ni	0.03 ± 0.04^{b}	0.04 ± 0.03^{ab}	0.15 ± 0.18^{ab}	0.06 ± 0.05^{ab}	0.07 ± 0.04^{a}	0.07 ± 0.03^{CD}
Sediment (µg/g) (n = 30)	Zn	0.43 ± 0.16^{c}	0.81 ± 0.30^{c}	2.53 ± 1.07^{ab}	1.48 ± 0.63^{bc}	3.28 ± 1.40^{a}	1.70 ± 0.7^{A}
	Pb	0.06 ± 0.10^{c}	0.17 ± 0.16^{b}	0.40 ± 0.15^{a}	0.20 ± 0.12^{b}	0.40 ± 0.16^{a}	0.25 ± 0.1^{B}
	Cd	0.02 ± 0.01^{b}	0.03 ± 0.02^{b}	0.11 ± 0.04^{ab}	0.16 ± 0.17^{a}	0.14 ± 0.06^{ab}	0.09 ± 0.04^{C}
	Cu	0.07 ± 0.05^{b}	0.07 ± 0.03^{b}	0.37 ± 0.24^{a}	0.15 ± 0.05^{b}	0.40 ± 0.24^{a}	0.21 ± 0.09^{B}
	Ni	0.08 ± 0.09^{b}	0.1 ± 0.06^{b}	0.27 ± 0.11^{a}	0.19 ± 0.16^{ab}	0.30 ± 0.21^{a}	0.19 ± 0.08^{B}

-Within row (Stations), mean ± sem with different superscript are significantly different at $P<0.05$.
-Within column (Total mean), mean ± sem with different superscript are significantly different at $P<0.05$.

Table 2 : Comparison of the total mean of heavy metal levels in the surface waters and sediments of this study with other related studies.

Media	Location	Metals					References
		Zn	Pb	Cd	Cu	Ni	
Surface Water (mg/l)	Bukuma oilfield	0.38	0.22	0.03	0.08	0.07	This study
	Lower Bonny Estuary	2.53	0.42	0.14	NA	0.09	Dambo, 2000
	Etelebou oilfield	0.23	0.18	0.01	NA	0.02	Agbozu and Ekweozor 2001
	Aquatic life water quality	NA	0.02	0.002	0.002-0.004	0.025-0.15	FMENV, 1991
Sediment (µg/g)	Bukuma oilfield	1.7	0.25	0.09	0.21	0.19	This study
	Lower Bonny Estuary	4.46	0.97	0.04	NA	0.08	Dambo, 2000
	Ikpoba River in Benin	7.65	6.51	0.10	8.35	0.49	Obasohan & Oronsaye (2000)
	Taylor creek	1.61	0.39	0.02	NA	0.24	Agbozu and Ekweozor 2004

NA – Not available

Lead: The range of lead levels in the surface waters and sediment during the sampling period are: (ND – 0.60; $\bar{X}$ = 0.22± 0.09mg/l) and (ND – 0.68; $\bar{X}$ = 0.25± 0.1µg/g) respectively. The highest value 0.60mg/l and 0.68µg/g in both media were noted in station C. In station E we also have another high value of 0.65µg/g of Pb (Sediment). As can be seen in Table 1, Stations E, C and D had higher Pb levels than the other stations without wellhead. This could be due to petroleum related contaminations. However, Station B ranks second in terms of stations' mean level for surface water (Table 1), but sediment Pb level is low. One of the plausible reasons for station B having a high level of lead in water could be from some domestic waste metal cans, drums etc, that were dumped on the mangrove shores of the station.

Based on the FMENV, (1991) aquatic life water quality - 0.1mg/l (Pb), and that of marine life standard (0.01mg/l) by McNeely *et al.*, (1979), the mean value of Pb in surface water of this study (0.22 ± 0.07mg/l) is high. Therefore the level of lead in the surface waters of the study area is likely to pose some environmental threat, especially where such area is being used for fermentation of cassava. The mean level of lead in the sediments of this study is 0.25µg/g and is lower than that obtained in similar studies by Obasohan and Oronsaye (2000) and Agbozu and Ekweozor (2004).

Cadmium: All the water samples investigated showed low level of Cd contamination. The range of Cd in sampled water was (ND – 0.07; $\bar{X}$ = 0.03±0.01mg/l) and (ND - 0.48µg/g;

$\bar{X}$ =0.09 ±0.04µg/g) for sediment. The sediment load of Cd is significantly different (P<0.05) from that of water. The implication of this is that sediment may cause surface water contaminate with Cd long after the source of pollutant has ceased. Again higher levels of Cd were recorded in stations E, C and D than the other stations.

However the mean value of surface water (0.03mg/l) and sediments (0.09µg/g) are higher than that obtained by Agbozu and Ekweozor (2001, 2004) and also the standard limits for aquatic life water quality (FMENV, 1991). With this high level of Cd in the surface waters and sediment of the study area, there is bound to be contamination of aquatic resources, which the local community depends on. Cd is non-essential but once it enters a biologic system, it is capable of remaining there, its excretion occurs very slowly and at certain concentrations it causes damage to human and other living organisms, especially when present as $CdCl^{+}$ or $CdCl_2$ in aqueous medium (Bryan, 1984). There have been reported cases of deaths in man through the consumption of aquatic resources with increased level of cadmium (Friberg, *et al.*, 1974).

Copper: The range of copper levels in the surface waters and sediments of this study are (ND -0.20; $\bar{X}$ = 0.08 ±0.03mg/l) and (ND – 0.83; $\bar{X}$ =0.21 ± 0.09µg/g) respectively. Though there were no significant stations' variations (P>0.05), but stations E, C and D have higher values than the other two stations in both media. This may be due to the to discharges of oily wastewater from the oil related activities in these stations. The level of copper in the sediment differs significantly (P<0.05) from that of the surface water. This is in agreement with findings of (Obashohan and Oronsaye 2000 and Oguzie 1996).

The mean value in surface water is higher than the national standard for drinking water (0.1mg/l) and aquatic water life quality, 0.002-0.004mg/l (FMENV, 1991). Cu is an essential element that has a biochemical role as an enzyme activator, but however high levels could accumulate in the liver (Wong, *et al.* 2001) thereby causing health disorders. Therefore the gradual addition of contaminants with Cu to the aquatic ecosystem may lead to public health disorder within the neighbouring communities of the study area.

Nickel: The surface water range of nickel was (ND – 0.5; $\bar{X}$ =0.07± 0.03mg/l), while that of the sediment was (ND – 0.63; $\bar{X}$ =0.19±0.08µg/g). The highest Ni level for surface water (0.50mg/l) was observed in station C in the month of May, which is the flow station, while that of the sediment (0.625µ/g) was in station E in the month of January. Stations E and C had the highest mean levels of Ni. The level of nickel in the sediment differed significantly (P<0.05) from that of surface water.

Ni has been classified as very toxic to aquatic life and relatively assessable to these organisms (Forstner and Wittman 1983), though it is now known to be essential in biological systems (Zerner, 1991; Nielsen, 1990). High levels of Ni have been reported in wastes from the petroleum industry (Horsfall and Spiff, 1998). Therefore the chronic discharges of such wastes into the aquatic ecosystem could result in accumulation of the metal in the environment. The mean water values for this study are higher than that obtained by Obasohan and Oronsaye (2000), Agbozu and Ekweozor (2001) and the national standard for aquatic life water quality (FMENV, 1991). These levels may be attributed to oily waste discharges that were conspicuously seen on the surface waters and sediments throughout the sampling period. If not checked it may definitely lead to gross pollution problems in the area over time.

Conclusion; For most of the metals, the levels in surface water and sediment are above that recommended for aquatic life water quality, water for domestic usage and similar studies within the Niger Delta, hence both aquatic life and man utilizing this media may be exposed to high risk of heavy metal poisoning. The level of risk may increase with the continuous discharge of pollutant sources of these metals into the environment. There is therefore the need to discourage the use of the area for fermentation of cassava for human consumption, and also the appropriate regulatory organ should reinforce stricter methods of waste effluents control/management to reduce further inputs into the area.

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