RADIONUCLIDES AND TRACE METAL POLLUTION IN SEDIMENTS FROM THE UPPER BONNY ESTUARY IN SOUTHERN, NIGERIA.

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Abstract
Surface Sediment cores collected from the Upper Bonny Estuary, located in Southwest Nigeria were analyzed by radiometric techniques. Gamma emitting radionuclides such as ^{226}Ra and ^{228}Ra were measured using gamma-ray spectrometer to determine spatio-temporal and vertical distributions of radionuclide activities expressed in Bq·kg^{-1} dry weight. The results of activities of naturally occurring radionuclide such as ^{226}Ra (15.37 ± 02 to 34.06 ± 03 Bq·kg^{-1}), ^{228}Ra (32.60 ± 05 to 48.57 ± 06 Bq·kg^{-1}) were all found to be within the range of typical values reported for coastal regions. Total ^{210}Pb in surface samples were determined via its daughter ^{210}Po by alpha spectrometry. The results ranged from 57.83 Bq.kg^{-1} dw to 131.69 Bq.kg^{-1} dw for the various stations. Ratios of ^{226}Ra to ^{228}Ra suggested accretion for all samples with low sediment accumulation registered during rainy season. The concentrations of trace metals (Ca, Mg, K, Zn, Pb, Cd, Co, Cr, Cu, Fe, Ni and Na) were determined using a Varian Atomic Absorption Spectrophotometer. Cr varied significantly ($p < 0.05$) with its range of mean values presented in mg/kg along with variations at statistically significant level.
Key words: Radionuclide, trace metals, sediment, gamma and alpha spectrometry, Bonny estuary

INTRODUCTION

Major indicators of pollution in aquatic environments are contaminated sediments. Sediment is an excellent archive which has the ability to store, uptake and release a variety of contaminants, including nutrients and heavy metals, over an extended period of time. Long-term changes of environmental conditions are often studied using sediment archives. Sediments are the primary repository of radionuclide and chemicals entering the marine environment (Sacan *et al*., 2010).

Marine sediments are commonly used as environmental matrices in metal and radioactive monitoring programmes because records of environmental changes are often preserved in them. Studies of these sediments allow an assessment to be made of the scale of pollution in aquatic ecosystems from past industrial and urban development (Valette-Silver, 1993)

Radionuclides and trace metals are important in environmental monitoring due to the impact they play in sediment in the marine environment. Metals occurring at 1000 mg kg−1 or less in the Earth's crust are referred to as trace elements. Depending on their densities, these elements can be classified as light or heavy (Ako¨zcan and Ug˘ur Go¨rgu¨n, 2013; Onojake and Frank, 2013). Several natural and artificial radionuclides have been used in environmental studies, especially in marine processes. ^{210}Po and ^{210}Pb are important natural radionuclides used in studies on the marine environment. These naturally occurring radionuclides are important because of their contributions to the natural radiation dose and technologically enhanced releases from sources of natural radioactivity (Vrec ˘ek *et al*., 2004).

^{210}Po ($t_{1/2}$=138 days), a high-energy α-particle emitter in the ^{238}U decay chain, is a naturally occurring radionuclide formed by the β- decay of its grandparent ^{210}Pb ($t_{1/2}$=22.3 years) via ^{210}Bi. In the aquatic environment, ^{210}Po is largely produced from the decay of ^{210}Pb deposited from the atmosphere (Stepnowski and Skwarzec, 2000).

Main anthropogenic sources of heavy and trace metal contamination in the environment are mining, agricultural wastes, disposal of untreated and partially treated industrial effluents, fossil fuels, petroleum exploration, indiscriminate use of metal-containing fertilizers, rock weathering, soil erosion, dissolution of water-soluble salts, wastewater-treatment plants, manufacturing industries, pesticides in agricultural activities and oil spillage (Hatje *et al.*; 1998; Osuji and Onojake, 2004 and Nouri *et al*., 2008).

The objectives of this study are to determine the pollution level of trace metals and radionuclide (^{226}Ra, and ^{228}Ra) that were measured in marine sediments from the Upper Bonny Estuary in Southern Nigeria.

Study Area

The study area stretched from the lower reach of Bonny River at Bonny town by Peterside community

to Choba town in the upper reach of the New Calabar River. The entire stretch from Bonny to Choba about 20 km is largely influenced by the tidal cycles, and lies between longitude 7° 00″ to 7°15″ E and latitude 4° 25″ to 4° 45″ N. The tidal amplitude is generally high and above 2 m at the Bonny terminal jetty. However, the water level increases and decreases depending on the lunar cycle. At high tides, salinity increases and decreases at low tides. Sea influence is experienced more at high tide regime than at low tide, when the effect decreases especially within the upper limits when fresh water input dominates the zone. The Bonny River system is characterized by the interaction of an estuarine and highly saline seawater located seaward of the river mouth (typical of the Niger Delta coastal region), and influenced by tide- and wind-driven surface currents.

The predominant coastal vegetation of the Bonny River due to its tidal influence is the mangrove, whose main species are the red and white mangroves which form more than nineteen percent of the saline swamps (Nwilo and Badejo, 2008). The white mangroves occur scattered among the red mangroves and thrive in less water-logged places.

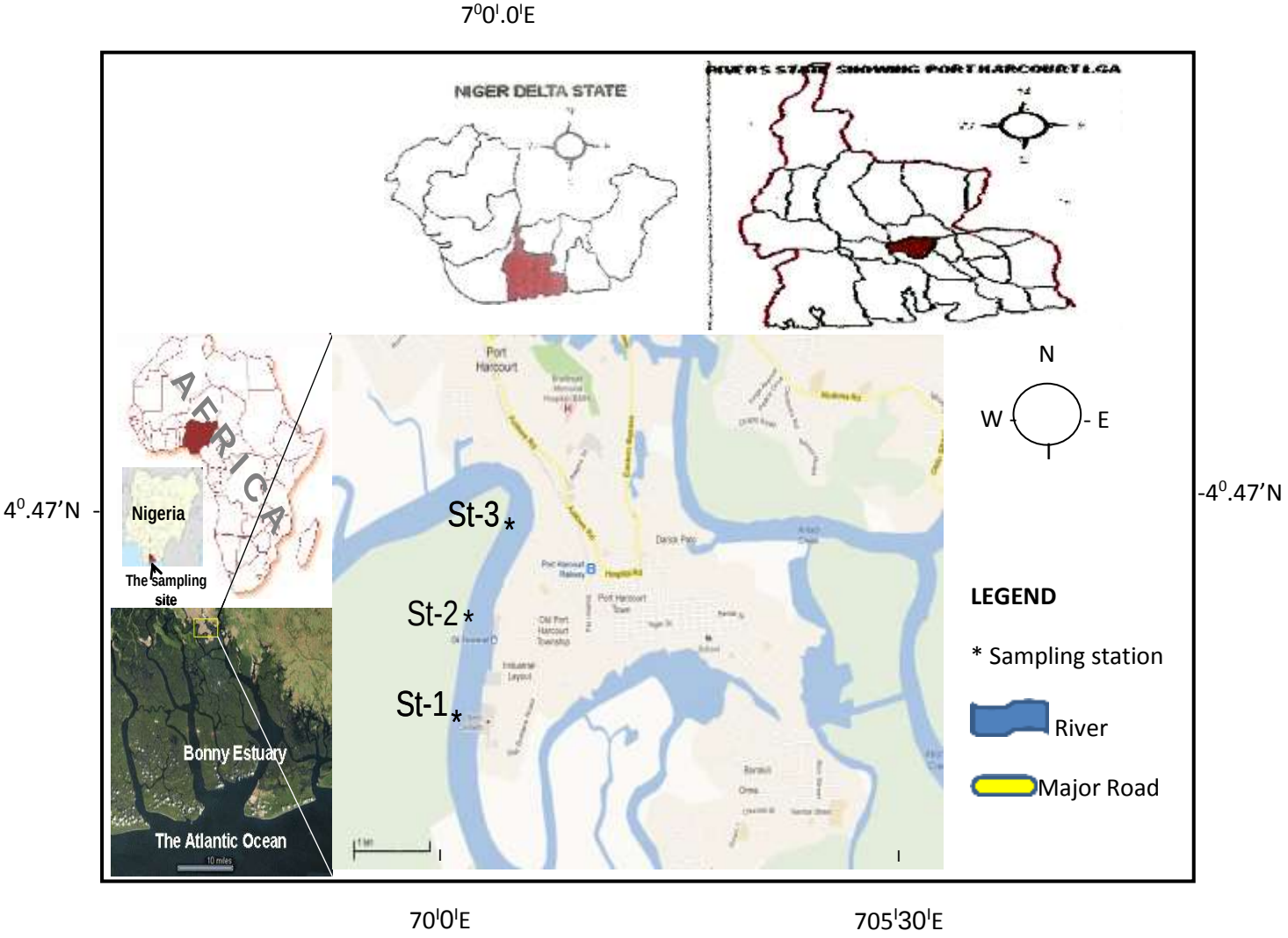

Figure 1. Map of the study area showing the sampling stations.

MATERIALS AND METHODS

Collection, Preparation and Analysis of Sediment Core Samples

During the period from August, 2011 to July 2012, sediment cores were retrieved from shallow marginal areas at three stations in the Bonny Estuary.

After collection trace metals were analyzed while during the month October 2012, the analysis of radionuclides was done. It was assumed that secular equilibrium was achieved between the daughter, Pb and parent, Ra radionuclides. Sampling locations are shown in Figure 1. In addition, subsurface sediment core samples (0-6 cm depth) were also collected from the three stations during different months covering dry and wet seasons. The cores were transported immediately after retrieval to the laboratory for pre-treatment and conditioning prior to analyses according to standard methods as reported by Onojake *et al.*, 2015.

Each core was sectioned into 2 cm slices and wet subsamples were weighed and then dried using a constant temperature drying oven for 24 h at 80 °C. Dry samples were weighed again and the content of water in each stratigraphic level was calculated for the three cores. Bulk densities were determined from water content and particle density of each slice. Finally, dried sediment was ground in a mortar to fine powder and homogenized for subsequent α and γ emitter analyses.

Radiometric Measurement

Activity of ^{210}Po was determined more than a year after sampling, so it was assumed that secular equilibrium with its parent ^{210}Pb had been achieved. Therefore, it was only possible to determine total ^{210}Pb activities at the sampling date. An aliquot of about 0.5 g of dry sediment was weighed in an acid cleaned beaker, spiked with a known activity of ^{209}Po yield tracer (the certified activity concentration is 0.357 ± 0.011 Bq·g-1) and totally digested using concentrated nitric and perchloric acids (Mathews *et al.*, 2007). The digested sample was evaporated to dryness and then finally, dissolved in 80 ml of 0.5M HCl. Ascorbic acid (50 mg) was added to reduce any iron present in the solution. Polonium was auto-deposited onto a Platinum coated disc after 6 hours of heating at 80° C and stirring the solution. The prepared α-sources were analyzed by α-ray spectrometry using silicon surface barrier detectors (EG & G) coupled to a PC running Maestro TM data acquisition software. The chemical recovery values ranged from 60 to 90%.Gamma emitting radionuclides [^{228}Ac (^{228}Ra), ^{214}Bi (^{226}Ra), ^{212}Pb (^{228}Th) and ^{40}K] were measured using γ-ray spectrometer.

The detector was a low background CANBERRA high-purity germanium p-type coaxial detector, housed in a 10 cm thick high-purity lead shield. The relative efficiency was 30% and the resolution was 2 keV for the 1332 keV 60 Co γ-peak. Weighed samples were introduced into 20 ml nalgene containers and sealed to trap the gaseous ^{222}Rn and ^{220}Rn emanating from in-situ ^{226}Ra and ^{224}Ra, respectively. The flasks were stored for over 21 days and then counted for 24 hours each. In some cases, and due to the small quantities of sediment in the upper layers of each core, two to three adjacent sub-samples were combined to reach the working geometry. ^{226}Ra activity was obtained from the ^{214}Bi photo peak at 609.3 keV. Due to the low activity of ^{137}Cs and the low amounts of sub-samples (around 20 g), a detector of HPGe of relative efficiency 70% was used for the determination of this radionuclide in each stratigraphic level.

Energy and efficiency calibrations of the gamma spectrometers were carried out using a multigamma source provided by Amersham and consisting of a mixture radionuclides emitting, each, one or two γ-rays in the energy range of 150–1800 keV. A known amount of the standard solution was diluted in the same geometry as the samples. The activity concentration (in Bq·kg-1) in each sample of all the studied radionuclides was determined from the net peak area, detector efficiency, gamma intensity and sample weight. The analytical procedure was checked using reference material (IAEA-327). Good agreement (>90%) was found between measured and certified values for ^{214}Bi, ^{228}Ac and ^{40}K.

Trace metals analysis

The sieved sediments (10g) was weighed into an acid-washed plastic polythene bottle and digested in a 100 ml solution of conc. HNO_3 and HCl acids (1:1 ratio). The mixture was vigorously shaken in a mechanical shaker and then filtered through No 42 Whatchman filter paper (Idodo-Umeh and Oronsaye, 2006). All acids used were of analytical grade quality and control was assured by the use of procedural blanks. Standard solutions of the metals were prepared from their 1000 ppm stock solutions for calibration. The concentrations of the metals (Ca, Mg, K, Zn, Pb, Cd, Co, Cr, Cu, Fe, Ni and Na) were determined using a Varian Atomic Absorption Spectrophotometer (Spectra AA-100).

RESULTS

Spatial and Temporal Trends in Surface Samples

Spatial and temporal variations of radium isotopes concentrations (^{226}Ra and ^{228}Ra) are plotted in Fig. 2. ^{228}Ra showed a fairly uniform distribution

among locations and months (within the error range), while ^{226}Ra displayed some variability with almost usually lower activity concentrations in dry months (February and December) than in rainy months (May, August and October). The highest values were registered during rainy months which could be attributable to the incorporation of ^{226}Ra- enriched particles eroded from the surrounding drainage area to the sediment.

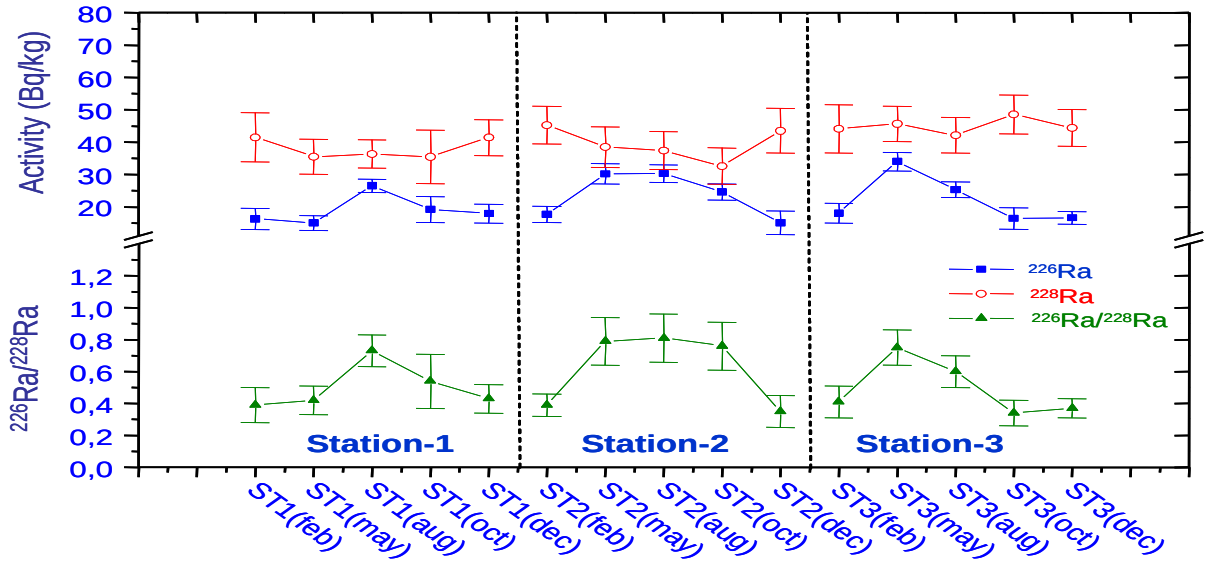

Figure 2: Spatial and Temporal Trends of ^{226}Ra and ^{228}Ra radioisotopes in subsurface sediment cores .Activities are in Bq.kg^{-1} dry weight

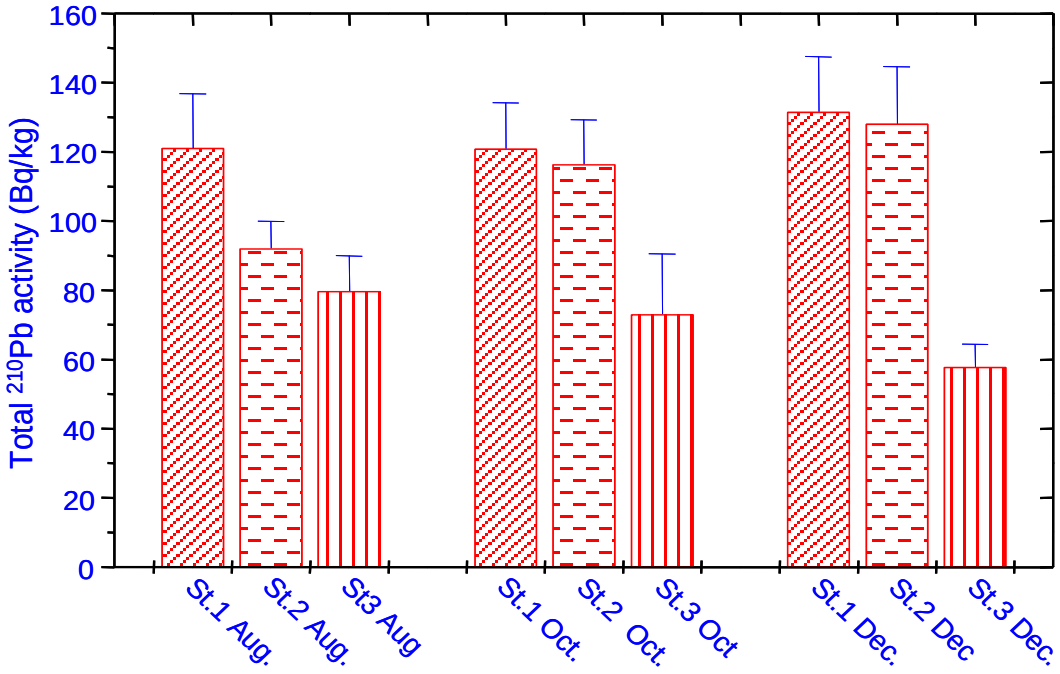

Figure 3: Spatial and Temporal Distribution of total ^{210}Pb (Bq.kg^{-1}, dry weight) in Subsurface Sediment Cores

Trace metals in sediments

The concentrations of all the metals measured in sediment apart from Co and Na, were slightly higher in 2012 than 2011. However, only Cr recorded significant variation in its concentration between the two years (Table 1, Figures 4).

Table 1. Range of values of trace metals concentration in sediment from the Bonny/New Calabar Estuary for 2011/and 2012

	Year			
Metals	**2011(**Mg/kg)	**mean**	**2012**	**mean**
Ca	3.10-10.50	6.10 ±1.10	7.50-10.90	9.70 ± 0.60
Mg	50.60-53.30	52.30 ± 0.40	52.20-53.40	53.00 ±0.10
K	18.70-28.30	24.20 ±1.50	18.30-57.10	28.10 ±3.30
Zn	1.50-3.30	2.70 ± 0.90	0.20-6.00	2.80 ± 0.70
Pb	0.20-0.60	0.60 ± 0.10	0.20-0.90	0.30 ± 0.06
Cd	0.00-0.10	0.06 ± 0.02	0.01-0.30	0.10 ±0.03
Co	0.40-0.70	0.50 ± 0.05	0.30-0.70	0.50 ±0.06
Cr	0.80-1.80	1.10 ± 0.20	1.00-3.80	2.00 ±0.30
Cu	1.40-1.90	0.90 ± 0.30	0.40-2.20	0.50 ±0.09
Fe	0.40-38.00	25.60 ±7.40	0.60-38.70	29.90 ±5.90
Ni	0.20-0.70	0.40 ± 0.09	0.20-0.80	0.50 ±0.08
Na	4.10-23.30	13.80 ± 3.20	5.10-18.70	12.80 ±1.80

Table 2. Range of values of Radionuclides in sediment from different stations.

Radionuclide (Bq.kg^{-1})	**Station 1**	**Station 2**	**Station 3**
^{226}Ra	15.37-27.34	14.46 – 30.21	16.11 – 34.06
^{228}Ra	35.46 – 41.49	32.60 – 45.29	42.11 – 48.57
^{210}Pb	117.41 -131.69	89.32 – 128.13	57.83 – 77.30

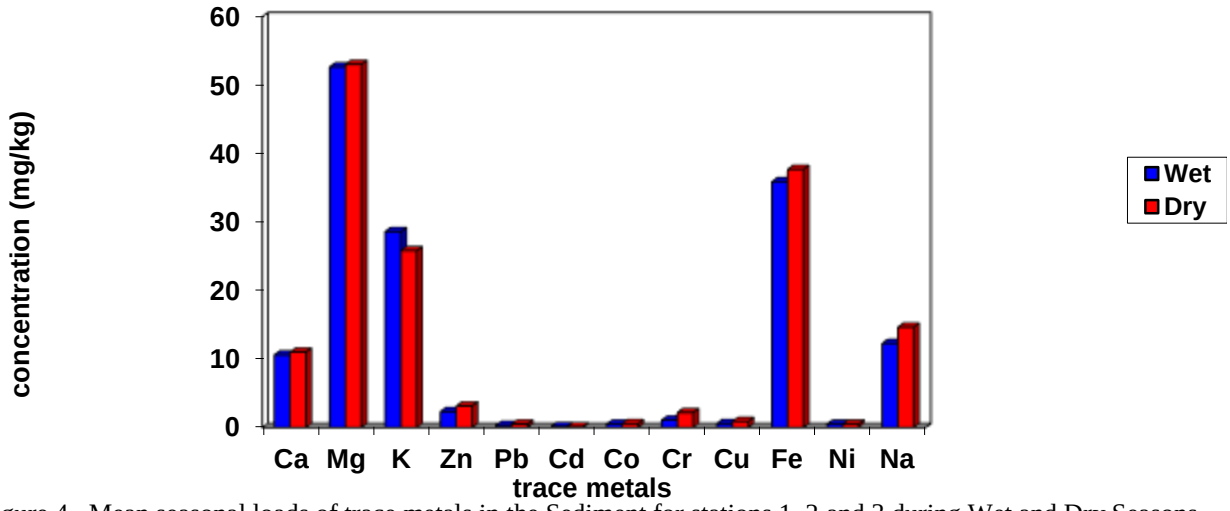

Figure 4. Mean seasonal loads of trace metals in the Sediment for stations 1. 2 and 3 during Wet and Dry Seasons

DISCUSSION

^{228}Radium can be more easily desorbed from particles than ^{226}Ra so that the mobility of the former should be less than that of ^{228}Ra. Furthermore, ^{226}Ra to ^{228}Ra ratios were also investigated for sediment erosion and accretion as suggested in previous studies (Bai *et al.*, 1997 and more recently Dai *et al.*, 2011). According to these authors, values less than 1, suggest accretion, and vice versa, and the larger sediment accumulation

rates yield lower ratio of $^{226}Ra/^{228}Ra$ in surface sediment.

The values found in this study are all less 1, ranging from 0.3 to 0.8, suggesting accretion and that the three studied sites are sedimentation zones with different sedimentation regimes. This result was in conformity with Dublin-Green (1985) where a net accretion was reported to be occurring in the upper Bonny Estuary using the distribution pattern of skewness and kurtosis. In addition, the highest values (lowest accumulation) registered during rainy months which could be attributable to two possible effects: desorption of ^{228}Ra to less contaminated water and to a minor extent, relatively strong water turbulence that reduce the settling of fine particles.

Total ^{210}Pb in surface samples was determined via its daughter ^{210}Po by α-spectrometry assuming that the secular equilibrium between both radionuclides was achieved. Activity concentrations, corrected to the sampling dates, are plotted in Fig. 3. The activities in St-3 were found lower than those in St-1 and St-2 with the lowest activity (56 ± 6 Bq·kg-1 dw) registered in the sample collected in December (dry month). The unsupported component of ^{210}Pb in estuarine sediment has two sources: the atmospheric, which should be the same for the three stations due to their proximity from each other, and sedimentation of ^{210}Pb adsorbed onto particles delivered by the river inputs and/or dredging activities. Therefore, low sedimentation could be responsible for the low ^{210}Pb activity concentration in surface sediment in St-3.

The values of trace metals obtained during the dry season for Ca Zn, Pb, Cd, Co, Cr, Cu, Fe, Ni and Na were slightly higher in dry season than the wet season (Fig. 4). This could be attributed to adsorption to sediment particles as a result of the reduced water volume usually associated with increased evaporation rate in the dry season. On the other hand, higher values recorded during dry season could also be attributed to low influx of fresh water and evaporation resulting in concentration of material in the river or as a result of slow current of water in dry season giving room for the particles to settle down. Subsequently, it may probably be due to dilution by rainwater which influences concentration and heavy metal mobility.

However, it has been reported that mobility of heavy metals depends not only on the total concentration in the soil and sediment but also on the soil or sediment properties; metal properties and environmental factors (Iwegbue *et al*., 2007). The intermittent high values of Ca, Mg, K, Cd, Co, Zn, Fe in wet season for stations 1 and 2 could be due to influence of run-off from rain water and human introduction.

Sediments are sinks for many pollutants including heavy metals. Bower (1979) reported that sediments are the major depository of metals; in some cases holding over 99% of the total amount of a metal present in amounts several times higher than their natural background levels and pollute sediments in regions near large industrial and urban areas (Ndiokwere, 1984). Consequently, sediments contaminated by heavy metals constitute a threat to the health of aquatic organisms (Forstner and Wittmann, 1983; Law and Singh, 1991).

CONCLUSION

This research studied the distribution of radionuclide and trace metals in surface samples collected from different locations and in three sediment cores retrieved from sites of diverse sedimentary patterns within the upper Bonny Estuary. ^{210}Pb activities were found relatively lower in station (St-3) than in the two other stations (St-1 and St-2). The two stations belong to an area characterized by intensive human activity (navigation, fishing and land-based industrial and commercial facilities) and physical disturbances in the sediment. This could be the reason for the differences observed in sedimentation rates. It is therefore concluded that the advent of Industrialization necessitated the fluctuating environmental conditions in the estuary. It was also observed that ^{226}Ra had higher concentrations than total ^{210}Pb due to the fact that Ra is relatively soluble in brackish and saline waters, such that sediment pore waters were usually enriched in Ra isotopes. Also enhanced levels of Ra were expected in the study area due to the massive pumping upwards of Ra-enriched particles with formation water during oil exploration.

Various studies from the study area have shown that trace metals from different sources are prevalent. Trace metal concentrations showed slight increase over the years of monitoring in sediment samples. The higher concentrations of trace metals in sediment reiterated the general believe that sediment are sink and archive for contaminants (Onojake *et al.*, 2015).

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