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SPATIAL AND TEMPORALVARIATION OF SOME HEAVY METALS AND TOTAL HYDROCARBON CONTENT OF SOILS FROM OKRIKA, RIVERS STATE, NIGERIA.

***[1]Amakiri,C.M, [2]Imafidor, H.O., Wokoma, O.A.F.**
*Ignatius Ajuru University of Education, Rumuoelumeni, Port Harcourt
[2]University of Port Harcourt, Choba. Rivers State.

***Corresponding Author (Email):** comfortmina06@gmail.com

Abstract
Spatial and temporal variations of some heavy metals and hydrocarbon content of soils from Okrika in Rivers State were carried out. Two crude oil-impacted communities in each of Okrika LGA (Alakiri and Abam) and Ogu/Bolo LGA (Bolo and Ogu) were selected for the study. One hundred and twenty soil samples were randomly collected from 4 locations, 30 samples each at depths of 0-5 cm, 6-10 cm and 11-15 cm .with the aid of a calibrated soil corer (50 mm in diameter) and covering both wet and dry seasons. Soil samples were taken to the laboratory for the determination of total hydrocarbon content (THC) and selected heavy metals. Total hydrocarbon content varied from 1343.2 – 85,565.11 mg/kg and that for heavy metals ranged from1.7-2.63mg/kg for cadmium 12.75– 30.48 mg/kg for lead, 1.98 -7.15mg/kg for copper and23.8 -47.0mg/kg for zinc. The study revealed that there were significant variations in the concentration of all the selected heavy metals across seasons but across study sites, differences were significant for copper and zinc only. Despite the obvious disparity in the magnitude of THC such differences were not statistically significant both across sites and seasons. Unlike copper and zinc, the concentration of lead and cadmium were above their stated limits thus suggesting a closer affinity to hydrocarbon. The observed concentration of THC which is far above the stated limit of 30mg/kg is indicative of severe hydrocarbon pollution in the study area and therefore the need for urgent remedial action.

Keywords: Soil, Hydrocarbon, Heavy Metals, Crude Oil, Pollution

Introduction
Crude oil and spent lubricating oil influence soil properties and growth of crops been previously reported (Osuji, et al. 2004). The presence of crude oil and spent lubricating oil in soil adversely affects their physical, chemical and microbiological properties, these in turn affect the germination of seeds and impedethe growth of cultivated crops. The impact of crude oil and spent lubricating oil pollution on soil properties and growth of the plant is dependent on their concentrations in a given soil. Beyond 3% concentration, these oils have been reported to be increasingly detrimental to the functional ability of the soil and plant growth (Ibiene et al., 2011). Abosede (2013) opined that oil pollution leads to a reduction in water filtration and soil aeration as a result of clogging of pore spaces, increasing bulk density and ultimately affecting plant growth. Earlier, Dendooven, (2011), had reported that contamination of soil with hydrocarbon could have a great effect on soil fauna. Other studies have reported inhibition of germination and growth of maize, okra and fluted pumpkin at higher doses. Increased concentration levels of hydrocarbons in contaminated sites could pose health hazards to animals, plants and even humans (Okop & Ekpo, 2012).

The oil spill is responsible for the continuous release of heavy metals into the Niger Delta environment (Ahiamadu et al., 2021). During oil production and or refining, heavy metals are grossly introduced into the soil as contaminants (Jennings, 2000). The major problem with heavy metals such as lead, mercury, and lead etc. is their toxicity (Jarup, 2003) as well as their inability to break down with ease into a non–toxic form, thus remaining a potential threat in the environment for a long (Isirimah, 2000). Ozcan et al. (2016) and Gebre and Debelie (2015) have reported that heavy metal accumulation in soil could negatively influence physiological activities such as gaseous exchange, photosynthesis and nutrient absorption which leads to a reduction in dry matter accumulation as well as a reduction in plant growth. It could also lead to reduced cation exchange capacity, insufficient nutrient, and organic content, and low water retention capacity (Singh and Kalamdhad, 2011).

Materials and Methods

The hydrocarbon-impacted sites investigated in the study are located in Okrika and Ogu-Bolo Local Government Areas of Rivers State. The local government areas are readily accessible by a network of roads, and footpaths and accessible to ships, boats, and canoes through the Bonny River and its tributaries. The LGAs are located within the humid-hot equatorial climate and their average annual temperature is between 180°C to 220°C with an annual range of about 200°C. There are two main seasons, the dry season(November-March) and the rainy season(April-October). The LGAs are neighbours inhabited by Okrikans (Wakirikese). The area lies between latitude 4°48'21.885" N and4°32'22.202" N and longitude 6°57'50.141"E and 7°15'19.895"E **covering a** land area of approximately 302.47 km² (Ogu-Bolo 114.58 km² and Okrika 187.8 km²). While Alakiri, Ogu and Bolo communities play host to one form of oil production/ processing activity (both legal and or illegal) and thus are heavily impacted /polluted, Abam on the contrary does not host any such activity and as such is the least/moderately impacted site.

Sample collection and Laboratory Analysis:

The collection of soil samples was done randomly with the aid of a calibrated soil corer. These soil samples were obtained at different depths from four(4) designated sites including Alakiri and Abam in Okrika LGA, and Bolo and Ogu in Ogu/Bolo LGA. From each core depth, samples were collected vertically at 0-5cm, 6-10cm, and 11-15cm. Ten(10)samples from each depth make a total number of 30 samples per site and 120soil samples in all. These samples were put directly into well labeled foil packs and black polythene bags with an open mouth of about 10cm immediately. This is done to prevent evaporation, and the samples were transported to the University of Port Harcourt laboratory for analysis. For heavy-metal analysis soil samples were digested using HCl/HNO3 following the method of the American Society for Testing and Materials (ASTM, 1986). The concentrations of copper, zinc, cadmium, and lead were determined using an atomic absorption spectrophotometer (AAS), a Unicam 969 with a UNICAM SOLAR data station V6.15.The total hydrocarbon content (THC) was determined following the method adopted by Okop and Ekpo (2012).

Results

The mean concentration of physicochemical parameters between the severely impacted sites as against the least impacted site is presented in Table 1. Total hydrocarbon concentration fluctuated from 1343.2 (middle soil – 6-10cm) to 1952.83 (topsoil – 0-5cm) mg/kg for the relatively unpolluted site (Abam) and 25,393.33 – 83,565.11 obtained respectively from the middle and top soils for the severely impacted stations. Figure1 shows the concentration of total hydrocarbon in the study sites during the wet and dry seasons. In the wet season, THC concentration was higher in Alakiri and Ogu while in the dry season, it was higher in Abam and Bolo. Two–way analysis of variance did show any significant difference between seasons and sites of study. The magnitude of Cadmium obtained at the various layers of soil across the different sites is presented in Table 1. For the severely and moderately polluted sites cadmium concentration varied from 1.73 – 1.9 mg/kg and 1.75 – 2.63 mg/kg respectively. In both cases, the topsoil had the least concentration. Generally, all the values of cadmium obtained in the dry season were uniform across all stations and lower than their wet season equivalents (Figure 2). Variations across seasons were shown to be significant at $p \leq 0.05$ but insignificant across sites when values of cadmium were subjected to a 2-Way ANOVA with replication.

Lead concentrations in soil obtained in all the sites at the different depths are displayed in Table 1. At the relatively unpolluted site, the value of cadmium increased with depth but this trend did not hold in the severely polluted site. Seasonal fluctuations were significantly different as shown by the 2- Way ANOVA with replication at $P \leq 0.05$. However, differences recorded across sites were not statistically significant. Values recorded during the dry season were uniform across all the sites and were significantly lower than those of the wet season, see Figure 3. The concentration of copper in this investigation varied across sites and seasons, see Table 1. At the severely polluted site concentration was seen to diminish with depth i.e. the lower the depth of soil the lower the concentration of copper. On the contrary for the moderately polluted site, the highest concentration of copper was recorded in the middle soil sample. Dry season values were generally higher than those of the wet season throughout the study (Figure 4). Variations across seasons and sites were found to be significantly different when subjected to a 2- Way Analysis of variance.

The concentrations of zinc in the different layers of soil in the moderately and severely polluted sites are shown in Table 1. For the severely polluted site concentration of zinc was reduced with increasing depth and varied from 40.35 mg/kg (bottom soil) to 47.0 (topsoil). The highest concentration of zinc in the moderately polluted site was observed at the bottom soil and the lowest at the middle soil. The magnitude of zinc recorded during the wet season was generally higher than the dry season values across all stations. Two Way analysis of the variance of the fluctuation between sites and seasons revealed that there was a statistically significant difference between sites and seasons at P≤ 0.05.

Table 1: concentration of heavy metals and total hydrocarb0n content of soil from moderately and severely polluted sites

SOIL PARAMETERS	MODERATLY POLLUTED			SEVERELY POLLUTED		
	0-5cm	6-10cm	11-15cm	0-5cm	6-10cm	11-15cm
THC(mg/kg)	1952.83	1343.2	1583.95	83565.11	25393.33	29081.68
Cd (mg/kg)	1.75	1.75	2.63	1.73	1.90	1.80
Pb (mg/kg)	12.75	14.96	18.01	30.48	21.00	27.66
Cu(mg/kg)	5.40	7.15	4.25	3.48	2.52	1.98
Zn(mg/Kg)	24.75	23.8	31.6	47	44.63	40.35

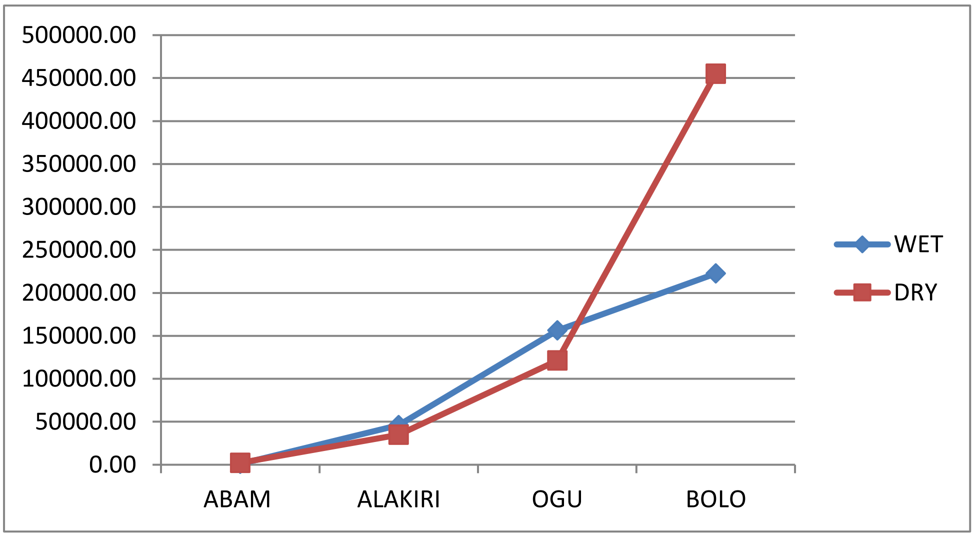

Fig. 1: Concentration of THC in both Wet and Dry seasons during the investigation

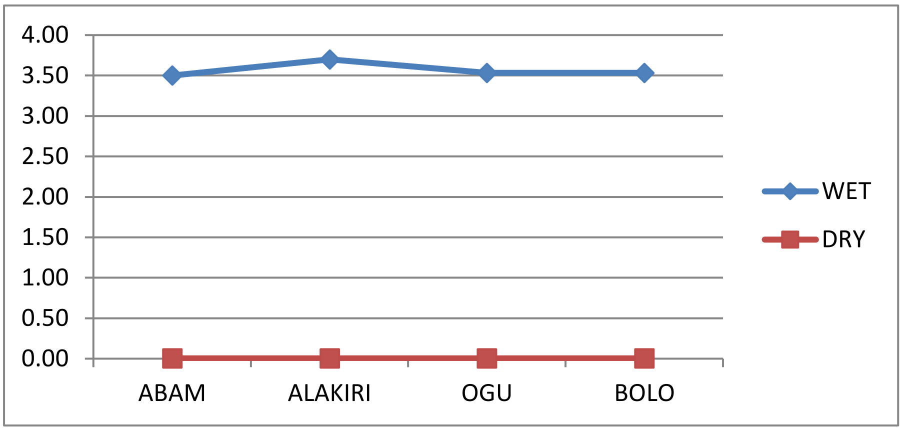

Fig. 2: Concentration of Cadmium in both Wet and Dry seasons during the investigation

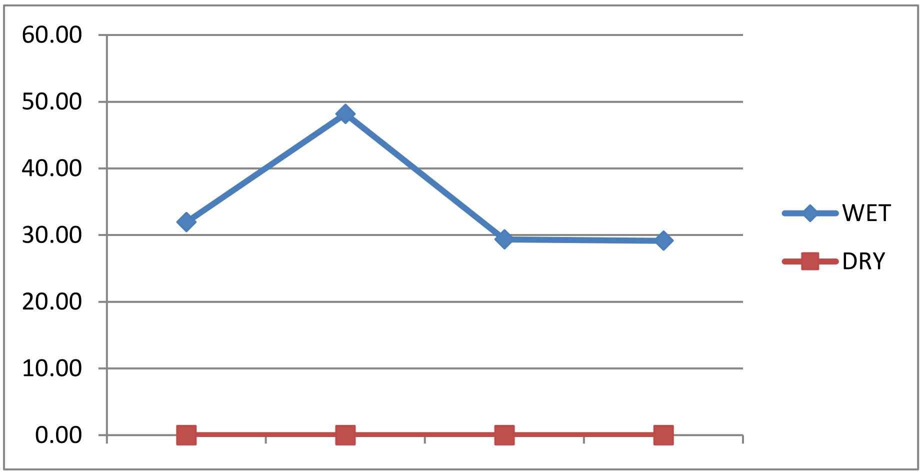

Fig. 3: Concentration of Lead in both Wet and Dry seasons during the investigation

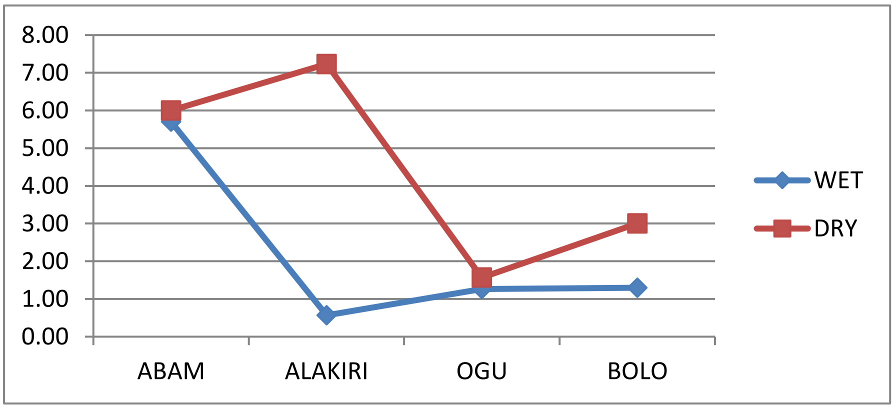

Fig. 4: Concentration of Copper in both Wet and Dry seasons during the investigation

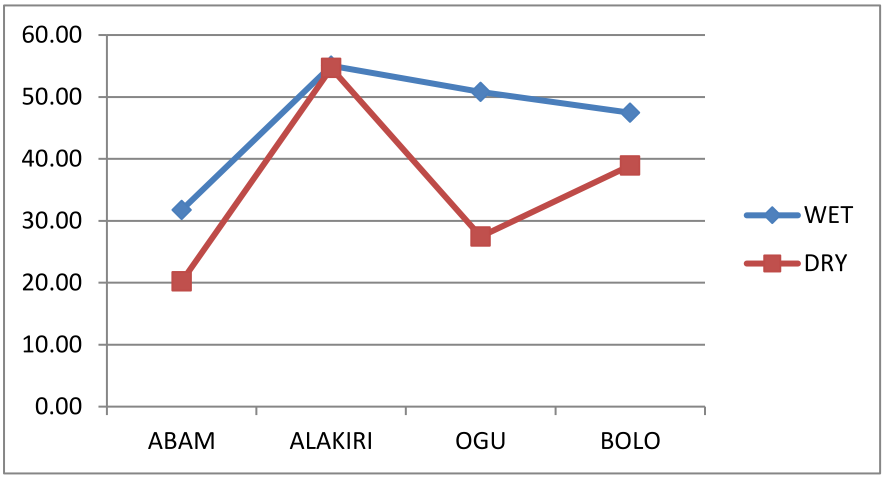

Fig. 5: Concentration of Zinc in both Wet and Dry seasons during the investigation

Discussion

Total hydrocarbon concentration observed in this investigation varied from 1343.20 – 83565.11mg/kg, this is significantly higher than the 17.04 – 61.85 mg/kg, 322.5±155.0–2178.50±64.50mg/kg and 67.5±20.7 – 361.8±327.7 mg/kg reported respectively by Ebong and John, (2021), Wokoma and Friday (2017) and Aigberua et al., (2016) in their separate studies of oil impacted sediments in the Niger Delta area, Nigeria. It is equally much higher than the 16.01 – 136.04 mg/kg obtained in sediments by Dumka and Kingdom (2018) and the 1403±80.61 – 3775.52±113.14 mg/kg by Wokoma (2014a),but closely related to the 126 – 52,000 mg/kg reported by UNEP (2011) in their assessment of Ogoni land. The occurrence of higher total hydrocarbon content (THC) in the topsoil of all the soil samples investigated agrees with the findings of Aigberua et al. (2016), Osuji et al. (2006) and Osuji and Adesiyan (2005) however THC did not generally decrease with depth in this study as earlier noted by Okop and Ekpo (2012) and Chukwujindu et al (2008). This could be attributed to the anaerobic degradation of hydrocarbon by indigenous bacteria. Aigberua et al (2016) reported higher values of THC during the wet season this is at variance with the observation of this investigation which revealed that there was no significant difference between seasons. The very high levels of THC as observed in this investigation could be detrimental to both flora and fauna that are associated with soil as well as ground and surface water, which is a result of legal and illegal oil production/refining activities.

The concentrations of Pb in the studied areas (12.75 – 30.48 mg/kg) were slightly higher than the permissible limit of RSMENR, (2002) and higher than the values reported by Ebong and John (2021) and Opaluwa et al. (2012). It is equally higher than the 0.87±0.15 – 2.69±0.17 mg/kg reported by Wokoma and Friday, (2017) in the sediments of Sombreiro River. However, the present magnitude of lead is lower than the mean value of 41.50±8.6 observed by Nwachoko et al. (2020). The higher concentration of lead in the soil samples of the studied sites could be attributed to the very high concentration of total hydrocarbon content (crude oil) in the area.

The concentration of copper in the various soils indicated that the moderately polluted site had a significantly higher concentration (4.25 – 7.15mg/kg) than the severely polluted sites which varied from (1.98 – 3.48mg/kg). This result is similar to the findings of Ebong and John (2021) that recorded a copper range of 2.34 – 6.33 mg/kg but is at variance with the reported mean value of 15.57±3.84 mg/kg by Nwachoko et al. (2020) in soils from an artisanal refining site in the Niger Delta. It is however significantly lower than the set permissible limits of 100 by RSMENR (2002).

Fosu-Mensah et al. (2017) in their study of heavy metal concentration and distribution in soils and vegetation at Korle Lagoon area in Accra, Ghana reported a cadmium concentration range of <0.001 - 103.66 mg/kg (with a mean value of 18.64 mg/kg), this is higher than that of this investigation. Equally higher than the present investigation is the report of a mean cadmium concentration of 55.58±12.2 by Ebong and John, (2021) in the Niger Delta. The value of cadmium observed in this study is however comparable to the range of 0.70 – 2.11

mg/kg recorded by Ebong and John (2021). The mean concentrations of Cd recorded at all sites were above the RSMENR (2002) permissible limit of 0.3 mg/kg.

The magnitude of Zinc (23.80 – 47.0) observed in this research conforms with that (23.46 – 67.36 mg/kg) recorded by Ebong and John, (2021) as well as the mean of 41.50±8.63 mg/kg reported by Nwachoko, et al., (2020). Comparatively, the range of values (2.70±0.007 – 10.42±0.01mg/kg) by Wokoma and Friday, (2017) and the mean of 1.33.34.±92 mg/kg and 5.37±1.918 reported by Wokoma (2014b) are lower than that of the current study.

Conclusion

The investigation has revealed that there are significant spatial (copper and zinc only) and temporal trends in the concentration of heavy metals in the study area. However, the wide disparity in the concentration of THC across stations and seasons was shown to be statistically insignificant, implying that the study sites are similar in their pollution load. While the magnitude of copper and zinc observed in this investigation are well below the Rivers State Ministry of Environment's stated limits, those of lead and cadmium are above their stated limits suggesting that the hydrocarbon from the study area contains more of these metals. The concentration of THC is multiple times the permissible limit of 30mg/kg in soil/sediments set by the Federal Ministry of Environment as well as the RSMENR, this suggests that the soils in the study area are severely polluted (even higher than that of Ogoni) and thus needs urgent clean up akin to that recommended by UNEP (2011) for Ogoni land. This is to forestall a possible breakdown and or loss of biodiversity resources, the hazard to both flora and fauna including man and the destruction of the means of livelihood of the people.

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