

# Total hydrocarbon profile and trace metal level in sediments from the upper Bonny estuary in southern Nigeria

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## Abstract

Sediment cores retrieved from shallow marginal areas at three stations in the New Calabar River Estuary in southern, Nigeria were evaluated for total hydrocarbon content and the level of trace metals between 2011 and 2012. Result of the core profiles of total hydrocarbon content ranged from 0.001 to 130.80 ppm. The observed profiles corresponded with severe environmental perturbations resulting from massive oil spills. The contamination levels of the respective metals varied and the range of mean values are presented in mg/kg along with variations at statistically significant level ( $P < 0.05$ ). In sediment, only Cr varied significantly ( $p < 0.05$ ) within two years. The constant rate of supply model which was employed to establish the age and date of sediment displayed increase in bulk sediment accumulation over the past 80 years.

**Key Words:** Total hydrocarbons, Sediment, trace metals, environmental perturbations, constant rate of supply.

## 1. Introduction

Industrialization and urbanization have affected the water bodies in the Port Harcourt metropolis negatively over the years. Heavy metals constitute one of the serious environmental pollutants due to their toxicity, persistent and bioaccumulation in sediments (Nouri *et al.*, 2008). These heavy metals from fresh water and tidal water are deposited in sediments (Samarghandi *et al.*, 2007). Sediment analyses have some advantages over surface water for the control and detection of metal pollution in estuaries (Forstner and Wittman 1983), because the rate of change of metal concentration in sediment is below that of water. 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 time period. Long-term changes of environmental conditions are often studied using sediment archives. The Bonny/New Calabar River Estuary is very important because it is the environment for fish, plants and animals, while the banks and nearby land support creatures such as otters, kingfishers, dragonflies and variety of water- living plants. The coastal areas of Bonny River host many fishing settlements while the river itself is a major navigational channel for oil vessels, countless outboard engine boats, maritime and oil-related activities. Hence this river is expected to be highly loaded with urban and industrial wastes. This has entailed a great increase in

discharge of pollutants to receiving marine waters bodies, causing undesirable effects on the aquatic environment. Marine water quality monitoring has become a subject of concern due to uncontrolled disposal of urban effluents, runoff, atmospheric deposition, municipal and industrial effluent into these water bodies (Onojake *et al.*, 2013).

The Bonny/New Calabar River is vital to the people of Niger delta and other surrounding regions. It is perhaps one of the largest arms of the River Niger discharging directly into the Atlantic Ocean and it is believed to also be the most environmentally stressed (Dublin-Green, 1985).

This study was conducted within the framework of the International Atomic Energy Agencies (IAEA) regional project and the objectives were to determine the historical trends of total hydrocarbon content and to determine the level of trace metal pollution in sediment from the Bonny/New Calabar River.

## 2. Materials and Methods

### 2.1 Description of Study Area

The study area stretched from 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 the Bonny to Choba is largely influenced by the tidal cycles, about 20km Figure 1 shows the study area and sampling stations and lies between longitude  $7^{\circ} 00''$  to  $7^{\circ} 15''$  E and latitude  $4^{\circ} 25''$  to  $4^{\circ} 45''$  N. The tidal amplitude is generally high and above 2m 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 (19%) of the saline swamps (Nwilo and Badejo 2008). The white mangroves occur scattered among the red mangroves and thrive in less water-logged places.

### 2.2 Collection, Preparation and Analysis of Sediment Core Samples

Sediment cores were retrieved from shallow marginal areas at three stations in the Bonny Estuary in 2011 and 2012 using an Uwitec gravity corer of 10 cm internal diameter. Sampling locations are shown in Figure 1.2. Thirty-two cm and 30-cm cores were taken from station 1 (St-1) and station 2 (St-2) respectively while the core from station 3 (St-3) was only 20-cm deep. In addition, subsurface sediment core samples (0-6cm 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. Each core was sectioned into 2cm slices and wet subsamples were weighed and then dried using a constant temperature drying oven for 24 h at  $80^{\circ}\text{C}$ . Dry samples were weighed again and the content of water in each stratigraphic level was calculated. Bulk densities were determined from water content of each slice while dried sediment was ground in a mortar to fine powder and then sieved through a  $650\mu\text{m}$  stainless sieve to remove ungrounded matter. 10grams of the sieved sediments was weighed into an acid-washed plastic polythene bottle and digested in a 100ml solution of conc.  $\text{HNO}_3$

and HCl (1:1 ratio). The mixture was vigorously shaken in a mechanical shaker and then filtered through No 42 Whatman filter paper (Idodo-Umeh and Oronsaye 2006). All acid used were of analytical grade quality and control was assured by the use of procedural blanks and spikes. The spike recovery for each element was greater than 94%. All samples were run in triplicates and the relative standard deviation for the triplicate analysis was less than 10%. 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). Subsequently, two grams of sediment was weighed into an amber coloured bottle and then 20 ml of chloroform was added to it. The solution was stirred with a rod and then poured into a funnel containing cotton wool and the funnel was placed in a beaker. A little quantity of sodium sulphate (dehydrating agent) was also added and then the solution was poured into a cell cuvette and finally inserted into the spectrophotometer and read for three consecutive times. Total hydrocarbon content was calculated by taking the average from the values obtained and then multiplied by the dilution factor, 10 (20 ml of chloroform/2g of soil)

### 2.3 Radiometric Measurement

Activity of  $^{210}\text{Po}$  was determined more than a year after sampling, so it was assumed that secular equilibrium with its parent  $^{210}\text{Pb}$  had been achieved. Therefore, it was only possible to determine total  $^{210}\text{Pb}$  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  $^{209}\text{Po}$  yield tracer (the certified activity concentration is  $0.357 \pm 0.011$  Bq·g<sup>-1</sup>) and totally digested using concentrated

nitric and perchloric acids. A review of  $^{210}\text{Po}$  determination can be seen in Mathews et al. (2007). The digested sample was evaporated to almost dryness and treated by evaporation with concentrated hydrochloric acid three times and, finally, dissolved in 80 ml of 0.5N HCl. About 50 mg of ascorbic acid was added to reduce any iron present in the solution. Polonium was auto-deposited onto a Platinum coated disc for 6 hours of heating at 80°C and stirring of the solution. The prepared alpha-sources were analysed by alpha-ray spectrometry using silicon surface barrier detectors (EG&G) coupled to a PC running Maestro™ data acquisition software. The chemical recovery values ranged from 60 to 90%. Gamma emitting radionuclides [ $^{228}\text{Ac}$  ( $^{228}\text{Ra}$ ),  $^{214}\text{Bi}$  ( $^{226}\text{Ra}$ ),  $^{212}\text{Pb}$  ( $^{228}\text{Th}$ ) and 40K] were measured using gamma-ray spectrometer. The detector was a low background CANBERRA high-purity germanium p-type coaxial detector, housed in a 10cm thick high-purity lead shield. The relative efficiency was 30% and the resolution was 2keV for the 1332keV  $^{60}\text{Co}$   $\gamma$ -peak. Weighed samples were introduced into 20 ml nalgene containers and sealed to trap the gaseous  $^{222}\text{Rn}$  and  $^{220}\text{Rn}$  emanating from in-situ  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$ , respectively. The flasks were stored for more than 21 days and then counted for 24 hours each one. In some cases, and due to the small quantities of sediment in the upper layers of each core, we combined two to three adjacent sub-samples to reach the working geometry.  $^{226}\text{Ra}$  activity was obtained from the  $^{214}\text{Bi}$  photopeak at 609.3 keV. Due to the low activity of  $^{137}\text{Cs}$  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, one or two  $\gamma$ -rays in the

energy range of 150–1800keV. A known amount of the standard solution was diluted in the same geometry as the samples. The activity concentration (in Bq·kg<sup>-1</sup>) 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 <sup>214</sup>Bi, <sup>228</sup>Ac and 40K.

### 3. Results and Discussions

#### 3.1 Core Profiles of Total hydrocarbon Content and Sedimentation Rates

The results shown in figure 2 illustrate the vertical distribution of total hydrocarbon content (THC), and the corresponding dates obtained with the CRS model for station 3. It was observed from the results, that the concentration of total hydrocarbon content were in the order of 0.001ppm, 0.07 ppm, 4.34 ppm, 80.1 ppm, 125.23 ppm 130.8 ppm and 75.43 ppm for sediments slices 18-20 cm, 10-12cm, 8-10 cm, 6-8cm, 4-6cm, 2-4cm and 0-2cm respectively, while sedimentation rates obtained in relation to the concentration of total hydrocarbon content were 0.064g/cm<sup>2</sup>.y (8-10cm), 0.055g/cm<sup>2</sup>.y (6-8cm), 0.039g/cm<sup>2</sup>.y (4-6cm), 0.109 g/cm<sup>2</sup>.y (2-4cm) and 0.074g/cm<sup>2</sup>.y (0-2cm) corresponding with 1938 (8-10cm), 1955 (6-8cm), 1973 (4-6cm), 1997 (2-4cm) and 2004 (0-2cm) obtained from the constant rate of supply (CRS) model respectively (Figure 4). A single relatively fast sedimentation (0.109 ± 0.004 g.cm<sup>-2</sup>.y<sup>-1</sup>) was reported for a depth of 2- 4cm in the core corresponding to the year 1997 ± 3. In addition, the sedimentation rates ranged from 0.019 - 0.034 g.cm<sup>-2</sup>.y<sup>-1</sup> and displayed minimal and maximal environmental perturbations between 1973 and 1997.

#### 3.2 The historical trends of total hydrocarbon (THC) and total phosphorus (TP)

The pollution assessment conducted using sediment cores revealed that the concentration of total hydrocarbon content ranged from 0.001 to 130.80 ppm; total phosphorus ranged from 0.01 to 0.499mg/g and the rate of sedimentation ranged from 0.039 g/cm<sup>2</sup>.y to 0.109 g/cm<sup>2</sup>.y at a depth of 0-10cm. The profiles displayed low concentrations of THC and TP in the late 1930s corresponding with almost a constant rate of sedimentation. This was attributable to the absence of oil and gas activity in the region and low nutrient level in the sediments which was earlier reported in the sediment of the Bonny Estuary and ascribed to high metabolic rate in the Niger Delta water bodies, where nutrients are quickly used up as soon as they are released (Chindah, 2004). Subsequently, the constant rate of sedimentation observed was in agreement with the report by Oyebande *et al.*, (1980) as the occurrence during the pre-dam (1915-1957) years where the annual sediment load delivered to the rivers was high and constant. The observable gradual increase in THC and TP corresponded with a slow sedimentation rate from the late 1950s. This could plausible be the heightened oil and gas activities following the discovery of crude oil in 1956 and the commercialization of oil in 1958. Furthermore, the decrease in sedimentation rate could be attributable to the construction of dams and reservoirs (1963-1977) as reported by Collins and Evans (1986). It was estimated that percentage reduction in sediment load as a result of dam construction was 70%.

Subsequently, maximum peaks observed between early 1970s and late1990s displayed; a relatively fast sedimentation rate (0.109 ± 0.004g.cm<sup>-2</sup>.y<sup>-1</sup>) which could be attributed to adverse weather conditions accompanied with flooding thereby suggesting flooding

events to have occurred in the 1990's; massive delivery of phosphorus from agricultural runoff which is sometimes indicative of flooding events and greater dimensions assumed with crude oil activities when it became the mainstay of the Nigerian economy in the early 1970s. It was also documented as years where massive oil spills occurred in Nigeria (Nwilo and Badejo, 2011).

Although reported cases of oil spill did not affect the Bonny estuary directly particles and suspended sediment might have been transported, modified and stored in the estuary. Dublin-Green (1985) reported that medium to fine sediments are being transported from the sea into the channel by strong tidal currents during high tide and back into the sea by ebb currents. In addition, Abam (2001) reported that the dense network of rivers and creeks, which creates a condition of delta-wide hydrological continuity, was the possible reason for disasters such as oil pollution which affects one part of the delta to be felt in other parts within the Niger Delta region. The gradual decrease in concentration in THC, TP and the sedimentation rate from the early 2000s was indicative of less quantity of oil spills and absence of flooding events. Adati (2012) reported that the annual oil spillage quantity has significantly decreased while the annual oil spill incidence is increasing yearly. However, no significant improvement was reported because the incidences are increasing with less quantity of oil being spilled.

Furthermore, the slow sedimentation rate was in conformity with Abam (2001) where it was reported that the emerging trends is that the dams have gradually silted up with the continuous entrapment of sediments, thus decreasing their capacity to impound water and increasing sediments delivery into the rivers.

### 3.3 Application of the Constant Rate of Supply Model

The Constant Rate of Supply model as described by Omokheyeke *et al.*, 2014 was successfully applied to calculate the ages and sedimentation rates for each stratigraphic level (figure 4). The sedimentation rates have fluctuated over the last 70 years due to anthropogenic activities in the surrounding area. A single relatively fast sedimentation ( $0.109 \pm 0.004 \text{ g}\cdot\text{cm}^{-2}\cdot\text{y}^{-1}$ ) was recorded for a depth of 2–4 cm in the core which could be explained as an effect of acceleration in sedimentation rate due to physical processes. Unlike St-1 and St-2, sediment accumulation at St-3 is relatively low ( $0.124\text{cm}\cdot\text{y}^{-1}$ ) because of the long distance (about 3 km) to the nearest site of intensive human activity. Nevertheless, high resolution core is required for a better quantitative description of historical sedimentation in this area (Omokheyeke *et al.*, 2014).

The age and sedimentation rates obtained from the constant rate of supply (CRS) model at each stratigraphic level are displayed in Figure 4. The data obtain from the CRS model revealed increase in bulk sediment accumulation rates over the past 80 years while sedimentation rates obtained were  $0.074 \text{ g}\cdot\text{cm}^{-2}\cdot\text{y}^{-1}$ ,  $0.109\text{g}\cdot\text{cm}^{-2}\cdot\text{y}^{-1}$ ,  $0.039\text{g}\cdot\text{cm}^{-2}\cdot\text{y}^{-1}$ ,  $0.550\text{g}\cdot\text{cm}^{-2}\cdot\text{y}^{-1}$  and  $0.064\text{g}\cdot\text{cm}^{-2}\cdot\text{y}^{-1}$  corresponding with 2004, 1997, 1973, 1955 and 1938. The sedimentation rates calculated suggested low sedimentation which has earlier been reported to signify a very calm environment. According to Dublin- Green (1985) it was reported that the shallow marginal area of the Bonny Estuary is a low energy environment characterized by weak tidal currents which promote the deposition of fine sediments while the deeper channel centres are areas of scouring; dominated by strong tidal currents.

### 3.4 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 (Figures 5 –7). Calcium ranged from 3.1-10.5 mg/kg in 2011 and 7.5-10.9 mg/kg in 2012 with mean values of  $6.1\pm 1.1$  and  $9.7\pm 0.6$  mg/L in 2011 and 2012 respectively. Magnesium concentrations ranged from 50.6-53.3 mg/kg in 2011 and 52.2-53.4 mg/kg in 2012 with mean values of  $52.3\pm 0.4$  and  $53.0\pm 0.1$  mg/kg in 2011 and 2012 respectively. Potassium ranged from 18.7-28.3 mg/kg in 2011 and 18.3-38.1 mg/kg in 2012 with mean values of  $24.2\pm 1.5$  and  $28.1\pm 3.3$  mg/kg in 2011 and 2012 respectively. Zinc ranged from 1.5-3.3 in 2011 and 0.2-6.0 in 2012 with mean values of  $2.7\pm 0.9$  and  $2.8\pm 0.7$  mg/kg in 2011 and 2012 respectively. Lead concentrations ranged from 0.2-0.6 mg/kg in 2011 and 0.2-0.9 mg/kg in 2012 with mean values of  $0.6\pm 0.1$  and  $0.3\pm 0.06$  mg/kg in 2011 and 2012 respectively. Cadmium ranged from below detection limit to 0.1 mg/kg in 2011 and 0.01-0.2 mg/kg in 2012 with mean values of  $0.06\pm 0.02$  and  $0.1\pm 0.03$  mg/kg in 2011 and 2012 respectively.

The concentrations of Co ranged from 0.4-0.7 mg/kg in 2011 and 0.3-0.4 mg/kg in 2012 with mean values of  $0.5\pm 0.05$  mg/kg and  $0.5\pm 0.06$  mg/kg in 2011 and 2012 respectively. Chromium ranged from 0.8-1.8 mg/kg in 2011 and 1.0-2.9 mg/kg in 2012 with mean values of  $1.1\pm 0.2$  mg/kg and  $2.0\pm 0.3$  mg/kg in 2011 and 2012 respectively. The concentrations of Cu and Fe in 2011 and 2012 ranged from 1.4-1.9 and 0.4-2.2 mg/kg, 0.4-38.0 and 0.6-38.7 mg/kg respectively with mean values of  $0.9\pm 0.3$  and  $0.5\pm 0.09$  mg/kg,  $25.6\pm 7.4$  and  $29.9\pm 5.9$  mg/kg for Cu and Fe in 2011 and 2012 respectively while that of Ni and Na ranged from 0.2-0.7 and 0.2-0.8 mg/kg, 4.1-

23.3 and 5.1-18.7 mg/kg respectively with mean values of  $0.4\pm 0.09$  and  $0.5\pm 0.08$  mg/kg,  $13.8\pm 3.2$  and  $12.8\pm 1.8$  mg/kg for Ni and Na in 2011 and 2012 respectively.

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 than the wet season with respect to station 3. 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. 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; Egborge 1986; Ademoroti 1996). Consequently, sediments contaminated by heavy metals constitute a threat to the health of aquatic organisms (Forstner and Wittmann 1983; Law and Singh 1991).

#### 4. Conclusion

The sedimentation rates obtained revealed that minimal and maximal environmental perturbation occurred for some years. The low sedimentation rates obtained are known to signify a very calm environment while the single relatively fast sedimentation rate observed was attributed to adverse weather conditions accompanied with flooding. Sedimentation rates obtained for stations 1 and 2 were effectively higher than that of station 3 indicating post-depositional mixing or reworking of sediment induced by physical disturbances. In addition, the historical inputs of total hydrocarbon content suggested massive oil spills during the period.

Trace metals from different sources are prevalent in coastal areas of the South Nigeria. The present study showed that sedimentary trace metals were of mixed biogenic, anthropogenic and industrial sources. Trace metal concentrations showed slight increase over the years of monitoring in sediment samples with statistical significance in the variation of some of them at ( $P < 0.05$ ) probability. The higher concentrations of trace metals in sediment showed the general belief that sediment are a sink and archive for contaminants. The study revealed the pollution records of the Niger Delta Basin over the last 80 years. The empirical data provided evidence of these conditions over the last 80 years. The sedimentation rates obtained revealed that minimal and maximal environmental perturbation occurred between 1973 and 1997. The low sedimentation rates obtained are known to signify a very calm environment while the single relatively fast sedimentation rate observed was attributed to adverse weather conditions accompanied with flooding. The concentration total hydrocarbon content suggested massive oil spills during the period from 1973 to 2003, while total phosphorus indicated low

nutrients and massive delivery of phosphorus from agricultural runoff which was sometimes indicative of flooding events. It is therefore concluded that advent of Industrialization necessitated the fluctuating environment conditions in the estuary.

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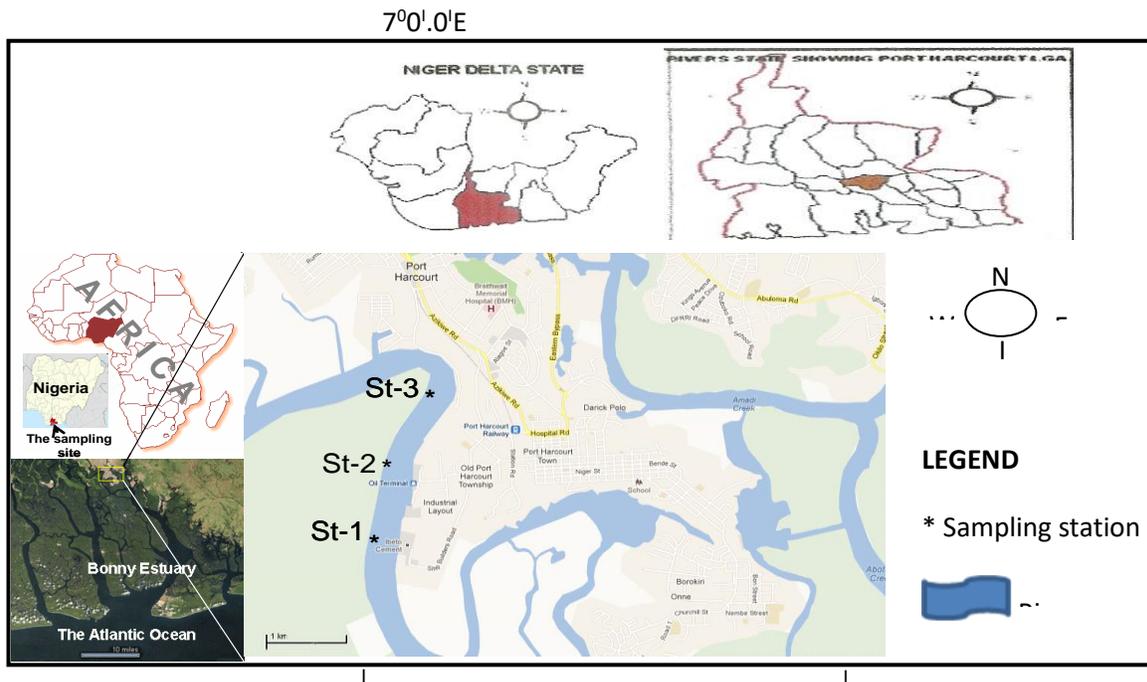


Figure 1. Map of the study area showing the sampling stations.

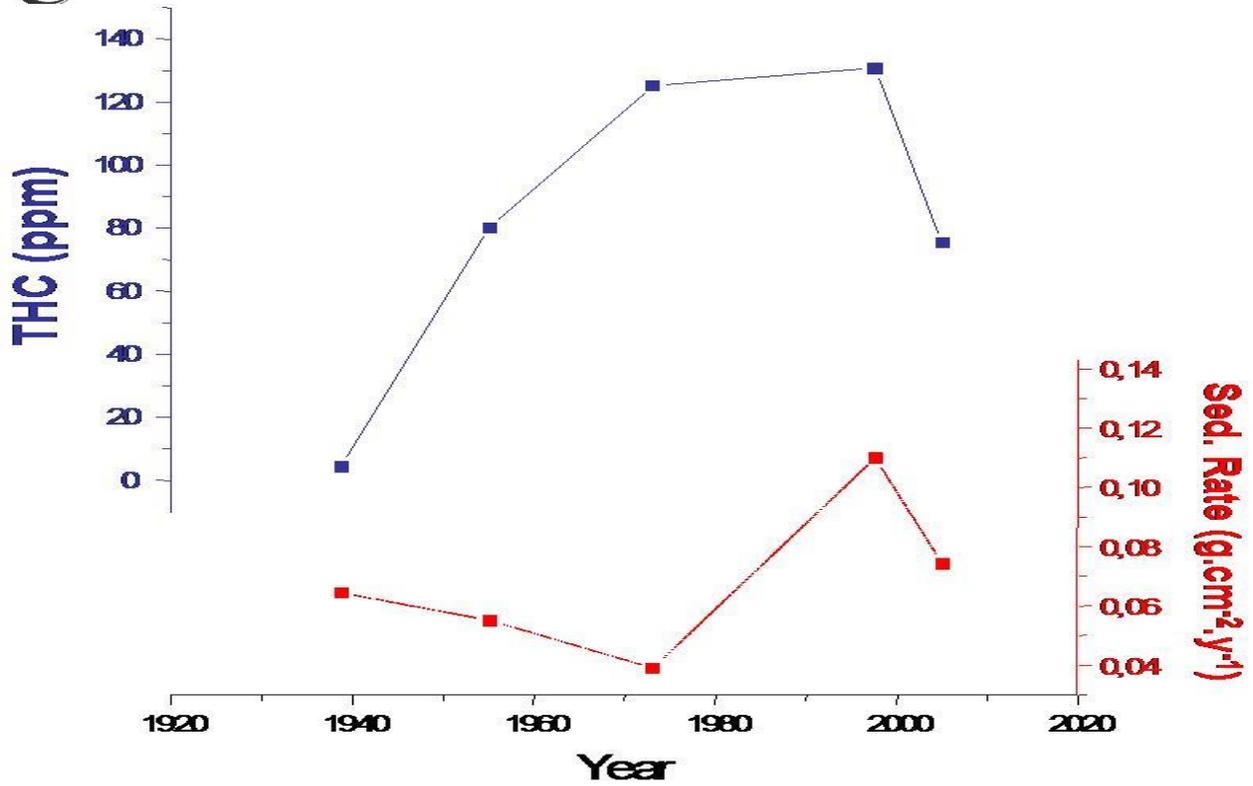


Figure 2. Core Profiles of total hydrocarbon content and sedimentation rates in sediment

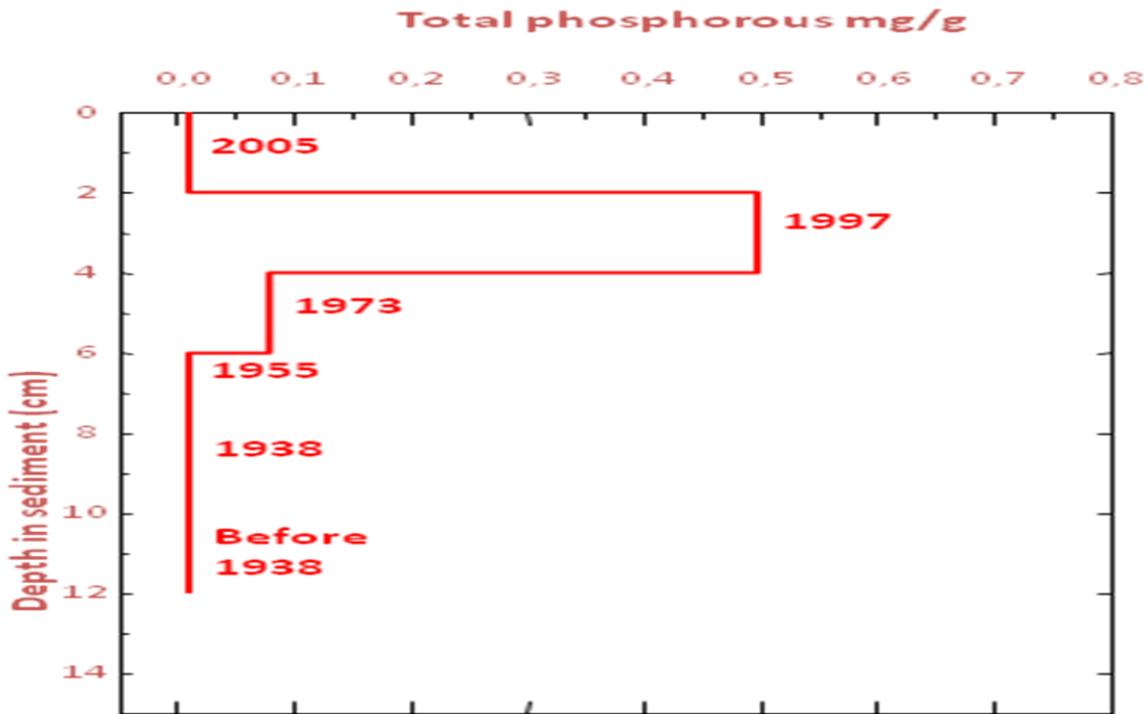


Figure 3. The Concentration of Phosphorus in sediment

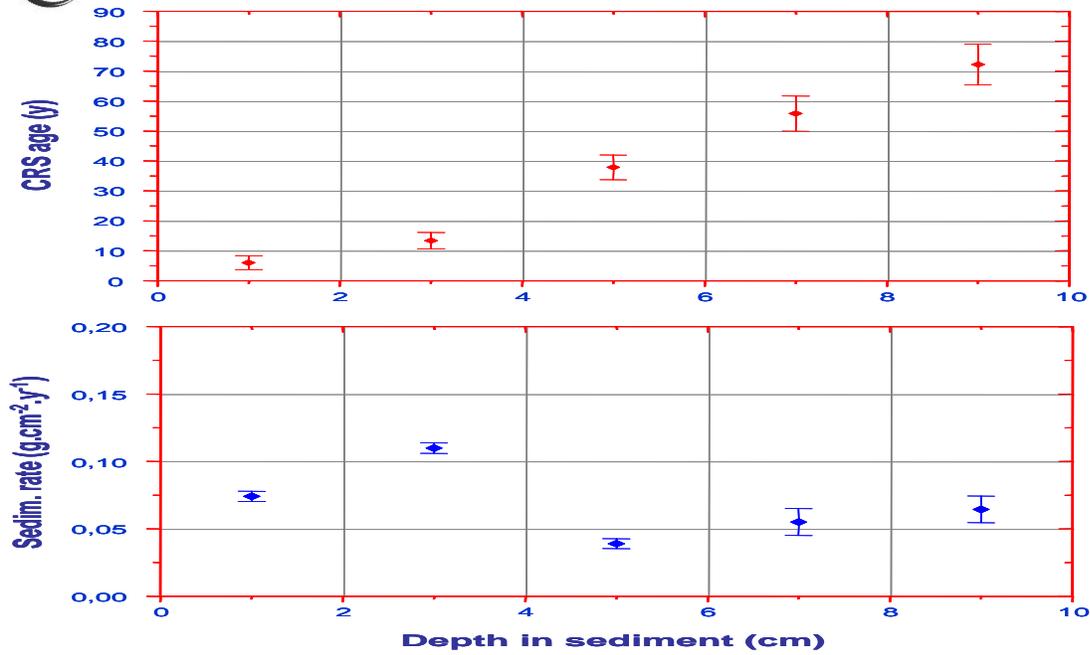


Figure 4. Age and sedimentation rate/depth relationships determined by CRS model.

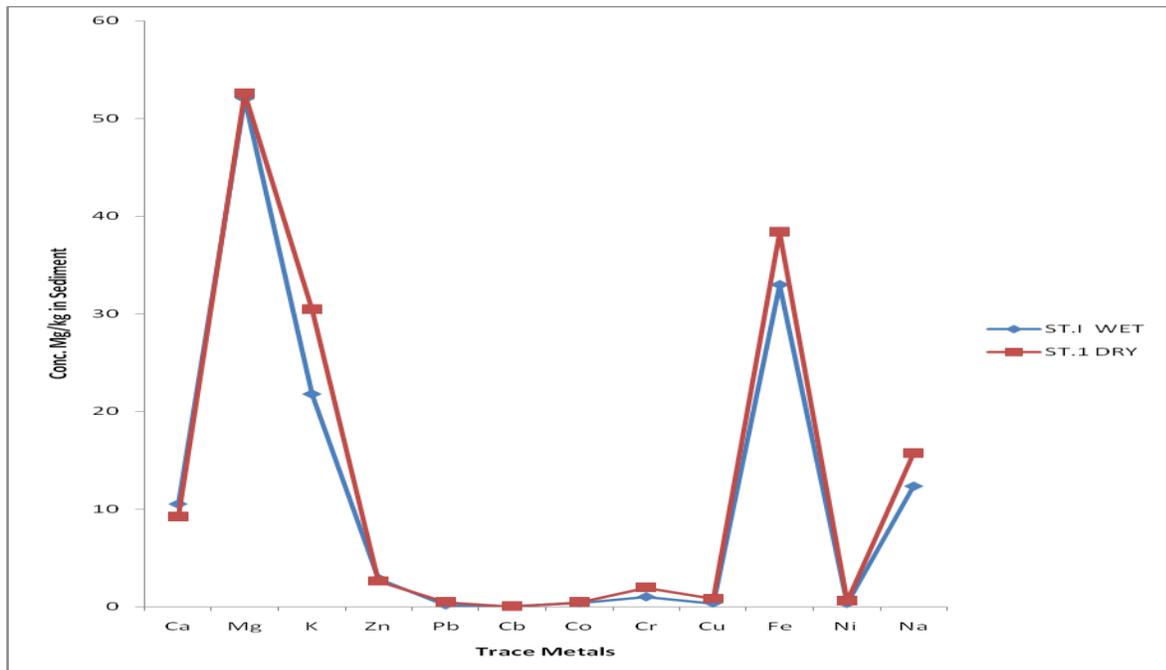
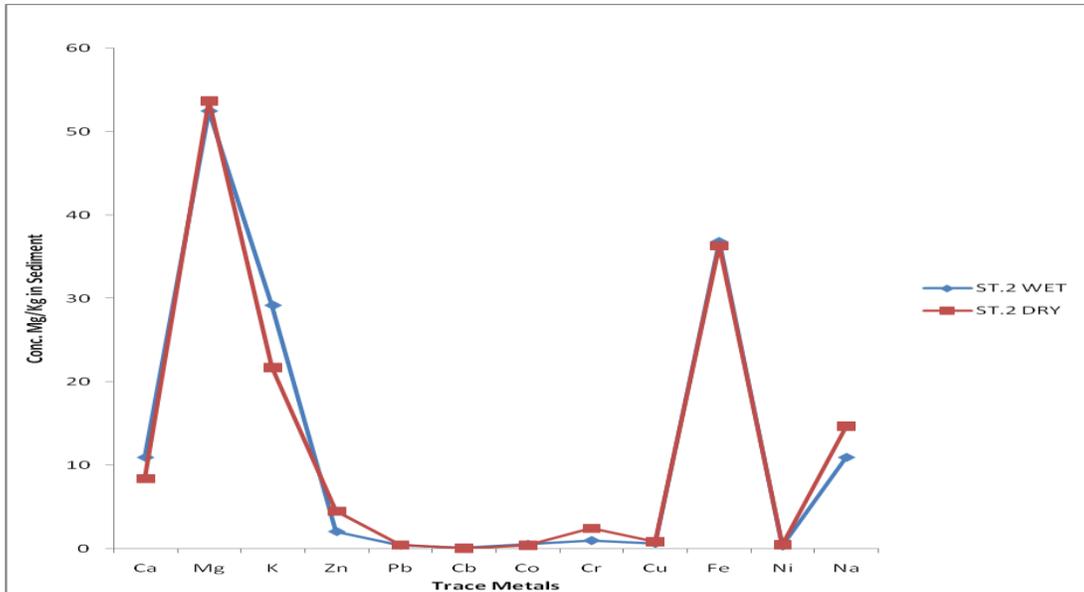
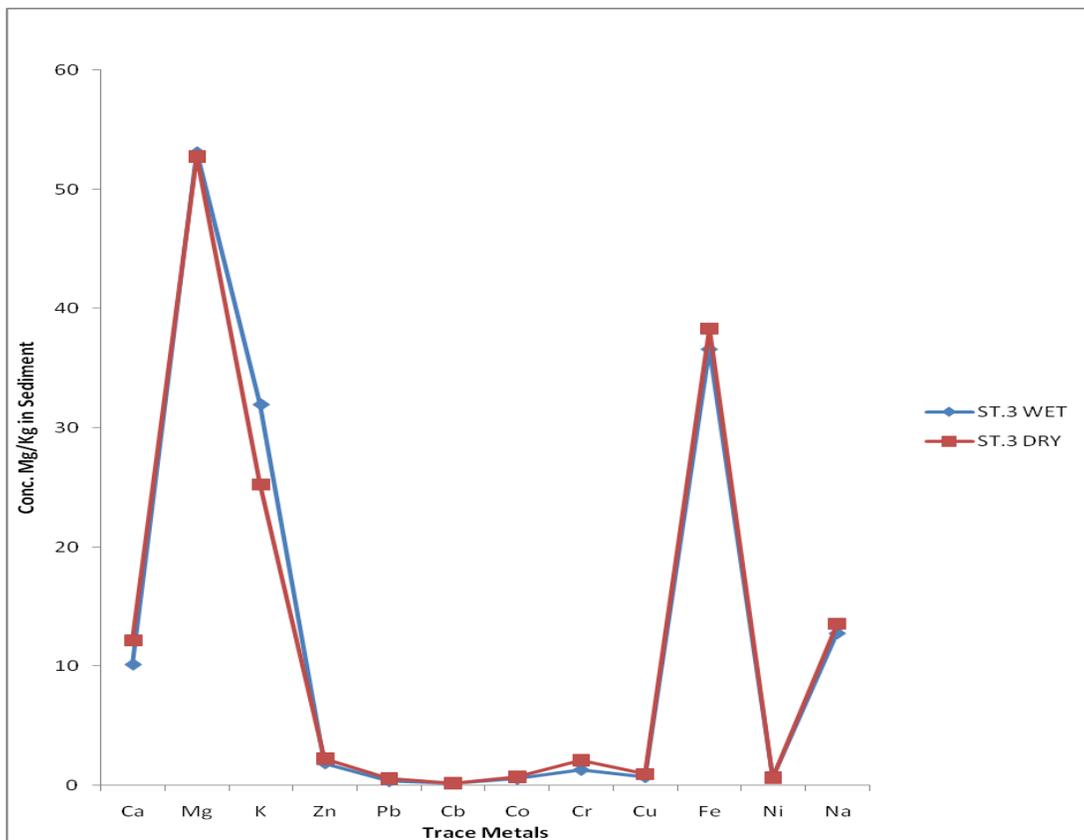


Figure 5. The level of trace metals in the sediment of Station 1 for 2011 and 2012



**Figure 6.** The level of trace metals in the sediment of Station 2 for 2011 and 2012



**Figure 7.** The level of trace metals in the sediment of Station 3 for 2011 and 2012