Effect of Polychlorinated Biphenyls (PCBs) Spills from Transformers on Soils Physico-chemical Properties

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Abstract: **Polychlorinated biphenyls are toxic persistent organic compounds primarily used in electrical and industrial application such as transformers, capacitors, and insulations. When leaked into the environment, they contaminate the soils, water and aquifers. Standard analytical procedures were employed in the determination of the concentration of polychlorinated biphenyls compounds from soil samples. Soil were collected using hand auger at various depths of 0-15cm, 15-30cm and 30-60cm at two transformer stations at Trans-Amadi and Manilla Pepple in Port Harcourt. Physico-chemical characteristic and heavy metal contents were analyzed accordingly using prescribed methods. The pH of 4.24 was obtained at 0-15cm while the organic matter content had 2.26% while heavy metal contents recorded higher values at same soil depths across both stations. Salinity had a significant positive correlation coefficient (r) of 0.908 and 0.956 with pH and electrical conductivity while Carbon/Nitrogen ratio had a significant similar correlation coefficient (r) of 0.852 with organic carbon. Available phosphorous had a significant correlation coefficient (r) of 0.833 with Carbon/Nitrogen ratio. The calibration factors of target polychlorinated biphenyls were estimated to test the linearity of the Gas Chromatography (GC) with Electron Capture Detector (GC-ECD) within a concentration of 0.025ng/µL to 0.400ng/µL. Relative standard deviation (RSD) of the calibration factors ranged from 4.6% to 12.3%, indicating a good response. . Results of this study revealed that Polychlorinated Biphenyls concentrations varied across various depths; Trans-Amadi was in the range of 12.95mg/kg – 52.05mg/kg while Manilla Pepple ranged from 4.70mg/kg - 12.95mg/kg, the mean of Σ28 polychlorinated biphenyls in soil samples from both transformer stations ranged from 4.7– 52.05mg/kg. However, these values were above standard limits for low persistent organic pollutants (POP) content in soils. The study reveals that continuous exposure of PCBs to the environment can affect the soils negatively by causing an imbalance in the soil structure and then pollute water resources through seepage into the ground water system because of the soil geologic formation. Regular exposure of the populace around the electrical transformer stations are predisposed to severe health risks through inhalation of particulate and gaseous depositions from the facility.**

Keywords: **Polychlorinated Biphenyls, Organic Pollutants, Transformer stations, Soils, Health risks.**

I. INTRODUCTION

Polychlorinated biphenyls (PCBs) are organic chlorine compound that are odourless, tasteless, and colourless or light colour synthetic chemical compounds. Polychlorinated Biphenyls are compounds consisting of 209 individual congeners differentiated by the position and number of chlorines that makes up the molecules [1]. Polychlorinated Biphenyls originate in the environment solely from anthropogenic sources including leakages from electrical transformers, waste disposals and spillage. They occur in soils and sediments as contaminants particularly from particulate and gaseous depositions from industrial applications or primarily as a result of spills, leaking toxic landfill or contamination from products containing the chemicals [1]. They may also be released into the environment by the burning of some wastes in municipal and industrial incinerators. Building materials such as caulking may also constitute a source of Polychlorinated Biphenyls contamination in the buildings and in the surrounding soils [2]. When these polychlorinated biphenyls in electrical transformers leaks, they enter the soil and can also enter the river/stream environment from a variety of sources including (i) direct deposition from the atmosphere, (ii) runoff from land, and (iii) directly from industrial and wastewater treatment plant discharges [3,4]. They bind very strongly to soil particles and resistant to physicochemical degradation. Generally the absorption of PCBs onto soil particles depends on factors such as the degree of chlorination of the individual congeners, the soil type, the organic matter content, the soil pH and the soil moisture [3]. The movement of PCBs in soil is directly proportional to the solubility of PCBs leaching solvent (Demnerova *et al.,* 2005 [5]; [6] [5]). Soils are tremendously heterogeneous environmental matrix with varying spatial and temporal gradients of organic carbon, pH, and particle size distribution [7]). Soil is an essential component of the terrestrial ecosystem and has an important ecological function in biogeochemical cycling of resources needed for plant growth. An individual plant depends on soil for anchorage, water, oxygen, and nutrients. Most soil matrixes consist of solid particles of mineral matter; with about 1-10% organic matter. Therefore, chemical pollution of soils, along with degradation processes such as erosion, combined with increased urbanization; pose a threat to the sustainability of soil resources [8]. Contaminated sites pose environmental and human health hazards [9]). The aim of this study therefore is to determine the effect of Polychlorinated Biphenyls into soils from transformers facilities in Port Harcourt.

Description of Area of study

The area of the study is situated around Trans-Amadi Industrial area and Manilla Pepple, Port Harcourt. The first transformer maintenance station in Trans-Amadi lies at latitude 4°48’48.05” and longitude 7°2’44.74” and the second lies at latitude 4°48’2.154” and longitude 6°59’53.178” at Manila Pepple Road, D-Line Port Harcourt.

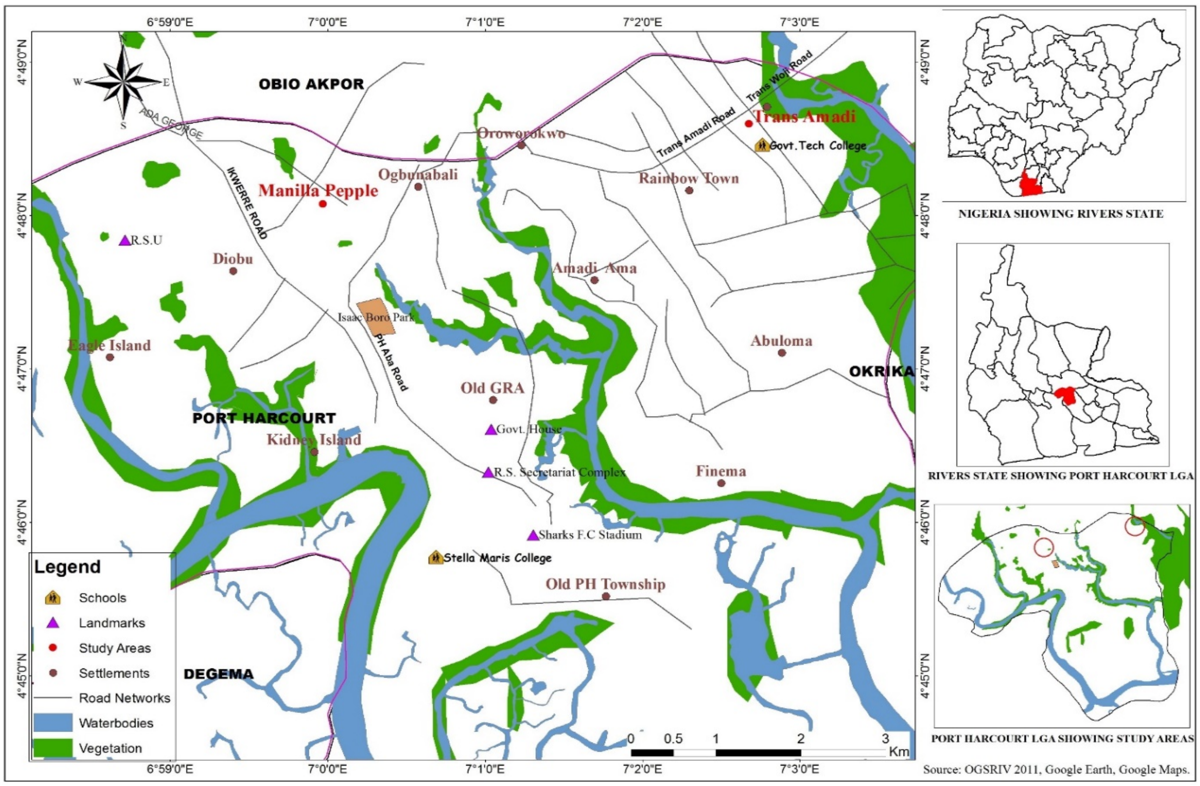

Fig 1: Map of Port Harcourt, showing the study Area

There is a beehive of business activities particularly shops, Hotels and Residential buildings around the Electrical transformer stations at Manilla Pepple in D-Line Diobu while in Trans Amadi the transformer station is situated around the Industrial Layouts with several multinational companies located in the area. Leakages from electrical transformers, indiscriminate waste disposals and spillages can result to contamination of soils, particulate and gaseous depositions from the industrial applications on the environment can cause severe health risks to residents doing business around the stations.

II. METHODOLOGY

Collection and Preparation of samples

Soil samples were collected from soils around transformer stations situated in Trans-Amadi industrial area and Manilla Pepple Road in D-Line Diobu, Port Harcourt where maintenance of electrical transformer facilities takes place. Six (6) soil samples were collected aseptically using a hand auger at sample depths of 0 -15cm, 15 - 30cm and 30 - 60cm from soils around transformer stations in Trans-Amadi and Manilla Pepple in D-Line, Diobu, Port Harcourt city. Samples were preserved in an ice packed cooler after collection before being transported to the laboratory for extraction and further analysis.

Preparation of Reagents for Polychlorinated Biphenyl (PCBs) Extraction

A total of 10µg/mL PCB standard mixture containing 28 PCB congeners PCB-8, 18, 28, 44, 52, 66, 77, 81, 101, 105, 114, 118, 123, 126, 138, 153, 156, 157, 167, 169, 170, 180, 187, 189, 195, 206 and 209, internal standard (PCB 209, 200µg/mL), were obtained from Sigma Aldrich, UK. The various calibration standard solutions were prepared according to manufacturer’s standards by adding the appropriate amounts of primary standards to hexane (97% purity, HPLC grade obtained from Sigma Aldrich). A constant concentration of 1µg/ml internal standard was added to the calibration standards and to the samples, prior to analysis. Sodium sulphate anhydrous (Merck, Germany) was first activated before use. Florisil cartridges (Supelco

6ml, 1gbed), purchased from Sigma Aldrich were used for the extract cleanup.

Sample Extraction and Clean-Up

According to the US Environmental Protection Agency (EPA) Standard method [10], safe operating procedure (SOP) for Polychlorinated Biphenyls (PCBs) extraction was adopted. Soil samples were mixed with equal weight of anhydrous sodium sulphate to form free flow mixtures which were then sonicated (subjected to ultrasonic vibration so as to fragment the cells, macromolecules, and membranes) for 15 minutes in three successive extractions, combined extracts were concentrated to about 5mL using a thermo-stated water bath, regulated at 40°C. Clean-up of extracts was achieved by transferring the 5mL of concentrated extract on a florisil cartridge, which had been conditioned with 5mL hexane. Finally, the elution of adsorbed analytes was achieved by passing hexane through the florisil cartridge. PCB 209, the internal injection standard was added to each of the cleaned extracts before the Gas Chromatography (GC) analyses. Cleaned extracts were stored at −4°C in a refrigerator prior to analysis.

Instrumental Analysis for Polychlorinated Biphenyls

Polychlorinated Biphenyls identification and quantification were performed on an Agilent 6890 series gas chromatograph equipped with a NiECD (Nickel Electron Chromatograph Detector) and a split/splitless injector. Chromatographic separation of the PCB congeners was carried out on a 30m Agilent Technologies (0.25mm I.D.; film thickness 0.25μm) fused silica capillary column (5% diphenylpolysiloxane, 95% dimethylpolysiloxane). The initial oven temperature was set at 60°C, held for 1min, then increased to 180°C at a rate of 30°C/min and then increased to 200°C at a rate of 2.5°C/min, this was further increased to 270°C at a rate of 7°C/min. The temperatures of the injector and detector were 280°C and 300°C, respectively. Splitless mode injection was employed. The following elution order of congeners was established PCB: 18, 28, 44, 52, 66, 77, 81, 101, 105, 114, 118, 123, 126, 128, 138, 153, 156, 157, 169, 170, 180, 187, 189, 195, 206 and 209, (internal injection standard).

Quality Control

The calibration factor which measures the detector response to varying concentrations of target analytes was estimated. The Relative Standard Deviation (RSD) of the calibration factors for target analytes from the five-point calibration standards were 4.6%, 9.2%, 3.8%, 5.9%, 5,4%,4.4%, 6.2%, 7.8%, 6.6%, 12.3% for PCB# 28 PCB congeners 8, 18, 28, 44, 52, 66, 77, 81, 101, 105, 114, 118, 123, 126, 138, 153, 156, 157, 167, 169, 170, 180, 187, 189, 195, 206 and 209, respectively, indicating a good instrumental method. This was done to ensure that instrument was operating up to manufacturer's specification. The limits of detections were estimated for target analytes from the calibration factors at a signal to noise ratio of 3:1. For samples in which target PCBs were absent, values < LOD (Limit of Detection) were reported. Blank determinations were carried out on every batch of sample and target analytes were absent. Internal injection standard (PCB 209) was added to the calibration standard as well as samples to correct for drift in retention times of the target analytes.

Soil Physico-Chemical Analysis

Physico-chemical analyses of soil samples from Transformer Facilities in Trans-Amadi and Manilla Pepple, D-Line, Port Harcourt city were carried out to determine the various parameters and its influence on the soil flora and fauna. The soil pH was determined by the electrometric method whereby the potential difference developed within a circuit consisting of a glass electrode, which was sensitive to hydrogen ions and a reference electrode immersed in the soil suspension was measured using a Pye Unican Model 290MK 2-pH meter. The inductivity bridge used for the measurement of electrical conductivity was Lovibond conductivity model, type CM-21. Conductivity was expressed as μS/cm [11]. Total Organic Carbon (TOC) was determined by wet combustion method of [11]. Total Nitrogen was determined by semi-micro Kjeldahl digestion method modified [11]. Ascorbic acid Molybdate blue method was used. This method consists of two reagents; consisting of Reagent A where 12g of Ammonium Molybdate mixed in 250ml of distilled water and 0.2908g of Antimony Potassium Tartrate mixed in 1000ml of H_2SO_4 and made up to 2 litres, Reagent B 1.056g of the ascorbic mixed in 200ml of reagent A. Five millilitres (5ml) of the soil extract was mixed with 8ml of reagent B and 40ml of distilled water, allowed to stand for 2 mins then absorbance was read at 882nm in the spectrophotometer. Heavy metals such as Iron, copper, chromium, lead and zinc were measured using Atomic Absorption Spectrophotometer (AAS).

III. RESULTS

The results of the physicochemical characteristics and heavy metals are presented in Tables 1 and Table 2 from the two different stations at Trans Amadi and Manilla Pepple stations. Polychlorinated Biphenyls concentrations varied across various depths in Trans-Amadi with a range of 12.95mg/kg – 52.05mg/kg while in Manilla Pepple it ranged from 4.70mg/kg - 12.95mg/kg. Table 3 showed that salinity had a significant strong positive correlation coefficient (r) of 0.908 and 0.956 with pH and electrical conductivity. Carbon/Nitrogen ratio had a significant strong positive correlation coefficient (r) of 0.852 with organic carbon. Available phosphorous had a significant strong positive correlation coefficient (r) of 0.833 with Carbon/Nitrogen Ratio. Chromium had a significant strong positive correlation coefficient (r) of 0.872 and 0.812 with electrical conductivity and copper. Zinc had a significant strong positive correlation coefficient (r) of 0.936 with lead.

Table 1: Physico-chemical Characteristics of Soils from Transformer Maintenance facilities in Trans-Amadi, Port Harcourt

	Physical characteristics		Chemical Characteristics							Heavy Metals				
Soil Depths	Temperature (°C)	Electrical Conductivity (µS/cm)	pH	Salinity (‰)	Organic Carbon (%)	Total Nitrogen (%)	Carbon/Nitrogen (C/N) Ratio	Available Phosphorous (mg/kg)	Nitrate (mg/kg)	Iron (Fe) (mg/kg)	Copper (Cu) (mg/kg)	Chromium (Cr) (mg/kg)	Lead (Pb) (mg/kg)	Zinc (Zn) (mg/kg)
0-15cm	29.6	141.3	6.66	0.06	2.3	0.02	115	0.84	0.09	12917.2	29.1	6.2	77.3	64
15-30cm	29.6	92.1	6.22	0.04	1.6	0.02	80	0.88	0.08	12523.2	7.5	0.003	47.6	53.2
45-60cm	29.6	82.4	5.45	0.04	1.95	0.02	97.5	0.86	0.08	14921.2	15.4	0.003	9	28
UNEP Standards										50000	50	200	200	250

UNEP – United Nations Environmental Programme, 2013

Table 2: Physico-chemical Characteristics of Soil from Transformer Maintenance facilities in Manilla Pepple, Port Harcourt

	Physical characteristics		Chemical Characteristics							Heavy Metals				
Soil Depths	Temperature (°C)	Electrical Conductivity (EC) (µS/cm)	pH	Salinity (‰)	Organic Carbon (‰)	Total Nitrogen (%)	Carbon/ Nitrogen (C/N) Ratio	Available Phosphorous (mg/kg)	Nitrate (mg/kg)	Iron (Fe) (mg/kg)	Copper (Cu) (mg/kg)	Chromium (Cr) (mg/kg)	Lead (Pb) (mg/kg)	Zinc (Zn) (mg/kg)
0-15cm	29.5	54.3	4.24	0.02	2.26	0.03	75.3	0.7	0.14	11579.2	16.5	0.003	25.6	36.7
15-30cm	29.2	57.6	5.59	0.03	1.56	0.02	78	0.52	0.11	14421.2	14.2	0.003	7.1	40.5
45-60cm	29.6	98.6	6.58	0.05	0.86	0.03	28.7	0.35	0.12	16549.2	8	1.1	0.01	22.4
UNEP Standards										50000	50	200	200	250

Table 3: Correlation Results Showing the Relationship between the Physicochemical Parameters of Soils from Manilla Pepple and Trans-Amadi, Port Harcourt

		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	pH														
2	Temperature (°C)	0.323													
3	EC (µS/cm)	0.808	0.604												
4	Salinity (‰)	.908*	0.53	.956**											
5	Organic Carbon (%)	-0.453	0.064	0.079	-0.163										
6	Total Nitrogen (%)	-0.324	0.161	-0.274	-0.274	-0.28									
7	Carbon/Nitrogen Ratio	-0.064	0.035	0.313	0.147	.852*	-0.725								
8	Avail. P (mg/kg)	-0.098	0.393	0.264	0.072	0.737	-0.599	.833*							
9	Nitrate (mg/kg)	-0.534	-0.326	-0.503	-0.525	-0.09	.853*	-0.547	-0.645						
10	Fe (mg/kg)	0.459	-0.012	0.092	0.374	-0.769	0.105	-0.544	-0.637	-0.073					
11	Cu (mg/kg)	0.034	0.036	0.496	0.343	0.762	-0.283	0.754	0.389	-0.094	-0.358				
12	Cr (mg/kg)	0.556	0.306	.872*	0.769	0.358	-0.208	0.467	0.204	-0.214	-0.115	.812*			
13	Pb (mg/kg)	0.323	0.357	0.685	0.459	0.601	-0.391	0.671	0.655	-0.38	-0.646	0.645	0.752		
14	Zn (mg/kg)	0.308	0.043	0.53	0.332	0.541	-0.56	0.689	0.592	-0.403	-0.652	0.577	0.64	.936**	

Note: N=6, *p<.05 **p<.01

IV. DISCUSSION

In Port Harcourt, there exist numerous transformer refurbishment facilities that make use of transformer oils which contain compounds known as polychlorinated biphenyls (PCBs) that are typical representative of chlorinated organic pollutants, identified as major environmental pollutants which absorb fast to the soil, more especially to dry soils because of its hydrophobic nature and may lead to contamination of vegetables and food chains [12]. Polychlorinated Biphenyls are used in transformer because they are very resistant to decomposition and have an excellent insulating property as well as high heat capacity. Soil temperature is the function of heat flux in the soil as well as heat exchanges between the soil and atmosphere [13]).Soil Temperature in this study varied slightly from 29.2 at Manilla to 29.6^{0}C at the Trans Amadi station. Soil temperature range of 10°C -28°C influences soil respiration by increasing the activity of extracellular enzymes that degrade polymeric organic matter in soils [14]). This indicates that the soil temperature of 29.6°C at Trans-Amadi stations and 29.2 ^{0}C Manilla Pepple was above the range of normal soil temperature values of 10^o-28^o prescribed by [14]).. This means that the presence of Polychlorinated Biphenyls (PCBs) may have altered the soil status thus making it not suitable to influence soil respiration which is important to increase the activity of extracellular enzymes that degrade polymeric organic matter in soils which may further influence microbial activities in soils because of their presence as pollutants [14].

Electrical conductivity (EC) is a measure of the amount of salts in soil (salinity of soil). It is an excellent indicator of nutrient availability and loss, soil texture, and available water capacity. It affects crop yields, the suitability of the soil for certain crops, the amount of water and nutrients available for plant use, and the activity of soil micro-organisms, which influences key soil processes such as the emission of greenhouse gases, including nitrogen oxides, methane, and carbon dioxide [15]. The electrical conductivity of soils at Trans-Amadi had 141.3 µS/cm and 98.6 µS/cm in Manilla Pepple which was lower than 1000 µS/cm as permissible limit indicating that the soils are non-saline and will not affect most crops and soil microbial processes but was higher in Trans Amadi station. Salinity can impede crop growth. Soils with EC of 1000 µS/cm are considered to be saline and this affects important microbial processes, such as nitrogen cycling, production of nitrous gases and other nitrogen oxide gases, respiration, and decomposition of organic matter including populations of parasitic nematodes and loss of nitrogen can be higher in these soils [15]. The pH of soils from Trans-Amadi station was in the range of 5.45 - 6.66 indicating that the soils are slightly acidic while the Manilla Pepple station had pH range of 4.24 - 6.58 at a depth of 0-15cm having a pH of 4.24 which is more strongly acidic. Phosphorus is never readily soluble in the soil but is most available in soil with a pH range of 6.5 [16]. Extremely and strongly acid soils of pH 4.0-5.0 can have high concentrations of soluble aluminium, iron and manganese which may be toxic to the growth of some plants [17]. The Organic Carbon content of 1.6% to 2.3% was recorded for Trans-Amadi station and 0.86% to 2.26% for Manilla Pepple station. However, as reflected by their low water solubility and high soil organic carbon partition coefficients (Koc), Polychlorinated Biphenyls bind strongly to soil and sediments and may persist in this phase for many years. In general, the rates of Polychlorinated Biphenyls dechlorination decrease as the degree of chlorination and the organic carbon content of the soil increases [17].The Available Phosphorous values ranged from 0.84 mg/kg to 0.88 mg/kg in transformer facilities/ stations at Trans-Amadi and 0.35 mg/kg to 0.7 mg/kg at Manilla Pepple. This showed that available phosphorous levels in soils from transformer facilities/ stations in Trans-Amadi and Manilla Pepple had low fertility in terms of available phosphorous because they were less than 20mg/kg. Soils possessing available phosphorous value of less than 20mg/kg is termed as low fertility soil, 20-40mg/kg is termed as medium fertility soil, while 40 – 100mg/kg is termed as high fertility soil and above 100mg/kg as excessive fertile soil [18].

For heavy metals, Iron content ranged from 12523.2mg/kg to 14921.2mg/kg in Trans-Amadi station while in Manilla Pepple 11579.2mg/kg to 16549.2mg/kg was recorded and this was below the acceptable value of 50,000 mg/kg in soils as prescribed by UNEP (2013) [19].

Copper is an essential micronutrient required in the growth of both plants and animals. In humans, it helps in the production of blood haemoglobin. Copper concentrations ranged from 7.5mg/kg to 29.1mg/kg in Trans-Amadi soils while in Manilla Pepple, the values ranged from 8mg/kg to 16.5mg/kg. This showed that Cu values of soils in Trans-Amadi and Manilla Pepple were below the permissible limit of 50 mg/kg [20]. This could be attributed to continuous activities of transformer refurbishment. Chromium had the highest concentration at soil depths of 0 – 15cm and 45 – 60cm Concentrations of chromium ranged from 0.003mg/kg to 6.2mg/kg in Trans-Amadi soils while in Manilla Pepple, values recorded ranged from 0.003mg/kg to 1.1mg/kg. This was below the permissible limits of 200mg/kg for soils. Concentrations of lead ranged from 9mg/kg to 77.3g/kg in Trans-Amadi soils while in Manilla Pepple, the values ranged from 0.01mg/kg to 25.6mg/kg. The mean values of lead recorded at all stations were below the acceptable value of 200 mg/kg in edible plants [21].

Zinc concentrations was highest at 0 – 15cm and 0 – 15cmin Trans Amadi and Manilla Pepple stations respectively with depths of 30 – 60cm for both stations had the lowest concentrations of zinc in soils. Concentrations of zinc ranged from 28mg/kg to 64mg/kg in Trans-Amadi soils while in Manilla Pepple, soils ranged from 22.4mg/kg to 40.5mg/kg. However, all the soil samples recorded mean values of zinc that were below the [21] permissible limit of 250 mg/kg for soils. Zinc is required nutrient and becomes toxic to plants only at high concentrations.

However, the concentrations of Polychlorinated Biphenyls from soils from transformer refurbishment facilities in Trans-Amadi ranged from 12.95mg/kg – 52.05mg/kg were above the provisional definition of low persistent organic pollutant (POP) content for PCBs of 50 mg kg-1 as defined in the guidelines on the management of POP waste of the Basel Convention (1992), this could be due to heavy usage of PCB oils in the transformers facility which may had leached into the soil over the years as a result of regular maintenance and possibly due to the persistent nature of PCBs while 4.70mg/kg - 12.95mg/kg recorded for Manilla Pepple were below the prescribed standards in soils [22]. The range of PCBs form soils from stations at Trans-Amadi and Manilla Pepple also exceeded those reported in urban soils in Nigeria [21] with a range of 8.71–26.28ng/g and other nations [22]' Polychlorinated Biphenyls can be transported to long distances and are among the most widespread environmental pollutants, having been detected in almost every corner of the globe [24]. Given the effective adsorption of PCB to soils and sediments, these contaminants can also be transported and bound to eroded soils and sediments.

These electric utilities use dielectic fluids (oils), which probably still contain PCB. Oil leakage to soil from electric utilities during regular operation has been identified as a PCB source to the environment, so it is likely that emissions to soil are also occurring in the study areas. PCBs are hydrophobic, so PCBs leaked to the soil are transported together with particulate material to the lower levels of the soil, where they accumulate together with sediments. This can explain the high PCB levels measured at accumulation site TP2 (15 – 30cm). The PCBs found in soil samples collected in the large electric power-transforming station also suggest that the transformer facilities are a point source for PCB pollution in the environment [23].

V. CONCLUSION

However, polychlorinated biphenyls are to known be recalcitrant in decomposition in soils and can percolate in soil layers and may attach to sediments which eventually seeps into the aquifers or most of the spills on soil surfaces because of its hydrophobic nature may enter water resources through runoffs or erosion to cause pollution. Pollution in this context can result to health risks associated with consumption of vegetables through the food chain to cause carcinogens and other related disease associated with inhalation of particulate and gaseous depositions within the environment.

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