

Research Article

Distribution of Organic Compounds (PAHs and BTEX) and Heavy Metals (Pb, Zn, Fe, Cd) in an Oil Impacted Soils, Rivers State Nigeria.

Osu Charles. I*¹, Okoro .I .A²¹ Department of Pure and industrial Chemistry, University of Port Harcourt, PMB, 5323, Port Harcourt, Rivers State.Nigeria.² Department of Chemistry, Michael Okpara University of Agriculture, Umudike, Nigeria.**Abstract**

This paper deals with the distributions of organic Compounds; Polyaromatic hydrocarbons (PAHs) and benzene toluene ethylbenzene xylene (BTEX)) and heavy metals (Pb, Zn, Fe, Cd) concentrations in an oil impacted soils of Rivers State, Nigeria. The concentrations of organic compounds ranged from $597.340 \pm 0.02 - 896.784 \pm 0.011$ Mg/Kg, for total PAHs; $0.030 \pm 0.006 - 0.057 \pm 0.003$ Mg/Kg, for BTEX and heavy metals ranged from $2.700 \pm 0.002 - 3.960 \pm 0.006$ Mg/Kg, Pb; $0.460 \pm 0.003 - 0.730 \pm 0.007$ Mg/Kg, Cd; $3.060 \pm 0.003 - 3.92 \pm 0.004$ Mg/Kg, Zn and $92.040 \pm 0.013 -$

129.400 ± 0.031 Mg/Kg, Fe. Soil samples from Bonny had the highest total PAHs concentration ($773.213 \pm 0.004 - 896.784 \pm 0.011$ Mg/Kg). The BTEX concentrations were of smaller values due to the time of crude oil spillage. A total PAHs concentrations increase as depth of the soil increase and distributions of the heavy metals in the various depths has no regular pattern.

***Correspondence**

Okoro .I .A
Email: okoroia@yahoo.com
Phone: +234-08052536054

Keywords: Oil spillage, PAHs, BTEX, Heavy metals and soils.**Introduction**

Environmental contaminants are widely distributed in our environment. Therefore, they have an effect on the tropic food chain. Soil may contain many organic compounds and heavy metals of natural as well as anthropogenic origin. The concentrations and toxicity of organic compounds [1] and heavy metals [2] present in such complicated mixtures range very widely and depend also on possible interactions among chemicals.

An oil spill is the release of a liquid petroleum hydrocarbon into the environment due to human activity, and is a form of pollution. The oil may be a variety of materials, including crude oil, refined petroleum products or by-product, ship's bunker, oily refuse or oil mixed in waste.

Polycyclic aromatic hydrocarbons (PAHs) is a chemical compound that contain more than one fused benzene ring e.g Naphthalene, Anthracene, Phenanthrene, benz(a) pyrene, benz (a) anthracene, Fluoranthene, pyrene, benz(a) Fluoranthene etc. The point sources of anthropogenic origin are: Coal gasification, heat and power generation, coke production, catalytic cracking, carbon – black production and use, asphalt production and use, refining/distillation of crude

oil, wood treatment and preservation, fuel operations, incineration and landfills/waste disposal [3-7].

Because of the very low water solubility and high octanol – water partition coefficient (K_{ow}) values, PAHs and BTEX will tend to be sorbed to the organic matter in the soil in stead of being solubilized in the infiltrating water and through the soil ; they will be transported downwards to the groundwater reservoirs [8]. It has been observed that a slow sorption following the initial rapid and reversible sorption lead to a chemical fraction that is very resistant to desorption [9]. This phenomenon is called aging, and the existence desorption-resistant residues may increase the time as the compound stay in the soil.

Carcinogenic PAHs are found in all surface soils[10], only the following are considered as possible human or animal carcinogens; benz(a) anthracene, benzo(K) fluoranthene, Chrysene dibenz(a,h) anthracene, indeno (1,2,3)pyrene [11]. The general population may be exposed to these compounds by inhalation of the compounds in tobacco smoke and contaminated air, as well as ingestion of contaminated food. Values in the order $1000 - 3000 \mu\text{g/Kg}$ are regarded as being in the upper range. Smokers consuming one pack of

nonfiltered cigarettes per day had an estimated additional intake of 1 – 5 μg /day [10].

BTEX is an acronym for benzene, toluene, ethylbenzene, and xylene. BTEX have in recent years attracted much attention, since they constitute one of the most common and serious threats to groundwater reservoirs and indoor climate deriving from contaminated sites. This is mainly due to the potential effects of benzene, which is considered a strong carcinogen, and is highly mobile in the soil and groundwater environment [12]. Benzene cannot be degraded with nitrogen as terminal electron acceptor [13]. The release of BTEX's to the environment is influenced by their fate and transport mechanisms. The remediation of BTEX in soil is affected by volatilization, dissolution, sorption and degradation by microorganism. The bacterial flora in soil has an ability to aerobically degrade the BTEX. This degradation will reduce the concentration in soil and groundwater [14].

Organic contaminants and heavy metals correlates significantly with the corresponding levels in soil [15- 16] and may provide important information. In this study, the level of soil contamination by PAHs, BTEX and heavy metals in an oil impacted soils of Rivers State, Nigeria were investigated.

Experiemental Procedures

Materials and Methods

The study areas, Bonny, Ogoni and Egbema are of major concern because of numerous crude oil fields. The soil samples were collected from three different towns; Bonny, Ogoni and Egbema at different depths (0 – 10 cm, 10 – 20 cm and 20 – 30 cm) using soil augar in September, 2010. The samples were labeled Aa, Ab, Ac, Ba, Bb, Bc, Ca, Cb, and Cc, where A, B, and C represent the study areas; Ogoni, Bonny and Egbema respectively and a, b, c represent the various depth; 0 – 10 cm, 10 – 20 cm and 20 – 30 cm respectively.

Soil PAH and BTEX Analysis:

The organic compound extraction was performed by the US EPA 3540 C and 3630 C method. The extraction was carried out by a soxhlet apparatus in the following manner: Soil samples were extracted with 100 ML methylene chloride for 24 hours. The extract was purified on a silica gel column where the compounds were eluted with 25 ML of methylene pentane mixture 2:3 ratio and dissolved for analysis in acetonitrile. The acetonitrile extract was analysed by gas chromatography (HP 5890).

Heavy metal analysis:

The digestion method proposed by the ministry of Agriculture, Fisheries and Food [17] with slight

modifications was used. One gram of dried and homogenized soil was weighed into a beaker (100 ml) and 10 ml nitric acid was added. This was then heated until dryness. Thereafter, 10 ml HNO_3 and 3 ml HClO_4 was added and the solution was heated until fuming. The sample solution was obtained by processing the residue with hot 6 M HCl (4ml) and then filtered and diluted with water to 50 ml. The solution was used for atomic absorption spectrophotometer (UNICAM SOIAAR 32) analysis for heavy metal determination.

Results and Discussion

Distribution of the total PAHs at various soil depths are shown in Figure 1. The total concentration ranged from 597.340 ± 0.021 – 896.784 ± 0.011 mg/kg. The total PAHs concentration in soil from B (773.213 ± 0.004 – 896.784 ± 0.011 mg/kg) was higher than the corresponding data from other sampling sites. This was attributed to the influence of the level of oil activities that is been carried out including oil spillage and the time it was dumped. The lowest concentration (597.340 ± 0.021 – 697.013 ± 0.081 mg/kg) of the total PAHs was found in soil sample C.

Soil samples collected from these areas were contaminated in varying degrees with respect to the depths of the soil by the organic compound. The total concentration of PAHs increases as the depth of the soil increases from 0 – 30 cm for all soil samples. Because of the very low water solubility, PAH will tend to be sorbed to the organic matter in the soil in stead of being solubilized in the infiltrating water and through this, it will be transported downwards to the groundwater reservoirs. The sorption process is therefore counteractive to efficient biodegradation since it will decrease bioavailability due to sorption, the compounds will be located in micro porous areas of the soil making it inaccessible to the bacteria, and the biodegradation will thus be controlled by the slow desorptive and diffusive mass transfer into the biologically active areas [8]. It has been reported that a slow sorption following the initial rapid and reversible sorption lead to a chemical fraction that is very resistant to desorption [9]. This phenomenon is called aging and the existences desorption – resistant residues may increase the time as the compound stay in the soil chemically. PAHs have also been shown to be partitioned or incorporated more or less reversibly into the humic substances of the soil after partial degradation and thereby be even more immobilized in the soil [18- 19].

PAHs show very low aerobic degradability depending on the environmental conditions and the available concentration. Very low concentrations have a strong influence on the biodegradation of such hydrophobic compounds, and some studies have indicated that the process stops below a certain threshold concentration [20]. Only two and three – ringed compounds have been shown to be degraded under

anaerobic conditions with nitrate or sulfate as the terminal electron acceptor [21-22]. The low mobility and high persistence means that they can stay in the soil for decades.

The results of this study show that the soils are highly contaminated with PAHs which have harmful health effects and are considerably higher compared to the range of $0.601 \pm 0.001 - 3.678 \pm 0.036$ mg/kg reported by Osu and Asuoha [23]. PAHs concentrations in uncontaminated and contaminated soils have also been reported [24-28]

From **Figure 2**, it was found that the concentrations of BTEX ranged from $0.030 \pm 0.006 - 0.057 \pm 0.003$ mg/kg. Sample B had the highest value (0.057 ± 0.003 mg/kg) while sample C had the lowest concentration value (0.036 ± 0.006 mg/kg) and the values were very small. This is due to volatilization, dissolution, sorption, biodegradation. These factors depend on the time the soils were impacted with crude oil. These values were lower than the concentrations (<

$0.001 - 0.013 \pm 0.003$ mg/kg) reported by OSU and Asuoha, [2].

The concentrations of heavy metals found in the contaminated soils studied, ranged from $2.70 \pm 0.002 - 3.96 \pm 0.006$ mg/kg, Pb; $3.06 \pm 0.003 - 3.92 \pm 0.004$ mg/kg, Zn; $92.040 \pm 0.013 - 129.40 \pm 0.031$ mg/kg, Fe and $0.490 \pm 0.001 - 0.730 \pm 0.007$ mg/kg, Cd (**Tables 3 - 6**). Iron had the highest concentration while cadmium had the lowest concentration in all the soil samples. There was no regular vertical pattern of distribution of these heavy metals along the depths in all the samples studied.

The result show significant lower values of cadmium and lead contents than the results reported by Osu and Okereke, [29] and similar with the values reported by Nwoko and Egunjobi, [30] The concentrations level of PAHs and heavy metals obtained in this study were above permissible level for soils as recommended by USEPA, [31] and ATSDR, [32]. This raises a lot of environmental concerns. The results of analysis are presented in **figures** below.

The results of the analysis are presented in the figures below:

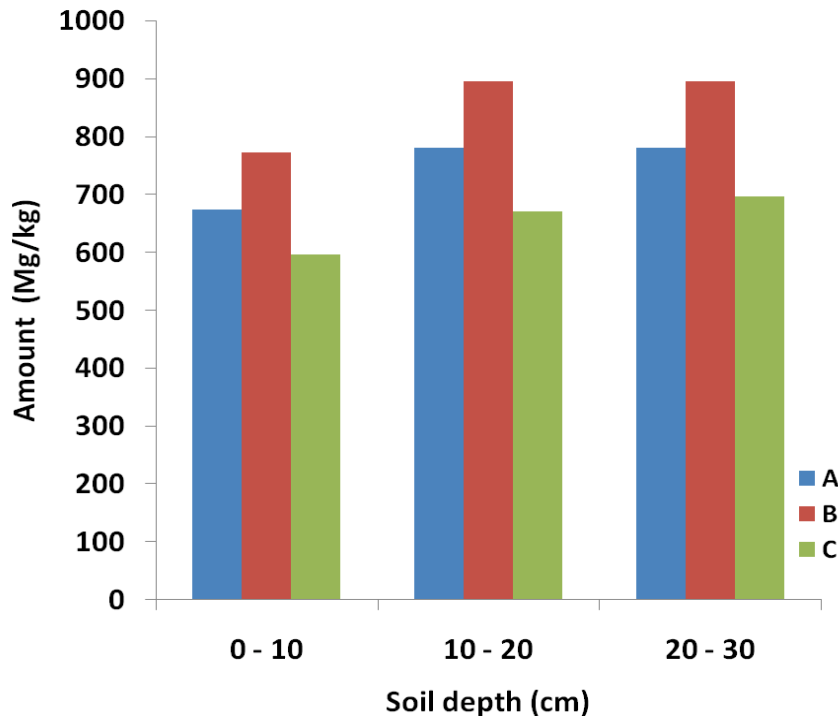


Figure 1 Total PAHs concentrations of some selected oil impacted soils in mg/kg.

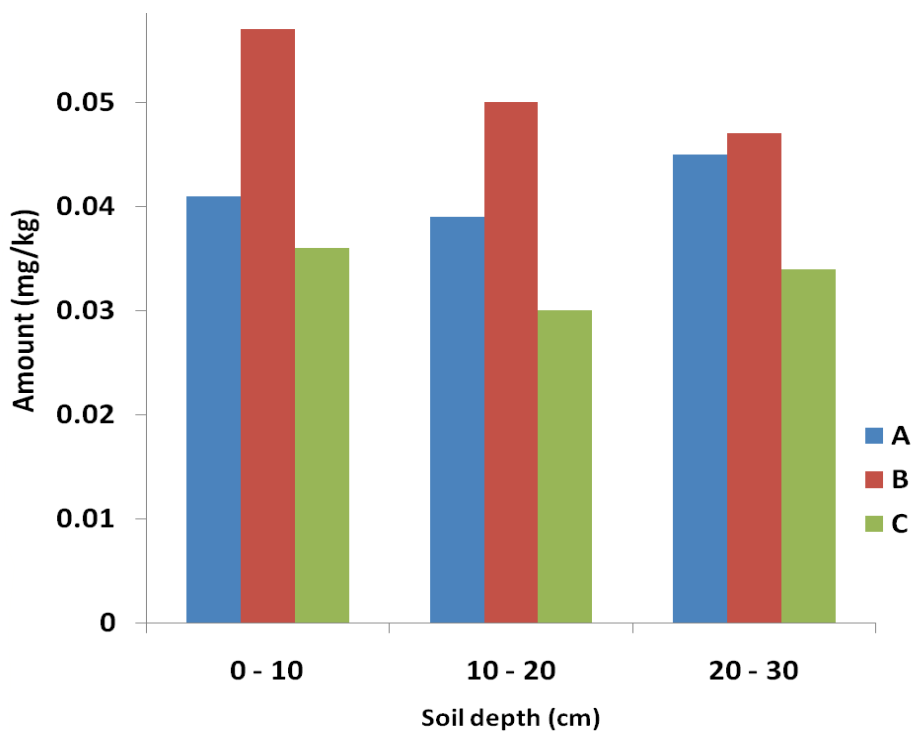


Figure 2 Total BTEX concentrations in some selected oil impacted soils in mg /kg.

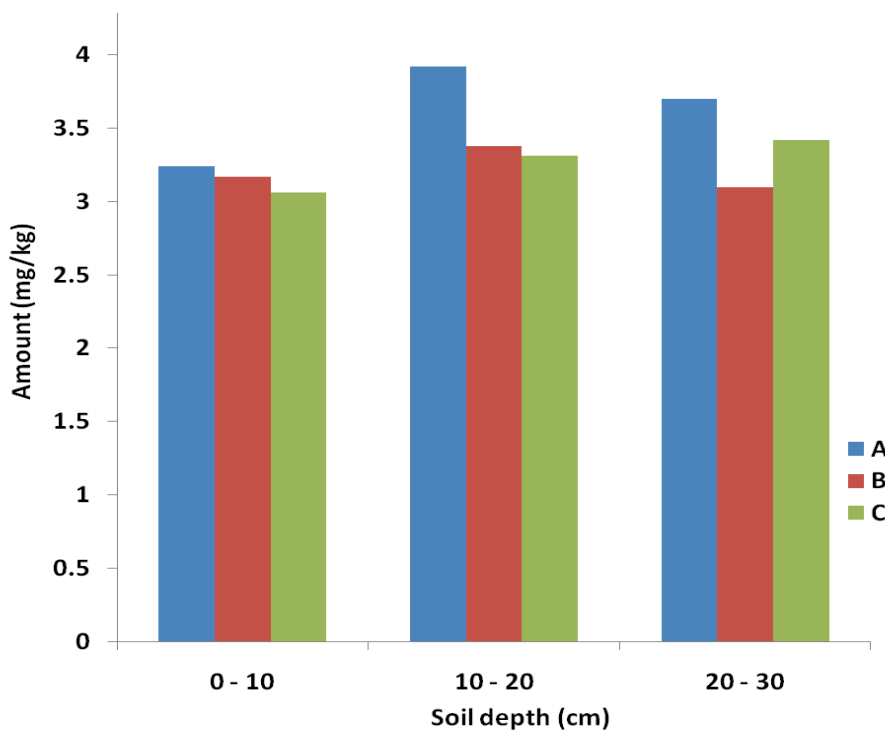


Figure 3 Pb concentrations in some selected oil impacted soils in mg/kg

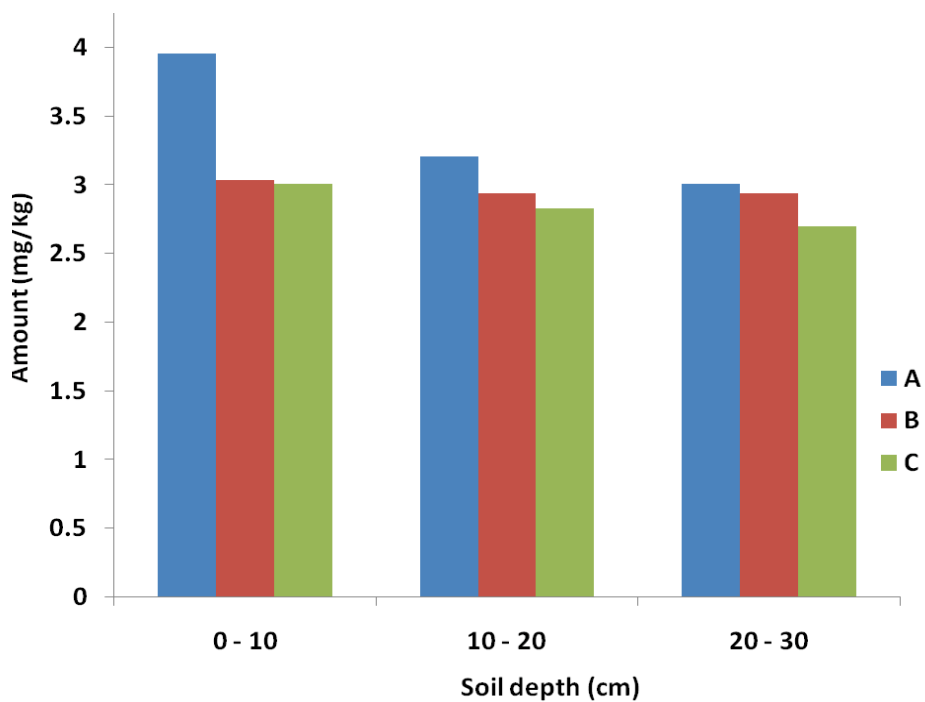


Figure 4 Zinc concentrations in some selected oil impacted soils in mg/kg.

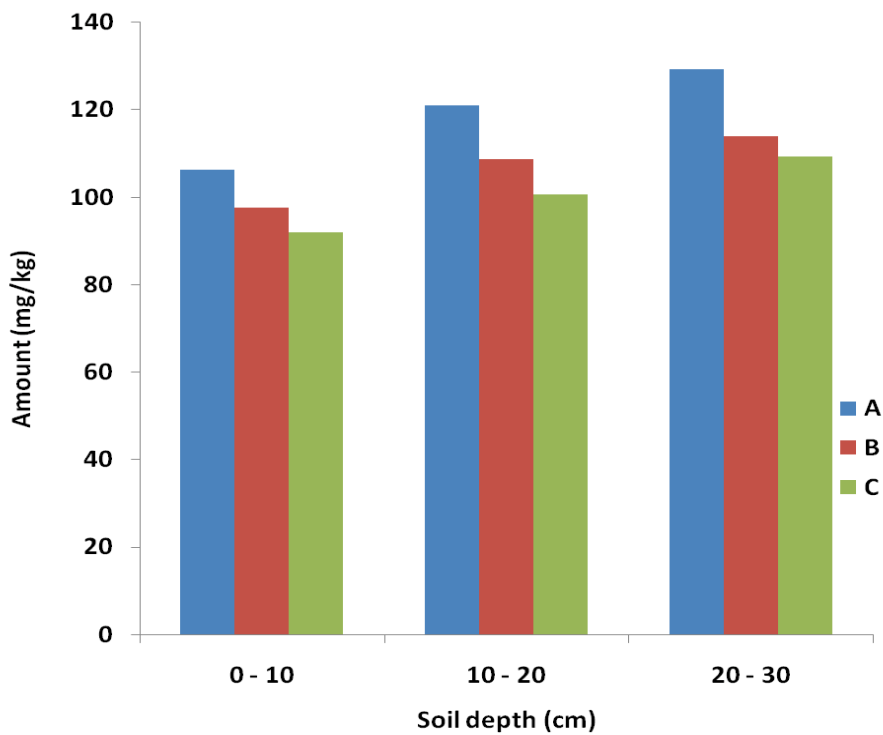


Figure 5 Fe concentrations in some selected oil impacted soils in mg/kg.

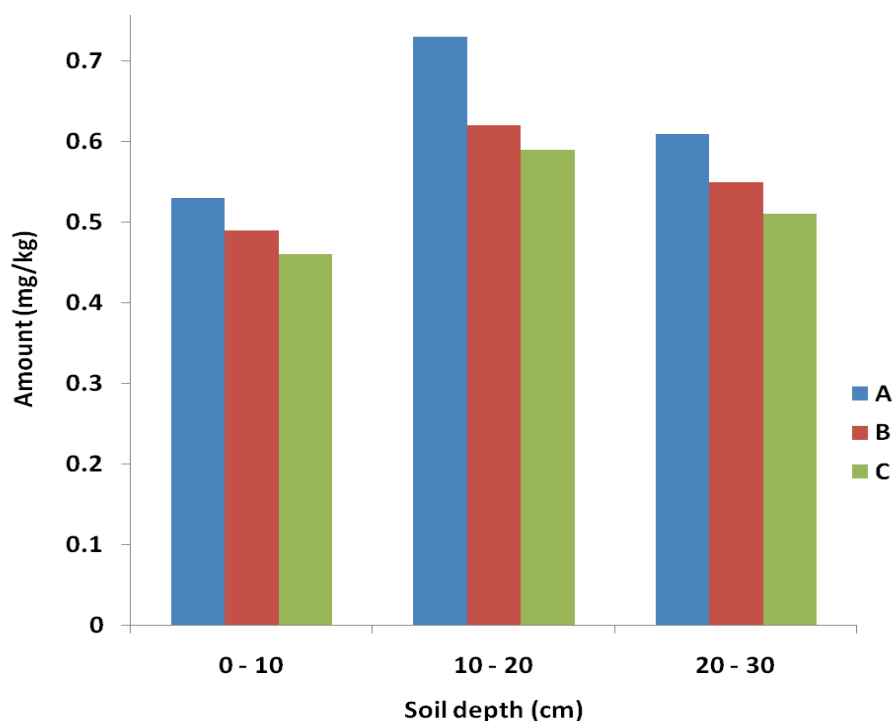


Figure 6 Cd concentrations in some selected oil impacted soils in mg/kg.

Conclusion:

The usual improper dumping of crude oil on the soil either through bunker or transportation now demands attention in order to protect the soil for agricultural purposes. High concentrations of total PAHs and heavy metals were found in all the soil samples. These were as result of crude oil spillage in the areas, which is the most common source of these contaminants. The BTEX concentrations were found to range from 0.030 ± 0.006 – 0.057 ± 0.003 mg/kg. The concentration of BTEX decreases as time increases due to evaporation, volatilization, adsorption and other factors.

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