Full Length Research Paper

# Inter-annual trends of heavy metals in marine resources from the Nigerian territorial waters

Nubi O. A.<sup>1\*</sup>, Oyediran L. O.<sup>2</sup> and Nubi A. T.<sup>3</sup>

<sup>1</sup>Nigerian Institute for Oceanography and Marine Research, Lagos, Nigeria. <sup>2</sup>Environmental Laboratories Limited, Lagos, Nigeria. <sup>3</sup>Environmental and Energy Management Department, University of Twente, Netherlands.

Accepted 5 January 2011

In an attempt to monitor and assess the pollution status of marine resources in the Nigerian territorial waters, this study was carried out to reveal the levels and inter-annual trend of heavy metals in marine resources from the Lagos lagoon marine ecosystem. Studies were carried out annually in the month of July between 2007 and 2009; and the observed levels and trends are herein reported and discussed. Drastic shoot up was observed in year 2009 at all locations in the levels of Fe, Zn, Cu, Cr, Pb, and Cd in surface water, with maximum values of 0.62, 1.14, 0.07, 0.06, 0.08, and 0.09 mg/L, respectively reported at the near shore locations. The maximum values recorded in year 2007 for Fe, Zn, Cu, Cr, Pb, and Cd in bottom sediments were 11533, 76.57, 16.23, 38.3, 41.29, and 0.94 mg/kg respectively. This study revealed a general inter-annual trends of 2009 > 2008 > 2007. This trend is alarming and it is of great concern considering the associated health and economic implications.

Key words: Gulf of Guinea, heavy metals, pollution, coastal water, seafood, human health, marine ecosystem.

## INTRODUCTION

Contamination of marine ecosystems with metals has been receiving global attention. In recent years, significant attention has been paid to the problems of environmental contamination by a wide variety of chemical pollutants including heavy metals (Eldemerdash and Elegamy, 1999). Although levels of these metals are monitored in water at such low levels that they are considered almost too insignificant to worry about. However recent research has discovered that even at extremely low levels, copper will disrupt the sense of smell of fish preventing them from detecting predators or recognising their eggs (Pollution Issues, 2010). The source of these heavy metals could be from the abandoned ships at the harbors, waste dumping into creeks and lagoons in the coastal areas, and also industrial effluent discharge into water bodies.

Pollution has clearly left its marks on the natural environment of the Gulf of Guinea coastal zone. Its impacts are concentrated around the coastal urban centres, which have been subject to an unbridled growth of population and industrial development in the past halfcentury (Scheren and Ibe, 2002). Despite the fact that the economy of most African countries is largely based on marine resources, pollution studies have shown elevated levels of some heavy metals in sediment and finfish samples from the Nigerian territorial waters (Kakulu and Osibanjo, 1988, 1992). Consequently, the concentrations of these metals in the marine resources from the Gulf of Guinea are presently of great concern.

There is therefore the need for a timescale monitoring of the levels of these metals in all the marine resources, so as to establish the trends that could be linked to anthropogenic activities particularly when the exploration of polymetallic nodules is yet to commence in the Atlantic. Apart from the level of heavy metal contaminants in fish, that is of particular interest because of the potential risk to humans who consume them, their levels in the environment they live are also important. Many studies had been carried out in the Nigerian coastal regions, the need to go a little farther off the coastal boundaries are therefore crucial for an excellent comparative study.

<sup>\*</sup>Corresponding author. E-mail: oanubi@niomr.org.



Figure 1. Map showing the sample stations in the offshore and nearshore regions.

This study was aimed at monitoring the levels, and inter-annual trend of heavy metals (Cd, Pb, Zn, Cu, Fe and Cr) in the Gulf of Guinea marine resources from 2007 to 2009. Data were compared with corresponding permissible limits for these metals in marine resources.

#### MATERIALS AND METHODS

Samples were collected shoreward at 10 locations (Figure 1). The sample stations were divided into two (2) namely, the offshore region (A) and the near shore region (B). Samples were collected for 3 years between 2007 and 2009 in the offshore region at five (5) locations (1 to 5) and also at the near shore region (6 to 10) in July when all maritime activities are believed to be at optimum operations. This was with a view to capturing the actual source of these heavy metals; either coastal or offshore. Fish samples were not taken in all the ten (10) locations due to difficulties in the catching process, but representative samples were taken for both regions.

Sample collection and analyses were carried out for surface water, bottom sediment, and fish samples using APHA-AWWA-WEF (2005) method, IITA Manual (1979), and FAO/SIDA (1983) method respectively.

#### **RESULTS AND DISCUSSION**

The results of this research work are presented in Figures 2a to 4b. Figures 2a to c present the levels and trends of Fe, Zn, Cu, Cr, Pb, and Cr between 2007 and 2009 for surface water, bottom sediment, and fish samples respectively. Comparisons were made in the levels of the metals in fish samples with some international standards such as United Kingdom and New

Zealand standards (Figure 3a), and European Commission EC standards (Figure 3b).

In year 2007, the levels of Fe, Zn, Cu, Cr, Pb, and Cd in surface water were observed to be higher in the nearshore locations (6 to 10) with maximum values of 0.42, 0.07, 0.05, 0.04, 0.05, and 0.05 mg/L, respectively. In year 2008, the levels of these metals were observed to have increased from their respective levels in year 2007. A further shoot up was observed in year 2009 at all locations in the levels of Fe, Zn, Cu, Cr, Pb, and Cd with maximum values of 0.62, 1.14, 0.07, 0.06, 0.08, and 0.09 mg/L, respectively reported at the near shore locations. Except for Zn which showed slight variations between 2007 and 2008, the studied metals showed annual increases in their levels. The maximum values reported in surface water for years 2007, 2008, and 2009 are presented in Table 1. The maxima for all the heavy metals appeared at the near shore locations. On the mean scale, the general observed trends for the metals at all locations and the inter-annual trend are Fe > Zn > Cd > Cu > Pb > Cr and 2009 > 2008 > 2007, respectively.

Except Zn and Cr, the mean for the maxima reported heavy metals in surface water for the periods of study was found to be higher than the values quoted by the European Commission environmental legislation for surface waters (Table 1) (GTZ, 1995). Except for Zn and Cu, the mean for the maxima reported heavy metals in surface water for the periods of study was found to be higher than the values quoted by WHO and USEPA as maximum limits (Mombeshora et al., 1981; WHO 1993).

The maximum values recorded in year 2007 for Fe, Zn, Cu, Cr, Pb, and Cd in bottom sediments are 11533, 76.57, 16.23, 38.3, 41.29 and 0.94 mg/kg, respectively. In

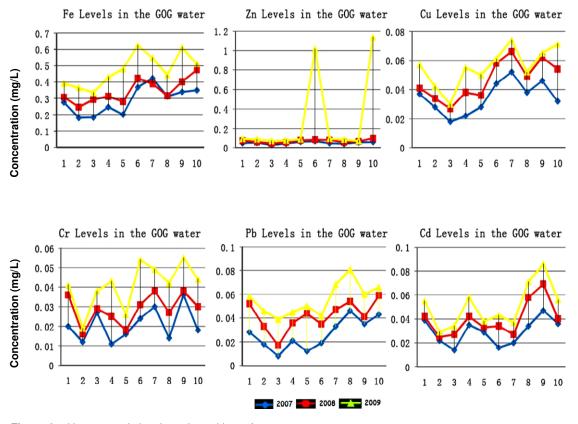


Figure 2a. Heavy metals levels and trend in surface water.

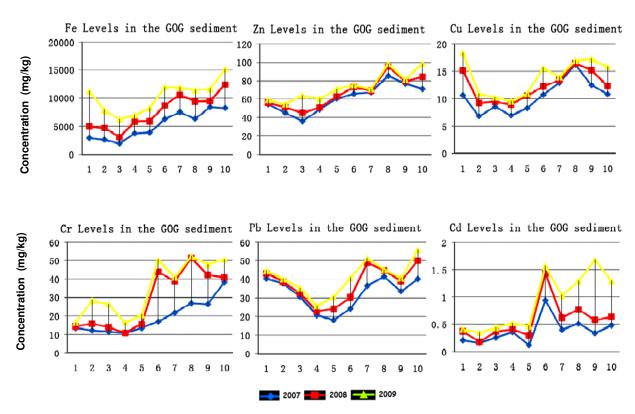


Figure 2b. Heavy metals levels and trend in bottom sediment.

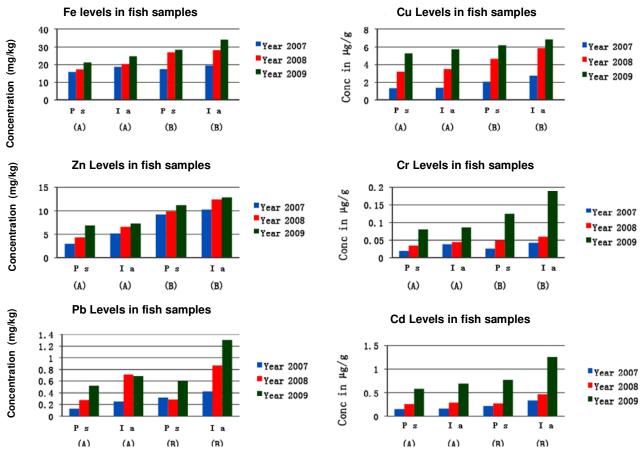
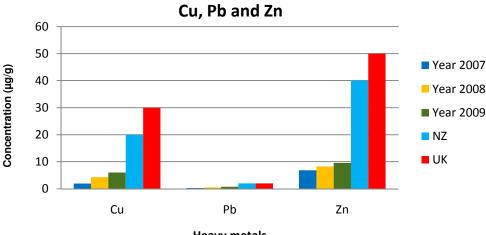


Figure 2c. Heavy metals levels and trend in fish samples. Ps: P. senegalensis; Ia: I. Africana.



**Heavy** metals

Figure 3a. Heavy metals mean levels in fish samples compared with UK, and NZ standards.

2008, the levels of these metals in bottom sediment were observed to have increased from their respective levels in 2007. A further increase was observed in 2009 at all locations in the levels of Fe, Zn, Cu, Cr, Pb, and Cd with

maximum values of 11926, 84.27, 18.42, 52.2, 55.82, and 1.68 mg/kg, respectively reported at the near shore locations.

Except for Zn and Cu, the levels of Fe, Cr, Pb and Cd

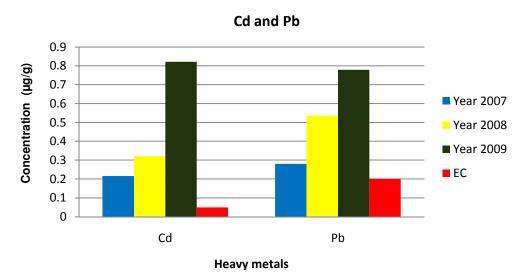


Figure 3b. Heavy metals mean levels in fish samples compared with EC standards (EC Directive, 1998).

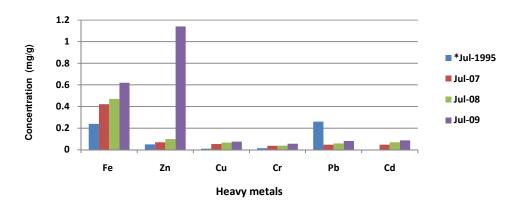


Figure 4a. Heavy metals maxima in Lagos Lagoon surface water for July 2007, July 2008, and July 2009, Compared with July 1995 (\*Don-Pedro et al., 2004).

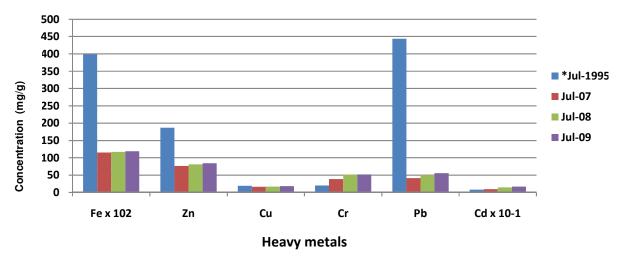


Figure 4b. Heavy metals maxima in Lagos Lagoon sediment for July 2007, July 2008, and July 2009, compared with July 1995 (\*Don-Pedro et al., 2004).

Metal (mg/L)	Year 2007	Year 2008	Year 2009	Mean	EC	WHO	USEPA
Fe	0.42 <sup>7</sup>	0.47 <sup>10</sup>	0.62 <sup>6</sup>	0.51	0.3	0.1	0.3
Zn	0.069 <sup>6</sup>	0.098 <sup>10</sup>	1.141 <sup>10</sup>	0.44	3	15	5
Cu	0.052 <sup>7</sup>	0.066 <sup>7</sup>	0.074 <sup>7</sup>	0.06	0.05	1.5	0.1
Cr	0.036 <sup>9</sup>	0.038 <sup>9</sup>	0.055 <sup>9</sup>	0.043	0.05	-	-
Pb	0.046 <sup>8</sup>	0.059 <sup>10</sup>	0.081 <sup>8</sup>	0.062	0.05	0.1	0.05
Cd	0.047 <sup>9</sup>	0.069 <sup>9</sup>	0.086 <sup>9</sup>	0.067	0.005	0.01	0.01

Table 1. Heavy metals maxima in surface water for years 2007, 2008, and 2009 (Locations in superscripts).

Table 2. Heavy metals maxima in sediment for years 2007 to 2009 (Locations in superscripts).

Metal (µg/g)	Year 2007	Year 2008	Year 2009	Mean	Pollution Std.
Fe	11533 <sup>7</sup>	11725 <sup>6</sup>	11926 <sup>6</sup>	11728	-
Zn	76.57 <sup>9</sup>	80.93 <sup>2</sup>	84.27 <sup>2</sup>	80.59	<90 (NP)
Cu	16.23 <sup>8</sup>	16.49 <sup>8</sup>	18.42 <sup>1</sup>	17.05	-
Cr	38.3 <sup>10</sup>	51.27 <sup>8</sup>	52.2 <sup>8</sup>	47.26	>25 (P)
Pb	41.29 <sup>8</sup>	50.02 <sup>10</sup>	55.82 <sup>10</sup>	49.04	>40 (P)
Cd	0.94 <sup>6</sup>	1.43 <sup>6</sup>	1.68 <sup>9</sup>	1.35	<25 (NP)

P: Polluted; NP: Non-polluted; Status of pollution in Sediment by Prater and Anderson (1970).

in bottom sediment were observed to be higher in the near-shore locations (6 to 10) in years 2007, 2008, and 2009. Zn and Cu were slightly different in their distribution by having some higher values recorded in the offshore region (1 to 5); particularly in 2008 and 2009 (Figure 2b). Table 2 presents the maximum values reported for heavy metals in bottom sediments in 2007, 2008 and 2009, and the general observed inter-annual trend for the metals is 2009 > 2008 > 2007.

While the mean for the maxima reported for Zn and Cd in bottom sediments for the periods of study classified the status of marine sediment in the GOG to be non-polluted, the mean for the maxima reported for Cr and Pb revealed the status to be polluted (Table 2).

Figure 2c presents the heavy metals levels and interannual trends between year 2007 and 2009. The species of fish samples identified for both regions were *Pseudotolitus senegalensis* (Ps) and *Illisha africana* (I a).

The highest levels of Fe (19.63  $\mu$ g/g), Zn (10.27  $\mu$ g/g), Cu (2.73  $\mu$ g/g), Cr (0.042  $\mu$ g/g), Pb (0.428  $\mu$ g/g), and Cd (0.329  $\mu$ g/g) in 2007 were observed in the near shore region, and in *I. africana*. These maxima rose significantly in 2009 having maximum values of Fe, Zn, Cu, Cr, Pb, and Cd shoot up to 34.06, 12.8, 6.86, 0.188, 1.306 and 1.247  $\mu$ g/g, respectively. At all locations, the levels of these metals were found to be higher in *I. africana* than in *P. senegalensis*. Except for the level of Pb in *P. senegalensis* that dropped in 2008 compared to 2007, but later rose in 2009, the observed inter-annual trends for the heavy metals was 2009 > 2008 > 2007; and of the

metals, Fe was found to be highest at all locations and for the periods of study.

In clear terms, the observable trend in the mean levels of Cr, Pb, and Cd in fish samples is 2009 > 2008 > 2007 (Figures 3a and b). It was also obvious for all the years that the mean levels of Cu, Pb, and Zn in fish samples were lower than their respective United Kingdom, and New Zealand standards for heavy metals in fish (Nauen, 1983). The disparity was seen clearly in both Cu and Zn as the UK and NZ standards were found to be appreciably higher than the observed mean levels (Figure 3b).

The mean levels of cadmium and lead were found to be significantly higher than the EC standards of 1998 (Figure 3b).

The trends in the levels of heavy metals observed in all the three principal media (surface water, sediment, and fish) of the Lagos lagoon were in agreement with the work carried out between 1989 and 1995 (Don-Pedro et al., 2004) on the trend of heavy metals concentrations in Lagos lagoon ecosystem which showed that there was a distinct upward trends in the levels of these metals in the lagoon. Impacts from both onshore and coastal activities are responsible for these increasing trends (Oyewo, 1998). Also, the non-degradable nature of heavy metals and possible slow rate of dispersion into the sea may be responsible for the higher levels observed in the near shore regions. The high depositional tendencies of these metals made the concentrations to be higher in the bottom sediment. Except for Pb, the concentration of metals reported in July 1995 by Don-Pedro et al. (2004) on the Lagos lagoon water were found to be markedly lower when compared with the present study (Figure 4a).

Except for Cr and Cd, the concentration of metals reported in July 1995 by Don-Pedro et al. (2004) on the Lagos lagoon sediment were found to be higher when compared with the present study (Figure 4b). Implementation of environmental management policies within the time gap, sediment transport, and dredging activities could be responsible for the lower levels in Fe, Zn, Cu, and Pb observed in the present study compared with July 1995 levels.

In line with the main objective of this research work, to know the recent levels, distribution, and the inter-annual trends of heavy metals in the marine resources from Gulf of Guinea, the higher levels observed in the near shore locations (6 to 10) was a clear cut case of impacts from coastal activities. Though some higher values were observed in bottom sediments in the offshore regions (1 to 5), this could be as a result of offshore activities such shipping, oil and minerals mining, etc. The upshot of this study also revealed the general inter-annual trends for all the metals studied to be 2009 > 2008 > 2007. This is alarming and it is of great concern, particularly when technology keeps advancing in response to meeting the unlimited human needs. Much has been done in the coastal region of the pollution status of aquatic environment, there is need to move farther into the offshore region to capture the impacts of maritime activities on the marine ecosystem. It might be useful to recall that exploration has started in the Pacific and India Oceans since the discovery of polymetallic noodles in the world ocean, there is therefore a great need to have baseline information on the heavy metals levels and trends in the Atlantic prior exploration.

Many issues such as climate change have gained global attention in the recent years; and at the expense of other seemingly less but equal environmental problems, much had gone into them. The same strength deployed in tackling global problems such as climate change should also be invested in cases relating to ocean and human health. The restoration and protection of the coastal and marine environment of the Gulf of Guinea should therefore be of great significance due to the richness of its productivity and biodiversity, and also for the livelihood of the countries which intrinsically depend on these resources for their economic development and future prosperity.

### ACKNOWLEDGEMENT

The authors are grateful to the Physical and Chemical Oceanography Department of the Nigerian Institute for Oceanography and Marine Research, and Environmental Laboratories Limited, for providing materials for sample collection and analyses.

#### REFERENCES

- APHA-AWWA-WPCF (2005). Standard Methods for the examination of water and wastewater. Edited by Anold, E.G. Joseph, J.C. and David J, 15th edition, Donelley RR and Sons Company, U.S.A, p. 547.
- Don-Pedro KN, Oyewo EO, Otitoloju AA (2004). Trend of heavy metals concentrations in Lagos lagoon ecosystem, Nigeria. West Afr. J. Appl. Ecol., 5: 103–114.
- EC Directive, 02/221EEC (1998). European commission for standardization. European standard, maximum levels for heavy metal concentration in marine fish, pp. 1–283.
- World Health Organisation (1993). Revision of WHO Guidelines for Water Quality. WHO Geneva.
- El-demerdash FM, Elegamy EL (1999). Biological effects in *Tilapia nilotica* fish as indicators of pollution by cadmio and mercury. Int. J. Environ. Health Res., 9(1999): 173-186.
- FAO/SIDA (1983). Manual of Methods in Aquatic Environmental Research, part 9. Analyses of metals and organochlorines in fish. FAO Fisheries Tech. Pap., p. 212.
- GTZ (1995). Environmental Handbook Volume III: Compendium of Environmental Standard Information sheets on EC environment legislation GTZ, p. 643.
- IITA (1979). Selected Methods for Soil and Plant analysis. Manual Series No. 1, International Institute for Tropical Agriculture, Ibadan Nigeria, p. 70.
- Kakulu SE, Osibanjo O (1988). Trace heavy metal pollution studies in sediments of the Niger delta area of Nigeria. J. Chem. Soc. Nig., 13: 9–15.
- Kakulu SE, Osibanjo O (1992). Pollution Studies of Nigerian Rivers. Trace metal levels in surface waters of the Niger Delta. J. Environ. Stud., 41: 287-292.
- Mombeshora C, Ajayi SO, Osibanjo O (1981). Pollution studies of Nigerian River I: Toxic heavy metals status of surface waters in Ibadan city. Environ. Int., 5: 49–53.
- Nauen CE (1983). Compilation of legal limits for hazardous substances in fish and fishery products, FAO Fish Circ., 764: 5-91.
- Oyewo EO (1998). Industrial sources and distribution of heavy metals in Lagos lagoon and their biological effects on estuarine animals. (PhD. Thesis), University of Lagos, p. 274.
- Pollution Issues (2010). Fish and Heavy Metal Contamination. http://www.pollutionissues.co.uk/fish-heavy-metal-contamination.html.
- Prater BL, Anderson MA (1977). Assessment of pollutional status of sediments according to metals concentration, J. Water Pollut. Canfr. 2: 2099.
- Scheren PAGM, Ibe AC (2002). Environmental pollution in the Gulf of Guinea: A regional approach. In: J. Mcglade, P. Cury, K. Koranteng and Nicholas J. Hardman-Mountford (eds). The Gulf of Guinea Large Marine Ecosystem--Environment Forcing and Sustainable Development of Marine Resources. Elsevier, p. 392.