DETERMINATION OF POLYCHLORINATED BIPHENYL RESIDUES IN SOIL OF SELECTED TRANSFORMER MAINTENANCE WORKSHOPS IN KADUNA AND ZARIA METROPOLIS, NIGERIA

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JANUARY, 2016

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A DISSERTATION SUBMITTED TO THE POSTGRADUATE SCHOOL

AHMADU BELLO UNIVERSITY, ZARIA.

IN PARTIAL FULFILLMENT FOR THE AWARD OF

MASTER OF SCIENCE DEGREE IN ANALYTICAL CHEMISTRY

DEPARTMENT OF CHEMISTRY

FACULTY OF SCIENCE

AHMADU BELLO UNIVERSITY,

ZARIA, NIGERIA

JANUARY, 2016

Declaration

I, Dauda Yakubu declare that the work in this dissertation entitled **''Determination of polychlorinated biphenyl residues in soil of selected transformer maintenance workshops in Kaduna and Zaria metropolis, Kaduna state, Nigeria"** has been carried out by me in the Department of Chemistry, Ahmadu Bello University, Zaria. The information derived from literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma in any other institution.

Dauda Yakubu	_____	_____
Name of Student	Signature	Date

Certification

This dissertation entitled "DETERMINATION OF POLYCHLORINATED BIPHENYL RESIDUES IN SOIL OF SELECTED TRANSFORMER MAINTENANCE WORKSHOPS IN KADUNA AND ZARIA METROPOLIS, KADUNA STATE, NIGERIA" by Dauda Yakubu meets the regulations governing the award of the degree of Master of Science in Analytical Chemistry of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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Dean, School of Postgraduate Studies _____ Signature _____ Date

Dedication

This work is dedicated to Almighty GOD from who strength was drawn to see to the successful completion of this course as well as my dear wife, Mrs. Elizabeth Dauda Yakubu and my children for their love and support.

Acknowledgement

My sincere gratitude goes to Almighty GOD for his protection, guidance and grace throughout the programme.

I wish to express my sincere appreciation to my Supervisors, Prof. V.O Ajibola and Prof. E.B Agbaji whose constructive criticisms, meticulous appraisal, valuable contributions and encouragement made it possible for the successful completion of this project. Your patience, cooperation and guidance are highly commendable.

My gratitude goes to the Coordinator of Postgraduate Studies in the Department, Dr. S.O Idris and other members of staff in the Department who worked hard at facilitating the programme.

My sincere appreciation goes to my classmates and colleagues at work. They have been good and very supportive.

Finally, my heart-felt gratitude goes to my parents, wife and children for their prayers, support and understanding.

ABSTRACT

As effective as polychlorinated biphenyls (PCBs) may be in achieving thermal stability as coolant in transformer oils; spills, decommissioning and poor handling of these transformer oils often results to contamination of PCBs on the environment. The attendant adverse effect of PCBs on the environment and humans has been of serious concerns. The residue levels of PCBs in soil of selected transformer maintenance workshops in Kaduna and Zaria metropolis, Kaduna State, Nigeria was determined. Two soil samples per site, one top-soil (0 – 5 cm) and one sub-soil (20- 30 cm), totalling fourteen (14) soil samples were collected in four (4) and three (3) different locations in Kaduna and Zaria metropolis respectively. Some soil physico-chemical properties such as particle size (sand, silt and clay) and total organic carbon (TOC) in the soil that may influence the dynamics of the pollutants was determined. In addition, the soil samples were analysed for residues of PCBs using the technique of gas chromatography-mass spectrometry (GC-MS). PCB concentrations were correlated (PEARSON) with the particle size and total organic carbon (TOC). The coefficient of variation of percent TOC was 45. The concentration of the PCBs measured showed significant correlation ($P< 0.05$) with TOC. PCB congeners CB 28, CB 52, CB 101, CB 153, CB 138 and CB 180 were detected at varied concentrations, occurring most frequently with highest sum PCB congeners of 8209.50 µg/kg at Arewa Metal Containers (AMECO) Kaduna, lowest sum PCB congeners of 0.81 µg/kg at Ahmadu Bello University (ABU) Main Campus, Samaru- Zaria, and absent at farmland near National Research Institute for Chemical Technology (NARICT), Zaria that serve as control. CB 153, CB 138 and CB 180 (hex- and hepta- chlorinated biphenyls) were dominant species in all the soil samples, accounting for more than 82 % and 68 % of total PCBs in the soil samples from Kaduna and Zaria respectively. The sum PCB congeners' residue levels down the soils in all the sites decreases due to soil binding effect and other weathering process. The percent hexa- and hepta- chlorinated biphenyls increased from top-soil to sub- soil except in AMECO. This finding reveals that higher molecular weight PCBs percolates down the soil which might offer an insight for ground water contamination. The measured Relative Retention Factors of all the samples were within the 6-11 percent (%) standard deviation retention time of the referenced standard PCB congeners, and was found satisfactory. The percent (%) recoveries of PCBs in topsoil and subsoil of AMECO, topsoil and subsoil of Mando are in the ranges of 83-145 % and 53-86 %, 52-92 % and 71-143 % respectively. The PCB residue levels in all the samples complied with the United Nations Environmental Programme (UNEP) set maximum limit of 50 ppm (50,000 µg/kg).

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Abbreviations and Symbols

∑	-	Sum
∑PCBs	-	Sum (total) of Polychlorinated biphenyls
µg/kg	-	Microgram per Kilogram
µL	-	Microlitre
%S.D RT	-	Percent Standard Deviation Retention Time
AMECO	-	Arewa Metal Company Limited, Kaduna.
AOAC	-	Association of Official Analytical Chemists
ATSDR	-	Agency for Toxic Substances and Diseases Registry
CB	-	Ballshmiter and Zell short-hand naming of PCB congeners
CEMP	-	Coordinated Environmental Monitoring Programme
DDT	-	Dichlorodiphenyltrichloroethane
DL – PCBs	-	Dioxin-Like Polychlorinated biphenyl(s)
DPR	-	Department of Petroleum Resources
EI	-	Electron Ionisation
ERA	-	Environmental Risk Assessment
FAO	-	Food and Agriculture Organisation
GC-ECD	-	Gas Chromatography – Electron-Capture Detector
GC-MS	-	Gas Chromatography – Mass Spectrometry
IARC	-	International Agency for Research on Cancer
ICES	-	International Council for the Exploration of the Sea
m/z	-	Mass Charge ratio
mg/kg	-	Miligram per Kilogram
MRL	-	Maximum Residual Limits
NIPs	-	National Implementation Plans

NIS	-	Nigeria Industrial Standard
OCP	-	Organochlorine Pesticides
OM	-	Organic Matter
PAH	-	Polycyclic Aromatic Hydrocarbons
PBT	-	Persistence bioaccumulation and Toxicity
PCBs	-	Polychlorinated biphenyls or Polychlorinated biphenyl Congeners
PCCD/Fs	-	Polychlorinated dibenzo-p-dioxins and dibenzo Furans
PHCN	-	Power Holding Company of Nigeria
POP	-	Persistence Organic Pollutants
PPM	-	Parts Per Million
PRC	-	Performance Reference Compounds
RF	-	Retention Factor
RRFs	-	Relative Retention Factors
SAEFL	-	Swiss Agency for the Environment, Forests and Landscape
SIM	-	Selected ion monitoring
SPMDs	-	Semi-Permeable Membrane Devices
SRM	-	Standard Reference Material
TCDD	-	2,3,7,8 – Tetrachlorodibenzo-p-dioxin
TEQ	-	Toxic Equivalent
TOC	-	Total Organic Carbon
TPCBs	-	Total Polychlorinated biphenyl(s)
UNEP	-	United Nations Environmental Programme
US EPA	-	United States Environmental Protection Agency
USDA	-	United States Department of Agriculture

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Polychlorinated biphenyls (PCBs) are a subset of synthetic organic chemicals known as chlorinated hydrocarbon that is to a large degree, chemically inert. PCBs have been produced in high volume by the chemical industry and used as additives to oils in electrical equipment, hydraulic machinery, and other applications where chemical stability has been required. These organic compounds can be transported for long distances, and have been detected in the furthest corners of the globe, including places far from where they are manufactured or used. Since PCBs exhibit a high degree of chemical and biological stability and also lipid solubility, they tend to accumulate in the food chains and have been detected in animal and human tissues (Breivik *et al*., 2007).

Commercial formulations of polychlorinated biphenyls (PCBs), such as Aroclor mixtures, were widely used in the past in transformers, capacitors, hydraulic fluids and as plasticizers in paints, plastics and sealants. It has been estimated that globally 1.3 million tonnes of PCB compounds have been produced (Breivik *et al.*, 2007).

Historically the main sources of PCBs in the marine environment include energy production, combustion Industries, production processes, and waste (landfill, incineration, waste treatment, and disposal). Due to concerns about the environmental impact of PCBs, production in Western Europe and North America ceased in the late 1970s and in Eastern Europe and Russia in the early 1990s. PCBs can still enter the marine environment following the destruction and disposal of industrial plants and

equipment or from emissions from construction materials (Kohler *et al*., 2005) and old electrical equipment (for example from landfill sites). PCBs are included in the Stockholm Convention (UNEP, 2009) due to their persistence, bioaccumulation, and toxicity (PBT).

Theoretically 209 individual PCB congeners can be produced, depending on the number and position of chlorine that is substituted onto the biphenyl moiety. Individual congeners are generally named according to the short-hand system developed by Ballschmiter and Zell (1980) for PCB congeners. For this naming system a number from 1 to 209, often prefixed with "CB", was applied to each congener after the congeners had been sorted on the basis of their structural names by Mills *et al.*, (2007). The molecular weight (g/molecule) of PCB ranges from 188.7 for monochlorobiphenyl to 498.7 for decachlorobiphenyl.

The seven ICES (International Council for the Exploration of the Sea) PCBs (CB28, 52, 101, 118, 153, 138, and 180) were recommended for monitoring by the European Union Community Bureau of Reference; these PCBs were selected as indicators due to their relatively high concentrations in technical mixtures and their wide chlorination range (3–7 chlorine atoms per molecule). The ICES-7 PCBs have been part of the OSPAR Co-ordinated Environmental Monitoring Programme (CEMP) since 1998 (Webster *et al*., 2013). Of the 209 PCB congeners, the most toxic are the so-called 'dioxin-like' PCBs (DL-PCBs). The DL- PCBs are the four non-*ortho* (CB77, 81, 126, and 169) and eight mono-*ortho* (CB105, 114, 118, 123, 156, 157, 167, and 189) PCBs that also have chlorines in both *para* and at least two *meta* positions. The non-*ortho* PCBs can obtain a planar configuration and the mono-*ortho* PCBs can obtain a near planar configuration. As

a result, the twelve DL-PCBs are stereo chemically similar to 2, 3, 7, 8-tetrachlorodibenzo-*p*-dioxin (TCDD) and therefore have similar toxic and biological responses to those of dioxins (Safe *et al*., 1985; Kannan *et al.*, 1989).

Chemical structures and physical properties of selected PCBs are well documented (Mackay *et al.*, 2006). Protection of human health and the environment requires that PCBs be disposed off in such a way that they do not enter the environment. The important step in the environmental management of PCBs is to identify their sources and develop strategies for reducing or eliminating their release to the environment (UNEP, 1999).

UNEP's Council in February 1997 and Stockholm Convention included PCBs among the 12 POPs identified for International action due to their persistence, bioaccumulation and toxicity (PBT) (UNEP, 2009).

Article 7 of the Stockholm convention requires National implementation plans (NIPs) to be developed by signatory Countries, with Nigeria being a signatory in 2002 (UNEP, 2001).

The empirical formula for PCBs is $C_{12}H_{(10-n)}Cl_n$, where n is a number of chlorine atoms within the range of 1-10. Theoretically, a total of 209 possible PCB congeners exist, but only about 130 of these are likely to occur in commercial products. These commercial PCBs are mixtures of PCB congener (Neumeier, 1998). Twelve of the 209 congeners: PCB 77, 81, 105, 114, 118, 123,126, 156,157,167, 169 and 189 are known to show toxic responses similar to those caused by 2,3,7,8- tetrachlorodibenzo-p-dioxin (TCDD) toxic dioxins and furans (Keon *et al*., 2007; Lynda *et al*., 2013).

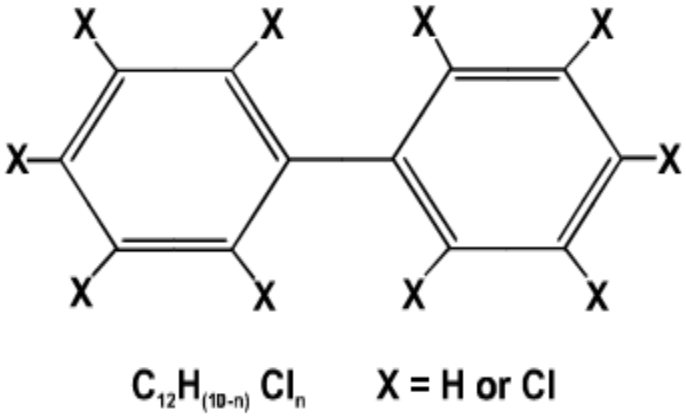


Figure 1.1: PCB molecular structure

PCB bio accumulate in the fatty tissues of exposed animals and humans (Fiedler, 1997) and this exposure is believed to be responsible for a wide variety of health effects, which includes skin rashes, eye irritation, disturbances in liver function and immune system, fatigue, impotence, depression, memory loss and possibly cancer. The US Department of Health and Human services as well as the International Agency for Research on Cancer (IARC) consider PCBs to be probable carcinogens in humans (IARC, 1987; ATSDR, 1989).

Many countries have developed classification and regulation for PCBs –containing fluids and materials. The benchmark level for PCB is considered as 50 mg/kg (or 50 ppm) as maximum permissible limit for regulation in many countries (UNEP, 1999).

Increasing awareness about the health and environmental effects associated with PCB exposure has resulted in a gradual withdrawal of use and an increase in production restrictions. Despite these efforts, PCBs continue to enter the environment. This is true

for developing nations like Nigeria that may have large quantities of PCB- containing electrical equipment still in service.

The various persistent cycles and pathways that led to widespread distribution of PCBs in the environment is represented in Figure 1.2, which may be a useful tool in the identification of specific focal areas for management or clean-up of PCBs (UNEP, 1999).

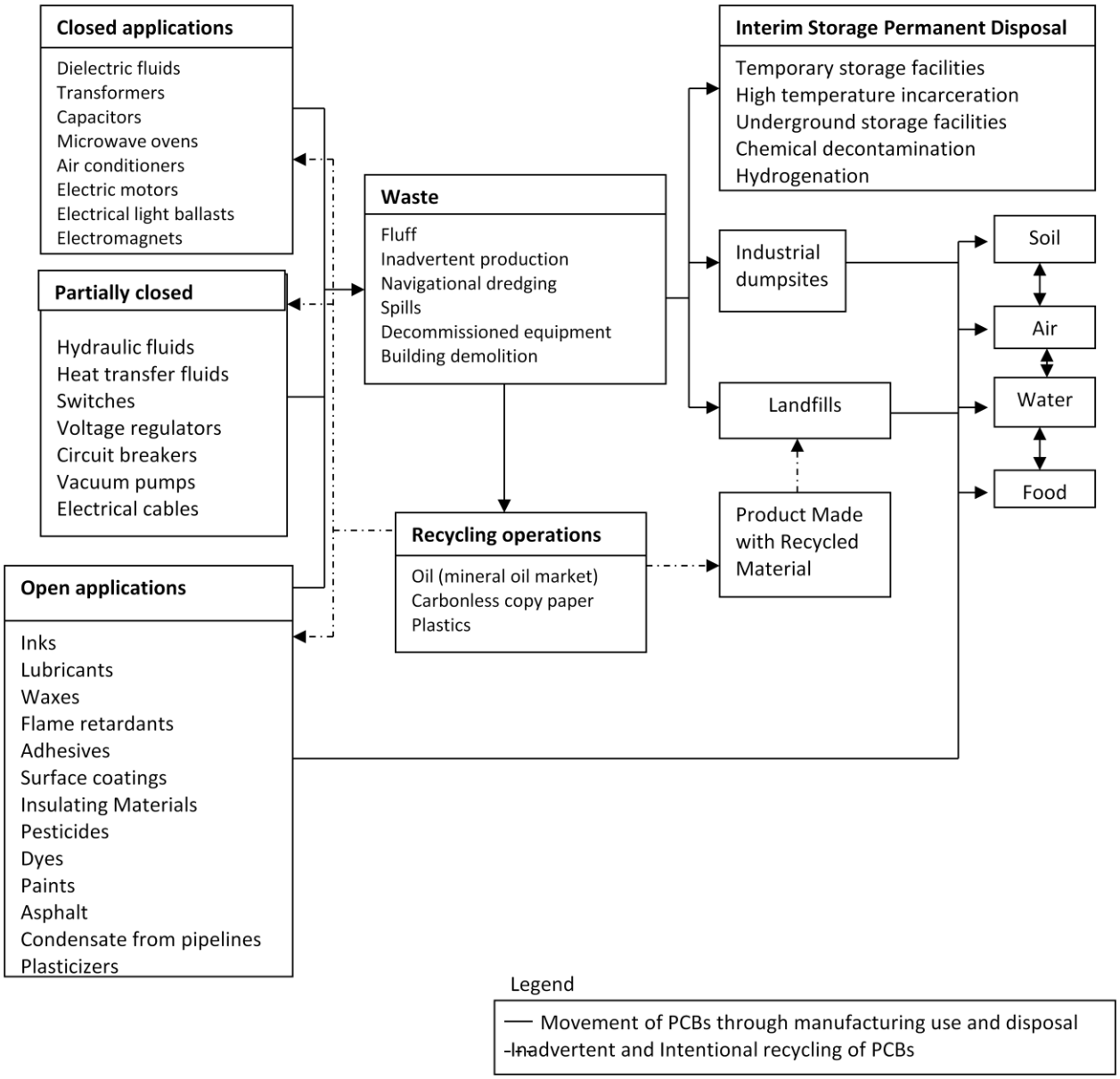


Figure 1.2: Distribution cycles and pathways of PCBs in the environment; **Source**:

UNEP, 1999

1.2 Justification of the Study

PCBs bio magnifies in the food chain and the health effects are numerous, such as tumours, cancer, liver damage, memory loss, impotence, reproduction and developmental effects. PCBs persistence once released into the environment, and its likely continual use means that PCBs could pose a threat for decade to come. Therefore, National action plan is required for the monitoring and management of PCBs towards Nigeria's obligation to the Stockholm convention on POPs (UNEP, 2001). Closed systems such as power transformers and transistors contain PCBs as dielectric coolant for electricity transmission. Maintenance/repairs of these transformers by Power Holding Company of Nigeria (PHCN) and their approved clients whenever technical malfunction arises often results to spills, accidental discharge or improper disposal of the spent PCBs transformer oils to the environment (UNEP, 1999).

1.3 Aim and Objectives of the Study

1.3.1 Aim of the Study

The aim of this study is to determine residue levels of PCBs in soils of selected transformer maintenance workshops in Kaduna and Zaria metropolis.

1.3.2 Objectives of the Study

The aim would be achieved by the following objectives:

i. Determine the soil particle size, and total organic carbon (TOC) content of the soil sample.

ii. Determine Polychlorinated biphenyls (PCBs) using Gas Chromatography/Mass Spectrometer (GC-MS).

iii. Determine relative response factor (RRF) and recovery (%) of PCBs in the soil samples.

iv. Correlation of results obtained at different sites with UNEP regulatory framework.

This research work focuses on chemical monitoring for Environmental Risk Assessment (ERA). The chemical monitoring of PCB residue levels in soils at the designated sampled sites in Kaduna and Zaria metropolis will serve as lead for further studies to link the bio availability of the measured PCBs with their concentrations at target organs and intrinsic toxicity.

CHAPTER TWO

LITERATURE REVIEW

2.1. History of PCBs

Historically, the first PCB-like chemical was discovered as a by-product of coal tar in 1865 and was synthesised in 1881. PCBs were first manufactured commercially in 1929 by Swan Corporation, which later became part of Monsanto chemical company of St. Louis Missouri (Peter *et al*., 1993). Monsanto later licence manufacturing of PCB to Caffarb(Italy), Prototec (France) and Kanega firm(Japan).

Many of the characteristics that make PCBs ideal in industrial applications create problems in the environment. Like many other chlorinated hydrocarbons, PCBs are soluble in fat, so they tend to accumulate in living things and enter food webs, where they concentrate. PCBs accumulation have been reported in mammal's fatty tissues and their milk, birds and their eggs, and was first recognised as an environmental problem in 1966 by Swedish researcher (Soren, 1966).

After U.S banned PCBs in 1976, according to statistics, the whereabouts of 30 % of all PCBs remain unknown, 30 % reside in landfills, in storage, or in the sediments of lakes, rivers and estuaries with the remaining 30-70 % remain in use with only 1 % estimated to have reached the oceans causing problems in food webs including humans (Christin *et al*., 1992)

2.2 Physical and Chemical Properties of PCBs

PCBs were produced and marketed as mixtures of many congeners. PCB mixtures are characterised by chlorine content. Less-chlorinated PCBs are odourless, tasteless, clear to pale-yellow, viscous liquids, while highly chlorinated mixtures are more viscous and

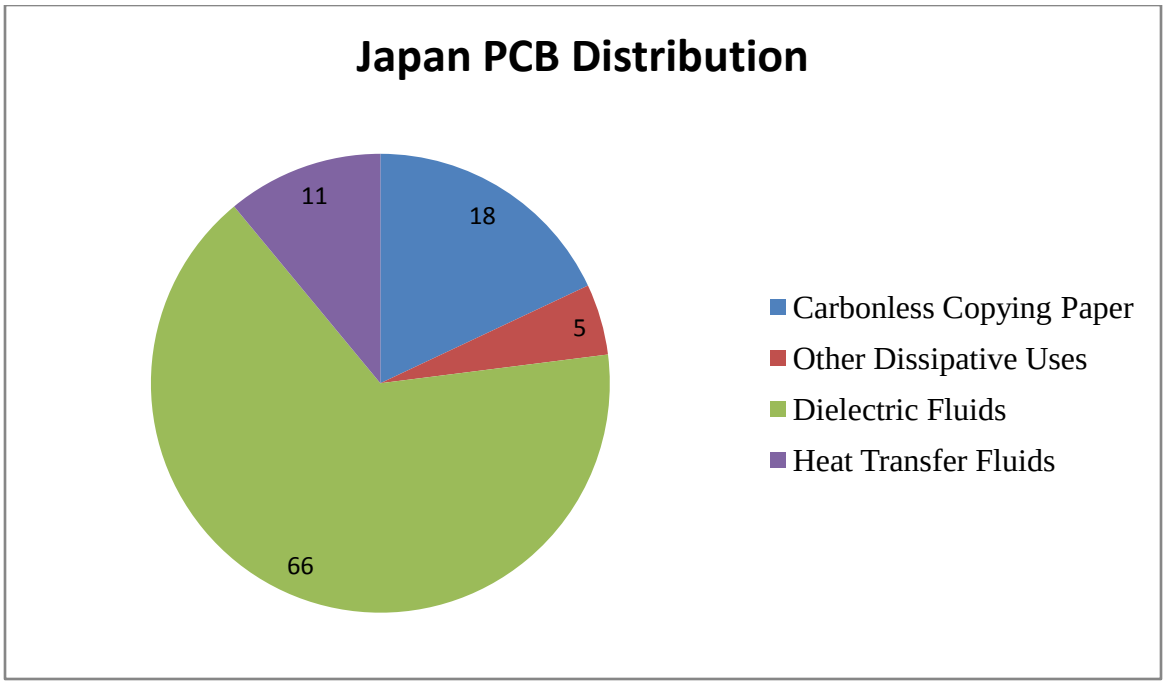
deeper yellow. PCBs have low water solubility of 0.0027 - 0.42 ng/L for Aroclors, density from 1.182 to 1.566 kg/L, low vapour pressures at room temperature, high solubility in most organic solvents and fats, high flash points from 170 to 380^{o}C , very high thermal conductivity and dielectric constants of 2.5 – 2.7 (UNEP, 1999)

PCBs are chemically inert, and resistant to oxidation, reduction, addition, elimination, and electrophilic substitution (Boate et al., 2004). PCBs have a half life of 8 to 15 years and are insoluble in water, which contributes to their stability (Mahan, 1998).

2.3 Uses and Applications of PCBs

PCBs have many useful physical and chemical properties that have led to their widespread use as dielectrics (mostly in transformers and capacitors) as heat exchange fluids, as paint and lubricants additives, in carbonless copying papers and in plastics as additives to oils in electrical equipment, hydraulic machinery and other applications where chemical stability has been required for safety, operation, or durability (Dobson and Van Esch, 1993; Neumeier, 1998).

The total PCBs application in Japan and Germany is characterised in the figure below:



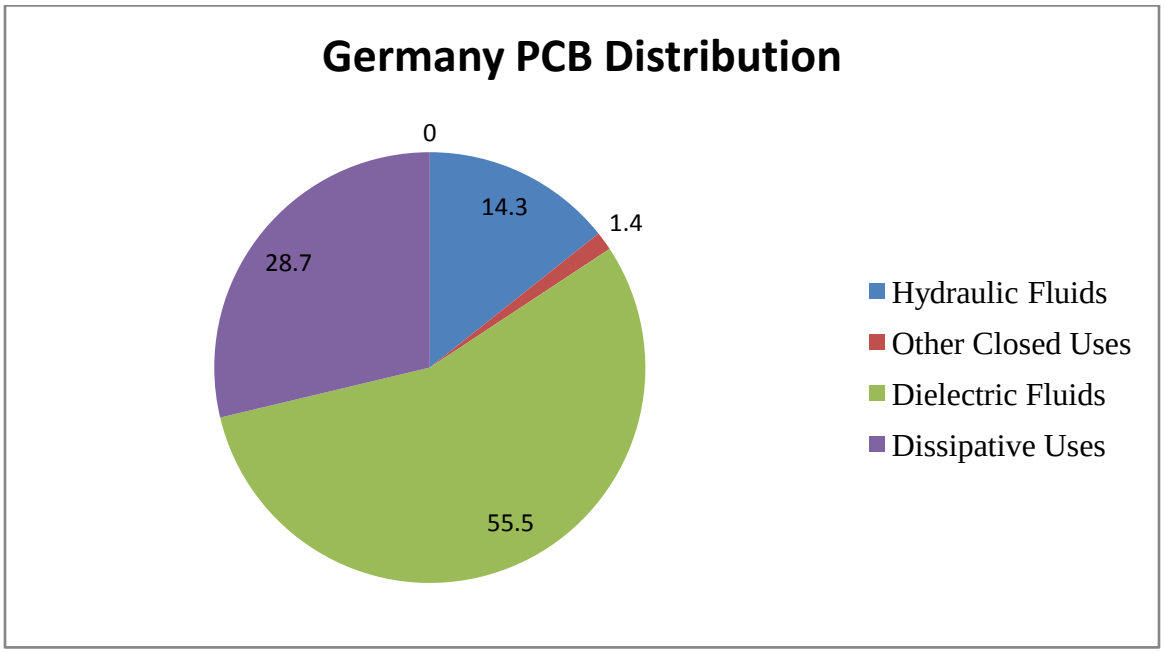


Figure 2.1: PCBs application and distribution in Japan and Germany

Although the chemical stability of many PCBs has been a benefit from the standpoint of commercial use, it has created an environmental problem because it translates into

extreme persistence when the PCBs are eventually released into the environment. In fact, PCBs have been reported among the most widespread environmental pollutants, having been detected in virtually all environmental media (indoor and outdoor air, surface and ground water, soil, and food) in almost every corner of the globe.

2.4 Health Effects of PCBs

Many PCB-mixtures are toxic. Exposure to low levels of PCBs is thought to cause various acute and chronic health effects (UNEP, 1999).

Bergeron *et al.* (1994) reported polychlorinated biphenyls (PCBs) as widespread, low-level environmental pollutants associated with adverse health effects such as immune suppression and teratogenicity; with an increasing evidence that some PCB compounds are capable of disrupting reproductive and endocrine function in fish, birds, and mammals, including humans, particularly during development. Research on the mechanism through which these compounds act to alter reproductive function indicates estrogenic activity, whereby the compounds may be altering sexual differentiation.

PCBs have been reported to bio-accumulate in the fatty tissues of exposed animals and humans and this is believed to be responsible for a wide variety of health effects. Acute exposures to high levels of PCBs have been associated with skin rashes, itching and burning, eye irritation, skin and fingernail pigmentation changes, disturbances in liver function and the immune system, irritation of the respiratory tract, headaches, dizziness, depression, memory loss, nervousness, fatigue, and impotence. Chronic effects of low-level PCB exposures reported include liver damage, reproductive and developmental effects, and possibly cancer (Fiedler, 1997; Neumeier, 1998).

United Nations Environmental and Protection Agency, in February 1997 included PCBs among the 12 POPs identified for International action. Article 7 of the Stockholm convention requires National implementation plans (NIPs) to be developed by signatory Countries, with Nigeria being a signatory. Many countries have developed classification and regulation for PCBs –containing fluids and materials. The benchmark level for PCB is considered as 50 mg/kg (or 50 ppm) in many countries (UNEP, 1999).

Nigerian Government through the instrumentality of standardisation have banned the use of the 12 POPs in mosquito coils and Household Aerosol insecticides marketed in Nigeria; however, these chemicals are still found marketed under different trade names for variety of application ignorantly (NIS, 1992; NIS, 2000).

Pavel *et al.* (1999) reported the PCBs that contributes to the toxic equivalents (TEQ) originated from PCB 156 (31.47%), PCB 126 (25.8%), and PCB 170 (20.28%). In a study concerned with documentation of human exposure to toxic PCBs in the Czech Republic, samples of human milk were collected in 1995 in the Prague area and were examined for the levels of toxic *non-*, *mono-*, and *di-ortho* PCB congeners. The concentrations of toxic PCBs found are comparable with data from other countries. The main contribution to the toxic equivalents (TEQ) originated from PCB 156 (31.47%), PCB 126 (25.8%), and PCB 170 (20.28%). Strong linear correlation was found for toxic equivalents (TEQs) with two major chlorobiphenyl congeners, PCB 153 and PCB 180.

2.5 Extraction and Clean up of PCBs

Gomez-Ariza *et al.* (2002) suggested a new pressurised liquid extraction method that automatically and rapidly achieves quantitative and selective (i.e., lipid-free) extraction of polychlorinated biphenyls (PCBs) in biota tissues was optimized. It consists of on-line clean-up by inclusion of sorbents in the extraction cell. The freeze-dried sample is dispersed with Florisil and loaded in the extraction cell containing an extra amount of Florisil. The extraction is performed under mild conditions using 55 ml of a dichloromethane: pentane (15:85) mixture, a temperature of 40^0 C, a static extraction time of 10 min and two extraction cycles. The Florisil retains co extracted lipids from the matrix, and the extract, after pre-concentration, is clean enough for direct injection into GC-MS and GC-electron-capture detection (ECD). Quantitative recoveries (from 90 to 106%) are obtained for both native and spiked PCB congeners in samples with high lipid content (up to 42% dry mass, in spoonbill eggs). The reproducibility of replicate extractions was better than 11% relative standard deviation. Method detection limits were in the ranges of 0.001-0.004 and 0.002-0.07 ng/g dry mass for GC-ECD and GC-MS-MS, respectively. The method was validated using the standard reference material SRM 2974 (a mussel tissue) from the US National Institute of Standards and Technology, compared to Soxhlet and matrix solid-phase dispersion extraction methods, and used to evaluate the contamination by PCBs in bivalves from South of Spain

Ligor *et al.* (2007) reported the presence of PCBs by means of a sensitive, rapid and robust monitoring method optimized for PCB in oils and fodders. The use of Ultrasonic assisted extraction allows for efficacious sample preparation. The clean-up method based on double layered SPE column provides a simplified approach for the removal of interferences from the raw sample. The GC/MS in SIM mode was used for final

determination of target congeners. This method fits the purpose of rapid screening of fodder and transformer oil samples. The PCBs were found in two transformer oils on the level of 760 and 630 mg/kg.

Wang *et al*. (2013) identifies PCBs 28, 52, 101, 138, 153, 180, 118 as the most abundant PCB congeners in water in a study to assess the bioavailability of polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and organochlorine pesticides (OCP) measured in the water column from Three Gorges Reservoir (TGR) collected in May 2008 using semi-permeable membrane devices (SPMDs). The sampling sites spanned the whole reservoir from the upstream to the great dam covering more than 600 km long distance with water flow velocities ranging from <0.05 to 1.5 m/s. This is the first experience of SPMD application in the biggest reservoir in the world. The results of water sampling rates based on performance reference compounds (PRC) were tested to be significantly correlated with water flow velocities in the big river. Results of back-calculated aqueous concentrations based on PRC showed obvious regional variations of PAH, PCB and OCP levels in the reservoir. Total PAH ranged from 13.8 to 97.2 ng/L, with the higher concentrations occurring in the region of upstream and near the dam. Phenanthrene, fluoranthene, pyrene and chrysene were the predominant PAH compounds in TGR water. The total PCBs ranged from 0.08 to 0.51 ng/L with the highest concentrations occurring in the region near the dam where PCBs 28, 52, 101, 138, 153, 180, 118 were the most abundant PCB congeners in the water.

2.6 Microbial Destruction of PCBs

Polychlorinated biphenyls (PCBs) are believed to be indestructible. However varieties of methods such as physical, chemical and microbial are used to investigate the destruction of PCBs in the environment. Recent findings have been shown to biodegrade PCBs under varieties of conditions. Two distinct classes of bacteria have now been identified that biodegrade PCBs by different mechanisms. The aerobic biodegradation of PCBs (natural strains, recombinant organisms, and soil applications) results demonstrated microbial reductive de-chlorination of even highly chlorinated PCBs under anaerobic conditions.

These two PCB degradative systems include aerobic bacteria which live in oxygenated environments and anaerobic bacteria which live in oxygen free environments such as aquatic sediments. The aerobes attack PCBs oxidatively, breaking open the carbon ring and destroying the compounds. Anaerobes, on the other hand, leave the biphenyl rings intact while removing the chlorines. This anaerobic de-chlorination degrades highly chlorinated compounds into less chlorinated derivatives. These two naturally occurring processes are complementary, and a two step treatment may permit the biological destruction of nearly all of the PCB mixtures commonly used (Daniel, 1990).

Marine sediments, in particular those with a high organic carbon content, accumulates hydrophobic compounds like PCBs to considerably higher levels than those of the surrounding waters. The sampling strategy depends on the purpose of the monitoring programme and the natural conditions of the region to be monitored. Typically sampling approaches include fixed-station sampling, stratified random sampling, or stratified fixed sampling. Muddy sediments, i.e. those containing a high proportion of fine material, are

preferable for organic contaminant monitoring, although sieving of sediments may be an alternative (OSPAR, 2002).

2.7 PCBs as Biomarkers in Environmental Risk Assessment

A wide array of bioaccumulation markers and biomarkers has been used to demonstrate exposure to and effects of environment in relation to their feasibility in environmental risk assessment (ERA). The most promising fish bioaccumulation markers are body burdens of persistent organic pollutants, like PCBs and DDTs. Since PCDD and PCDF levels in fish tissues are very low as compared with the sediment levels, their value as bioaccumulation markers remains questionable. In order to assess exposure to or effects of environmental pollutants on aquatic ecosystems, the following suite of *fish biomarkers* may be examined: biotransformation enzymes (phase I and II), oxidative stress parameters, biotransformation products, stress proteins, metallothioneins (MTs), MXR proteins, haematological parameters, immunological parameters, reproductive and endocrine parameters, genotoxic parameters, neuromuscular parameters, physiological, histological and morphological parameters. All fish biomarkers are evaluated for their potential use in ERA programs, based upon six criteria. This evaluation demonstrates that phase I enzymes (e.g. hepatic EROD and CYP1A), biotransformation products (e.g. biliary PAH metabolites), reproductive parameters (e.g. plasma VTG) and genotoxic parameters (e.g. hepatic DNA adducts) are currently the most valuable fish biomarkers for ERA. The use of bio monitoring methods in the control strategies for chemical pollution has several advantages over chemical monitoring. Many of the biological measurements form the only way of integrating effects on a large number of individual and interactive processes in aquatic organisms. Moreover, biological and biochemical

effects may link the bioavailability of the compounds of interest with their concentration at target organs and intrinsic toxicity. Based upon this overview there is little doubt that measurements of bioaccumulation and biomarker responses in fish from contaminated sites offer great promises for providing information that can contribute to environmental monitoring programs designed for various aspects of Environmental Risk Assessment (Ron van der, *et al.,* 2003)

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

3.1.1 Apparatus and Equipment

The apparatus and equipment used for the experimental work are presented below.

i. Analytical balance
ii. Round bottom flask
iii. Conical flask
iv. Beakers
v. Glass cylinders, 1000-mL capacity
vi. Thermometer
vii. Hydrometer, Bouyoucos (Fisherbrand model no. 14-331-5c)
viii. Electric mixer with dispensing cup
ix. Plunger
x. Rotary evaporator
xi. Microwave
xii. Crucible
xiii. Desiccators
xiv. pH meter (Jenway 2000)
xv. Sample containers (glass bottles)
xvi. Oven: Capable of operating at 130 $\pm$20^{o}C
xvii. Muffle furnace: Capable of operating at 500$\pm$50^{o}C

xviii. Desiccator

xix. Filter papers; whatman 542, 125 mm diameter.

xx. Chromatography column for clean up: Glass, 130 mm by 5.6 mm internal diameter.

xxi. Micro-syringes; Used for sample spiking and preparation of standard solutions.

xxii. Ultrasonic bath

xxiii. Gas chromatography-mass spectrometry equipment. Capable of operating at a resolution of 5000 (i.e. 10% valley definition) with a heated injector system.

xxiv. Gas chromatography column; Fused silica capillary column (DB-5 ms column), with a dimension of 30 m by 0.25 mm internal diameter, 0.25 µm film thickness.

xxv. Pasteur pipette for clean-up chromatography; Glass, 150 mm by 5 mm internal diameter.

3.1.2 Reagents

All reagents for this work are of the Analar grade with sufficient purity that will not give rise to significant interfering peaks in the chromatographic analysis; and solvents suitable for high performance liquid chromatography were employed.

i. Distilled water

ii. Hexane

iii. Acetone

iv. Dichloromethane

v. Nonane

vi. Acetone:dichloromethane mixture: Equal volume of acetone and dichloromethane were thoroughly mixed (a ratio of 50:50 v/v).

vii. Sodium sulphate: Traces of organic material were removed by washing the anhydrous and granular sodium sulphate with dichloromethane and allowed to dry, prior to heating to $500 \pm 50^{o}C$ in a muffle furnance for 4.0 ± 5.0 hours. It was then cooled to $200^{o}C$ in a muffle furnace and then finally to ambient temperature in a dessicator; and stored in a sealed glass container ready for use.

viii. Air (filtered and dried)

ix. Standard PCB stock solutions: Stock solutions (in nonane) of all the PCBs to be determined were prepared within a concentrations range 1-10 mgl^{-1}. A single solution (in nonane) containing $1mgl^{-1}$ of each of the PCBs of interest was also prepared.

x. Mixed internal standard 13C12-PCB solutions: A mixed internal standard solution (in nonane) of isotopically labelled PCBs was prepared, typical of the PCBs being determined. 13C12-PCB 52 and 13C12-PCB 153, each at a nominal concentration of 2 $mgl^{-1}$was used.

xi. Recover standard 13C12-PCB solution: A recovery standard solution (in nonane) of an isotopically labelled PCB. 13C12-PCB 118 at a nominal concentration of 2 mgl^{-1} was used.

xii. Mixed calibration and internal standard solutions (see 3.6.1)

xiii. Florisil 60-100 mesh

xiv. Glass wool: It was pre-washed with dichloromethane and allowed to dry prior to use.

xv. Silica gel 60

xvi. 5 % Hexametaphosphate solution (Dispersing solution): 50 g of sodium, hexametephosphate, $Na_6(PO_3)_6$, was dissolved in deionised water and diluted to 1000 mL.

3.2 Methods

3.2.1 Sample Collection

The likely contamination to the environment on poor management of transformer maintenance/repairs sites by PHCN/and their approved clients, informed the choice of the sampling locations for this study. Two soil samples per site, one top soil (0-5 cm) and one subsoil (20-30 cm), from seven different places in Kaduna and Zaria metropolis, totalling 14 samples were taken. The four different sampling locations in Kaduna were coded K1, K2, K3 and K4, and three different locations in Zaria metropolis were coded Z1, Z2, and Z3 as presented in Table 3.1.

Composite samples of 800 g for each topsoil and subsoil were separately taken from the sampling locations and manually mixed and transferred into glass sample bottles, sealed and labelled before it was transported to the laboratory, and stored in a refrigerator (SAEFL, 2003). This is to ensure reproducibility of result and precision.

3.2.2 Sample Pre-treatment for Analysis

Representative soil samples of 400 g were air-dried; lump samples were gently crushed in porcelain mortal with a pestle, sieved to a particle size of 2.00 mm and air-dried at ambient temperature to enable a more homogeneous sub-sample to be taken for analysis.

Table 3.1: Showing the seven sampling locations and their respective point coordinates.

S/no	Point Coordinates	Sample locations	Codes
1	10º38□20.5□ □N 7º36□38.8□ □E	PHCN main maintenance workshop outlet closed to River Kaduna, Station Market, Kaduna.	K1
2	10º35□00.7□ □N 7º39□50.7□ □E	Individual transformer maintenance workshop by AMECO, Kakuri Road, Kaduna	K2
3	10º39□00.6□ □N 7º37□36.11□ □E	Individual transformers maintenance workshop opposite Television Garage, Kaduna	K3
4	10º39□03.9□ □N 7º37□46.9□ □E	PHCN power transmission substation, Mando, Kaduna	K4
5	11º39□05.7□ □N 7º35□31.3□ □E	Transformer substation within ABU, Samaru- Zaria (transformer substation near department. of Economics)	Z1
6	11º33□04.2□ □N 7º35□01.6□ □E	Transmission substation Dogarawa, near old Kano road overhead bridge, Zaria	Z2
7	11º33□10.7□ □N 7º34□03.7□ □E	Farm remote from possible PCBs source (as the control) near NARICT	Z3

3.3 Determination of Physicochemical Properties

3.3.1 Determination of soil particles size (Bouyoucos Hydrometer method)

3.3.2 Method:

For the test sample, 50 g of soil sample was weighed and treated with 100 mL of 5 % sodium hexametaphosphate (5 % dispersing solution) and the sample was mixed for 30-60 seconds in electric mixer with dispersing cup. The suspension was quantitatively transferred from the dispersing cup to 1000 mL glass cylinder, filled to mark with deionised water and allowed to stand overnight to equilibrate. The plunger was inserted into suspension and carefully mixed for 30 seconds until a uniform suspension was obtained. A timer was set at 40 seconds, the plunger was removed and the hydrometer was gently inserted into the suspension for a recorded reading at 40 seconds to give the amount of silt and clay suspended. After 6 hours, 52 minutes when the silt has settled to the bottom of the cylinder, the hydrometer reading was recorded as the amount of clay in suspension.

For blank sample, 100 mL of 5% dispersing solution was mixed with 880 mL of deionised water in 1000 mL glass cylinder. The temperature and the hydrometer readings were recorded at the beginning of each set of test.

Corrections are made for the density and temperature measurement of dispersing solutions as described by the method (Bouyoucos, 1962).

(1) Percent clay(< 0.002 mm) was calculated as

% clay = corrected hydrometer reading at 6 hours, 52 minutes x 100/wt of sample

(2) Percent silt(0.05-0.002 mm):

% silt = corrected hydrometer reading at 40 sec. x 100/wt. of sample - % clay

(3) Percent sand (2-0.05 mm):

% sand = 100 % - % silt + % clay

The soil texture is reported based on the USDA textural triangle chart (Bouyoucos, 1962) presented in Appendix III.

3.4 Determination of Total Organic Carbon (TOC)

Soil sample of 10.0 g was taken from the representative sample, weighed and in a ventilator oven first dried at 40 ^{o}C for 1 hour to attain a constant weight and then the temperature was increased to 105 ^{o}C and allowed to stand for 6 hours as described in the procedure of Association of Official Analytical Chemists (AOAC, 1980).

The total organic carbon was calculated as:

$$\% \text{ Total organic carbon} = \frac{W_2 - W_3}{W_2 - W_1} \times 100$$

Where W_1 = weight of empty crucible

W_2 = weight of sample and crucible before drying

W_3= weight of sample and crucible after drying

3.5 Sample Extraction

Soil sample of 10.00 g was transferred into a 100 mL beaker. 0.02 µg (i.e. 10 µL of 2mg/L) of each of the mixed internal standards (C13PCB 52 and C13PCB 153) was added, followed by the addition of 30 mL of 50:50 v/v acetone: dichloromethane mixture into the beaker and ultra-sonicate for about 3 minutes to allow the soil particles to settle.

The supernatant liquid was transferred into a 250 mL round bottomed flask and extracted with 30 mL of the mixture of acetone and dichloromethane. The solvent extraction and transfer process was repeated twice and all the extracts were combined together in the round-bottomed flask. A blank sample, comprising a similar matrix to the soil under investigation was similarly treated with the same internal standard and procedure above.

The extracts (i.e. blank sample and analyte sample) were dried by filtering through a filter containing 10.00 g of sodium sulphate. The filter paper containing the sodium sulphate was further washed with 30 mL of solvent mixture and the filtrate collected in the round-bottomed flask. The volume of dried extract was reduced to between 3.00 and 5.00 mL using a rotary evaporator; and was further reduced to 1.00 – 2.00 mL using a stream of air. 1.00 mL of the reduced dried extract was transferred to a glass vial and the container was rinsed with 2.00 – 3.00 mL of hexane. The solvent washings were then added to the vial. The volume of the solvent was finally reduced at ambient temperature to approximately 1.00 mL (Environment Agency, 2003; EASCA, 2003; Roose and Brinkman, 2005).

3.6 Clean-up

Florisil column was prepared by packing a Pasteur pipette with a small amount of glass wool, the column was first packed with Florisil to a depth of 65 mm and then with sodium sulphate to a depth of 50.00 mm. The column was then eluted with about 5.00 mL of dichloromethane and allowed to drain before heating the column at 130 ± 10 °C for excess of 16 hours, and the column stored at this temperature until ready for use.

The column was removed from the oven and allowed to cool. The column was set up in a retort stand and bottom flask placed below the base of the column. The extract was added to the top of the column and container containing the extract rinsed with 5 mL of hexane and the solvent washings added to the column. This procedure was then repeated. A further quantity (10.00 mL) of hexane was then added to the column and the column eluted until the solvent meniscus reaches the top of the column. The eluate was collected and labelled hexane fraction (This extract usually contains all PCBs present except the non-ortho PCBs.). Eluate was concentrated to 1.00 – 2.00 mL using a rotatory evaporator followed by stream of air.

50.00 mL of dichloromethane (DCM) was added to the column and the elute collected in a separate container and was labelled DCM fraction (This fraction usually contains the four non -ortho PCB congeners). The eluate was then concentrated to 1.00 – 2.00 mL using rotator evaporator followed by stream of air.

Each extract was transferred to a separate vial from their containers and rinsed with about 2.00 – 3.00 mL of hexane and the solvent added to their respective vials. To each vial, 10.00 µl of the recovery standard solution (C13 PCB 118) were added; and the volume of the solvent reduced to approximately 1.00 mL using a blow down apparatus ((Environment Agency, 2003; EASCA, 2003; Roose and Brinkman, 2005).

3.7 Gas Chromatography-Mass Spectrometry

Aliquots samples of 10.00 g were spiked with labelled PCBs as internal and recovery standards, extracted with 30 mL mixture of 50:50 v/v acetone: dichloromethane in a microwave , and extracts were then dried by filtering through a filter containing 10.00 g of anhydrous sodium sulphate. The dried extract was clean up with florisil and then

analysed by GC-MS in the ion recording mode performed at a mass resolution of 5000. The GC-MS was operated according to the set analytical conditions in Table 3.2 to monitor a minimum of two mass fragmentation ions per level of chlorination based on SAL modified US EPA method 1668 (1999). The method was used because of its suitability for determination of PCB congeners based on the following reasons:

i. The machine is capable of detecting up to 0.01 ug/kg of the PCBs in soil samples.
ii. The relative high concentration in technical mixtures of the seven (7) PCB congeners and their wide chlorination range (3-7 chlorine atoms per molecule).
iii. Microwave (fast, efficient and economical)
iv. Isotopic dilution (precision and accuracy)
v. Good recovery % (reproducibility or repeatability)

3.7.1 Calibration (mixed calibration and internal standard solutions)

Multi-point calibration was undertaken by injecting 1µl of each of the PCB calibration standard solutions (a, b and c) below; and blank (nonane) solution into the gas chromatograph, and the calibration responses obtained for the series of standard solutions.

a. Into a 2 mL crimp-capped vial, 0.02 µg of the internal standard (C13 PCB 52 and C13 PCB 153) was added with 0.02 µg of the recovery standard (C13 PCB 118) and 500.00 µL of the 1.00 mg/L standard PCB stock solution and 480 µL of nonane and labelled as 0.50 mg/L PCB calibration standard.

b. Into a 2 mL crimp-capped vial, 0.02 µg of internal standard, (C13 PCB 52 and C13 PCB 153) was added with 0.02 µg of recovery standard (C13 PCB 118) and 50.00 µL of the 1.00 mg/L standard PCB stock solution, then 930.00 µL of nonane added and labelled as the 0.05 mg/L PCB calibration standard.

c. Into a 2 ml crimp-capped vial, 0.02 µg of internal standard (C13 PCB 52 and C13 PCB 153) was added, followed by 0.02 µg of recovery standard (C13 PCB 118), then 5.00 µL of 1 mg/L standard PCB stock solution. And finally, 975.00 µL of nonane. Labelling the standard as 0.005 mg/L PCB calibration standard.

3.7.2 GC-MS Analytical Cconditions

The GC-MS was set at analytical conditions given in Table 3.2 below:

Table 3.2: GC-MS Analytical Conditions

Machine make and model	**GC-MS, QP 1020 PLUS**
Injection temperature and mode	280^0C, splitless
Flow control mode	Linear velocity
Sampling time, split ration	1.0 min, 1.0
Pressure	51.0 KPa
Total flow and purge flow	2.8 mL/min, 1.0 mL/min
Column flow	0.92 mL/min
Linear Velocity	35.0 cm/sec
Ionisation	EI, ACP mode-scan and sim. Threshold-5000, ion source-200^0C, interface temperature- 260^0C, solvent cut time-1.5min and micro scan width-0.000mμ.
Oven temperature programme for both instrument	Initial 60^0C (hold for 2 min), then ramp (i) 30^0C/min to 190^0C,then ramp (ii) 3^0C/min to 280^0C hold (10 min)
Carrier Gas	Hydrogen

3.8 Quantification

Quantification of the selected PCBs was carried out via the isotope dilution technique since an isotopically labelled internal standards was used. Prior to the gas chromatographic-mass spectrometric analysis of the test sample, extraction and clean-up recovery were determined from the addition of the recovery standard, C13 PCB 118, to the extract after the final concentration stage.

3.8.1 Preparation of PCB standard

A suite of 'ICES 7' congeners (consisting of PCBs 28, 52, 101, 118, 138, 153, 180) was purchased from Sigma Aldrich chemical company, UK. These suites of PCB EC7 has LOD of 0.05 µg/kg for each congener with a sum calculated LOD of 0.35 µg/kg.

3.8.2 Calibration of Analytes PCBs 28, 52, 101, 118, 138, 153 and 180

1. Triple calibration of analytes PCB 28, 52, 101, 153 and 138 of concentrations 5.0, 50.0 and 500.0 ng/µL, and analytes PCB 118 and 180 of concentrations 15.0, 100.0 and 600.0 ng/µL was carried out to obtain the average values of RF (RT) and RRF in Table 3.2 below.
2. 12.0 ng/ µL of C13 PCBs of the corresponding PCBs were used as internal standards, except C13 PCB118 and C13 PCB180 that 24.0 ng/ µL was used as internal standard.
3. 12.0 ng/ µL of C13 PCB54 and C13 PCB141 were used as recovery standard.
4. 1.00 g of each of the 14 samples and 12.00 ng/µL of PCBs standard addition were employed in the analysis.

Multiple calibrations by replicate determination of RRF values using PCB 54 and PCB 141as recovery standards are in Appendix I. A summary of PCB congener standard extracted from Appendix 1 is presented in Table 3.3 below:

Table 3.3: Polychlorinated Biphenyl (PCB) Standard

PCB Congener	M/Z	RT (min.)	RRF	% S.D RT	Chemical Name
CB28	256	16.2	1.11	8	1,1□-Biphenyl,2,4,4□-trichloro
CB52	292	15.4	1.05	7	1,1□-Biphenyl,2,2□,5,5□-tetrachloro
CB101	326	17.6	1.18	9	1,1□-Biphenyl,2,3□4,4□,5-pentachloro
CB118	326	10.5	1.11	6	1, 1□-Biphenyl,2,3□,4,4□,5-pentachloro
CB153	360	18.4	1.27	11	1,1□-Biphenyl,2,2□,4,4□5,5□-hexachloro
CB138	360	18.4	1.27	10	1,1□-Biphenyl,2,3,3□,4,4□,5-hexachloro-2,3
CB180	394	11.0	1.17	8	1,1□-Biphenyl,2,2□,3,4,4□,5,5□-heptachloro

3.8.3 Acceptance criteria and sample quality control measures

The conformation of a PCB of interest is based upon these criteria:

(i) The peaks in the individual ion chromatograms for the ions monitored for each PCB group should maximize within 1 second of each other.

(ii) The retention times of corresponding peaks should be within 3 seconds, relative to an isotopically labelled PCB.

(iii) The isotope ratio should be within 20.00% of the theoretical value. If the ratio is above this value, then interference may be suspected.

a. Relative response factors (RRF)

The relative response factor (RRF) is defined and calculated by the following equation:

$$(\text{RRF}) = \frac{\text{Signal (analyte)x Amount (internal standard)}}{\text{Signal (internal standard)x Amount (analyte)}}$$

Where the signal is the sum of the areas of the two isotope peaks (mass 1 and mass 2) for the specific isomer.

For recovery calculations

$$(\text{RRF}) = \frac{\text{Signal (internal standard)x Amount (recovery standard)}}{\text{Signal (recovery standard)x Amount (internal standard)}}$$

The average relative response factor is simply the mean of the RRFs obtained for each of the calibration standard solutions.

b. PCB Quantification

Prior to extraction, a known amount of internal standard is added to a known amount of sample. Using these values and the calibration-based RRFs, the amount of each PCB was calculated in the test sample as:

$$\text{Amount of PCB} = \frac{\text{Signal (PCB)} \times \text{ Amount (internal standard added)}}{\text{Signal (internal standard)} \times \text{ Amount (sample extracted)} \times \text{RRF}}$$

To determine the recovery of the internal standard, the equation below was used

$$\text{Recovery (\%)} = \frac{\text{Signal (internal standard)} \times \text{Amount (recovery standard added)}}{\text{Signal (recovery standard)} \times \text{Amount (internal standard added)} \times \text{RRF}}$$

CHAPTER FOUR

RESULTS

4.1 Physicochemical Properties of Soil Samples from Kaduna and Zaria.

4.1.1 Texture of Soil

The % clay in Table 4.1 increases from top soil to subsoil in the soil samples from AMECO, TV Garage, Mando, and Dogarawa, while, the % clay decreases from top soil to subsoil in the soil samples from main work shop and ABU Samaru. The % clay for both top soil and subsoil in the soil samples from the control farmland near NARICT was 16. The % clay is highest in both top soil and Subsoil in the soil samples from ABU Samaru,, and lowest in soil samples from Dogarawa.

In Table 4.1, the % silt decreases from top soil to subsoil in the soil samples from main work shop Mando, ABU Samaru, Dogarawa and Farmland near NARICT. However, an increase in % silt was observed from top soil to subsoil in the soil samples from AMECO. While, the % silt remains the same for both top soil and subsoil in the soil samples from TV Garage and Dogarawa. The % silt in topsoil and subsoil samples from TV Garage and Dogarawa was 14 and 8 respectively. The % silt is highest in top soil and subsoil samples from ABU Samaru and AMECO respectively, and least in both top soil and subsoil samples from Dogarawa.

In Table 4.1, the % sand decreases from top soil to subsoil in the soil samples from AMECO, TV Garage and Dogarawa, while, the % sand increases from top soil to subsoil in the soil samples from main work shop, ABU Samaru and Farmland near NARICT. The % sand for both top soil and subsoil in the soil samples from Mando is 70%. The %

sand is highest in both top soil and subsoil in the samples from Dogarawa, and least in the topsoil and subsoil samples from ABU Samaru.

4.1.2 Total Organic Carbon (TOC)

The % TOC in Table 4.1 decreases from top soil to subsoil in the soil samples from AMECO, TV garage, Mando, Dogarawa and farmland near NARICT. However, the % TOC increases from top soil to sub soil in the soil samples from main workshop and ABU Samaru. The % TOC is highest in the subsoil from main workshop, and least in both the top and sub soil from farmland near NARICT.

Generally, the physicochemical properties of the soil samples reveals that the % sand increases with decrease in % clay and % silt in the soil samples from the study locations. Also the % TOC increases with increase in % sand in the soil samples from the study locations.

4.2 Range and Mean of Physicochemical Characteristics of Soil Samples.

In Table 4.2, the % clay range was 10-22 with mean value of 14.43 and standard deviation was 3.20. The % silt range was 8-20 with mean value of 15.43 and standard deviation was 3.80. While, % sand range was 58-82 with mean value of 69.43 and standard deviation was 6.54. The % TOC range was 0.31- 1.68 with mean value of 1.17 and standard deviation 0.49.

The calculated coefficient of variation (%) for clay, silt, sand and total organic carbon (TOC) was 84, 97, 78 and 45 respectively. This shows a coefficient of variation (%) for % silt is highest and least for %TOC in the samples under investigation.

Table 4.1: Physicochemical Properties of Soil Samples of Transformer Maintenance Workshop in Kaduna and Zaria

Location	Sample	% clay	% silt	% sand	% Total organic carbon(TOC)
Main w/shop	Topsoil	14	18	68	1.46
	Subsoil	12	14	74	1.68
Ameco	Topsoil	16	18	66	1.59
	Subsoil	18	20	62	1.50
TV Garage	Topsoil	12	14	74	1.52
	Subsoil	16	14	70	1.19
Mando	Topsoil	14	16	70	0.89
	Subsoil	16	14	70	0.59
ABU Samaru	Topsoil	22	20	58	0.70
	Subsoil	18	18	64	1.50
Dogarawa	Topsoil	10	8	82	1.67
	Subsoil	12	8	80	1.35
NARICT	Topsoil	16	18	66	0.38
	Subsoil	16	16	68	0.31

Table 4.2 Range and Mean of Physicochemical Characteristics of Soil Samples

Characteristics	Range	Mean	Standard deviation	Coefficient of variation (%)
Clay, %	10 – 22	14.43	3.20	84
Silt , %	8 - 20	15.43	3.80	97
Sand, %	58 – 82	69.43	6.54	78
TOC, %	0.31 – 1.68	1.17	0.49	45

4.3 PCB Residue Levels or Contents

4.3.1 PCBs in Kaduna and Zaria Metropolis

In Table 4.3, the PCBs EC-7 (µg/kg) in top soil sample from AMECO is highest with recorded value of 8209.50, and least with a value of 21.90 in subsoil sample from TV garage. The recorded PCB concentrations at top soils are higher than the sub soils in all the samples, which may be attributed to higher binding effect of the soil and hence less percolation of PCBs down the soil depth.

The PCBs EC-7 (µg/kg) in Table 4.4 of top soil and subsoil samples in ABU Samaru is the least with recorded values of 0.82 and 0.19 respectively. The PCB concentration in topsoil and subsoil sample in Dogarawa is 413.20 and 469.30 respectively. The increase in PCB concentrations recorded from topsoil to subsoil samples in Dogarawa may be attributed to less binding effect of the top soil. The control samples in a farmland near NARICT had PCBs (sum) measured values of 0.00 for both top soil and sub soil which indicate the soils are not contaminated..

PCB 118 congener has been classified among the twelve toxic PCBs with toxic equivalent of 0.0001 based on 2, 3, 7, 8-TCDD value of 1(EASCA, 2003); therefore the relatively high content of 5.70 ug/kg, 90.40 ug/kg and 4.50 ug/kg, 15.30 ug/kg, and 44.30ug/kg and 45.40ug/kg recorded in main w/shop(topsoil), AMECO (top and subsoil), TV Garage (topsoil), and Dogarawa (top and subsoil) respectively is of great concern.

The maximum permissible limit set for PCB in the environment is 50 mg/kg (or 50 ppm) (UNEP, 1999). Therefore the determined PCBs residues level in all the samples complied with the UNEP set maximum limit in the study.

Table 4.3: Result of PCB Content (µg/kg) in Soil Samples of Transformers Maintenance Workshop in Kaduna

PCB	Main w/shop		Ameco		TV Garage		Mando	
	A	B	A	B	A	B	A	B
PCB101	17.20	1.20	213.40	11.20	40.20	1.90	1.50	0.10
PCB118	5.70	0.40	90.40	4.50	15.30	0.80	1.10	0.10
PCB138	107.10	13.60	1587.80	137.40	123.10	6.70	252.40	43.40
PCB153	84.30	12.00	2962.80	186.00	126.20	6.50	192.30	20.20
PCB180	91.00	14.00	3528.30	301.00	101.30	5.60	303.80	56.30
PCB28	0.45	BDL	4.30	0.10	0.10	BDL	0.03	0.01
PCB52	0.88	0.05	36.90	0.50	6.80	0.30	BDL	BDL
PCB EC7(Sum)	306.63	41.63	8209.50	641.60	413.00	21.90	751.13	120.11

BDL – Below detection limit of 0.01µg/kg

A – Topsoil

B - Subsoil

Table 4.4: Result of PCB Content (µg/kg) of Soil Samples in Zaria

	ABU Samaru		Dogarawa		NARICT	
PCB	**A**	**B**	**A**	**B**	**A**	**B**
PCB101	0.07	0.02	80.20	76.70	BDL	BDL
PCB118	0.04	0.01	44.30	45.40	BDL	BDL
PCB138	0.19	0.05	99.20	107.00	BDL	BDL
PCB153	0.22	0.06	103.70	124.70	BDL	BDL
PCB180	0.17	0.04	60.40	83.30	BDL	BDL
PCB28	0.09	0.01	5.80	7.70	BDL	BDL
PCB52	0.04	0.01	19.60	24.50	BDL	BDL
PCB EC7(Sum)	0.82	0.19	413.20	469.30	BDL	BDL

BDL- Below detection limit of 0.01µg/kg

A – Topsoil

B - Subsoil

4.4 Pearson Correlation (r) of Soil Physicochemical Properties with Total PCB Residue Concentrations

The Pearson correlation (r) of topsoil physicochemical properties with Total PCB residue concentrations show positive correlation in % Clay, % Silt and % TOC and negative correlation in % Sand. The correlation coefficient (r) revealed significant difference ($p<0.05$) in Top soils.

For the Subsoil, there is negative correlation in % Clay and % Silt and positive correlation in % Sand and % TOC. Except % TOC in the Subsoil, % Clay, % Silt and % Sand recorded no significance difference ($p>0.05$).

Table 4.5: Pearson Correlation (r) of Soil Physicochemical Properties with Total PCB Residue Concentrations

Sample	% clay	% silt	% sand	% TOC
Top soil (T PCBs)	0.0774	0.1795	-0.1355	0.3986
Sub soil (T PCBs)	-0.0052	-0.0126	0.0101	0.3243

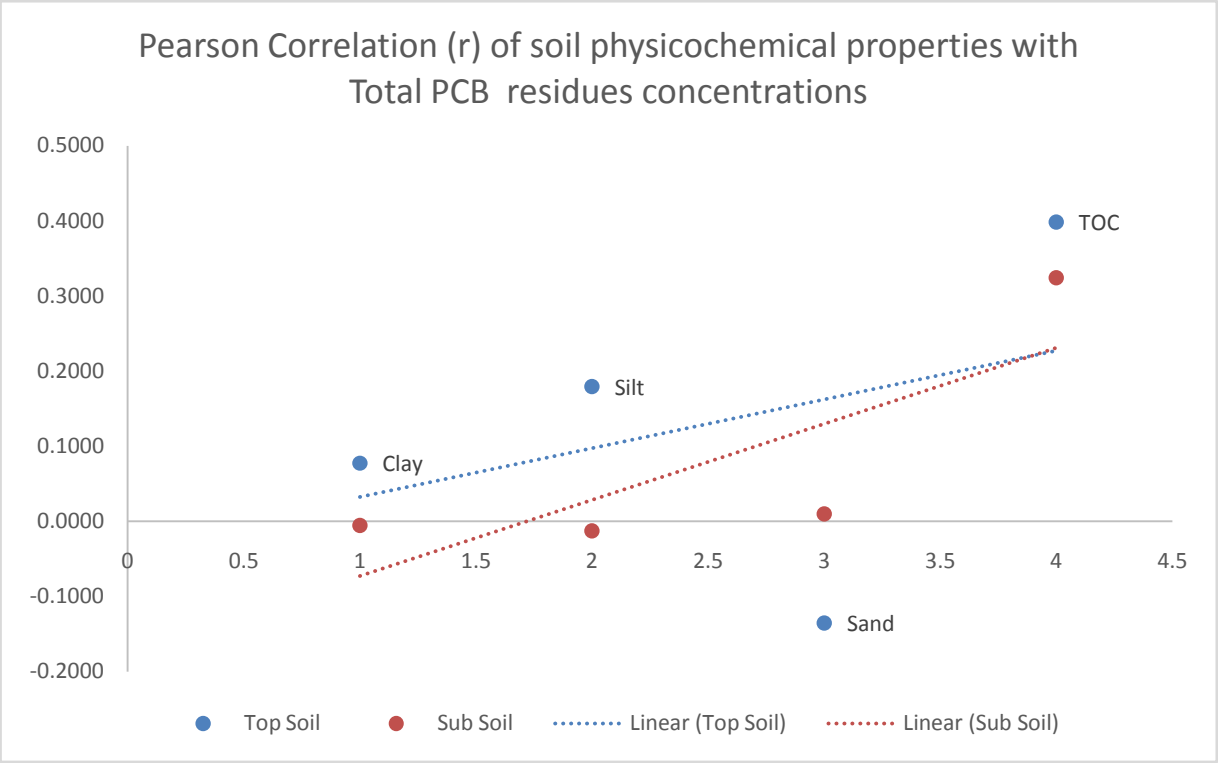


Figure 4 .1 Graph of correlation of physico-chemical properties with TPCB residues

Significant correlation at $P < 0.05$

T PCB = Total PCB

4.5 Percent (%) Hexa- and Hepta-biphenyls in Total PCB Concentrations.

Table 4.6 show the total amount (µg/kg) and percent (%) of hexa- and hepta-chlorinated biphenyls (CB 153, CB 138 and CB 180) in ∑ PCB of soil samples. The results obtained show hexa- and hepta- chlorinated biphenyls are dominant species in all the soil samples, accounting for more than 82% and 63% of PCBs- EC7(sum) in the soil samples from Kaduna and Zaria respectively. While, the total amount (µg/kg) and percent (%) of hexa- and hepta-chlorinated biphenyls (CB 153, CB 138 and CB 180) in ∑ PCB of topsoil and subsoil samples was not detected in a farmland near NARICT.

The soil samples shows increase in % hexa- and hepta- chlorinated biphenyls from top-soil to sub- soil except in AMECO. This finding reveals that higher molecular weight of PCB percolates down the soil which might offer an insight or explanation for ground water contamination.

The wide disparity in % abundance of PCB congeners in each of the soil sample might be governed by congener's properties such as vapour pressure, water solubility and bio degradation and weathering processes.

Table 4.6: Percent (%) of Hexa-and Hepta- biphenyls in Total PCB Concentrations on Topsoil (0-5 cm) and Subsoil (20-30 cm).

Sample	Location	Total amount of PCB (µg/kg)	Total amount of hexa-and hepta-biphenyls(CB 153,138 and 180)	Percent (%) of hexa-and hepta-biphenyls
Mainw/shop	Top soil (A)	306.63	282.40	93
	Sub soil (B)	41.63	39.60	95
Ameco	Top soil(A)	8209.50	8078.90	86
	Sub soil (B)	641.60	624.40	82
TV Garage	Top soil (A)	413.00	350.60	85
	Sub soil (B)	21.90	18.80	87
Mando	Top soil (A)	751.13	748.50	99
	Sub soil (B)	120.11	119.90	94
ABU Samaru	Top soil (A)	0.82	0.58	70
	Sub soil (B)	0.19	0.15	79
Dogarawa	Top soil (A)	413.20	263.30	63
	Sub soil (B)	469.30	315.00	68
NARICT	Top soil(A)	BDL	BDL	-
	Sub soil(B)	BDL	BDL	-

BDL- Below detection limit of 0.01µg/kg

4.6 Relative Response Factor (RRF), in Minutes and Recovery (%) of PCB in Soil Samples

Tables 4.7 and 4.8 below, show the respective sample locations in Kaduna and Zaria, congeners, and the determined mass to charge ratio (M1, M2), theoretical and measured M1/M2, and theoretical and measured relative retention time (RRT) and recoveries (%).

The measured higher value of 2.33 as against 1.55 was at great variance with the theoretical M_1/M_2 value for CB101 in subsoil of ABU Samaru. This might be attributed to gain in charge fragmentation of target ion. Also, the measured lower value of 1.23 as against 1.55 was at variance with the theoretical M_1/M_2 value for CB118 in the same sample. This might be attributed to loss in mass to charge ratio of target ion.

The relative retention times (RRF) for congeners CB28, CB52, CB101 and CB118 in topsoil of AMECO, CB28 and CB138 in topsoil and subsoil of Mando in Table 4.7 are not within the % standard deviation retention time (%S.D RT) of the corresponding PCB congener standard in Table 3.3. This might be attributed to slight interference.

The percent recoveries of the PCB congeners in topsoil and subsoil of main w/shop, topsoil and subsoil of TV Garage and topsoil and subsoil Dogarawa was 0%. While, the PCB congeners were recovered in the range of 83- 145%, 53- 86%, 52- 92% and 71- 143% in topsoil and subsoil of AMECO, topsoil and subsoil of Mando respectively.

Table 4.7: Result of Soil Relative Response Factor (Rrf), in Minutes and Recovery (%) of Samples from Kaduna

Sample Code	PCB Congener	M_1	M_2	M_1/M_2		Retention Time		RRF	% Recovery
				Theoretical	measured	Theoretical	Measured		
Main	CB28	256	258	1.05	1.04	07:07	07:04	1.15	0
s/shop	CB52	290	292	0.78	0.79	07:50	07:46	1.11	0
(topsoil)	CB101	326	328	1.55	1.64	10:02	09:58	1.15	0
	CB118	326	328	1.55	1.63	11:54	11:49	1.12	0
	CB153	360	362	1.24	1.22	12:29	12:25	1.18	0
	CB138	360	362	1.24	1.29	13:21	13:17	1.20	0
	CB180	394	396	1.05	1.04	15:31	15:26	1.17	0
Main	CB28	256	258	-	-	-	-	-	-
w/shop	CB52	290	292	0.78	0.94	07:50	07:45	1.11	0
(subsoil)	CB101	326	328	1.55	1.62	10:02	09:58	1.15	0
	CB118	326	328	1.55	1.71	11:54	11:49	1.12	0
	CB153	360	362	1.24	1.24	12:29	12:25	1.18	0
	CB138	360	362	1.24	1.19	13:21	13:17	1.20	0
	CB180	394	396	1.05	1.07	15:31	15:26	1.17	0
Ameco	CB28	256	258	1.05	0.89	07:07	07:07	0.87	99
(topsoil)	CB52	290	292	0.78	0.69	07:50	07:50	0.95	85
	CB101	326	328	1.55	1.62	10:02	10:02	1.31	142
	CB118	326	328	1.55	1.58	11:54	11:54	1,27	141
	CB153	360	362	1.24	1.24	12:29	12:30	1.35	83
	CB138	360	362	1.24	1.12	13:21	13:20	1.36	97
	CB180	394	396	1.05	0.95	15:31	15:27	1.14	145
Ameco	CB28	256	258	1.05	1.11	07:07	07:11	1.11	86
(subsoil)	CB52	290	292	0.78	0.74	07:50	07:55	1.05	79
	CB101	326	328	1.55	1.62	10:02	10:09	1.18	68
	CB118	326	328	1.55	1.58	11:54	12:02	1.11	62
	CB153	360	362	1.24	1.28	12:29	13:38	1.08	74
	CB138	360	362	1.24	1.34	13:21	13:30	1.27	76
	CB180	394	396	1.05	1.04	15:31	15:40	1.17	53

TV	CB28	256	258	1.05	0.81	07:07	07:07	1.15	0
Garage	CB52	290	292	0.78	0.63	07:50	07:50	1.11	0
(topsoil)	CB101	326	328	1.55	1.60	10:02	10:02	1.15	0
	CB118	326	328	1.55	1.58	11:54	11:54	1.12	0
	CB153	360	362	1.24	1.23	12:29	12:30	1.18	0
	CB138	360	362	1.24	1.21	13:21	13:21	1.20	0
	CB180	394	396	1.05	1.05	15:31	15:29	1.17	0
TV	CB28	256	258	-	-	-	-	-	
Garage	CB52	290	292	0.78	0.73	07:50	07:47	1.11	0
(subsoil)	CB101	326	328	1.55	1.61	10:02	09:58	1.15	0
	CB118	326	328	1.55	1.60	11:54	11:50	1.12	0
	CB153	360	362	1.24	1.21	12:29	12:26	1.18	0
	CB138	360	362	1.24	1.18	13:21	13:17	1.20	0
	CB180	394	396	1.05	0.98	15:31	15:26	1.17	0
Mando	CB28	256	258	1.05	0.95	07:07	07:07	1.24	92
(topsoil)	CB52	290	292	-	-	-	-	-	-
	CB101	326	328	1.55	1.60	10:02	09:57	1.09	63
	CB118	326	328	1.55	1.66	11:54	11:48	1.05	52
	CB153	360	362	1.24	1.34	12:29	12:24	1.13	88
	CB138	360	362	1.24	1.34	13:21	13:15	1.12	79
	CB180	394	396	1.05	1.01	15:31	15:24	1.09	56
Mando	CB28	256	258	1.05	1.03	07:07	07:05	1.24	143
(subsoil)	CB52	290	292	0.78	-	-	-	-	128
	CB101	326	328	1.55	1.30	10:02	10:02	1.09	88
	CB118	326	328	1.55	1.53	11:54	11:50	1.05	71
	CB153	360	362	1.24	1.33	12:29	12:26	1.13	122
	CB138	360	362	1.24	1.33	13:21	13:16	1.12	133
	CB180	394	396	1.05	1.00	15:31	15:26	1.09	94

Table 4.8: Result of RRF in Minutes and Recovery (%) of Soil Samples from Zaria

Sample Code	PCB Congener	M_1	M_2	M_1/M_2		Retention Time		RRF	% Recovery
				Theoretical	measured	Theoretical	Measured		
ABU Samaru (topsoil)	CB28	256	258	1.05	1.06	07:07	07:09	1.11	94
	CB52	290	292	0.78	0.65	07:50	07:52	1.05	80
	CB101	326	328	1.55	1.50	10:02	10:04	1.18	70
	CB118	326	328	1.55	1.43	11:54	11:56	1.11	58
	CB153	360	362	1.24	1.27	12:29	12:32	1.27	81
	CB138	360	362	1.24	1.20	13:21	13:24	1.27	80
	CB180	394	396	1.05	1.11	15:31	15:34	1.17	57
ABU Samaru (subsoil)	CB28	256	258	1.05	1.08	07:07	07:08	1.11	91
	CB52	290	292	0.78	0.74	07:50	07:50	1.05	78
	CB101	326	328	1.55	2.33	10:02	10:02	1.18	71
	CB118	326	328	1.55	1.23	11:54	11:54	1.11	64
	CB153	360	362	1.24	1.17	12:29	12:31	1.27	82
	CB138	360	362	1.24	1.30	13:21	13:22	1.27	79
	CB180	394	396	1.05	1.21	15:31	15:32	1.17	61
Dogara wa (topsoil)	CB28	256	258	1.05	1.05	07:07	07:05	1.15	978
	CB52	290	292	0.78	0.77	07:50	07:48	1.11	982
	CB101	326	328	1.55	1.60	10:02	10:01	1.15	1053
	CB118	326	328	1.55	1.61	11:54	11:53	1.12	1050
	CB153	360	362	1.24	1.23	12:29	12:29	1.18	1020
	CB138	360	362	1.24	1.33	13:21	13:20	1.20	1116
	CB180	394	396	1.05	1.06	15:31	15:29	1.17	1403
Dogara wa (subsoil)	CB28	256	258	1.05	1.08	07:07	07:08	1.11	0
	CB52	290	292	0.78	0.71	07:50	07:51	1.05	0
	CB101	326	328	1.55	1.59	10:02	10:05	1.18	0
	CB118	326	328	1.55	1.59	11:54	11:57	1.11	0
	CB153	360	362	1.24	1..33	12:29	12:34	1.27	0
	CB138	360	362	1.24	1.32	13:21	13:25	1.27	0
	CB180	394	396	1.05	1.06	15:31	15:34	1.17	0

CHAPTER FIVE

DISCUSSION

5.1 Physicochemical Property Analysis

The physical properties of the soil samples from selected sites in Kaduna and Zaria provided an insight into the nature of the soils being investigated (Table 4.1). The soil particle size distribution reveals the textural class of the soils as mainly sandy loam (sand- silt) which is characteristic of most arable lands in the region., while the soil texture in ABU Samaru, and Dogarawa reveals that the soils are loamy sand and sandy clay loam respectively (based on USDA classification). The samples have relatively low organic matter content (OM) with reference to FAO classification of soil organic matter (FAO, 1990). Soil organic matter and clay contents are known to influence the dynamics and behaviour of both inorganic and organic pollutants in soil (Department of Petroleum Resources (DPR), 2002; Huang, 2004; Aiyesanmi and Idowu, 2012). The coefficient of variation (%) is least for %TOC in the samples under investigation. For soils containing more than 15% humus, the pollutant content is considered to be significant (Schumacher, 2002; Leach *et al.*, 2008).

5.2 PCB Congeners' Residue Levels (contents) Analysis

The results obtained for PCB 28, 52, 101, 118, 153, 138 and 180 and their %S.D RT is within the ±20% difference when compared to the mean response factor from the initial calibration (8082A-19). This infers that there were minimal interferences on the RF and RRF values obtained. This could be attributed to adequate sensitivity and effective clean-up of the soil samples prior to analysis.

All the soil samples showed decrease in PCB residue levels from top- soil to sub- soil in each of the site. This may be attributed to the presence of 10-22% clay in the soil (Table 4.2) which influences the dynamics and behaviour of the pollutants (PCBs).

Aiyesanmi and Idowu (2012) reported same findings in their works on organochlorine pesticide residues in soil.

Also, the decrease in PCB residue levels down the soils indicates that PCB are strongly retained in soils due to binding effect despite being subjected to a lot of loss to environmental processes and reaction. Such environmental processes and reactions include volatilization, leaching, solubilisation, bio concentration, biodegradation and runoff that significantly change PCB compositions. Zhang Jian-ying *et al.,* (2007) also reported same findings in their work on PCB residue levels in a farmland in China.

The total PCB congeners residue levels obtained in all the sampled sites were below the benchmark of 50 ppm (50,000 µg/kg) set by member countries under the Stockholm convention (UNEP, 1999).

The results obtained show hexa- and hepta- chlorinated biphenyls are dominant species in all the soil samples, accounting for more than 82% and 63% of PCB- EC7(sum) in the soil samples from Kaduna and Zaria respectively(Table 4.6).

The soil samples show increase in % hexa- and hepta- chlorinated biphenyls from top-soil to sub- soil except in AMECO. This finding reveals that higher molecular weight PCBs percolate down the soil which might offer an insight or explanation for ground water contamination. The finding also agree with the literature report that PCBs are the most widespread environmental pollutants, having been detected in virtually all

environmental media (including ground water) in almost every corner of the globe (UNEP, 1999)

PCB congeners' distribution is governed by congener properties such as vapour pressure, water solubility and bio degradation (Zhang Jian-ying *et al.*, 2007). This, explains the wide disparity in % abundance of PCB congeners in each of the soil sample.

The RRF values obtained in all soil samples compared favourably with %S.D RT of PCB standard in Table 3.3 and are within the ±20% of the theoretical values for isotope ratio of PCB congeners in literature (8082A-19).

The results of recoveries for soil samples showed that the method has suitable range with good reproducibility.

5.3 Correlation Analysis

Correlation analysis was carried out to examine the relationship between the soil physical properties and total quantity of PCB residues obtained in corresponding soil samples matrices.

The results obtained for % clay, %silt, %sand and %TOC for top-soil and sub-soil samples in Table 4.1 are correlated with the total amount of PCB residues in the corresponding samples matrices in Tables 4.3 and 4.4. The correlation analyses are as presented in Table 4.5 and in graph in figure 4.1.

The correlation coefficients (r) revealed significant difference ($p < 0.05$) in top soils and %TOC in subsoil, while there was no significant difference ($p > 0.05$) for % clay, % silt and %sand in sub soils.

Therefore, it can be inferred that the correlations coefficients between the measured physicochemical properties of the soil and the PCB showed positive and negative correlations.

Also, the recorded highest correlation value of %TOC in both the top soil and sub soil suggests that PCB residue levels in the soil are possibly more associated with organic matter content of the soil, which could be attributed to the fact that PCB molecules have high tendency of binding to organic carbons in soil, similar to fats or lipids of animals and plants as reported by Swackhamer *et al.*, (1988).

CHAPTER SIX

6.0 SUMMARY, CONCLUSION AND RECOMMENDATION.

6.1 Summary

The adverse health effects of PCBs biomagnifications in the food chain and its consequences such as: tumours, cancer, liver damage, memory loss, impotence, reproduction and developmental effects along with the prolong shelf life of PCB congeners in the environment necessitated this study.

Samples from top soil (0- 5 cm) and sub soil (20-30 cm) were collected in four (4) and three (3) different locations in Kaduna and Zaria metropolis respectively. The samples were pre- treated prior to physical and chemical analysis.

Aliquots of samples were spiked with labelled PCBs as internal and recovery standards, extracted, clean up with florisil and then analysed by GC-MS in the ion recording mode performed at a mass resolution of 5000.

The soil particles size distribution revealed the textural class of the soils as mainly sandy loam (sand- silt), characteristic of most arable lands in the region except ABU, Samaru-Zaria and Dogarawa that are loamy sand and sandy clay loam soils respectively.

PCB congeners were detected in all the sampled sites in Kaduna and Zaria except for the control sample drawn from a farmland near NARICT, Zaria. However, the values obtained were below the 50,000 µg/kg set by UNEP. The hexa- and hepta- chlorinated biphenyls(CB153, 138 and 180) were the dominant species in all the soil samples, accounting for more than 82% and 63% of PCB- EC7(sum) in the soil samples from Kaduna and Zaria respectively. The % hexa- and hepta- chlorinated biphenyls increase

from top-soil to sub- soil except in AMECO. This finding revealed that higher molecular weight PCBs percolates down the soil which might offer an insight for ground water contamination.

The measured RRFs were within the referenced standard values of PCB congeners used and the Percent (%) Recoveries were good.

The correlation coefficients (r) revealed significant difference ($p < 0.05$) in top soils and %TOC in subsoil, while there was no significant difference ($p > 0.05$) in sub soils.

6.2 **Conclusion**

Spills, decommissioning and poor handling of transformer oils during use and maintenance often results to incidence of PCB residues on the environment which poses serious concerns on the environment and humans.

Physicochemical properties such as soil particle size and total organic carbon (TOC) influence the dynamics of the pollutants (PCBs) in the soil. The decrease in PCB congeners' residue levels down the soils indicates that PCBs are strongly retained in soils due to soil binding effect despite being subjected to a lot of loss in environmental processes and reactions. Therefore, there is correlation ($P < 0.05$) between PCBs concentrations and these physicochemical properties.

PCB congeners detected at varied concentrations include CB 28, CB 52, CB 101, CB 153, CB 138 and CB 180, occurring most frequently with highest ∑ PCB congeners of 8209.50 µg/kg at AMECO, Kaduna, lowest ∑PCB congeners of 0.81µg/kg at Ahmadu Bello University (ABU) main campus, Samaru- Zaria, and absent at farmland near NARICT, Zaria that serve as control sample.

CB 153, CB 138 and CB 180 (hex- and hepta- chlorinated biphenyls) were dominant species in all the soil samples, accounting for more than 82% and 68% of ∑ PCBs in the soil samples from Kaduna and Zaria respectively.

PCB 118 congeners has been classified among the twelve toxic PCBs with toxic equivalent of 0.0001 based on 2, 3, 7, 8-TCDD value of 1; therefore the detection levels of 5.70 ug/kg, 90.40 ug/kg, 4.50 ug/kg, 15.30 ug/kg, and 44.30 ug/kg and 45.40 ug/kg recorded in main workshop (topsoil) , AMECO (topsoil and subsoil), TV Garage(topsoil), and Dogarawa (topsoil and subsoil) in Kaduna and Zaria respectively is of concern.

The determined PCB residue levels in all of the samples comply with the UNEP set maximum limit of 50 ppm (50,000 µg/kg).

These findings provide information on the current and potential health risks of PCB residue levels in soil from these locations.

6.3 Recommendation

This research work on the chemical monitoring of PCB residue levels in soils at the coded sampled sites in Kaduna and Zaria metropolis serves as lead for further studies to link the bio availability of the measured PCBs with their concentrations at target organs and intrinsic toxicity in biota.

The Federal Government is advised to completely phase out the use of PCB as additives to oils in electrical equipment and substitute it with silicone or hydrogenated compounds which are environmentally friendly.

For further studies, the contaminated sites at former PHCN main workshop, Kaduna and Dogarawa transmission substation, Zaria that have their main drain channels discharge into river Kaduna and fadama farmland in Zaria, provide an ideal environment to monitor bioaccumulation and biomarker responses in fish for environmental risk assessment (ERA).

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APPENDIX I

Table 4.1a: Multiple calibrations by replicate determination of RRF values using PCB 54 as recovery standard

Determinant	IUPAC No	1	2	3	Mean	S.D.	Retention Time Standard
Recovery standard	PCB 54	1.00	1.00	1.00	1.00	0.000	0
Internal standard	PCB 28	1.14	1.18	1.23	1.19	0.045	4
Analyte	PCB 28	1.22	1.06	1.04	1.11	0.098	8
Internal standard	PCB 52	0.823	0.835	0.879	0.846	0.029	4
Analyte	PCB 52	1.13	1.01	0.998	1.05	0.072	7
Internal standard	PCB101	0.55	0.57	0.586	0.569	0.018	3
Analyte	PCB101	1.30	1.10	1.15	1.18	0.104	9
Internal standard	PCB118	1.38	1.51	1.58	1.49	0.101	7
Analyte	PCB118	1.17	1.11	1.04	1.11	0.065	6

Table 4.1b: Multiple calibrations by replicate determination of RRF values using PCB 141 as recovery standard

Determinant	IUPAC No	1	2	3	Average	S.D.	Retention Time Standard
Recovery standard	PCB141	1.00	1.00	1.00	1.00	0.00	0
Internal standard	PCB153	1.15	1.22	1.24	1.20	0.047	4
Analyte	PCB153	1.44	1.18	1.20	1.27	0.144	11
Internal standard	PCB138	1.03	1.09	1.11	1.08	0.041	4
Analyte	PCB138	1.42	1.19	1.19	1.27	0.132	10
Internal standard	PCB180	0.534	0.616	0.724	0.625	0.095	15
Analyte	PCB180	1.27	1.13	1.10	1.17	0.09	8

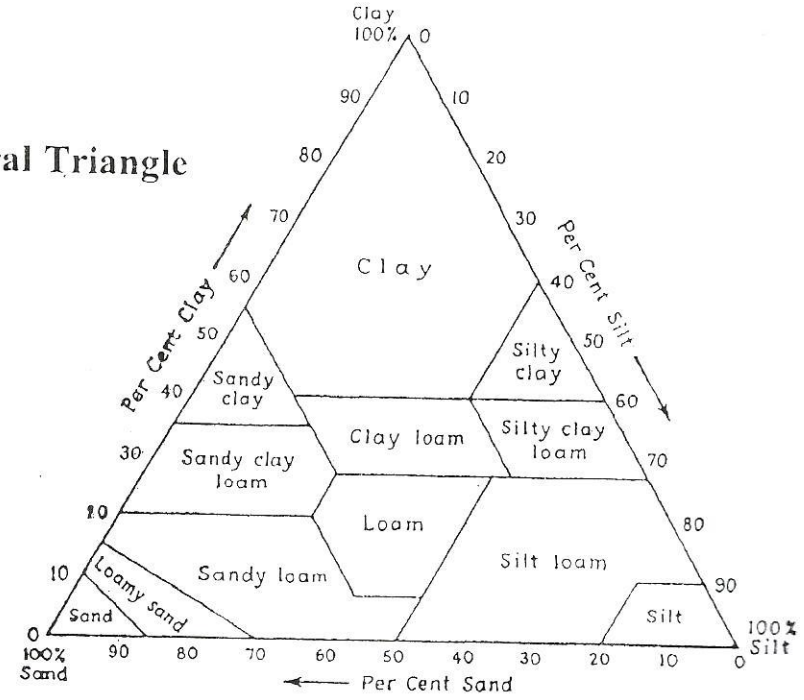
APPENDIX II

PARTICLE SIZE ANALYSIS (HYDROMETER METHOD)

Reporting

Results are reported as percentages of the mineral fraction, % sand, % silt, % clay. Soil texture is based on the USDA textural triangle as presented in the chart below:

Textural Triangle



APPENDIX III

Photographs of Sample locations and sampling:



KI- Independent maintenance transformers workshop, opposite Television Garage, Kaduna



KI- Independent maintenance transformers workshop, opposite Television Garage, Kaduna



K2 - Independent maintenance transformers workshop by AMECO, Kakuri, Kaduna



K2 - Independent maintenance transformers workshop by AMECO, Kakuri, Kaduna



K3- PHCN main maintenance workshop, station market, Kaduna



K3- PHCN main maintenance workshop, station market, Kaduna



K3- PHCN main maintenance workshop, station market, Kaduna



Z1- Transformer substation within ABU, Samaru Zaria (transformer substation near department of Economics)



K4- PHCN Power transmission substation, Mando, Kaduna



Z2- Transmission substation dogarawa, near Kano road overhead bridge, Zaria