

Seasonal Variations of Heavy Metals Concentrations in Sediment Samples Around Major Tributaries in Ibeno Coastal Area, Niger Delta, Nigeria

Nwadinigwe, Chukwuemeka A., Udo, Godwin J., Nwadinigwe, Alfreda O.

Abstract: Seasonal Variations of Heavy Metals Concentrations in Sediment Samples around major Tributaries in Ibeno Coastal Area, Niger Delta, Nigeria was investigated using Atomic Absorption Spectrophotometer Unicam 939 model. Fifteen composite sediment samples were collected in February 2013 and June 2014 representing dry and wet seasons respectively. The concentrations (mg kg^{-1}) of heavy metals in sediment for dry and wet seasons were in decreasing order of (dry) Fe (22.18 ± 14.82) > Mn (9.67 ± 2.75) > V (3.39 ± 3.30) > Ni (2.18 ± 0.78) > Cd (0.48 ± 0.75) > Co (0.10 ± 0.01) > Zn (0.49 ± 0.08) > Pb (0.05 ± 0.07) and (wet) Fe (23.28 ± 0.24) > Mn (9.45 ± 2.63) > V (3.31 ± 3.34) > Ni (1.94 ± 1.48) > Cd (0.48 ± 0.74) > Pb (0.03 ± 0.04). The mean concentrations of Mn, Ni, Pb, Zn, in dry season were higher when compared to the mean concentrations of the heavy metals in wet season except, Fe, V, and Co. The mean concentrations of Cd for dry and wet seasons were the same in dry and wet seasons. All the heavy metals were detected in all the sediment samples. The mean concentrations of all the heavy metals were higher than the control sediment in both dry and wet seasons but below the World Health Organization standards. Iron was found to be the most abundant metal in sediment for both seasons. The average pH (6.170) of the sediment was slightly acidic and below WHO and DPR standards. Frequent monitoring of aquatic environments is necessary in order to detect and prevent cumulative consequences of heavy metallic pollutants which may lead to sub-lethal effects in the aquatic fauna and clinical poisoning to man and farm animals that depend on them for food.

Keywords: Environment, Concentrations, Heavy metals, pollutants, Sediment,

1. INTRODUCTION

The increase in industrialization, urbanization and population has led to scientific researches on the Niger Delta Rivers System. Studies on heavy metals in rivers, lakes, fish and sediments have been a major environmental focus especially during the last decade and heavy metals contaminations of coastal water and sediment have been identified as a serious pollution resulting from industrialization [1]. Protecting sediment quality is an important part of restoring and monitoring the biological integrity of our Nation's water as well as protecting aquatic life, wild life and human health [2]. The investigation of sediments from the water bodies is of great interest in aquatic systems research. Once introduced into the water, metals tend to become incorporated into the underlying sediments hence sediments are good indicators of metal contamination levels.

Sediments reflect the current quality of the system as well as providing information on the impact of pollution sources. Sediment is an integral component of aquatic ecosystem providing habitat, feeding, spawning and rearing areas for many aquatic organisms. Extensively study of sediments all around the world indicated that sediments act as sinks and sources of contaminants in aquatic systems because of their variable physical and chemical properties. Trace metals can accumulate in the upper sediment. Heavy metals in aquatic system can be naturally produced by the slow leaching from soil/rock to water, which are usually at low levels, causing no serious deleterious effects on human health [3], [4]. Heavy metals are produced from a variety of natural and anthropogenic sources. In fluvial environments, however, metal pollution can result from direct atmospheric deposition, geologic weathering or through the discharge of agricultural, municipal, residential or industrial waste products [5]. Heavy metals discharged into the environment rapidly associate with particulates and ultimately settles in bottom sediments of water bodies either through direct discharge or surface run-offs. The accumulation of metals from the overlying water to the sediment is dependent on a number of external environmental factors such as pH, electrical conductivity and the available surface area for adsorption caused by the variation in grain size distribution [6]. Being an integral part of the dynamic hydro-geochemical system involved in the cycling of elements, sediment can accumulate and store, or release heavy metals and other toxic elements to the watershed, depending on conditions defined by the pH, redox potential, organic matter and grain size distribution of the sediment. As a result, aquatic sediments are used to monitor environmental and natural changes occurring in local, regional or global watersheds and/or changes in aquatic ecosystems forced by anthropogenic factors [7] The indiscriminate discharges of effluents by the petroleum companies into the environment constitutes one of the main

- Prof. Nwadinigwe, Chukwuemeka A.
- Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka, Nigeria.
- Udo, Godwin J. Department of Pure and Industrial Chemistry
- University of Nigeria, Nsukka, Nigeria., email acmejames@yahoo.com Phone: +2348083661932
- Dr. Nwadinigwe, Alfreda O. Department of Plant Science and Biotechnology, University of Nigeria, Nsukka, Nigeria.

factors of degradation of the aquatic and terrestrial ecosystem located near major urban centers and contribute to the increase of the concentrations of heavy metals in these environments [21]. More and more attention has been drawn due to the wide occurrence of metal pollution in aquatic system. Some heavy metals may transform into the persistent metallic compounds with high toxicity, which can be bioaccumulated in the organisms, magnified in the food chain, thus threatening human. Among environmental pollutants, metals are of particular concern; due to their potential toxic effect and ability to bio accumulate in aquatic ecosystems [8]. Considering of the use of some rivers and lakes as water supplies, threats are thus posed on human health via drinking water, polluted vegetable, foodstuff and disruption of the natural environment. Understanding the dynamics of the environment through chemical assessment of heavy metals in environmental matrix is crucial in determining pollution status of the environment. The objective of our study was to investigate the impact of a crude oil exploration and exploitation in sediment with respect to heavy metals pollution by: determining dry and wet seasons concentration of heavy metals in surface sediment of tributaries around Qua Iboe Rivers coastal area and comparing metal concentrations in sediment with standards for sediment quality, and relevant recorded in literatures.

2. MATERIAL AND METHODS

2.0 STUDY AREA

Ibena Local Government Area has a coastal area of over 1,200 square kilometers. It is situated on the eastern flanks of Niger Delta which in turn is part of gulf of Guinea. It is located at the south end of Akwa Ibom State with latitude $7^{\circ}54'$ and $4^{\circ}34'$ North of equator and longitude $7^{\circ}54'$ and $8^{\circ}02'$ east of Greenwich Meridian. The communities on the west bank of Qua Iboe River do not have access to the hinterland except by boat through the river and creeks. Qua Iboe River estuary which lies within the study area coordinates, has Douglas Creek emptying into it. This creek is about 900m long and 8m deep. It is the point where petroleum exploration and production (E and P) waste from the Exxon Mobil Qua Iboe Terminal (QIT) tank farm are transferred to the lower Qua Iboe River Estuary and adjoining creeks through two 24 cm diameter pipes. The Exxon Mobil oily sludge dumpsite is located adjacent to this creek and the flare stack, where gas is flared continuously is also situated. Some communities in Ibena Local Government Area are located at the bank of Qua Iboe River while others are located on the Atlantic Littoral, Mkpanak, Upenekang, Iwu-achang, are located on the east bank of Qua Iboe River, Okoritip and Ikot Inwang are located on the west bank while Iwokpom-Opolom, Itak Abasi, Akete, Okoritak are located on the Atlantic Coast line. Qua Iboe River estuary situates in close proximity to the Exxon Mobil oil effluent treatment and discharge plant. The wastes are discharged into the Atlantic Ocean but may recede into the estuary due to tidal motion [9].

2.1 SAMPLING PROCEDURE

The study area was divided into 15 sampling locations, identified as : Location-1(Atabrikang), Location-2(Ntafre),

Location- 3 (IkotInwang), Location- 4 (Okoritip), Location-5 (Ukpenekang), Location-6 (Okpolom), Location-7 (IwoOkpom), Location-8 (Okoritip), Location-9 (Afia), Location-10 (AdahaUsuk), Location-11 (InuaEyetIkot), Location-12(ItakAfaha), Location-13 (Iwokwang), Location-14 (Okom Ita), and Location-15(Mkpanak) as shown in the map of the study area (Fig. 1).

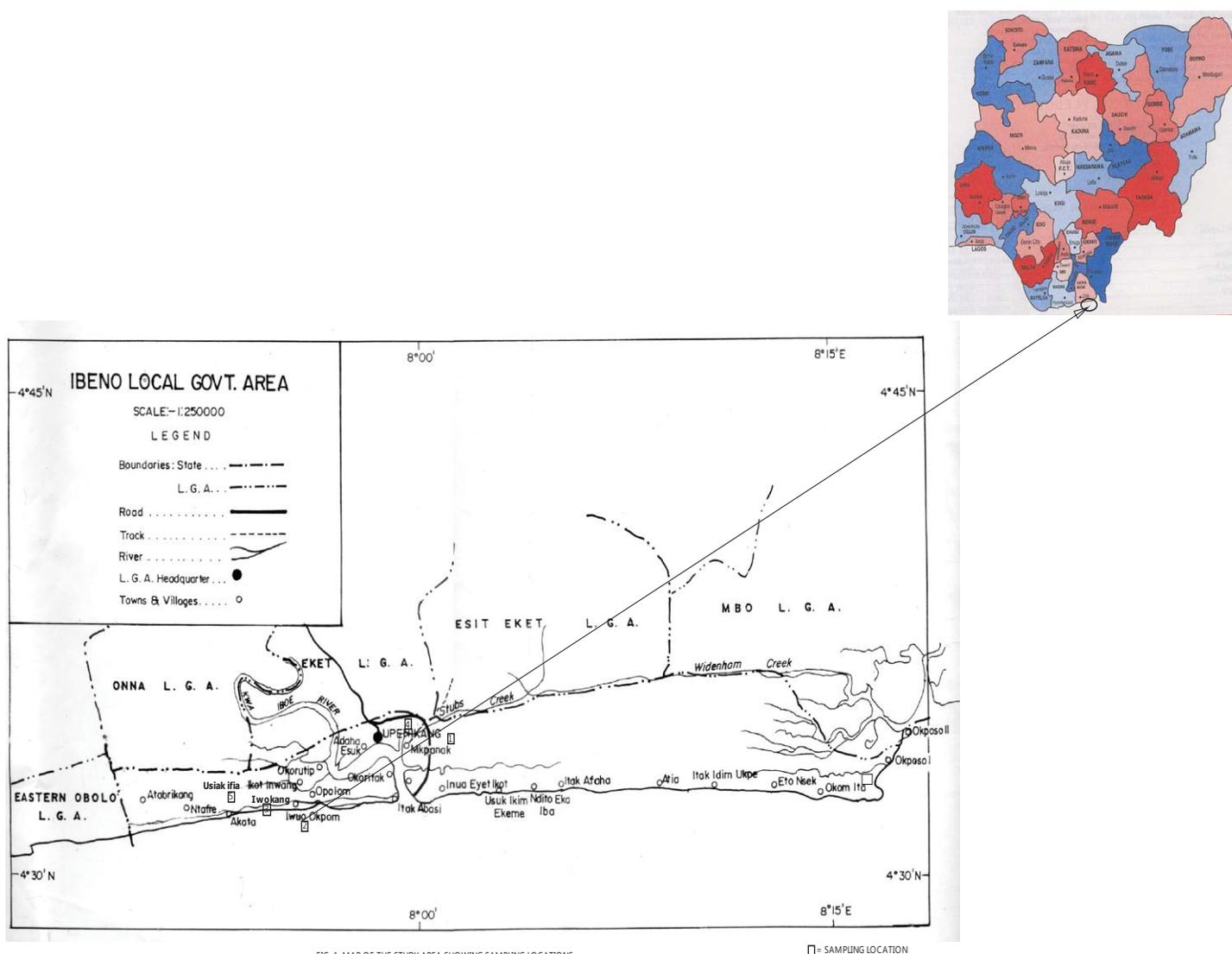


Fig. 1. Map of the study area showing sampling locations. Adapted from Survey Department, Ministry of Land and Housing Akwa Ibom State, Nigeria.

Triplicate sediment samples from three (3) points of each location were collected and mixed together to form a composite sample representation of that location. A total of fifteen (15) composite sediment from 15 geo-referenced points in 15 tributaries in the study area were collected and analyzed for heavy metal concentrations during dry and wet seasons. The surface sediment samples were obtained with a 6.5 m diameter corer to a depth of 10 cm between each sampling location the corer was rinsed with distilled water. Sediments samples collected were extruded from corer into a tray before stored in clean plastic plates in a cold container taken to the laboratory for pretreatment and analysis.

2.2 ANALYTICAL PROCEDURE

Sediment sample was sun dried; pulverized and sieved to pass through a 2 mm mesh size. 1.0 g of the sediment sample was weighed into a Kjeldahl flask. 15 ml of aqua regia was added and stirred to wet the sample. The sample was kept overnight. The next day, the flask was placed on a hot plate and heated to 50 °C for 30 mins. The temperature was raised to 120 °C and heating continued until the

disappearance of the white fume. The sample was cooled and 10 ml 0.2 M HNO₃ was added. The resulting mixture was filtered through a filter paper (Whatman no 541). The flask and filter paper were washed with small aliquots of 0.2 M HNO₃. The filtrate was transferred into a 50 ml flask and made up to the mark with 0.2 M HNO₃. A blank sample was made using the same methods but without the sediment. The concentrations of Ni, V, Cd, Pb, Co, Fe, Mn and Zn were determined using Flame Atomic Absorption Spectrophotometer (AAS) [10]. The pH of sediment samples was determined as described by Radojvic and Bashkin (1999), [10].

3 RESULTS AND DISCUSSION

The concentrations of the eight heavy metals (Ni, V, Cd, Pb, Mn, Fe, Co, and Zn) in the fifteen (15) geo-referenced points in surface sediment samples from the study area for dry and wet seasons in are presented in Tables 1-3. The results indicated that the order in mean concentrations (mg kg⁻¹) of heavy metals in the sediment samples during dry and wet seasons was : Fe (22.18 ± 14.82) > Mn (9.67 ± 2.75) > V (3.39 ± 3.30) > Ni (2.18 ± 0.78) > Cd (0.48 ± 0.75)

> Co (0.10 ± 0.02) > Zn (0.05 ± 0.08) > Pb (0.05 ± 0.07) and Fe (23.28 ± 0.25) > Mn (9.45 ± 2.64) > V (3.31 ± 3.34) > Ni (1.94 ± 1.48) > Cd (0.48 ± 0.74) > Co (0.13 ± 3.34) > Pb (0.03 ± 0.04) respectively. All the heavy metals were detected in all the sediment samples. The mean concentrations of all the heavy metals were higher than the control sediment in both dry and wet seasons but below the World Health Organization standards. The mean concentrations of Mn, Ni, Pb, Zn, in dry season were higher when compared to the mean concentrations of the heavy metals in wet season except, Fe, V, and Co. This may be due to slow movement of water in the sediment and the possible high absorption ability of the heavy metals by the sediment. The mean concentrations of Cd for dry and wet seasons were the same in dry and wet seasons. The most obvious anthropogenic impact was observed in location 5 (Ukpenekang). The concentration of most of the metals appears higher in the dry season than those recorded for

the wet season. Of all the metal examined, iron was found to be the most abundant metal in sediment for both seasons. From the results obtained, it could be observed that the concentrations of heavy metals in the samples locations and between dry and wet seasons were variables. This could be attributed to the geological distribution of minerals that varies from one location to the other. Among the metals detected Pb had the lowest concentration and was higher during the dry season, this may be because of efficient sedimentation since the water is only disturbed by tidal current during the dry season. Kpee et al. (2009) [11], revealed that the average metal concentrations in sediment in both seasons in the study area were in the order: Pb ($25.73 \mu\text{g g}^{-1}$) > Cu ($18.48 \mu\text{g g}^{-1}$) > Ni ($2.91 \mu\text{g g}^{-1}$) > Cd ($1.35 \mu\text{g g}^{-1}$). The potentially bio-available heavy metals include those that can be accessed by man through ingestion and are usually considered as being of anthropogenic origin [11].

Table 1: Mean concentrations (mg kg^{-1}) of heavy metals in sediment during dry season

Heavy Metals	HSD ₁	HSD ₂	HSD ₃	HSD ₄	HSD ₅	HSD ₆	HSD ₇	HSD ₈	HSD ₉	HSD ₁₀	HSD ₁₁	HSD ₁₂	HSD ₁₃	HSD ₁₄	HSD ₁₅	HSD _c	Mean±SD
Ni	2.12	0.04	0.020	4.20	2.02	2.80	4.20	2.10	0.38	1.10	0.08	1.17	4.00	4.78	3.75	0.01	2.18±0.78
V	4.28	2.28	10.00	5.33	11.13	2.95	3.42	0.66	0.73	2.95	0.35	0.21	1.23	1.28	3.28	0.02	3.30±3.30
Cd	1.02	0.03	0.250	0.18	0.33	0.35	0.20	0.23	0.30	0.05	0.03	0.66	0.20	3.04	0.30	0.38	0.48±0.75
Pb	0.16	0.02	0.020	0.02	0.02	0.01	0.07	0.03	0.03	0.04	0.27	0.02	0.02	0.02	0.02	0.02	0.05±0.07
Mn	8.03	9.50	9.060	8.31	8.31	9.51	11.26	7.20	3.09	9.95	11.95	12.02	9.07	13.25	14.50	13.17	9.67±2.75
Fe	24.02	8.90	9.980	10.92	49.47	49.47	8.99	7.80	11.09	18.72	19.09	21.09	25.52	24.27	46.42	30.10	22.83±14.8
Co	0.08	0.08	0.067	0.08	0.08	0.058	0.05	0.05	0.07	0.02	0.02	0.22	0.24	0.22	0.22	0.24	0.10±0.078
Zn	0.03	0.04	0.041	0.03	0.02	0.06	0.05	0.05	0.05	0.06	0.07	0.07	0.06	0.06	0.05	0.05	0.05±0.02

HSD = Heavy metals in sediment samples, HSDC = Heavy metals in control sediment samples, ND = Not detected

Table 2: Mean concentrations (mg kg^{-1}) of heavy metals in sediment during wet season

Heavy metals	HSD ₁	HSD ₂	HSD ₃	HSD ₄	HSD ₅	HSD ₆	HSD ₇	HSD ₈	HSD ₉	HSD ₁₀	HSD ₁₁	HSD ₁₂	HSD ₁₃	HSD ₁₄	HSD ₁₅	HSD _c	Mean±SD
Ni	2.00	0.10	0.01	3.99	2.00	2.02	3.89	2.09	0.30	1.08	0.05	1.07	3.08	4.00	3.39	0.90	1.94±1.48
V	4.19	2.00	10.20	5.55	10.99	3.00	3.30	0.59	0.70	2.90	0.28	0.20	1.18	1.29	3.27	0.06	3.31±3.34
Cd	1.00	0.13	0.330	0.18	0.30	0.32	0.09	0.19	0.28	0.10	0.03	0.69	0.20	3.30	0.30	0.32	0.48±0.74
Pb	0.15	0.01	0.020	0.01	ND	ND	0.06	0.02	0.03	0.03	0.03	0.02	0.01	0.01	0.02	0.06	0.03±0.03
Mn	8.00	9.50	9.00	7.99	8.31	8.98	11.19	7.07	3.00	9.89	10.85	12.00	9.00	13.00	13.90	12.99	9.45±2.64
Fe	25.69	10.05	9.99	11.90	50.50	49.49	9.00	8.00	12.00	20.20	21.01	23.00	25.40	25.01	48.00	28.09	23.28±0.25
Co	0.07	0.08	0.07	0.07	0.08	0.04	0.03	0.03	0.06	0.02	ND	0.02	0.99	0.19	0.22	1.00	0.13±0.25
Zn	0.02	ND	0.04	0.01	0.01	0.02	0.04	0.05	0.05	0.02	0.04	0.07	0.06	0.05	0.04	0.10	0.04±0.20

HSD = Heavy metals in sediment samples, HSDC = Heavy metals in control sediment samples, ND = Not detected

Table 3: Average concentrations of heavy metals (mg kg^{-1}) for wet and dry seasons in sediment of the study area.

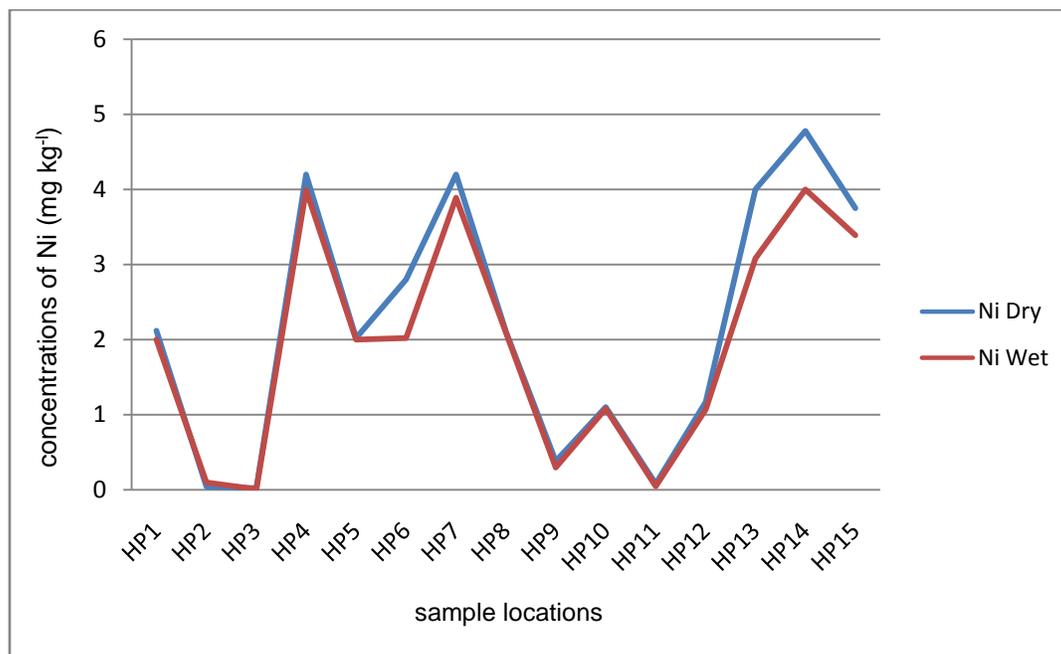
Heavy metals	Mean concentration for dry season	Mean concentration for wet season	Average concentrations for dry and wet seasons
Ni	2.184	1.938	2.06
V	3.339	3.300	3.34
Cd	0.478	0.476	0.47
Pb	0.051	0.027	0.04
Mn	9.668	9.445	9.56
Fe	22.383	23.283	22.83
Co	0.103	0.131	0.12
Zn	0.049	0.035	0.04

3.0 SEASONAL DYNAMICS OF INDIVIDUAL ELEMENT

3.1 NICKEL (Ni)

Ni level in sediment samples investigated in the study area recorded a mean \pm SD ($2.18 \pm 1.69 \text{ mg kg}^{-1}$) and % CV (77.59 %) for dry season (Table 1). Similarly, mean \pm SD ($1.93 \pm 1.47 \text{ mg kg}^{-1}$) and % CV (76.23 %) Ni was recorded in the sediment of the study area for wet season (Table 2). The total average concentration of Ni in the sediment of the study area was 2.061 mg kg^{-1} (Table 3). The highest concentration of 4.78 mg kg^{-1} was recorded at location 14 (Okom Ita) and the lowest of 0.04 mg kg^{-1} at location 2 (Ntetre) Fig. 2. In the study of Chindah et al. (2009)[12], nickel concentration ranged between $3.50 \pm 2.4 \text{ mg kg}^{-1}$ and $3.50 \pm 2.5 \text{ mg kg}^{-1}$ for dry and wet seasons respectively. Also, Osoji et al.(2010)[13], reported that Ni had higher concentrations in the dry seasons as compared

to the rainy seasons with mean concentration of 14.33 mg kg^{-1} and 9.75 mg kg^{-1} for dry and wet seasons respectively. In a study "Survey of heavy metals in sediments of Kolo creek in the Niger Delta, Nigeria" by Inengite et al. (2010)[14], mean concentrations of Ni (11.13 – 14.33 ; 5.52 and 9.75) mg/Kg for dry season, late dry season, rainy season and late rainy season respectively were obtained. In a related study, Obasohan (2008) [15], reported Ni range of (0.020 - 0.35) mg kg^{-1} . Nickel has been classified as very toxic to aquatic life and relatively assessable to aquatic organisms. Petroleum wastes contain high concentration of Nickel. Chronic discharges of the wastes into the aquatic ecosystem could result in accumulation of the metal in the environment. Potentially bio-available heavy metals comprise of those heavy metals that can be accessed by man through ingestion and are usually considered as anthropogenic in origin.

**Fig. 2:** Seasonal variations of Ni within the study locations

3.2 VANADIUM (V)

The mean concentration and % CV of V in sediment samples of the study area during dry season were $3.34 \pm 3.30 \text{ mg kg}^{-1}$ and 77.13 % respectively (Table 1). Also, the study revealed mean concentration of $0.0379 \pm 0.0349 \text{ mg kg}^{-1}$ and % CV of 100.8 % vanadium in the wet season (Table 2). Total average of concentration of 3.319 mg kg^{-1} V was obtained in the sediment samples of the study area and is presented in Table 3. The total average concentration of 3.319 mg kg^{-1} was high and exceeded the concentration of V in control sediment sample of 0.002 mg kg^{-1} . The highest concentration of 11.13 mg kg^{-1} was recorded in location 5 (Ukpenekang) and the lowest of 0.03 mg kg^{-1} was recorded in location 9 (Afia) Fig. 3. Essien et

al. (2012) [16], reported a mean concentration of 16.23 mg kg^{-1} V in the sediment of the study area. Also, Chindah et al. (2009)[12], observed that vanadium concentrations were relatively high for both seasons with slight variations observed between dry (0.04 mg kg^{-1}) and wet (0.13 mg kg^{-1}) season respectively. The relatively high concentration of V trapped in the sediment may be due to crude petroleum oil spillages, which is common in the area. The level of vanadium as indicated in this study especially in Ukpenekang is high enough to cause serious threat, which implies pollution. There is need to prevent this trend since there is a high tendency of heavy metals to accumulate in the environment

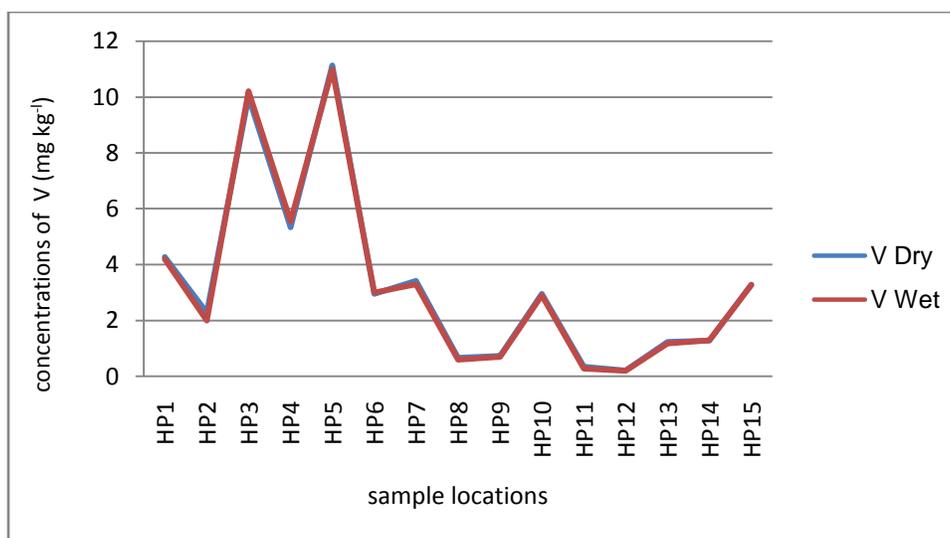


Fig. 3: Seasonal variations of V within the study locations.

3.3 CADMIUM (Cd)

The mean concentration of Cd in surface sediment samples was ($0.48 \pm 0.75 \text{ mg kg}^{-1}$) and % CV of 157.54 % was obtained for dry season (Table 1). Similarly, mean \pm SD ($0.476 \pm 0.741 \text{ mg kg}^{-1}$) and CV % (155.71 %) were recorded in the surface sediment samples of the study area during wet season (Table 2). The total average concentration of Cd in sediment for dry and wet seasons was 0.477 mg kg^{-1} (Table 3). The highest concentration of 3.04 mg kg^{-1} was recorded in location 14 (Okom Ita) and the lowest 0.03 mg kg^{-1} Fig. 4. The mean concentration of Cd was higher than the control sediment sample (0.38 mg kg^{-1}). In a study conducted by Olatunji et al. (2012) [7], the concentration of Cd in sediment ranged between ($0.17 - 0.51 \text{ mg kg}^{-1}$). Ideriah et al. (2013)[17], recorded following percentage composition of heavy metals in sediments samples Pb (22.27 %), Cu (25.41 %), Cd (37.78 %), Cr (

22.24 %), Ni (24.84 %), Mn (21.43 %) and Zn (22.43 %) respectively during dry season. Also, Chinda et al. (2009) [12], recorded Cd concentration which ranged between (0.030 and 0.014 mg kg^{-1}) in the wet season while in the dry season, a uniform concentration of $0.0005 \text{ mg kg}^{-1}$ was recorded. In a related study by Ikpee et al. (2009)[11], concentration of Cd in sediment sample from the study area ranged between $1.5 \pm 1.0 \mu\text{g g}^{-1}$ to $1.8 \pm 1.2 \mu\text{g g}^{-1}$ and $1.2 \mu\text{g g}^{-1}$ and $1.5 \mu\text{g g}^{-1}$ in the dry and wet seasons respectively. Cd is non-essential and once it enters biological system is capable of remaining there, its excretion occurs very slowly and at certain concentrations it causes damage to human and other living organism especially when present as CdCl_2 in aqueous medium. There have been reported cases of deaths in man through the consumption of aquatic resources with increased level of Cd.

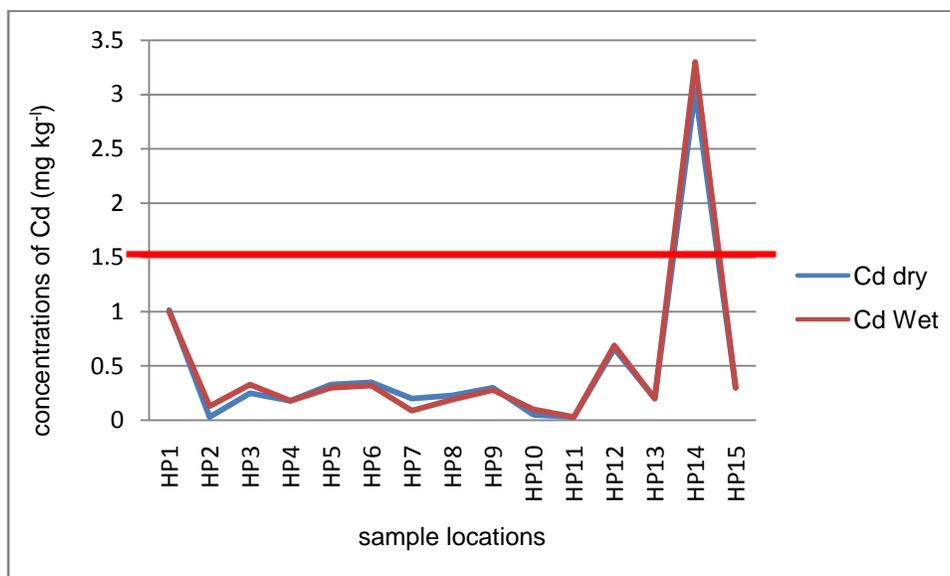


Fig. 4: Seasonal variations of Cd within the study locations.

3.4 LEAD (Pb)

The mean concentration and % CV of Pb in surface sediment samples of the study area during dry season were $0.05 \pm 0.07 \text{ mg kg}^{-1}$ and 138.53 % respectively (Table 1). During wet season, sediment samples revealed mean \pm SD ($0.03 \pm 0.04 \text{ mg kg}^{-1}$) and % CV (134.20 %) of Pb in the study area. Total average of Pb in dry and wet seasons in the surface sediment samples of the study area was 0.039 mg kg^{-1} Table 3. Lead was not recorded in locations 4 (Okoritip) this was contrary to study of Oladoye et al. (2014)[24], who recorded a maximum value of $232.95 \mu\text{g/g}$ of Pb in the sediment at the study location (Okorutip); the highest concentration was recorded in location 1 (Atabrikang) during wet season (Table 2), Fig 5. Similarly, during dry season, the highest concentration was 0.16 mg kg^{-1} location 1 (Atabrikang) and lowest concentration of 0.01 mg kg^{-1} was recorded in location 6 (Okpolom), (Table 2), Fig. 5. In a research related conducted by Ikpee et al. (2009)[11], in the study area, the mean concentration of Pb in sediment samples ranged between $42.0 \pm 20.0 \mu\text{g g}^{-1}$ to $25.54 \pm 22.56 \mu\text{g g}^{-1}$ in dry and wet seasons respectively. The results revealed that the average metal concentrations in sediment samples in both seasons was in the order $\text{Pb} > \text{Cu} > \text{Ni} > \text{Cd}$ which were $25.73 \mu\text{g g}^{-1}$, $18.48 \mu\text{g g}^{-1}$, $2.91 \mu\text{g g}^{-1}$ and $1.35 \mu\text{g g}^{-1}$ respectively. Olatunji and Osibanjo

(2012)[7], recorded concentration of Pb in sediment at the range of (13.67 to 18.11 mg kg^{-1}) with mean levels of $15.75 \pm 1.49 \text{ mg kg}^{-1}$ during dry season, and (14.92 - to 19.08 mg kg^{-1}) with mean Pb level of $16.96 \pm 1.45 \text{ mg kg}^{-1}$ during wet season. Also, Essien et al. (2012) [9], recorded a mean concentration of 2.94 mg kg^{-1} in sediment of the study area. In a related research by Chindah et al. (2000) [12], lead concentrations in the sediment were higher in wet season (0.003 - 0.027 mg kg^{-1}) than dry season (0.01 mg kg^{-1}). The presence and detection of Pb in the sediment of the study area may be attributed to Pb – laden effluent discharged into ecosystem. The use of lead in industrial processes and consumers product (e.g. batteries, gasoline additives, rolled and extruded products, cable sheathing, paints, alloys and pigment may also account for this. Toxic levels of lead may adversely affect sperm shape, motility, and DNA integrity, thereby giving rise to infertility in males. There are reports that lead accumulation can also lead to altered cellular functions including growth and immune functions [18-19]. The presence of lead is risky to aquatic life since fishes and aquatic fauna are particularly very vulnerable to Pb and often retain about a percent of ingested Lead, which could be taken up by man through food chain. The seemingly increased level of Pb in study area suggests gradual pollution of the study area by Pb.

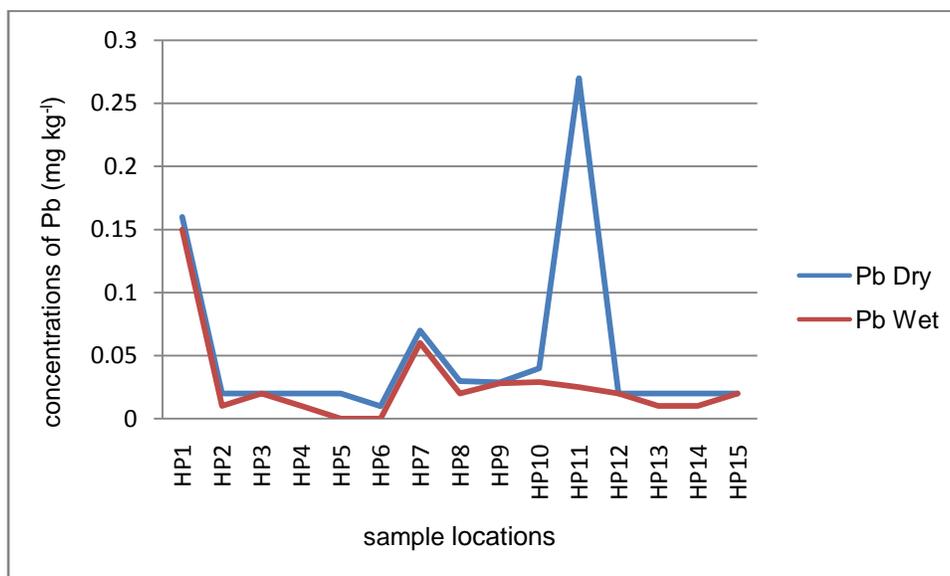


Fig. 5: Seasonal variations of Pb within the study locations

3.5 MANGANESE (Mn)

The level of Mn in surface sediment of the study area was $(9.67 \pm 2.75 \text{ mg kg}^{-1})$ and % CV (28.47 %) for dry season Table 1. Mean concentration of $9.45 \pm 2.64 \text{ mg kg}^{-1}$ and % CV (27.94 %) were recorded in the sediment samples of the study area for wet season (Table 2). The total average concentration of Mn in the sediment samples of the study area was 9.56 mg kg^{-1} Table 3. The concentrations were lower than the concentration of 13.17 mg kg^{-1} of Mn in control sediment samples. The highest concentration of 14.50 mg kg^{-1} was recorded in location 15 (Mkpanak), and

lowest concentration of 3.09 mg kg^{-1} was recorded in location 9 (Afia) Fig. 6. In a study by Osakwe and Peretiemo-Clarke 2013 [22], 0.25 mg kg^{-1} and 0.16 mg kg^{-1} of Mn were recorded in River Ethiope, Delta State, Nigeria for dry and wet seasons respectively. A very important fact about heavy metal poisoning is the fact that they are not easily excreted out of the body, and their effect on the body is not immediate, so individuals can go on accumulating the heavy metal over a long period of time without knowing, only to manifest much later in life.

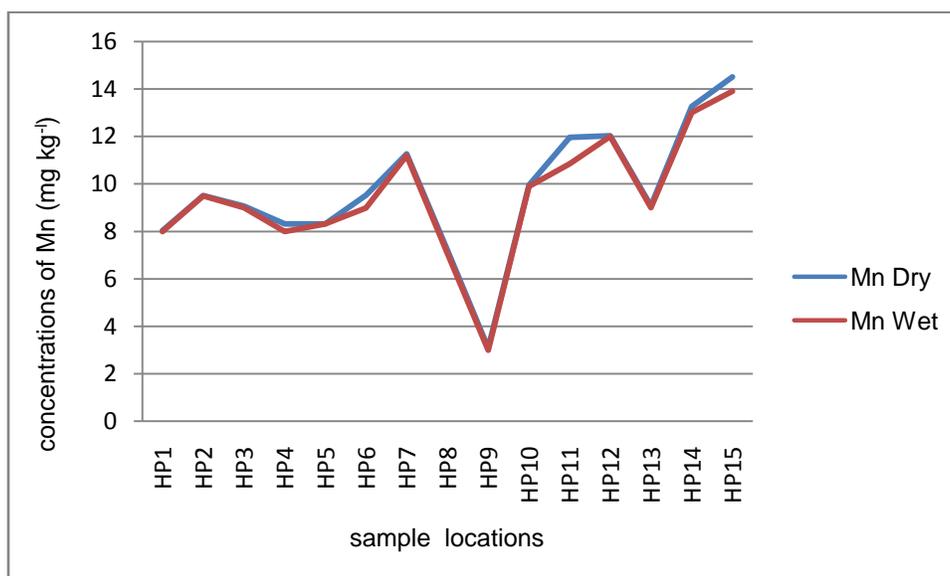


Fig. 6: Seasonal variations of Mn within the study locations.

3.6 IRON (Fe)

The mean concentration and % CV of Fe in surface sediment samples of study area during dry season were $22.383 \pm 14.817 \text{ mg kg}^{-1}$ and 66.198 % respectively Table 1. During wet season, mean concentration of $23.28 \pm 14.91 \text{ mg kg}^{-1}$ and CV % (64.04 %) of Fe were recorded Table 2.

Total average concentration of $22.833 \text{ mg kg}^{-1}$ of Fe was recorded for dry and wet seasons Table 3. The highest concentration of 49.47 mg kg^{-1} was observed in location 6 (Okpolom) and the lowest concentration of 7.80 mg kg^{-1} was recorded in location 8 (Okoritip) Fig. 7. This agreed with the work of Essien et al. (2012) [9] who recorded a

mean concentration of 35.40 mg kg^{-1} of Fe in the sediment samples of the study area. In a related study by Upadhi et al. 2013[23], the concentrations of heavy metals was in the order $\text{Fe} (674 \pm 12.31) > \text{Cu} (8.31 \pm 0.31) > \text{Pb} (6.22 \pm 0.16) > \text{Cd} (0.01 \pm 0.01)$ with iron leading. The concentration of Fe to an extent is usually determined by the nature of soils along the river course which is eventually leached into the river system and its sediments [22]. The high level of Fe in sediment samples of the study area may be attributed to

the discharge of Fe-laden waste and effluent replete with corroded iron pipes, containers and scrapes into the water body and lithological or crustal origin [1]. The prevalent and high concentration of Fe in all the samples analyzed in this research work show it abundant in the study area though industrial activities may contribute, and the high concentration of Fe in sediment sample may suggest possible contamination by iron.

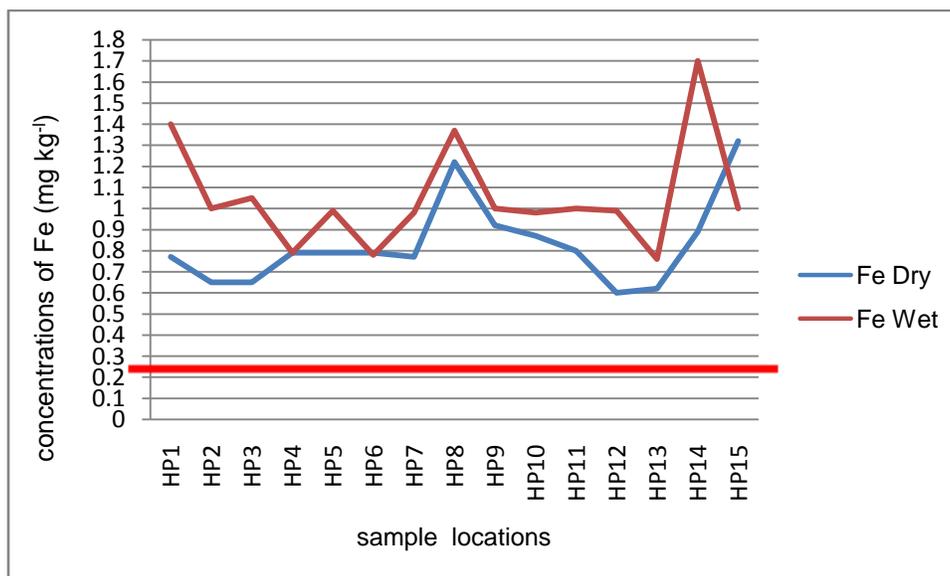


Fig. 7: Seasonal variations of Fe within the study locations.

3.7 ZINC (Zn)

The findings also recorded a mean concentration of $0.05 \pm 0.01 \text{ mg kg}^{-1}$ and % CV of 30.44 % of Zn in surface sediment samples as presented in Table 1 for dry season. Comparatively mean concentration of $0.03 \pm 0.02 \text{ mg kg}^{-1}$ and CV % of 58.17 % of Zn were recorded in sediment samples during wet season Table 3. Total average concentration of 0.04 mg kg^{-1} of Zn was obtained from sediment samples of the study area for dry and wet seasons Table 3. The highest concentration of 0.07 mg kg^{-1} Zn was recorded at location 11 (Enea Eyet Ikot) and lowest concentration of 0.02 mg kg^{-1} was recorded at location 5 (Ukpenekang) Figure 8. In the report by Chindah et al. (2009) [12], concentrations of Zn in the sediment samples of the study area were higher in dry season ($1.03 - 2.04 \text{ mg kg}^{-1}$) than in wet season ($0.063 - 0.277 \text{ mg kg}^{-1}$). Essien et al. (2012) [9], reported a mean concentration of 5.68 mg kg^{-1} in the sediment samples from Tributary of Qua Iboe River Estuary. Osakwe and Peretiemo-Clarke 2013[22], recorded mean concentrations of 2.25 mg kg^{-1} and 2.23 mg

kg for wet and dry seasons respectively in Sediments of River Ethiope, Delta State, Nigeria. Oladoye et al (2014) [24], in their study "Comparative assessment of lead and zinc in the Coastal Areas of Niger Delta" recorded a range of $24.26 \mu\text{g/g}$ to $131.52 \mu\text{g/g}$ of zinc in the sediment samples of Qua Iboe river, Akwa Ibom. The concentration of Zinc in sediment samples was generally low in all the locations investigated compared to previous research conducted in the area. Although zinc is not a human carcinogen, ingestion of large doses (390 mg kg^{-1} per day for (3 – 13) days or about 27 mg kg^{-1} of Zn per day) can cause death. Vomiting, diarrhea, abdominal cramping and in some cases, intestinal hemorrhage can occur from long-term exposure to high dosage of zinc. Zinc is widely used in industries to make dye, paint, rubber, wood preservatives and ointments. Plants and animals require zinc for normal growth. At high concentration, zinc is very toxic, its toxicity being caused by interactions in plant uptake of other essential elements like phosphorus and iron [22]

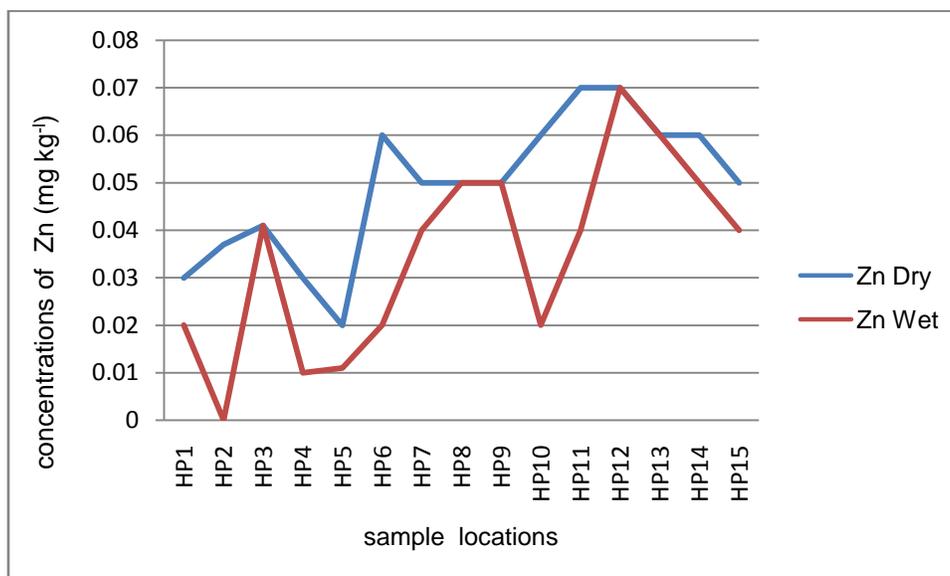


Fig. 8: Seasonal variations of Zn within the study locations.

3.8 COBALT (Co)

Mean concentration of $0.10 \pm 0.08 \text{ mg kg}^{-1}$ and % CV of 75.95 % were recorded in the sediment of the study area during dry season Table 1. Also, mean concentration of $0.13 \pm 0.24 \text{ mg kg}^{-1}$ and % CV 186.72 % of Co were obtained in surface sediment samples of the study area during wet season Table 2. Total average concentration of 0.12 mg kg^{-1} was recorded for dry and wet seasons Table 3. In a related study by Essien et al. (2012) [9], a mean concentrations of 0.09 mg kg^{-1} and 0.27 mg kg^{-1} of Co in surface water and sediment samples respectively. In a study by Owamah 2013 [21], $0.49 \pm 0.001 \text{ mg kg}^{-1}$, $0.46 \pm 0.002 \text{ mg kg}^{-1}$, and $0.49 \pm 0.001 \text{ mg kg}^{-1}$ of Co were recorded in Warri River in the months of December, January and February respectively representing wet season. Also, during dry season, $0.62 \pm 0.002 \text{ mg kg}^{-1}$, $0.64 \pm 0.001 \text{ mg kg}^{-1}$, $0.59 \pm 0.002 \text{ mg kg}^{-1}$ of Co for the months May, June and July respectively. Cobalt is an essential element introduced anthropogenically into the aquatic environment via run off through application of fertilizer. The toxicity of Co is quite low compared to many other heavy metals, exposure to very high level can cause health effect.

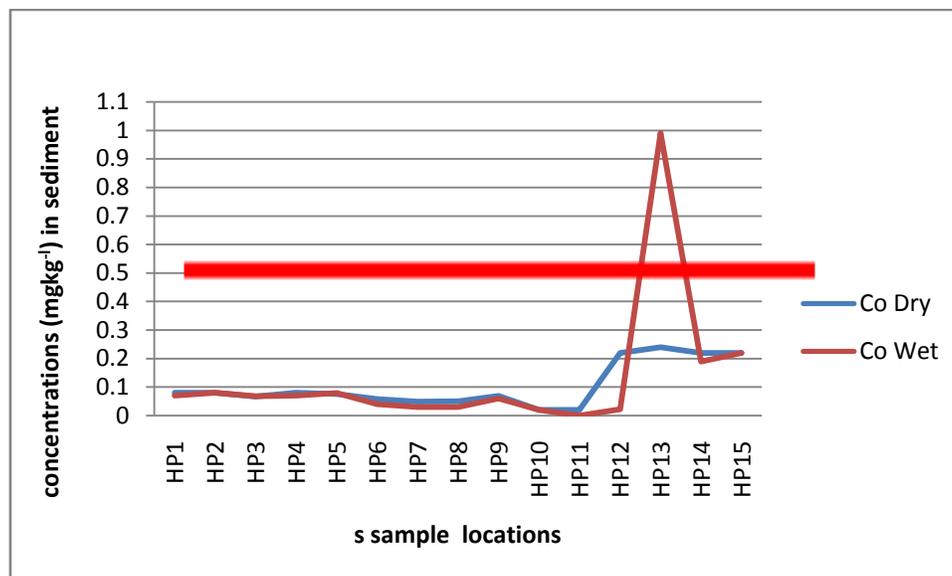


Fig. 9: Seasonal variations of Co within the study locations.

3.9 pH

The mean pH of sediment for wet and dry seasons were 6.226 and 6.113 respectively, with average pH of 6.170 slightly acidic but below WHO and DPR threshold standards of 6.5 - 8.5. There was no significant difference in pH levels of the sediment during dry and wet seasons. This was similar to the research of Jamabo 2011[20]. The slightly acidic pH is peculiar to Nigerian soil and sediment [1]. Jamabo 2011[20], in "Sediment characteristics of the mangrove swamps of the upper Bonny River, Niger Delta, Nigeria" reported a higher range of pH (2.90 – 4.60) and (3.10 - 4.60) during and wet seasons respectively. Olatunji and Osibanjo (2012)[7], recorded pH range of 5.90-7.29 with mean value of 6.84 ± 0.28 , the concentration levels of heavy metals found in sediments are dependent on the prevailing pH condition of the hypolimnion water column [3]. Low pH condition affects metal speciation and may enhance metals' solubility and possible leaching into the water column. High acidity of sediment has been attributed to a combination of possible oxidation of FeS₂ in the sediment to produce sulfuric acid, depleted calcium level or increased aluminum concentration in sediment [1].

4. CONCLUSION

The concentrations of the heavy metals varied within the studied locations and from one season to another, dry season recorded higher concentrations of most of the heavy metals compared to wet season. The average concentrations of all the heavy metals were higher than concentrations in control samples and may not be lethal to the environment since there were below the maximum permissible range as recommended by WHO and Department of Petroleum resources, Nigeria. The concentration of Fe was the highest compared to other metals. This implied threat especially when viewed in perspective of community health issue. The elevated Ni/V concentrations in sediment might be attributed impacts of oil operations in the study area since Ni and V are the major

metallic component in crude oil. The increased concentrations of the heavy metals in sediment of the study area could be attributed influence of oil exploration and exploitation, domestic waste discharge and other anthropogenic activities in the study area. It is recommended that appropriate proactive and periodic measures be put in place by government and petroleum companies to check possible bioaccumulation of the heavy metals in the aquatic biota. This is to prevent the local populace from the threat of bioaccumulation of the heavy metals. The findings from this investigation can serve as baseline environmental data for monitoring of heavy metals accumulation in aquatic the fragile environment.

ACKNOWLEDGMENTS

The authors wish to thank the staff of post graduate laboratory, Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka and staff of research and development laboratory Ministry of Science and Technology, Akwa Ibom State for their technical assistance, provision of equipment and glassware necessary for this work.

References

- [1] P.E. Ndimele, C.A. Kumolu-Johnson. Some Aspects of the Physicochemistry and Heavy Metal Content of Water, Sediment and *Cynotherissa mento* (Regan, 1917) from Badagry Creek, Lagos, Nigeria. Trends in Applied Sciences Research, 7, 724-736, 2012
- [2] O.A. Davies and C.C. Tawari. Season and tide effects on sediment characteristics of trans-okpoka creek, upper bonny Estuary, Nigeria. Agric. Biol. J. N. Am., 1(2), 89-96, 2010.
- [3] Z. Qunfang, Z. Jianbin, F. Jianjie, S. Jianbo, J Guibin. Biomonitoring: An appealing tool for assessment of

- metal pollution in the aquatic ecosystem. *Analytica chimica acta*. 606, 135–150, 2008.
- [4] L. Taoze, L. Bangyu, , Z. Wei. Nutrients and Heavy Metals in Biochar Produced by Sewage Sludge Pyrolysis: Its Application in Soil Amendment. *Pol. J. Environ. Stud.* 23(1), 271-275, 2014.
- [5] B.R. Issa, F.O. Arimoro, M. Ibrahim, G.J. Birma, E.A. Fadairo. Assessment of Sediment Contamination by Heavy Metals in River Orogo (Agbor, Delta State, Nigeria) *Current World Environment*, 6(1), 29-38, 2011.
- [6] A.K. Inengite, N.C. Oforka, L.C. Osuji, Survey of heavy metals in sediments of Kolo creek in the Niger Delta, Nigeria. *African Journal of Environmental Science and Technology*, 4(9), 558-566, 2010.
- [7] O.S. Olatunji, and O. Osibanjo. Distribution and temporal variation of selected heavy metals in sediment of River Osara mainstream drainage in North Central Nigeria. *African Journal of Pure and Applied Chemistry*, 6(13), 188-194, 2012.
- [8] D.O. Onwuli, G. Ajuru, B. Holy, F.C. Amadi. The concentration of Lead in Periwinkle (*Tympanotonos fuscatus*) and River sediments in Eagle Island River, Port Harcourt, Rivers State Nigeria. *American Journal of Environmental Protection*, 2(2), 37-40, 2014.
- [9] J.P. Essien, and N.U. Benson, Trend in Heavy Metals and Total Hydrocarbon Burdens in Sub creek, a Tributary of Qua Iboe Estuary, Nigeria. *Trends in Applied Science Research*, 2, 312 – 319, 2012.
- [10] M. Radojvic, V.N. Bashkin .*Practical Environmental Analysis*. The Royal Society of chemistry. Thomas Graham House, Science park, Milton Road, Cambridge UK. pp 405-500, 1999.
- [11] F. Ikpee, E. Ozioma, L. Ihunwo. Seasonal Variation of Cd, Ni, Cu and Pb in Catfish, Sediment and Water Samples from Ipo Stream in Ikerre District of Rivers State, Nigeria. *Pakistan Journal of Nutrition*, 7, (3), 67-79, 2009.
- [12] A.C. Chindah, S.A. Braide, J. Amakiri, S.O.N. Chikwendu. Heavy Metal Concentrations in Sediment and Periwinkle –*Tympanotonus fuscatus* in the Different Ecological Zones of Bonny River System, Niger Delta, Nigeria. *The Open Environmental Pollution & Toxicology Journal*, 1, 93-106, 2009.
- [13] C.L. Osuji, and M.O. Chukwunedum. The Ebocha-8 oil spillage fate of Associated Heavy Metals six months after. *Petroleum chemistry research group, Department of industrial and pure chemistry, University of Port Harcourt, Choba, Port Harcourt, Nigeria*. 2010.
- [14] A.K. Inengite, N.C. Oforka, L.C. Osuji. Survey of heavy metals in sediments of Kolo creek in the Niger Delta, Nigeria. *African Journal of Environmental Science and Technology*, 4(9), 558-566, 2010.
- [15] E.E. Obasohan. Heavy metals in the Sediment of Ibiekuma Stream in Ekpoma, Edo State, Nigeria. *African Journal of General Agriculture*, 4, p 2, 2008.
- [16] J.P. Essien. and N.U. Benson. Trend in Heavy Metals and Total Hydrocarbon Burdens in Sub creek, a Tributary of Qua Iboe Estuary, Nigeria. *Trends in Applied Science Research*, 2, 312-319, 2012.
- [17] T. Ideriah, J.K. Ikpee, F.N. Nwanjoku. Distribution and Speciation of Heavy Metals in Crude Oil Contaminated Soils from Niger Delta, Nigeria. *World Environment*, 3(1), 18-28, 2013.
- [18] N. Juha, H. Heidi, H. Jukka. Water pH and sediment resuspension regulating internal phosphorus loading in a shallow lake – field experiment on diurnal variation. *J. Limnol.*, 70(1), 3-10, 2011.
- [19] A. Jakimska, P. Konieczka, K. Skora, K. Namiesni. Bioaccumulation of metals in tissues of marine Animals, Part 1: Role and impact of heavy metals on organisms. *Poland Journal of Environmental Studies*. 20(5), 1117-1125, 2011.
- [20] A. Jamabon. Sediment characteristics of the mangrove swamps of the upper Bonny River, Niger Delta, Nigeria. *New Clues in Sciences*, 1, 74-79, 2011.
- [21] H.I. Owamah. Heavy Metals Determination and Assessment in a Petroleum Impacted River in the Niger Delta Region of Nigeria. *J. Pet Environ Biotechnol*, 4(1), 1-4, 2013.
- [22] S.A. Osakwe. Peretiemo-Clarke, B.O. (2013). Evaluation of Heavy Metals in Sediments of River Ethiope, Delta State, Nigeria. *IOSR Journal of Applied Chemistry (IOSR-JAC)*, 4(2), 1-4, 2013. www.iosrjournals.org.
- [23] F. Upadhi, O.A.F. Wokoma, J.A. Edoghotu. Levels of Bioaccumulation of Some Heavy Metals in Fish (*Tilapia zilli*) and Their Concentration in Water and Sediment of Owubu Creek, Niger Delta, Nigeria. *Resources and Environment*, 3(3), 59-64, 2013.
- [24] P.O. Oladoye, and O.O. Adewuyi, Comparative assessment of lead and zinc in the Coastal Areas of Niger Delta. *Journal of Research in Environmental Science and Toxicology*, 3(3), 39-45, 2014.