DISTRIBUTION OF METALS AND POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN THE FLOODPLAIN SOILS OF THE LOWER REACHES OF RIVER NIGER, NIGERIA

BY

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CERTIFICATION

We certify that this dissertation was done by TESI, Godswill Okeoghene under our supervision. It is adequate in scope and quality in partial fulfillment of the requirement for the award of Doctor of Philosophy (Ph.D) Degree in Analytical Chemistry in the Department of Chemistry, Faculty of Science, Delta State University, Abraka.

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DEDICATION

This work is dedicated to the Most High God and to my uncle Late Rev. (Barr) Moses Ese Mukoro.

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ABSTRACT

The main objective of this study was to investigate the distribution of metals (Pb, Cd, Ni, Zn, Mn, Cr, Fe, Co, Al, Ba and Cu) and USEPA 16 priority polycyclic aromatic hydrocarbons (PAHs) in floodplain soils of the lower reaches of River Niger, Nigeria. Soil samples were collected three months after the Ladgo dam flood disaster of 2012 when the flood water has receded completely and a year after the major flooding. Soil samples were collected from different locations between Asaba and Aboh floodplains of the lower reaches of River Niger at different depths. Some physiochemical properties of the soil profiles were analysed. The concentration of metals was determined using inductively coupled plasma atomic emission spectrometry (ICP-AES) after digestion with aqua regia. The chemical forms of metal in the soil were determined using the BCR sequential chemical extraction method while the measurement of the concentrations of PAHs was performed using gas chromatography equipped with mass spectrometer (GC-MS) after extraction by ultrasonication with hexane/dichloromethane and clean-up. The concentrations of metals were in the range of 0.2-2.8, 1.1-40.5, 0.8-69.0, 1.1-26.3, 0.5-29.4, 1.0-14.4, 18.7-1490, 8.0-147, 5.1-790, 41-32200 and 848-24000 $\mu g\ g^{-1}$ for Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn, Ba, Al, and Fe respectively three months after the major flooding and 0.2-8.5, 0.5-17.4, 1.1-108.9, 0.9-21.4, 1.1-674.0, 0.6-93.6, 0.7-24.1, 0.1-1141, 0.3-177, 100-27270 and 47.0-33050 $\mu g\ g^{-1}$ for Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn, Ba, Al, and Fe respectively a year after the major flooding. The concentration of $\sum 16$ PAHs were in the range of 811.8 to 10651.4 $\mu g\ kg^{-1}$ and 12.2 to 2634 $\mu g\ kg^{-1}$ three months after the major flooding and a year after respectively. The chemical fractionation of metals indicated that residual and Fe-Mn oxides/hydroxides phases were the predominant forms of metals in the soil profiles in the two sampling periods with high potential mobility. The results showed that the concentrations of metals in the soil profiles in both sampling periods were below their respective regulatory control limits except for Cd and Zn in some sites. The potential ecological risk values of metals indicate that these soils fall within the low ecological to moderate ecological risk categories with significant impact from Cd pollution. The non-carcinogenic risks expressed in terms of the hazard index (HI) for the majority of the sites and depth were < 1 for the adults and children scenarios suggesting that the probability of health effects arising from metal contamination in these sites is low. The average cancer risk values were lower than the potentially acceptable target risk value of 10^{-6} set by the US EPA. The Incremental Lifetime Cancer Risk values obtained were higher than the potentially acceptable target risk value of 10^{-6} set by the US EPA signifying a high potential human carcinogenic risk in the study area.

CHAPTER ONE

INTRODUCTION

1.1   Background of the Study

River floodplains are highly dynamic systems resulting from frequent flood inundations. Tinny layers of sediment are deposited in floodplains when flood water recedes. The deposited sediment layers consist of nutrients, soil particles and organic matter, but may also contain significant amounts of contaminants such as polycyclic aromatic hydrocarbons, pesticides, metals, etc (Klok *et al.,* 2008). Floodplain sedimentation and erosion processes are mainly caused by floods which is one of the factor that can control the redistribution of anthropogenic contaminants in the floodplains (Malmon *et al.,* 2002). Therefore, beside atmospheric inputs of pollutants, flooding events strongly influence the contamination of the soils of floodplains.

Polycyclic aromatic hydrocarbons (PAHs) are a large group of more than 100 hundred organic compounds containing of two or more fused aromatic rings organized in linear, angular or cluster formation. PAHs are of environmental and health concern because a number of them have known mutagenic and carcinogenic properties as well as long range transportation capabilities. They tend to be associated with particles and are widely transported by flooding and atmospheric pathways, resulting in elevated concentrations in sediments and soils (Yang *et al.,* 2006). PAHs in the environment originate from two main sources namely natural sources (which include forest fire and volcanic eruption) and anthropogenic sources (such as incomplete complete combustion of fossil fuel, coke production, oil spillage and may other industrial processes) (Yang *et al.,* 2012). Anthropogenic sources are by far the greatest contributor to the global PAHs load. PAHs comprising two or three fused aromatic rings are refer to as low molecular weight PAHs while those consisting of more than three rings are refer

to as high molecular weight PAHs. The high molecular weight PAHs are more recalcitrant and toxic than the low molecular ones (Wenzl *et al.,* 2006). The solubilities of PAHs decrease linearly with increased in molecular weight (Zhang *et al.,* 2006). PAHs are persistent and stable in the environment because of their low aqueous solubility and high soil sorption capabilities (Parrish *et al.,* 2004). The persistent and recalcitrant nature of higher molecular weight PAHs are also related to the high resonance energies due to their dense clouds of π electrons surrounding the aromatic rings (Johnsen *et al.,* 2005).

United States Environmental Protection Agency (US EPA) has listed sixteen PAHs as 'priority pollutants' that need constant monitoring in the environment even though there are hundreds of them. The sixteen PAHs have been further classified as follows; benzo(a)pyrene(BaP)as group 1A (carcinogenic to humans), dibenzo(a,h) anthracene(DahA) group 2A (probably carcinogenic to humans) and naphthalene (NaP), benzo(a)anthracene (BaA), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), chrysene (Chry) and indeno(1,2,3-cd)perylene (IndP) as group 2B (possibly carcinogenic to human), while acenaphthene (Ace), acenaphthylene (Acy), anthracene (Ant), benzo(ghi)perylene (BghiP), fluoranthene (Flt), fluorine (Flu), phenanthrene (Phen) and pyrene (Pyr) are not classified as to their carcinogenicity to humans (Banger *et al.,* 2010).

The presence of metal in humans and environment is of a great environmental and health concern because of their toxicity and persistence in the environment (Li *et al.,* 2008, Ma *et al.,* 2009; Rizo et al. 2011; Li *et al.,* 2012; Sheng et al. 2012). The distribution of metals in soils is influenced by many environmental factors such as parent materials, soil properties and human activities which include industrial production, traffic, farming, and irrigation, released from smelters, waste incinerators, industrial waste water, and from the application of sludge or municipal compost, pesticides, and fertilizers (Iwegbue *et al.,* 2012; Hu *et al.,* 2013). Regardless of their origins in the soil, accumulation of metals can lower soil quality, reduce

crop yield and the quality of agricultural products, thereby resulting negatively impacting the health of humans, animals, and the ecosystem (Nagajyoti *et al.,* 2010).

Metal content of soil is of major significance in relation to soil fertility and nutrient status. Some metals such as Zn, Cu, and Sr are essential for the growth and development of plants and other living organisms. Nevertheless, high concentrations of these metals in living organisms might detrimental. Other metals, which are not essential such as Pb or Cr, may be tolerated by the ecosystem in low concentration, but become injurious in higher concentrations (Machender *et al.,* 2011). The availability of metals in soil is controlled by factors such as pH, temperature, redox potential, cation exchange capacity, competition with other metal ions, component and quality of the soil (Moon et al. 2000; Mapanda et al. 2005; Skordas and Kelepertsis 2005). Soil acts as a sink for contaminants and natural buffer for transportation and distribution of chemical materials and elements in the atmosphere, hydrosphere and biomass. Thus, soil is considered as the most significant part of biosphere (Benhaddya and Hadjel 2014). Thus it is important to quantify the concentrations and identify the sources and spatial variability of pollutants in the soils.

1.2   Statement of the Problem

Rivers Benue and Niger are transnational rivers. The anthropogenic activities in the upstream countries greatly influence the contaminant status of the lower reaches of these rivers especially that of the River Niger in which all the content are deposited. In 2012, an extreme flooding event took place between the months of September and October in Nigeria due to the release of uncontrollable volumes of water from the Ladgo dam in Cameroon, coupled with excessive rainfall into the River Niger. These events pushed the River Niger over its banks and submerged hundreds of kilometres of land including communities, dumpsites, industries, oil installations and others. During flooding, pollutants such as metals and polycyclic aromatic hydrocarbons present in various chemical forms are transferred from water to the area covered

by flood. Thus, flood events represent an important contamination pathway for floodplain soils (Kruger *et al.*, 2005).

However, there are few published data around the world and Nigeria in particular on the concentrations of metals (Bojakowska and Sokolowska, 1996; Albering et al., 1999; Middlekoop, 2000; Saint-Laurent et al., 2001; Benson, 2006; Ahsan et al., 2008; Shasheen et al., 2013; Ande et al., 2014; Rosolen et al., 2015) and PAHs (Gotch et al., 2001; Witter *et al.,* 2003; Hilscherova *et al.,* 2007; Pies et al., 2007; Sartori et al., 2010) in floodplain soils. A survey of the literature indicates that there are no published data on the distribution of metals and PAHs in the soils of the floodplain of the lower reaches of the River Niger. Against this background is this research work instituted.

1.3   Objectives of the Study

The main objective of this study was to investigate the distribution of metals and polycyclic aromatic hydrocarbons (PAHs) in floodplain soils of the lower reaches of River Niger. The specific objectives of the study are to:

i.   determine the concentrations and forms of metals such as Pb, Cd, Ni, Zn, Mn, Cr, Fe, Co, Al, Ba and Cu in the floodplain soils of lower reaches of River Niger.

ii.   evaluate the chemical fractionation patterns of the metals in the soils of the floodplain.

iii.   evaluate the extent of contamination/pollution of the floodplain soils using different pollution indices.

iv.   identify the sources of metals and PAHs in the floodplain soils using multivariate statistics.

v.   evaluate human and ecological risk of metals and PAHs in soils of the floodplain soils of lower reaches of River Niger.

vi.   determine the concentrations and profiles of the 16 United State Environmental Protection Agency (USEPA) priority PAHs in the soils of the floodplain of the lower reaches of River Niger.

vii.   examine the changes in the composition patterns with respect to the two flooding regimes.

1.4   Significance of the Study

The knowledge of concentrations and forms of metals and polycyclic aromatic hydrocarbons in soils provide information on the sources of these contaminants, bioavailability, human and ecological risks of exposure to these contaminants. Such information is useful for pollution history, local environmental quality and risk management, establishing pollution control measures and guidance for remediation/cleanup and for environmental forensic studies.

1.5   Scope of this study

This study is restricted to the distribution and chemical forms of metals (Cd, Pb, Ni, Cr, Co, Cu, Ba, Fe, Mn, Zn and Al) and the USEPA 16 priorities PAHs in the floodplain soils of the lower reaches of the River Niger.

CHAPTER TWO

REVIEW OF RELEVANT LITERATURES

2.1   Sources of metals in the environment

Metals are defined as any element with a silvery luster, and have the ability to conduct heat and electricity (Issa, 2008). Metals are classified into essential and non-essential metals. Essential metals are those that are required by humans and other living organisms in little amounts for proper functioning of life processes e.g. Zn, Fe, Co, Mo, Ni, etc (Orhue and Frank, 2011). Inadequate supply of essential metals in living organism results in retarded growth and inability to complete life cycle while excess of these metals on the other hand causes toxic effects and health (Wuana and Okieimen, 2011). The non-essential can be tolerated by humans and other organisms at very low concentrations but at higher concentrations they become toxic and pose health problems e.g. As, Ag, Cd, Hg, Pb, etc (Orhue and Frank, 2011)

The sources of metals in the environment are both natural and anthropogenic. Metals occur naturally in the soil environment from the pedogenetic processes of weathering of parent materials and volcanic eruption (Kabata-Pendias and Pendias, 2001; Orhue and Frank, 2011; Wuana and Okieimen, 2011; Okoro *et al.,* 2012). Anthropogenic sources arises from industrial activities such as mining, smelting of metallic and ferrous ores, electroplating, traffic emissions, energy and fuel production, fertilizer and pesticides application and waste disposal (Liu *et al.,* 2007; Morton-Bermea *et al.,* 2009; Sherene, 2010; Wei and Yang, 2010; Orhue and frank, 2011; Okoro *et al.,* 2012; Abbas *et al.,* 2014).

Metal pollution in urban soils and agricultural soils has serious consequence on the health of humans and the surrounding ecosystem. The rate at which metals are generated through anthropogenic cycles are more rapid relative to natural ones.

Metals are present in one of four forms in the soil. These are mineral, organic, sorbed or dissolved forms. Sorbed metals represent the third largest pool and are generally very tightly

bond to soil surfaces (Issa, 2008). The movement of metals in soils is influenced by physical and chemical characteristics of each metal and other environmental factors. The most important environmental factors influencing the migration of metals in soils are pH, soil type, total organic content, redox potential, cation exchange capacity (Moon et al. 2000; Mapanda et al. 2005; Skordas and Kelepertsis 2005; Issa, 2008).

2.2   Fate and/or behaviour of metals in soils and environment

Metals once release into the environment are distributed among the various environmental matrices such as water, soil, suspended solids and biota. The behavior of metals in the environment is governed by dilution, dispersion, sedimentation, sorption and desorption reactions with different soil constituents (Appel and Ma, 2002; Issa, 2008; Orhue and Frank, 2011). The fate of metals in soil is controlled by soil pH, soil composition, cation release from contamination source materials, cation exchange, adsorption onto surfaces of minerals, soil organic matter and precipitation of secondary minerals (Manceau *et al.,* 2000). In the environment, metals undergo bioaccumulation, solubility and mobility, bioavailability and toxicity.

2.2.1   Bioaccumulation

Bioaccumulation is the phenomenon in which the concentration of a chemical in a biological organism becomes higher relative to the environmental concentration (Kampa and Castanas, 2008). The presence of elevated concentration of metals in soil enhances the uptake of metals thereby leading to accumulation in plant community (Gimmler *et al.,* 2002; Issa, 2008). However, metals uptake by plants can be hindered by complex formation between nutrient and metal ions in soils, with high nutrient levels (Gothberg *et al.,* 2004). One of the parameters used to evaluate the possible accumulation of metals through food ingestion is the soil to plant transfer factor (El-ghawi *et al.,* 2005). Plants grown on soils contaminated with

metals have higher concentrations of metals than those grown on uncontaminated soil (Nabulo, 2006; Issa, 2008).

Direct and indirect accumulation of metals in soil and through plants respectively enter the food chains and cause detrimental effects to herbivores, carnivores and humans (Issa, 2008). Metals are continuously released into the soils through various anthropogenic sources thereby causing accumulation in agricultural soils. This pose a threat to food safety issues and potential health risks as a result of soil to plant transfer of metals (Khan, 2005).

2.2.2 Solubility

Metal mobility is related to metal solubility, which is further governed by adsorption-desorption processes in soils (Ma and Dong, 2004). Parameters which significantly affect the movement of metals in soils include pH, total organic matter and ionic strength. The mobility of metals is low at a neutral to slightly alkaline pH condition while the retention of metals in soil is high with increase pH (Sherene, 2010). Organic matter is significant for the sorption of metals by soils hence decreasing their movement and availability. Formation of complexes by organic matter and metals after ionization of weak acid groups have been associated with higher solubility of metals in soil solution at alkaline pH. For example, it was reported that Cd is readily mobile in sandy loam soils but organic matter in the surface layer will act as a sink for Cd and will slow the mobility (Carrillo et al., 2000). Naidu and Harler (1998) reported that, the function of organic acids in the movement of Cd is very important since modern agriculture involves minimum tillage particles that recycle plant residues. Organic ligands play an important role in controlling metal solubility during complexation of metals.

The amount of metals adsorbed decreases with increasing ionic strength for minerals with permanent surface charge density (Sherene, 2010). Casagrande et al. (2001) reported that regardless of pH, Zn adsorption was always superior to the most diluted $CaCl_2$ solution used. Soil texture reflects the particle size distribution of the soil and thus the content of fine particles

like oxides and clay. These components are important adsorption media of metals in soil. The clay soil holds higher concentrations of metals in comparison with sandy soil (Sherene, 2010).

2.2.3 Bioavailability

The bioavailability of metals in soils is a function of the biological parameters and physicochemical properties that is their ions and compounds. The bioavailability of metals in natural systems is controlled mainly by adsorption-desorption reactions at the particle solution interface (Issa, 2008). The bioavailability of metals such as Co, Ni, Cu and Zn decrease in horizon B of soils with clay illuviation due to their enhanced adsorption capacity. As a result of improved buffering capacity of calcerous soil horizons, metals availability is reduced in these soil horizons (SIPOS, 2004). Soil pH also influence the bioavailability of metals such that at low pH many metals become less available to plants while others become toxic to plants (Hollier and Reid, 2005).

2.2.4 Toxicity

Metals are present in agricultural soils and cannot be degraded. They also have deleterious effects on plants and human health because of their overall toxicity and behaviour. Both pH and redox potential affect the toxicity of metals by limiting their availability (Issa, 2008). High concentrations of metals in soils is toxic for organisms such as bacteria, fungi and higher organisms. Short term and long term effects of pollution varies depending on metal and soil characteristics (Nemeth and Kadar, 2005). Metal bonding and leaching increases bioavailability and toxicity (Mathe-Gaspar *et al.,* 2005). Increase in acidity of soil leads to increase in the levels of aluminium ions in the soil solution which invariably become toxic to plant roots. Most of the serious consequences of the high metals concentrations is their negative effect on many of the decomposers that live in the soil (Elvingson and Agren, 2004). Metals

such as Hg, Se, As and Cr can be transformed to other oxidation states in soil thereby influencing their toxicity (Issa, 2008).

2.3   Toxic and health effects of investigated metals

The health effects of metals pollution on humans ranged from morphological abnormalities, neurophysical disturbances, gene mutation among others. The presence of metals affects enzymes and hormonal activities as well as growth and mortality rate (Idris *et al.,* 2007; Okoro *et al.,* 2012).

2.3.1   Cadmium

The sources of cadmium mining, smelting, refining, paint pigments, electroplating, manufacturing of batteries and plastic (Abbas *et al.,* 2014). It had also be found in insecticides, fungicides, sludge and commercial fertilizers that use cadmium compounds (Okoro *et al.,* 2003). Cadmium has no beneficial biological importance in the human body, hence it is a pollutant of global concern (European Commission, 2002). Cadmium is toxic even at small concentration and is attributed to renal dysfunction, cadmium pneumonitis, bone defects, increased blood pressure and myocardic dysfunction (WHO, 2001; Singh *et al.,* 2006; Duruibe *et al.,* 2007). There is also some evidence that cadmium can replace zinc in zinc containing enzymes which causes Itai-Itai disease with lethal consequences (European Commission, 2002). In addition, Cadmium has carcinogenic, mutagenic and teratogenic effects in human health (Vukojevic *et al.,* 2006). Cadmium affect reproduction in both humans and animals because it interfere with the rate of ovarian and placental steroidogenesis and as such it was included among the endocrine disruptors (Chadrese *et al.,* 2006). Severe exposure to cadmium may result in pulmonary odema and death. Pulmonary effects such as emphysema, bronchiolitis and alveolitis may occur due to exposure to sub chronic dose of cadmium and its compounds (Young, 2005; Duruibe *et al.,* 2007).

2.3.2 Chromium

Major sources of chromium contamination include releases from electroplating processes, pigment for photography, pyrotechnics, plastics, textile, dyeing, paints and steel fabrication and the disposal of chromium containing wastes (Wuana and Okiemen, 2011; Gadd, 2010; Abbas *et al.,* 2014). Chromium is usually present in two forms; the hexavalent chromium which is the most form and extremely toxic and the trivalent chromium which is non-toxic. Exposure to chromium (VI) overtime can be hazardous to human health. Inhaling or ingesting chromium (VI) overtime can cause nose bleeding, ulcers, convulsion, kidney and liver damage, cancer, gene mutation and teratogenicity (Gadd, 2010; Abbas *et al.,* 2014). Chromium is also associated with allergic dermatitis in humans (Scragg, 2006; Wuana and Okieimen, 2011).

2.3.3 Zinc

Zinc occurs naturally in soil, however, the concentration of Zn is on the increase as a result of anthropogenic activities. Anthropogenic sources of Zn include industrial activities such as mining, refineries, brass manufacturing and plumping (Manohar *et al.,* 2002; Wuana and Okieimen, 2011; Abbas *et al.,* 2014). Excessive intake of Zn may lead to vomiting, dehydration, abdominal pains, nausea, lethargy, "metal-fume fever", gastrointestinal distress (Manohar *et al.,* 2002; Okoro *et al.,* 2012). Ingestion of higher concentration of Zn has also be associated with bloody urine, icterus (yellow mucus membrane), liver failure, kidney failure and anaemia (Duruibe *et al.,* 2007). As a result of high accumulation of Zn in soils, there is excessive Zn uptake by plants. Zn alters the various activities taking place in soil because it influences the activities of microorganisms and earthworms negatively and as such slow down the breaking down of organic matter (Greany, 2005; Wuana and Okieimen, 2011).

2.3.4 Lead

Lead is one of the earliest metals recognized and used by humans. It has a long history of beneficial use to mankind but now has been recognized as toxic and posing a widespread threat to humans and wildlife (Rashed, 2003). The major sources of Pb include mining, paint pigments, electroplating, manufacturing of batteries and burning of coals (Godt *et al.,* 2007). Lead has a lot of toxic effects which include injury to the peripheral nervous system, dysfunctions in the kidney, joints and reproductive systems, teratogenicity, inhibition of the synthesis of haemoglobin, cardiovascular system and acute and chronic damage to the central nervous system and (Ogwuegbu and Muhanga, 2005; Duruibe *et al.,* 2007). Other effects are loss of appetite, anorexia, liver damage, gastrointestinal damage, anemia, and malaise (Godt et al., 2007). Exposure of children to lead results in hyperactivity and mental deterioration, impaired development, lower intelligent quotient and shortened attention span (National Safety Council, 2009; Wuana and Okieimen, 2011). Lead absorption in the body is enhanced by Ca and Zn deficiencies promotes lead absorption in the body even as the acute and chronic effects of lead bring about psychosis (Duruibe *et al.,* 2007). In many cases, the effect of lead is due to its acting as an anti-nutrient, hindering the utilization of Zn, Mg, vitamin B1 etc.

2.3.5 Manganese

Manganese is an essential trace metal that is umbiquitous in the environment. This implies that manganese is not only important for humans' survival, but it is also toxic when its concentrations in human body is in excess. The health effects of Mn occurs mostly in the respiratory tract and in the brain. Signs of Mn poisoning includes forgetfulness, hallucinations, and damage to the nerve. It has also be reported that Mn can cause lung embolism, Parkinson disease, and bronchitis. It may cause impotency in men due to long term exposure (ATSDR, 2006). Manganese alters the absorption of dietary iron when in excess thereby resulting in iron deficiency anemia for long-term exposure to excess levels. High ingestion of Mn reduced

copper metallo-enzymes activity (Blaurock-Busch, 2009). For animals, manganese is an all-important element of over thirty-six enzymes that are utilized for the carbohydrate, protein and fat metabolism. With creatures that feed too little manganese, interference of normal development, bone formation and reproduction will come about. For some animals the lethal dose is rather depressed, which implies they possess little opportunity to make it even at smaller doses of manganese when these exceed the essential dose. Manganese substances can cause lung, liver and vascular disturbances, decline in blood pressure, failure in development of animal fetuses and brain damage (Lenntech, 2008). Manganese ions moved to the leaves after taken up from soils and can result in toxicity and deficiency symptoms in plants. Highly toxic concentrations of manganese in soils can cause swelling of cell walls, withering of leaves and brown spots on leaves (Anonymous, 2004).

2.3.6   Cobalt

Cobalt is distributed widely in the environment and this increased humans' exposure to cobalt via inhalation of air, dermal contact and ingestion. Cobalt is not readily available in the environment, but when cobalt particles are not bound to soil or sediment particles, the consumption by plants and animals is high and plants and animals may accumulate it. Cobalt is beneficial for humans because it is a component of vitamin B12, which is indispensable for human health. But, excess concentrations of cobalt may be deleterious to the health humans. When we ingest high concentration of cobalt, we experience lung effects, such as asthma and pneumonia (ATSDR, 2006). Cobalt and its compounds has been listed within the group 2B as agents which are possibly carcinogenic to humans by the International Agency for Research on Cancer (IARC). In plants, only very high concentrations cause abnormalities (Vukojevic *et al.,* 2006).

2.3.7 Copper

Copper is the third most utilised metals in the world (Van Commodities Inc., 2011). Copper originates from printing operations, copper polishing, plating and painting (Abbas *et al.,* 2014). Copper occurs in drinking water from copper pipes as well as from additives designed to control algal growth (Wuana and Okieimen, 2011; Ok\oro *et al.,* 2012). It is an essential metal needed by plant, animals and humans. Copper assist in the manufacture of blood haemoglobin in humans and in seed production, resistance to diseases and control of water in plants. High concentrations of Cu results in anaemia, liver and kidney damage, dizziness and diarrhea (Wuana and Okieimen, 2011; Okoro *et al.,* 2012).

2.3.8 Nickel

Nickel is present in the environment in small amounts but Ni can be hazardous when the maximum tolerable limits are exceeded (Wuana and Okieimen, 2011). The sources of nickel in the environment are metal plating industries, combustion of fossil fuels, nickel mining, electroplating, porcelain enameling, non-ferrous metal and paint formulation (Khodadoust *et al.,* 2004; Abbas *et al.,* 2014). Nickel toxicity include cancer of the lungs, chronic bronchitis, reduced lung function and dermatitis (Abbas *et al.,* 2014). Headache, dizziness, nausea, and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness all results from acute ingestion of Ni (Kadirvelu, 2000).

2.3.9 Aluminium

Aluminium is the third most plentiful element in the earth crust. It is accessible to humans through nasal sprays, food additives, buffered aspirin astringents, antacids, and antiperspirants from drinking water (Bakare-Odunola, 2005; Okoro *et al.,* 2012). Aluminium causes senility and presenile dementia (Bakare-Odunola, 2005). According to Okoro et al.

(2012) Aluminium has been linked with developing Alzheimer's and Parkison's diseases as researchers found what they considered to be significant amounts of aluminium in the brain tissue of Alzheimer's patients.

2.4   Distribution of Metals in floodplain soils

Bojakowska and Sokolowska (1996) evaluated the distribution of metals in Bystrzyica River floodplain and reported that the concentration of Cd, Pb, Ni, Cu, Co, Zn, Ba and Mn ranged from <0.5-40.6, 10.0-91.0, 6.0-45.0, 6.0-45.0, 6.0-74.0, 7.0-83.0, 2.0-32.0, 27.0-488, and 23.0-111 mg kg^{-1} respectively. The concentration of metals in River Meuse floodplain was determined by Albering et al. (1999). They found out that the concentrations of metals ranged from 5.6-14.0, 157-326, 62-116, and 705-1239 mg kg^{-1} for Cd, Pb, Cu, and Co respectively.

Middlekoop (2000) determined the concentration of metals in Rhine and Meuse floodplain soils and reported concentrations in the ranged of 70-490, 30-130 and 170-1450 mg kg^{-1} for Pb, Cu and Zn respectively. Ali et al. (2003) investigated the concentration of metals in floodplain soils in Bangladesh and found concentrations in the ranged of 14.3-31.0, 61-176, 14-134, 8.7-65.7 and 27.8-138 mg kg^{-1} for Pb, Cr, Ni, Cu and Zn respectively.

Korfali and Davies (2004) carried out a comparative study on the composition of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) of bed sediments with the adjacent flood soils of River Nahr-Ibrahim, Lebanon. The results revealed that the concentrations of Cd, Cr, Cu and Pb in the upstream sediments were higher than that of soil. The authors suggested that sources of metals in the bed sediments were due to direct discharge of these metals into river channel.

Schroder et al. (2005) compared mechanistic geochemical modelling with a statistical approach in the partitioning of metals in embanked floodplain soils of the Rivers Rhine and Meuse. The authors measured the concentrations of As, Cd, Cr, Cu, Ni, Pb and Zn in 194 soil samples at 133 sites distributed in the Dutch part of the Rhine and Meuse river systems. The

authors found a strong correlation between heavy metal contamination and organic matter content, which was almost identical for both river systems.

Abderahman and Abu-Rukah (2006) investigated metal concentrations in Zarga River basin, Jordan and found that the concentration of Pb, Cr, Ni, Cu, Co and Zn ranged from 61-112, 62-120, 66-100, 33-61, 35-71 and 78-140 mg kg^{-1} respectively.

Metal distribution in Cross River floodplain soils was investigated by Benson (2006). The author found concentrations in the ranged of 21.39-22.60 mg kg^{-1} for Pb, 10.4-22.38 mg kg^{-1} for Ni, 14.09-22.61 mg kg^{-1} for Cu, 5.09-11.52 mg kg^{-1} for Co and 33.6-42.92 mg kg^{-1} for Mn.

Krishna and Govil (2008) investigated the levels of metals in soils in the vicinity of Manali industrial area in Chennai, Southern India. The authors reported high concentrations ranging from 149.8-418.0 mg/kg for Cr, 22.4-372.0 mg/kg for Cu, 11.8-78.8 mg/kg for Ni, 63.5-213.6 mg/kg for Zn and 2.3-15.3 mg/kg for Mo while the levels of other metals were comparable to background levels.

The distribution of metals in Faridpur floodplain soils was investigated by Ahsan et al. (2008). They reported metal concentrations in the range of 0.12-0.17, 24.32-33.95, 73.5-108.14, 42.21-61.01, 38.20-63.35, 14.60-22.09, 82.69-117.36 and 374.09-575.17 mg kg^{-1} for Cd, Pb, Cr, Ni, Cu, Co, Zn and Mn respectively. Ahsan et al. (2008) also investigated metal concentrations in Dhamrai floodplain soils in Bangladesh and found that the concentration of metals ranged from 0.11-0.22 mg kg^{-1} for Cd, 23.22-26.61 mg kg^{-1} for Pb, 45.60-84.38 mg kg^{-1} for Cr, 43.80-47.94 mg kg^{-1} for Ni, 29.61-33.71 mg kg^{-1} for Cu, 15.41-17.26 mg kg^{-1} for Co, 78.88-125.87 mg kg^{-1} for Zn and 471.09-655.24 mg kg^{-1} for Mn.

Rogan et al. (2010) reported that the level of contamination of paddy soil by metals in Kacani field (Macedonia) was in the order of Pb>As>Cd>Zn>Cu however, their mobility potential was in the order of As<Cu<Pb<Zn<Cd.

Wu and Zhang (2010) in their survey of metals in paddy soils of the modern agricultural zone in southeastern China found that the total concentrations of metals in these soils ranged from 15.30 to 78.40 mg kg-1 for Cu, 20.10 to 41.40 mg kg-1 for Pb, 54.98 to 224.4 mg kg-1 for Zn, 0.04 to 0.24 mg kg-1 for CD, 54.90 to 197.1 mg kg-1 for Cr, 0.03 to 0.61 mg kg-1 for Hg, 3.44 to 15.28 mg kg-1 for As, and 7.17 to 19.00 mg kg-1 for Co.

Ibraginov et al. (2010) determined the concentration of metals in Odra River floodplain (Poland) and found out the concentration of metals ranged from 1.4-7.0 mgkg^{-1}, 24.5-242, 5.4-81, 9.2-60, 23.6-1006 mg kg^{-1} for Cd, Pb, Cr, Ni and Zn respectively.

Germershausen (2010) investigated the ecological impacts of land use on the heavy metal and nutrient budget in the floodplain of the Innerste between Langelsheim and Ruthe. The results suggest that the mobility of heavy metals in the soils of the study area is low and also showed that most Cu, Zn, Pb and Cd total contents were significantly above average in the floodplain, and decreased from south to north within the study area.

Karanlik et al. (2011) reported that the concentration of Cd, Pb, Ni and Co in Amik floodplain soils in Turkey ranged from 0.02-0.65, 0.60-20.94, 46.6-3965.32 and 0.4-74.0 mg kg^{-1} respectively.

Tidball (2012) investigated geochemical dispersion in soils on the Alamosa River floodplain, San Luis Valley, Colorado. Soil samples were collected in 1993 from 762 sites in the south western part of the San Luis Valley encompassing the Alamosa River floodplain and adjacent drainages between the Conejos River and the Rio Grande. The results showed that the concentrations of heavy metals ranged from 4.9-26 mg/kg for As, 7-140 mg/kg for Cu, <0.02-0.77 mg/kg for Hg, 2.8-380 mg/kg for Pb, <0.1-2.9 mg/kg for Se and 40-590 mg/kg for Zn.

Zovko et al. (2012) looked into the spatial variability of metals in the floodplain soils of the Neretva River valley in Croatia. The authors found that except Cu, metal concentrations were lower than the threshold value set by the Croatian government regulation.

Metal concentrations in the floodplain soils of Harz Mountains in Germany was assessed by Gabler and Schneider (2013). The authors found metal concentrations in the range of <0.2–200 mg kg^{-1} for Cd, <10–30,000 mg kg^{-1} for Pb, 7–10,000 mg kg^{-1} for Cu and 50–55,000 mg kg^{-1} for Zn.

Saint-Laurent et al. (2013) reported metal concentrations in the ranged of <0.5-0.9, 5.0-490, <2.0-55, <1.0-120, <2.0-46 and 38.0-310 mg kg^{-1} for Cd, Pb, Cr, Ni, Cu and Zn respectively.

Shasheen et al. (2013) determined the concentration of Cd, Pb, Ni Cu and Zn in River Nile floodplain soils in Egypt. The authors reported that the average concentrations for these metals were 1.7, 27.5, 71.6, 65.0 and 90.0 mg kg^{-1} respectively. Shasheen et al.(2013) also reported average concentrations of 7.9, 100 66.6, 168 and 861 mg kg^{-1} for Cd, Pb, Ni, Cu and Zn respectively in Elbe River floodplains in Germany. The authors also reported average concentrations of 1.5, 21.5, 232, 29.7 and 4.3 for Cd, Pb, Ni, Cu and Zn respectively for Penios floodplain soils in Greece.

Ande et al. (2014) investigated metal concentrations in River Ona floodplain in Ibadan, Southwest, Nigeria and found that the concentrations of metals ranged from nd-0.01 mg kg^{-1}, for Cd, 33-40 mg kg^{-1} for Pb, 0.21-1.21 mg kg^{-1} for Cr, 4.57-17.87 mg kg^{-1} for Cu, 3.09-263.5 mg kg^{-1} for Zn, 7.9-34.6 mg kg^{-1} for Mn and 86.2-181 mg kg^{-1} for Fe.

Shumo et al. (2014) reported concentrations in the ranged of 0.48-2.58 for Cd, 6.85-11.8 mg kg^{-1} for Pb, 48.93-110.86 mg kg^{-1} for Cr, 35.28-48.93 mg kg^{-1} for Ni, 46.93-63.77 mg kg^{-1} for Cu, 25.03-37.35 mg kg^{-1} for Co, 11.40-121.42 mg kg^{-1} for Zn, 896.48-1337 mg kg^{-1} for Mn and 54.21-72.42 mg kg^{-1} for Fe in the River Nile floodplain soils in Sudan. Also, Shumo et al. (2014) determined the concentrations of metals in the White Nile and Blue Nile floodplain soils in Sudan and found that the concentration of metals in the White Nile ranged from 1.97-2.02, 10.03-12.46, 41.45-85.19, 0.29-36.23, 29.59-37.29, 16.03-20.51, 67.45-72.15, 571.25-

632.19 and 34.08-42.79 mg kg^{-1} for Cd, Pb, Cr, Ni, Cu, Co, Zn, Mn and Fe respectively while the concentration of metals in the Blue Nile floodplain ranged from 0.97-1.51, 4.19-7.91, 43.63-82.76, 19.67-48.16, 45.21-51.10, 25.0-34.36, 67.19-101.17, 911.75-1048.81 and 54.14-62.38 mg kg^{-1} for Cd, Pb, Cr, Ni, Cu, Co, Zn, Mn and Fe respectively.

The distribution of metals in the floodplain soils of Cerrado Biome floodplains in Brazil was investigated by Roselen et al. (2015). The authors reported that the concentration of metals ranged from nd-50.3 for Pb, 43.6-145.6 mg kg^{-1} for Cr, 7.0-17.3 mg kg^{-1} for Ni, 30.6-88.0 mg kg^{-1} for Cu, 5.0-36.3 mg kg^{-1} for Zn and 9.0-35.0 mg kg^{-1} for Ba.

2.5   Chemical speciation and speciation analysis of metals

There have been confusion in the use of the terms "speciation" and "speciation analysis" by researchers in the field of environmental and analytical chemistry, biology, geochemistry among others. They find it difficult to differentiate between the two concepts and thus they use them interchangeably. Many researchers have defined speciation to reflect their field. Speciation according to the International Union of Pure and Applied Chemistry (IUPAC) is the distribution of an element amongst defined chemical species as to electronic or oxidation state, complex or molecular structure and isotopic composition. While speciation analysis is an analytical activity of identifying and/or assessing the quantities of one or more individual chemical species or patterns in an environmental sample or a biosystem (Templeton et al., 2000). A good comprehension of environment-organism interactions can be gotten from the distribution patterns and bioavailability of metals in the environment. Therefore, bioactivity and bioavailability of metals is a function of their chemical co-existing forms and thus their speciation (Benson *et al.,* 2013).

2.5.1   Analytical significance of metal speciation analysis

Analytical measurements of metals expressed as total concentrations in environmental and biological samples are insufficient to assess the environmental impact of polluted soils and

sediments since metals may exist in different chemical forms and only a fraction of the total metal can be remobilized (Ramirez *et al.,* 2005; Benson *et al.,* 2013). According to Benson et al. (2013), one major importance of speciation analysis is the qualitative and quantitative sign it has given to individual metal forms, which could be used in the evaluating the index of metal toxicity.

Metal distribution, mobility, bioavailability, reactivity and toxicity in environmental matrices depends strongly on the mineralogical and chemical forms in which they are present (Baeyens *et al.,* 2003; Okoro *et al.,* 2012). Thus, it is important to find out the chemical forms of metals in environmental matrices employing speciation analysis.

Speciation analysis provides additional information on collected results through characterizing some of the most important chemical species of metals with a view to understand the transformations between species that are likely to occur and to deduce from such informations the associated environmental and health effects (Benson *et al.,* 2013). Likewise, metal speciation analysis is a necessary tool in analytical and environmental chemistry for predicting the fate of metals in aquatic ecosystems and designing effective and efficient methods for water quality monitoring.

2.5.2   Techniques for the study of speciation

A broad range of sensitive and specific analytical techniques has been designed and developed for speciation studies. Among these techniques are hyphenated techniques such as GC-ICP-MS for the analysis of organometallic elements, x-ray spectroscopic techniques and sequential leaching techniques (Koschinky and Hein, 2003; Ohnuki *et al.,* 2005; Hirata *et al.,* 2006). Although the various techniques originated by various researchers are capable of quantifying the amount of free and bound metal, Benson et al. (2013) noted that only the most sensitive techniques are suitable for speciation analysis. For Zaporozhets and Linnik (2004), speciation techniques using inductively coupled plasma in combination with mass

spectrophotometry (ICP-MS), inductively coupled plasma combined with atomic emission spectrophotometry (ICP-AES) and electrothermal technique combined with atomic absorption spectrometry (ET-AAS) are the most sensitive and selective.

Initial speciation analysis on environmental matrices were directed mainly on separation of specific elemental species (Adamu *et al.,* 2013). Species were separated using the observing techniques; liquid chromatography (LC), gas chromatography (GC), capillary electrophoresis (CE) and gel electrophoresis (GE) (Rosen and Hieftje et al., 2004; Adamu et al., 2013). In recent times, separation methods have been incorporated with highly sensitive and powerful detection methods for reliable quantitative measurements (Benson *et al.,* 2013). High performance liquid chromatography (HPLC) is one major and readily available methods utilized in separating non-volatile species of interest and has been widely coupled to atomic spectroscopy for quantification. A long list of resin supports have been utilized as the stationary phase with size exclusion, cation exchange, chelating, anion exchange, and reversed phase (Adamu et al., 2013). In this way, analytes with different oxidation states e.g. Cr^{3+} and Cr^{6+} are separated and qualified. Other suitable techniques for on-line coupling are inductively coupled plasma combined with atomic emission spectrometry (ICP-AES) and inductively coupled plasma with mass spectrometry (ICP-MS). ICP-MS has helped greatly in multi-element determinations, isotopic discernment with very high sensitivity. In the same vein, electroanalytical techniques such as anodic stripping voltammetry (ASV), amperometry and potentiometry have also been utilized for determination of the various oxidation states of metals, metals' organometallic species and their complexes (Adamu *et al.,* 2013).

Mathematical models and computer assisted programs have likewise been designed for speciation analysis. The Free Ionic Activity Model (FIAM) has been employed to determine metal speciation in soil, which involves the uptake of metal by target organisms (Campbell, 1995). The FIAM was later changed into the Biotic Ligand Model (BLM) so as to admit the

influence of completing cations like Ca^{2+} and H^+ (Di-Toro et al., 2001). Continuing development in this regard, Donnan membrane Technique (DMT) Diffusive Gradient in Thin films (DGTs) have been designed and successfully used in speciation analysis. The Windermere Humic Aqueous Model (WHAM VII) is the latest variant of the mathematical model and computer assisted program developed and generally accepted worldwide (Tipping, 1998; Adamu et al., 2013). According to Adamu et al. (2013), the WHAM VII model contains a database for cation binding to humic and fulvic acids, including all rare earth elements and silver; and also mimics the precipitation of iron (III) and aluminium hydroxides, and binding of irons to precipitate. The binding activity of dissolved organic matter is used to generate distributions of predicted free ions concentrations (Lofts and Tipping, 2011).

2.5.3   Speciation studies in sediment and soils

To understand metal speciation in sediment and soils several approaches including as the phase-selective chemical extraction which involved multi steps extraction procedures have been employed (Tessier *et al.,* 1979; Barnah *et al.,* 1996; Li and Thornton, 2000; Okoro *et al.,* 2012; Benson *et al.,* 2013). The number of steps in these extraction procedures varies from 3 to 8 steps. For example, Li and Thornton (2000) (3 steps), Tessier et al. (1979) (5 steps), Kersten and Fronstier (1986) (6 steps) and Krishnamauti et al. (1995) (8 steps). These extraction procedures varies in their extraction reagent, types and experimental conditions. The 5-step Tessier et al. (1979) is one of the widely utilized sequential extraction procedure. This sequential extraction procedure demarcates the metal forms sequentially as exchangeable, carbonate-bound, iron and manganese oxide-bound, organically-bound and residual. However, following this basic procedure, a number of modified procedures have been developed which uses different reagents or experimental conditions to separate individual fractions (Gomez-Ariza *et al.,* 2000; Ma and Rao, 1997; Zdenek, 1996; Camparella *et al.,* 1995; Borovec *et al.,* 1993). The type of reagents used in extracting when it comes to speciation analysis is based on

selectivity and specificity towards a particular physicochemical form of metals (Gitari *et al.,* 2010). According to Benson et al. (2013), the reagent cocktail for respective extraction steps are capable of disrupting the binding agents between individual elements and the sediment/soil thereby enabling the release of the metal species into the solution. Since sequential extraction procedures were not standardized, researchers use schemes developed by themselves.

However, in an effort to harmonized and standardized the extraction procedures the Community Bureau of Reference (BCR) (now Standards, Measurement and Testing Programme (SMTP) sequential extraction method was developed (Moc'ko and Waclawek, 2004; Jung *et al.,* 2010; Okoro *et al.,* 2012). The BCR method is a 3-step method which delineate metals into exchangeable, reducible and oxidizable fractions which are extracted with reagents. A summary of this approach is displayed in Table 2.1. A sediment certified reference material BCR-701 was used to validate this method employing certified and indicative extractable concentration of Cd, Cr, Cu, Ni, Pb and Zn (Rauret and Lopez-Sanchez, 2001; Okoro *et al.,* 2013). This method was applied and taken over by a large group of scientists, despite some shortcomings in the sequential extraction steps (Usero et al., 1998; Ho and Evans 1997; Agnieszka and Wieslaw, 2002).

Table 2.1: Three-step sequential extraction procedure developed by BCR

Species	Regent	Extraction time/temp.
Exchangeable, Water- and acid-soluble	40 cm^3 11 M CH_3COOH per 1.0 g of sample	Shake using mechanical shaker overnight at $25^{\circ}C$
Reducible species (metal oxides- and hydroxides-bound)	40 cm^3 0.1 M $NH_2OH.HCl$ (adjusted to pH $= 2$ with HNO_3) added to residue.	300 min at $25^{\circ}C$
Oxidisable species (organic matter and suphides-bound)	10 cm^3 5.8 M H_2O_2 added to residue in water bath. Evaporate solution to few cm$_3$. After cooling, add 50 cm^3 1 M CH_3COONH_5 (adjusted to pH $= 2$ with HNO_3) to residue.	60 min at room temperature 60 min at $85^{\circ}C$ 360 min ($25^{\circ}C$)

The application of sequential extraction procedures abound in the literature. For instance, Iwegbue (2007) in investigating the chemical speciation and likely mobility of Cd, Cu, Pb, Zn, Cr and Ni in the soils of automobile mechanic waste dumps in Port-Harcourt, Nigeria uses a sequential fractionation protocol that generated six different fractions into which soil metal could partition. The author found out that for surface soil, Cd was partitioned among all the fractions except residual fraction, Cu was dominant in the organic fraction, Zn and Pb were predominant in the reducible fraction while Cr and Ni were associated with the residual fraction.

Osakwe (2012) studied selected heavy metals Fe, Cd, Ni, and Cr in contaminated refuse dumpsites soil samples collected from South – Eastern Nigeria, for their geochemical differentiation into different chemical fractions, using Ma and Rao six steps sequential chemical extraction. The author found that the residual fraction was the most important phase for the four heavy metals under study with the following average percentage values 74.43 for Fe, 37.69 for Cd, 70.11 for Ni and 62.47 for Cr.

Shasheen et al. (2013) studied the fractionation of metals in floodplain soils from Egypt, Germany and Greece using sequential extraction to delineate Cd, Cu, Ni, Pb and Zn into five phases. The authors reported that the predominant phase of the metals is the residual phase for Egyptian and Greek soils while for the German soil non-residual phase predominated for all metals. Katana et al., (2013) carried out a speciation analysis utilizing the modified Community Bureau of Reference (BCR) sequential extraction procedure for Ni and Cr in soils of open-air garages in Ngara, Nairobi, Kenya. The authors found that the metals partitioned in the order of; exchangeable > oxidisable > residual > reducible for Ni and exchangeable = residual > reducible > oxidisable for Cr. The % of non-residual Ni and Cr was 76.37 and 74.25 respectively while the mobility factors for the heavy metals were 29.10% and 25.82% respectively.

Ajala et al. (2014) evaluated the chemical fractionation of iron, manganese, copper, zinc, nickel, lead, cadmium and chromium in floodplain soils of Eke-Mgbom, Afikpo Nigeria the authors employed the sequential extraction procedure of Horowitz (1991). The authors reported that the metal fractions is are in the order of Oxidizable >> Exchangeable >> Carbonate > Residual > Reducible.

2.6   Formation of polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are produced from two primary mechanisms which are pyrosynthesis and pyrolysis (Sun, 2004; Pakpahan *et al.,* 2009; Ravindra *et al.,* 2008). Pyrosynthesis encompasses the formation of PAHs from saturated hydrocarbons under oxygen-lacking conditions (Ravindra *et al.,* 2008).

At temperature above $500^{\circ}C$, carbon hydrocarbon and carbon-carbon bond in lower hydrocarbons (e.g. ethane) are broken to form free radicals. These free radicals formed combine with acetylene which then condenses into aromatic ring structures which are stable and resistant to thermal degradation (Ravindra et al, 2008).

In pyrolysis, a macromolecular aromatic hydrocarbon is broken into smaller fragments. Through the process of pyrosynthesis, these small fragments which are mainly free radicals undergo cyclization and aromatization to form polycyclic compounds (Pakpahan *et al.,* 2009). The formation and transportation of PAHs is influenced by temperature, type of fuel and amount of oxygen (Sun, 2004; Lima *et al.,* 2005). PAHs formation from hydrocarbons heating and combustion is possible at temperatures as low as $300\ ^{\circ}C$ to $500\ ^{\circ}C$ for high molecular weight and $1000\ ^{\circ}C$ or more for low molecular weights whenever vapour phase of pyrolysis and partial oxidation proceed readily. Pope et al. (2000) stated that inspite of structural complexity of PAHs they have significant number of isomers and as the temperature increases, the relative abundance of all PAH isomers in mixture other than the most stable isomer also increases.

Kwon and Castaldi (2006) in their study on PAHs formation through thermal degradation of styrene butadiene copolymer (SBR) in the range of 300 to 500 °C revealed that the substituted aromatic PAHs, 2, 3, and 4 rings, reached their maximum concentrations at temperatures of 380, 400 and 450 °C respectively. On their part, Richter et al. (2000) confirmed observations by Pope et al. (2000) and Kwon and Castaldi (2006) through their work on pyrene-contaminated soil and its contribution to PAHs formation using oxygen-free heating process at a temperature range of 250 and 1000 °C showed that all of the treatment temperatures resulted in the formation of volatile PAHs by-products which contain pyrene. Also, Alfe et al. (2010) reported progressive increase in concentration profiles of PAHs in the pyrolysis region of the lower temperature range. Liu et al. (2001) investigated the emission of PAHs from combustion of coals in Fluidized Bed Conductor (FBC) bench-scale at the temperature range of 790 to 900 °C with excess air ratio range of 1.13 to 1.34. The authors showed that high molecular weight PAHs of 4 and 5 rings were produced at temperature below 850 °C while low molecular weight PAHs of 2 and 3 rings were formed at above 850 °C. Wey et al. (2006) studied the effect of lower operating temperature on PAHs formation. They found that formation of gas phase PAHs was increased by inclusion of CaO additive at 600 and 700 °C but then decreased at 800 °C. In addition, the formation of solid phase of PAHs was effectively suppressed by CaO additive at 600 and 700 °C, but it was poor at 800 °C.

2.7 Sources of polycyclic aromatic hydrocarbons

PAHs sources in the environment are categorised into five major sources. These are domestic, mobile, industrial, agricultural and natural sources (Beegle *et al.,* 2001; Marchand *et al.,* 2004; Ravindra *et al.,* 2008; Wick *et al.,* 2011).

2.7.1 Domestic sources

Domestic sources of PAHs are related with the combustion of garbage, wood, coal crude oil, and municipal waste incineration and other organic substances like tobacco, cigarette

and char-cake meat (Ravindra *et al.,* 2008; Wick *et al.,* 2011). WHO (2002) reported that wood, diesel, animal-dung cake and crop waste are mainly used for cooking in under-developed countries. The report also stated that over 75 % people in China, India and South East Asia and 50-75 % of people in parts of South America and Africa use these solid fuels for daily cooking. In their study, Venkatanaman et al. (2002) reported the emission factors of total PAH from wood, briquette and dung-cake combustion. They found out that the emission factors ranged from 2.0 to 3.2 mg kg^{-1}, 2.8 to 3.0 mg kg^{-1} and 3.1 to 5.5 mg kg^{-1} respectively. The emissions of the 16 USEPA PAHs plus B[e]P was estimated by Oanh et al. (2005) from 12 selected cook-stoves burning wood fuel, rice husk briquettes and anthracite coal. They found out that the emission factors of PAHs ranged from 24 to 114 mg kg^{-1} and 140 mg kg^{-1} from wood fuel and rice husk briquettes fuel respectively.

2.7.2   Mobile sources

The mobile sources of PAHs include emissions from aircraft, ships, railway, automobiles, off-road vehicles and machineries. These sources of PAHs depends on factors such as the type of engine, load and age of engine, type of fuel and quality of fuel used, PAH accumulation in lubricant oil, lubricant oil combustion and driving mode including cold starting and emission control (Ravindra *et al.,* 2008). For instance, diesel is a source of lighter molecular weight PAHs while gasoline is a source of heavy molecular weight PAHs (Juhasz and Naidu, 2000; Wick *et al.,* 2011). Schauer et al. (2002) reported that the make-up of the fuel sways PAH emissions for diesel vehicles. According to Ravindra et al. (2008), diesel fuelled vehicles have higher particulate emissions than gasoline fueled vehicles. These particles consist of combustion-generated soot, a solvent extractable hydrocarbons fractions and a mineral fraction. The PAHs are found within the solvent extractable fractions (Ravindra *et al.,* 2008).

The emission of PAHs from gasoline automobiles is a function of the air/fuel ratio. It had be reported that as the air/fuel ratio increased, the high molecular weight PAHs decreased

rapidly (Jones *et al.,* 2004). Duran et al. (2001) in their study showed that engine speed was a better decisive factor for PAHs emission than torque and also reported an increase in aromatic content in PAHs emission at high engine speed. Two stroke fuel is a mixture of gasoline and oil and two stroke engines are essential in motor scooter and motor cycle (Ravindra *et al.,* 2008). The engines are usually small and not designed with additional emission control systems. Gambino et al. (2000) estimated that unrestricted PAH emissions are 1.6 mg km^{-1} for the sum of 29 PAHs with 2-6 rings and 28.8 µg kg^{-1} for 6 carcinogenic PAHs. The relationship between PAH concentrations and traffic composition was evaluated by Wingfors et al. (2001) and they found significant relationship between tricyclic PAHs, heavy duty vehicles and naphthalene as well as association between heavy PAHs and light duty vehicles. The authors nevertheless found out that the total amounts of PAHs linked with particles did not increase with increasing percentage of heavy duty vehicles. Traffic congestion in urban areas in which vehicles travelled short distances, engine deterioration and high mileage also contributes high emissions of PAHs (Ravindra *et al.,* 2008). Many studies have showed that the emissions from vehicles exhaust are the largest contribution of PAHs in urban areas (Marchand *et al.,* 2004; Ravindra *et al.,* 2006; Marr *et al.,* 2006).

Ships, trains and aircrafts also contribute significant amounts of PAHs to the environment. Cooper et al. (2003) estimated the exhaust emission from a ship during normal real world operation – hoteling, unloading and loading activities. He found that the concentration of 29 PAHs ranged from 0.15 to 2 mg kWh^{-1} except for a ship using heavier residual oil (9.5 to 11 mg kWh^{-1}). The author also reported that PAH emissions from ships comes from the production of electrical power by smaller diesel engines. According to Ravindra et al. (2008), PAH emissions from larger ships/ferries may releases significant amounts of PAHs into the atmosphere depending on geographical conditions of the local harbor and the route but further investigations would be needed. Kohler and Kunniger (2003) reported

that about 139 tons of USEPA PAHs are emitted by the creosoted ties of the Swiss railway network every year. PAHs emissions in rail transportation is due to the utilization of diesel and diesel/electric locomotives (Ravindra *et al.,* 2008). Chen et al. (2006) reported that PAHs emission from aircrafts exhaust may be substantial since about 227 billion liters of jet fuels are used up worldwide yearly. The release of PAHs from aircrafts is a correlate of fuel constituent and on the power setting of the engine and tend to reduce as the power setting increases (Ravindra *et al.,* 2008). Also, Ravindra et al. (2008) reported that the mean emission factors for an aircraft gas turbine engine is 1.24 mg per landing-take off (LTO) cycle for BaP. The emission of PAHs from a helicopter turbo-shaft engine was characterized by Chen et al. (2006). They found that the mean total PAH concentration in engine exhaust was 843 μg m^{-1}. They also reported that two and three benzene ring PAHs dominate the total PAHs emission. Ray et al. (2008) in their study of PAH concentrations in International Airport in Delhi, India found out that the total of 12 PAHs ranged from 2.39 μg g^{-1} to 7.53 μg g^{-1} with a mean concentration of 4.43$\pm$1.45 μg g^{-1}. Other sources of PAHs due to mobile emissions are abration of rubber tyres, asphalt road surfaces and brake linings (Boulter, 2005; Ravindra *et al.,* 2008).

2.7.3 Industrial emissions

Industrial sources of PAHs have been identified to comprised creosote and wood preservation, primary aluminium production, bitumen and asphalt industries, coke production, waste incineration and cement manufacture. Others are rubber tyre manufacturing, petrochemical and related industries, and commercial heat/ power production (PAHs Position paper; Ravindra *et al.,* 2008). The release of PAHs via bench-scale and small industrial, water tube boilers was carried out by Pisupati et al. (2000). The authors detected only acenaphthene, fluoranthene and napthalene at concentrations which ranged from 85 to 320 μg kg^{-1} of fuel fired. Yang et al. (2005) investigated the release of PAHs from furnaces combusting recycled paper and virgin bamboo. They found out that the individual PAH emission factors ranged

from < 1mg kg^{-1} fuel to several tens of mg kg^{-1} fuel. PAHs generated in waste-tire pyrolysis process was investigated by Chen et al. (2007) and found a mean content of total PAHs of 77 µg g^{-1} dominated by indeno (1,2,3-cg)pyrene, dibenzo(a,h)anthracene and BaP. Furthermore, they reported that the emission rate of gaseous, particulate and residual PAHs in the flare exhaust were 25, 1.6 and 3.0 mg min^{-1} respectively and corresponding emission factors of 3.4, 0.2 and 0.4 mg kg^{-1} for tires while the PAHs emission rate and factor estimated for a scrap tire pyrolysis plant were 42 g day^{-1} and 4.0 mg kg^{-1} tire respectively.

2.7.4   Agricultural sources

Agricultural sources of PAHs include burning of brushwood and straw, open burning of biomass, moorland heather for regeneration purposes and stubble burning, (Godoi *et al.,* 2004; Ravindra *et al.,* 2008). Godoi et al. (2004) found that PAHs emitted during sugarcane burning were comparable to those of some urban centres. Kakareka and Kukharchyk (2003) evaluated the emission of PAHs in open burning and found that the concentration of PAHs ranged from 240 to 571 mg kg^{-1} with significant contribution from phenanthrene. Hays et al. (2005) simulated the agricultural fires of surface residuals of rice and wheat and found that n-alkane, PAHs and lignin dimmer molecules predominate in the organic carbon fraction of the PM2.5 emissions. The wheat and rice straw particulates were improved by eight-fold of high molecular weight PAHs. Kumata et al. (2006) predicted that the combustion of biomass burning adds 17-45 % of PAHs load of fine particles in Tokyo and the increase in the biomass PAH contributed about 27 % and 22 % of winter-time elevation of 3-4 ring PAHs and 5-6 ring PAHs respectively.

2.7.5   Natural sources

PAHs can be naturally released into the environment through forest fires, volcanic eruption, cosmic source as well as burning of forest wood land or moorland as a result of lightning strike (Baumard *et al.,* 1999). Volcanic eruptions also release PAHs, but no

information with respect to these releases into the atmosphere have been documented (Ravindra *et al.,* 2008). Some Researchers have argued that PAHs can be produced by unicellular algae, higher plants or bacteria, but others believed that these organisms accumulate PAHs rather than synthesising (Wilcke *et al.,* 2000). Carbonaceous chondrites, which originate in the main asteroid belt is the cosmic source of PAHs (Halasinski *et al.,* 2005; Ravindra *et al.,* 2008).

2.8   Priority PAHs

The United State Environmental Protection Agency (USEPA) has placed 16 PAH compounds on the Priority Pollutants List created under the Clean Water Act (Wick *et al.,* 2011). Furthermore, the USEPA 16 PAHs were categorised as follows; benzo(a)pyrene(BaP)as group 1A (carcinogenic to humans), dibenzo(a,h) anthracene(DahA) group 2A (probably carcinogenic to humans) and naphthalene (NaP), benzo(a)anthracene (BaA), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), chrysene (Chry) and indeno(1,2,3-cd)perylene (IndP) as group 2B (possibly carcinogenic to human), while acenaphthene (Ace), acenaphthylene (Acy), anthracene (Ant), benzo(ghi)perylene (BghiP), fluoranthene (Flt), fluorine (Flu), phenanthrene (Phen) and pyrene (Pyr) are not classified as to their carcinogenicity to humans(IARC, 2010). According to Ravindra et al. (2008), these PAHs were considered to be in the priority list because more data are available on them than on the toxic effects, regularity of occurrence in environmental matrix, concentrations and distribution patterns and greater chance for exposure to these PAHs than to the others; and of all the PAHs analysed, these demonstrated the highest concentrations. The molecular structures of these PAHs are shown in Figure 2.1 while selected properties of the priority PAHs are shown in Table 2.2.
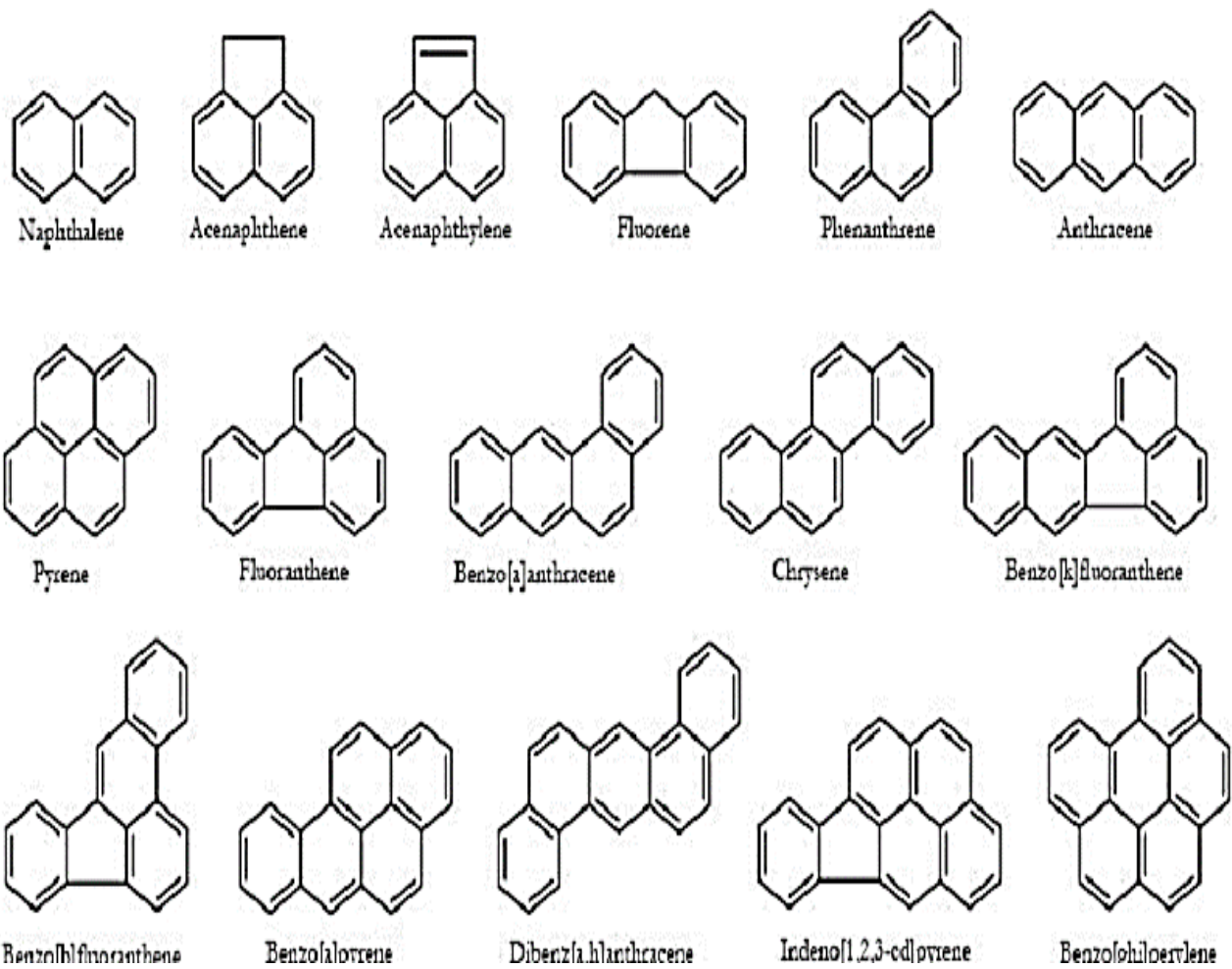
Figure 2.1: Structures of 16 priority PAHs

The structures shown, left to right and top to bottom, are labelled:

Naphthalene, Acenaphthene, Acenaphthylene, Fluorene, Phenanthrene, Anthracene, Pyrene, Fluoranthene, Benzo[a]anthracene, Chrysene, Benzo[k]fluoranthene, Benzo[b]fluoranthene, Benzo[a]pyrene, Dibenz[a,h]anthracene, Indeno[1,2,3-cd]pyrene, Benzo[ghi]perylene

Table 2.2: US EPA's 16 priority PAHs and selected properties (Adapted from Lundstedt, 2003; Bojes and Pope, 2007)

PAH Name	No. of rings	Molecular weight (g mole^{-1})	Solubility in water (mg L^{-1})	Vapour pressure (Pa)	Log Kow
Naphthalene	2	128.17	31	11.866	3.37
Acenaphthene	3	154.21	3.8	0.500	3.92
Acenaphthylene	3	152.2	16.1	3.866	4.00
Anthracene	3	178.23	0.045	3.40×10^{-3}	4.54
Phenanthrene	3	178.23	1.1	9.07×10^{-2}	4.57
Fluorene	3	166.22	1.9	0.432	4.18
Fluoranthene	4	202.26	0.26	1.08×10^{-3}	5.22
Benzo(a)anthracene*	4	228.29	0.011	2.05×10^{-5}	5.91
Chrysene*	4	228.29	0.0015	1.04×10^{-6}	5.91
Pyrene	4	202.26	0.132	5.67×10^{-4}	5.18
Benzo(a)pyrene*	5	252.32	0.0038	6.52×10^{-7}	5.91
Benzo(b)fluoranthene*	5	252.32	0.0015	1.07×10^{-5}	5.80
Benzo(k)fluoranthene*	5	252.32	0.0008	1.28×10^{-8}	6.00
Dibenzo(a,h)anthracene*	5	278.35	0.0005	2.80×10^{-9}	6.75
Benzo(g,h,i)perylene*	6	276.34	0.00026	1.33×10^{-8}	6.50
Indeno(1,2,3-cd)pyrene*	6	276.34	0.062	1.87×10^{-8}	6.50

*Classified as possible human carcinogenic by the U.S. EPA

2.9   Chemistry of polycyclic aromatic hydrocarbons

The behaviour of PAH compounds in the environment is influenced by their specific characteristics. The molecular weight, structure, water solubility and vapour pressure of the PAHs controls the transport properties, degradation and sequestration (Pierzynski *et al.,* 2000; Reid *et al.,* 2000; Wick *et al.,* 2011).

2.9.1   Molecular weight

PAHs are classified as low molecular weight (LMW) and high molecular weight (HMW) PAHs. Low molecular weight PAHs have two or three fused rings while high molecular weight have four or more fused rings (Wick *et al.,* 2011). Increased in molecular weight of PAH compounds leads to increase in hydrophobicity and lipophilicity whereas increased in molecular weight leads to decrease in water solubility and vapour pressure. Thus, the PAH compound will be become more recalcitrant (Wick *et al.,* 2011). Low molecular weight PAH compounds are broken down and volatilized faster than high molecular weight PAH compounds. The persistent nature of HMW PAHs in the environment is due to low volatility, resistance to leaching and recalcitrant nature (Wick *et al.,* 2011). The molecular weight of PAH compounds are shown in Table 2.3.

2.9.2   Structures

PAHs are classified into two groups based on ring structures. These are alternant and non-alternant PAHs. Alternants are derived from benzene by fusion of additional six membered benzoid ring and contain fewer than eight benzoid rings (Harvey, 1998). Examples of alternant PAHs include anthracene, phenanthrene and chrysene. Non-alternant PAHs on the other hand may contain rings with fewer than six carbon atoms in addition to six membered rings. This group is extremely broad in structure and greatly increases PAH diversity (Harvey, 1998). Examples of non-alternant PAHs are fluorine, fluoranthene, benzo(b)fluoranthene etc.

2.9.3 Solubility

PAHs solubility in water depends on factors such as temperature, pH, ionic strength and other organic chemicals (Pierzynski *et al.,* 2000). According to Wick et al. (2011), solubility is assessed by chemical structure and octanol-water partition coefficients. Increasing the number of benzene rings in a PAH compound results in decrease in solubility. Nevertheless, these are exceptions as symmetry, planarity and the presence of substituents affect PAHs solubility in organic solvents (Wick *et al.,* 2011). Harvey (1997) found out that solubility increased in linearly-fused PAH as the number of rings increase due to the bonds becoming weaker in character, but was not observed in angularly-fused PAH. Similarly, Dabestani and Ivanov (1999) reported that planar PAHs are less soluble and biologically less toxic. Alternant PAH compounds that are planar and symmetrical needs a relatively high energy of solubilization due to their ability to fit closely in a lattice. Hence, they are less soluble (Harvey, 1997; Wick *et al.,* 2011). As PAH compounds deviate from planarity or symmetry they tend to be more soluble in organic solvents. Methyl and polar substitution may also increase the solubility of PAHs in certain solvents (Harvey, 1997).

2.9.4 Octanol-water partition coefficient

Similarly, increased in the octanol-water partition coefficients (Kow) of PAHs results in decrease in solubility (Wick *et al.,* 2011). The solubility and Kow of selected PAHs are shown in Table 2.1. The octanol-water coefficient is often expressed as the log Kow. Napthalene has a log Kow of 3.37 while Indeno (1,2,3-cd)pyrene has log Kow of 6.50. Thus, naphthalene is more soluble than Indeno(1,2,3-cd)pyrene.

2.9.5 Vapour pressure

The vapour pressure of PAH compounds are important for determining risk associated with contaminated soils and sediments, transfer between two resources(soil and air) as well as field sampling and laboratory safety (Wick *et al.,* 2011). Vapour pressure is the point at which

PAHs in the solid state either evaporate into a gaseous from or condense back to a solid state. The higher the vapour pressure at normal temperature, the more volatile the compound is. The vapour pressure of naphthalene is 11.866 Pa while that of dibenzo(a,h)anthracene is 2.8×10^{-9} Pa at normal temperature. Thus, naphthalene is more volatile and would readily evaporate more rapidly than dibenzo(a,h)anthracene (Mackay and Callcott, 1998; Wick *et al.,* 2011).

2.9.6   Bioavailability of PAHs

Bioavailability have been defined as the possibility of a substance to negatively or positively affect an organism (Pierzynski *et al.,* 2000). The transportation, degradation and sequestration of PAHs in the environment is a function of their bioavailability. However, adequate tests to evaluate the bioavailability of PAHs in contaminated soil and sediments are not available (Wick *et al.,* 2011). According to Stokes et al. (2006) and Harmsen (2007), the bioavailability of PAHs is influenced by;

a)   The physical properties of the specific PAH compound (LMW or HMW)

b)   The soil characteristics (clay and organic matter content, structure) and

c)   The receptor organisms (bacteria, earthworms, arthropods etc)

As a result of their high solubility and volatility as well as the ability of different micro-organisms to use them as a sole carbon source, LMW PAHs are removed faster by physicochemical and biological processes while HMW PAHs are more stable, recalcitrant and less bioavailable in the environment (Alexander, 1999). The characteristics of soil such as texture and aggregation, organic matter and heterogeneity of soil also tremendously affects the bioavailability of PAHs. For instance, Nam and Alexander (1998) reported declining PAH availability to phenanthrene degraders with time in soils with ≥ 2 % organic matter. Hundai et al. (2001) reported on the retention of large amounts of phenanthrene by smectite. However, according to Chung and Alexander (2002), single or multiple soil properties such as organic matter content and/or clay content does not always correlate with the bioavailability of PAHs.

The bioavailability of PAHs also depend on the receptor organisms. For instance, in an environment dominated by microbial population "A", a certain compound may bioavailable and readily degraded; however, in that same environment with microbial population "B", that same compound may not be bioavailable to that specific group of microorganisms and the compound will persist in the soil (Alexander, 1999; Wick *et al.,* 2011).

2.10   Occurrence and composition of polycyclic aromatic hydrocarbons in soils

The concentrations of PAHs in soil resulting from natural processes and sources have been estimated to range between 1 and 10 μg kg^{-1} (Edwards, 1983). However, the concentration of PAHs in soils have increased in recent times due to human activities. Juhasz and Naidu (2000) reported total PAH concentration of 5863 mg kg^{-1} at a creosote production site, 18704 mg kg^{-1} at a wood preserving site, 821 mg kg^{-1} at a petrochemical site and 451 mg kg^{-1} at a gas manufacture plant site. Chen *et al.* (2005) investigated the contents and distribution of PAHs in 43 surface and subsurface soils around the urban Guangzhou where several kinds of vegetables are grown. They found out that the contents of PAHs (16 US EPA priority PAHs) ranged from 42 to 3077 μg/kg.

A detailed and systematic research was undertaken to evaluate the levels of PAHs in urban soils in Beijing, China (Tang *et al.,* 2005). They found high concentrations of $\sum$PAHs ranging from less than 366 to 27,825 ng g^{-1}. The distribution of PAHs in soil contaminated with human wastes in the Niger Delta area of Nigeria has been investigated (Olajire *et al.,* 2005). The authors reported PAHs concentrations in the ranged of 182 $\pm$ 112 to 433 $\pm$256 μg/kg dw. The total concentration of 16 EPA-PAHs ranging from 0.467 to 5.470 μg/g have been reported in urban surface soils from Beijing (Li *et al.,* 2006). Olajire et al (2007) reported total concentrations of 10 PAHs which varied from 101.5 to 209.7 μg g^{1} dry weight in soils from the vicinity of Agbabu bitumen field of Southwestern Nigeria.

Okoro and Ikolo (2007) carried out an investigative study of PAHs in soils in Effurun metropolis in the Niger Delta Area of Nigeria. They found out that pyrene was observed to be the most abundant compound in all sites (20%) followed by fluoranthene (14%) phenanthrene (12%) chrysene (10%) benzo(ghi) perylene (6%).

Hilscherova et al. (2007) investigated the redistribution of organic pollutants in River sediments and alluvial soils in Czech Republic. The authors found that the concentrations of PAHs as well as organic carbon content in both sediment and floodplain soils were considerably influenced by the flooding, which caused a decrease in all studied contaminants in sediments and substantial rise of the PAH pollution in the flooded soils.

Pies et al. (2007) studied the distribution of polycyclic aromatic hydrocarbons (PAHs) in floodplain soils of the Mosel and Saar River and found out that the sum of nineteen PAHs in the soil samples was up to 81 mg kg^{-1} dry weight (dw). Most soil samples showed a relationship between the presence of coal particles and PAH concentrations. Sartori et al. (2010) quantified the concentration and distribution of 41 PAH, organic C, total N, and S of floodplain soils under a natural vegetation succession. The authors found out that the concentration (ΣPAH) ranged from 16 ng g^{-1} to 12000 ng g^{-1} with a mean of 1300 ng g^{-1}.

Post flooded forest soil profile samples obtained near Afam power station, contiguous to Imo River were analysed for quantitative determination of polycyclic aromatic hydrocarbons (PAHs) by Oyo-Ita et al. (2011). The authors reported that PAHs content for the top soil horizon appeared similar to that of one of the point-source samples and variation in PAHs content for the lower soil horizons reflected a record of past PAHs deposition as a consequence of differences in Imo river current trajectory.

Wang et al. (2008) studied the sources and distribution of PAHs in urban soils from two US cities (New Orleans and Detroit) and reported that the average total PAH (sum of 17 PAH concentrations) of Detroit soils was 7,803 µg/kg, compared to 5,100 µg/kg for New Orleans soils.

Argawal (2009) examined the impact of vehicular traffic on the contamination status of urban traffic sites in Delhi with respect to polycyclic aromatic hydrocarbon (PAH). Total PAH concentration at traffic sites ranged from 1062 µg kg^{-1} to 9652 µg kg^{-1} with an average value of 4694 ± 3028 µg kg^{-1}. At the rural site average concentration of total PAHs was found to be 886 ± 303 µg kg^{-1}. PAH pattern was dominated by five- and six-ring PAHs (contributing >50% to the total PAHs) at all the three traffic sites.

Banger et al. (2010) determined the depth-wise distribution of 16 PAHs compounds in four urban soils of different land uses in Miami, Florida, USA. They found out that total PAHs were significantly greater at surface (1,869 µg/kg) than sub-surface soil (478–1,079 µg/kg). The distribution of polycyclic aromatic hydrocarbons (PAHs) in surface soils from communities in oil exploration areas of the Niger Delta of Nigeria was examined by Sojinu et al. (2010). The concentration of 28 target PAHs ranged from 24 to 120 ng/g (average: 80 ng/g) in the soil samples. Two-ring PAHs were the dominant components accounting for approximately 45% of the total PAHs detected.

Soil samples of semi-urban zones in Tianjin, China were evaluated for 16 polycyclic aromatic hydrocarbons (Lv *et al.,* 2010). The total concentrations of tested polycyclic aromatic hydrocarbons in Xiqing, Dongli, Jinnan, Beichen ranged from 58.5—2,748.3, 36.1—6i34.7, 58.5—4,502.5, 29.7— 852.5 ng/g and the averages of total concentration of polycyclic aromatic hydrocarbons were 600.5, 933.6, 640.8, 257.3 ng/g, respectively.

Wang et al. (2010) reported a total concentrations of 16 PAHs which ranged from 31.6 to 1475.0 ng/g, with an arithmetic average of 336.4 ng/g in soils of Beijing, Tianjin and surrounding areas, North China. Orecchio (2010) assessed the concentrations of PAHs in soil of a Natural Reserve in Italy situated in front of a plant used in manufacturing of cement and found out that the $\sum$PAHs in the soil of investigated area, ranged from 35 to 545 µg/kg.

A study of PAHs contamination in roadside soil was conducted in fast growing city in India during autumn and winter seasons (Kumar and Kothiyal, 2011). They found a total average concentration of 4.04 µg/g and 16.38 µg/g during winter and autumn respectively. Dibenzo(a,h)anthracene and Benzo(a)pyrene were the individual polycyclic aromatic hydrocarbons found in highest concentration at all the intercepts ranging between 0.008 to 28.4 µg/g during winter and 0.01 to 252.85 µg/g during autumn. Peng et al. (2011) studied the concentration and spatial distribution of 16 polycyclic aromatic hydrocarbons (PAH5) in urban soils of Beijing. The total mass concentration of 16 PAHs ranged from 93 to 13141 µg kg^{-1} with a mean of 1228 µg kg^{-1}.

Surface soils affected by forest fires from Igbanko mangrove forest in Nigeria were analyzed for 16 EPA priority polycyclic aromatic hydrocarbons (PAHs) (Sojinu *et al.,* 2011). The total PAHs concentrations in the soils ranged from 63 to 188 µg kg^{-1} dry weight (average: 108 µg kg^{-1}). The three predominant PAHs in the soils were naphthalene (Nap), fluoranthene (Flu), and benzo(b)fluoranthene (BbF).

Nganje et al. (2012) investigated the concentration of polycyclic aromatic hydrocarbons in topsoil in the location of fuel-oil spillage from a tank farm in Esuk Utan, Calabar municipality, Nigeria. The authors reported total concentrations of PAHs in soil ranged from 16.06 to 25547.75 µg/kg with a mean concentration of 2906.36 µg/kg. The ΣPAH concentrations of the seven carcinogenic PAH compounds in the soil varied between 0.02 and 97954 µg/kg.

Yang et al. (2012) investigated the profiles and distribution of polycyclic aromatic hydrocarbons (PAHs) in agricultural surface soils from the Huanghuai plain, China. The total concentrations of 16 PAHs varied from 15.7 to 1247.6 µg/kg, with an average of 129.5 µg/kg.

The concentration of PAHs in soils of the Niger Delta region of Nigeria was determined by Olawoyin et al. (2012). They found out that the concentration of the 7 potential carcinogenic PAHs ($\sum_{carc}^{soil}$7PAHs) in the soils varied from 297-4080.6 ± 546.3 mg/kg with median of 419 mg/kg and the concentrations for non-carcinogenic PAHs ranged from 315-1339±300 mg/kg with a median of 497.5 mg/kg.

Jiao et al. (2012) investigated polycyclic aromatic hydrocarbons (PAHs) in surface soils collected from coastal and estuarine areas of the northern Bohai and Yellow Seas (CEANB YS), China and found total concentrations of PAHs which ranged from 6.6×10^1 to 9.2×10^2 ng g^{-1} dry weight, with an average of 3.1×10^2 ng g^{-1} dw.

The distribution of polycyclic aromatic hydrocarbons (PAHs) in urban roadside soils of Kurukshetra, a developing city in Haryana, India was studied by Kumar et al. (2012). The concentration of $\sum$16PAHs ranged from 16.1 to 2538.0 µg kg^{-1}. The average concentration of total PAHs and total possible carcinogenic PAHs was 631.6±44.5 µg kg^{-1} and 568.8±38.8 µg kg^{-1} respectively.

Kwon and Choi (2013) investigated the concentrations and spatial distribution of PAHs in soil of Ulsan, Korea. They reported total concentrations of PAHs which ranged from 65 ng/g to 12,000 ng/g. The levels and distribution of PAHs indicated that industrial areas were more contaminated compared to those of rural and urban areas. PAH levels of soils from the Yellow River Delta, China were measured by Yuan et al. (2014) and they found out that the total concentrations of $\sum$PAHs ranged from 27 to 753 ng/g dw., with a mean of 118 ± 132 ng/g.

Yang et al. (2014) determined the concentration of PAHs in the soils from Jiaozhou Bay Wetland and the total concentration of PAHs ranged from 176.1–563.3 ng/g dry weight, with a mean of 345.3 ng/g dry weight. Kumar et al. (2014) studied the distribution of selected PAHs in residential street soils from an industrial city. The concentrations of $\sum$PAHs ranged from 36 – 898 µg kg^{-1} with an average value of 315 ± 67 µg kg^{-1}.

According to Wick et al. (2011), the main mechanism of PAHs removal in soil is degradation by microbial metabolism. However, microbial degradation of PAHs in soil is influenced by the physical and chemical properties of the particular PAH compound being degraded, soil temperature, moisture, pH and oxygen concentration.

2.11   Source identification of PAHs

In environmental studies, PAHs sources can be determined by the use of multivariate statistical methods such as Principal component analysis (PCA) and cluster analysis (CA) and diagnostic source ratios (Miranda et al., 1996; Dıaz et al., 2002).

2.11.1 Principal component analysis (PCA)

PCA is generally utilised to decrease data and to bring out a small number of underlying factors (principal components) for analyzing associations among the observed variables (Loska and Wiechuya, 2003; Yongming et al., 2006). If large variations is observed in the standard deviations of variables, PCA results will vary significantly depending on whether the covariance or correlation matrix is employed (Farnham et al., 2003). PCA is applied to a correlation matrix when variables vary by different orders of magnitude and each variable is normalized to unit variance and therefore contributes equally. To make the results of PCA more easily interpretable, the PCA with VARIMAX normalized rotation is employed, which can take care of the variances of the factor loadings across variables for each factor. Factor loadings > 0.71 are typically regarded as excellent and < 0.32 very poor (Garcıa et al., 2004; Yongming et al., 2006). When PCA with VARIMAX normalized rotation is carried out, each PC score comprised information on all of the variables put together into a single number, while the loadings indicate the relative input each element makes to that score. The PC loadings are plotted and the plot inspected for similarities observed as clusters in the PC loading plot.

2.11.2 Cluster Analysis (CA)

Cluster analysis (CA) is employed to further categorise variables of different origins on the basis of the resemblances of their characteristics. Hierarchical cluster analysis, assist in identifying relatively homogeneous groups of variables, using an algorithm that starts with each variable in a separate cluster and combines clusters until only one is left (Yongming et al., 2006). When the variables have large differences in scaling, standardization is performed before computing proximities, which can be done automatically by the hierarchical cluster analysis procedure. A dendrogram is designed to evaluate the cohesiveness of the clusters produced, in which associations among elements can freely be seen. The CA is complementary to PCA.

2.11.3 Diagnostic source ratios

Source apportionment of PAHs employing diagnostic source ratios entails an understanding of the relative thermodynamic stability of different parent PAHs, the properties of different PAHs origins as well as the variations between the components of PAHs and origins (Yunker et al., 2002). Budzinski et al. (1997) and Yunker et al. (1999) have utilized parent PAH ratios to determined combustion originated PAH. However, to decrease confounding factors such as variations in volatility, water solubility, adsorption among others, the ratio estimations are usually limited to PAHs within a given molecular mass (Yunker et al., 2002). For parent PAHs, combustion and/or anthropogenic input is often derived from an increase in the amount of the less stable "kinetic" PAH isomers in relation to the more stable "thermodynamic" isomers (Yunker and Macdonald, 1995; Yunker et al., 2002) and the stability of the lighter PAH isomers has been evaluated to buttress such interpretations (Budzinski et al., 1997).

The following diagnostic/isomer ratios Flu/(Flu + Pyr), Ant/(Ant + Phe), BaA (Chry + BaA), Phe/Ant, LMW/HMW and IndP/(IndP+ BghiP) have been used to distinguished between

combustion and petroleum sources. Based on the PAH isomer pair ratio measurement compiled by Yunker *et al.,* (2002), Flu/(Flu + Pyr) < 0.4 implies petroleum origins, 0.4–0.5 implies petroleum combustion and >0.5 implies combustion origins of coal and biomass; Ant/(Ant + Phe) ratio < 0.10 are seen in petroleum input whereas value > 0.1 are characteristic of combustion process; BaA (Chry + BaA) ratio < 0.2 indicates petroleum, 0.2 – 0.35 petroleum combustion and > 0.35 indicates combustion of coal and biomass and Iper/(Iper + Bper) ratio < 0.2 were from petroleum origin input, between 0.2 and 0.5 were from petroleum combustion and > 0.5 were typical of combustion of coal, wood and grassed matter.

Many studies have developed and used a specific value of PAH diagnostic ratio for source apportionment of PAHs. For instance, Chen et al. (2005) investigated the possible sources of PAHs in 43 surface and subsurface soils around the urban Guangzhou where variable kinds of vegetables are grown. The ratios of methylphenanthren to phenanthrene(MP/P), anthracene to anthracene plus phenanthrene (An/178), ben[a]anthracene to benz[a]anthracene plus chrysene (BaA/228). indeno[1,2,3-cd]pyrene to indeno{1,2,3-ed/pyrene plus benzo[ghi]perylene suggested that the source of PAHs in the soil samples are mixed with a dominant contribution from petroleum and combustion of fossil fuel.

Tang et al. (2005) evaluated the sources of PAHs in urban soils in Beijing, China employing the ratios of phenanthrene to anthrene and fluoranthene to pyrene to ascertain pyrogenic and petrogenic sources, respectively. They found out that in majority of the soils, the sources of the PAHs were pyrogenic. These sources included motor vehicle exhausts, industrial activities and coal combustion. These information can be further used to assess the health risk associated with soils contaminated with PAHs.

Source identification of PAHs in urban surface soils from Beijing was carried out by Li et al. (2006) and characteristic ratios of anthracene (An)/(An+ phenanthrene (Phe)), fluoranthene (Flu)/(Flu+pyrene(Pyr)) and benzo[a]pyrene (BaP)/benzo[g,h,i]perytene (BghiP)

showed that the PAHs came from coal combustion however vehicular emission could not be ignored.

PAH compound ratios, such as phenanthrene/anthracene and fluoranthene/pyrene, were calculated to estimate the relative significance of different sources of PAHs in soil from the locality of Agbabu bitumen field of Southwestern Nigeria (Olajire *et al.,* 2007). The collected data indicate pyrolytic and petrogenic origins. The anthropogenic PAHs, i.e., pyrene and benzanthracene showed parallel distribution forms in the studied area, indicating that these compounds originated from a similar source.

Wang et al. (2008) in their study on the origin of PAHs in urban soils from two US cities employed diagnostic PAH concentration ratios to determine the sources of PAHs in Detroit and New Orleans, respectively: phenanthrene/anthracene ratios (2.97 and 5.36), benz(a)anthracene/chrysene ratios (0.99 and 0.85), benzo(b)fluoranthene/benzo(k) fluoranthene ratio (1.51 and 1.53), and benzo(a)pyrene/benzo(e)pyrene ratios (0.98 and 0.92). The ratios revealed that PAH concentrations are from pyrolytic sources, majorly vehicle exhaust as information from travel and gasoline usage in Detroit and New Orleans supported these findings.

Principal component analysis was used to find the potential sources of PAHs in soils of semi-urban areas in Tianjin, China (Lv *et al.,* 2010). It turned out that the burning of coal was the most significant source in the three districts except Beichen. To an extent, cooking, coking, traffic, and biomass burning also contributed to the polycyclic aromatic hydrocarbons pollution in these districts.

The source determination of PAHs in soils of oil exploration areas of the Niger Delta of Nigeria was examined by Sojinu et al. (2010). Assessment of the PAH compound ratios, phenanthrene/anthracene (Phen/Ant) and fluoranthene/pyrene (Flu/Pyr), suggested that the PAHs in most soil samples were predominantly of pyrogenic samples, an indication that gas flaring associated with oil exploration work in the Delta mostly affected the surface soils.

Peng et al. (2011) studied the sources of 16 polycyclic aromatic hydrocarbons (PAHs) in urban soils of Beijing. The results of sources identification suggested that the primary sources of PAHs were vehicle exhaust and coal combustion and the secondary source was atmospheric deposition of long-range transported PAHs.

Sojinu et al. (2011) evaluated the source of PAHs in surface soils affected by forest fires from Igbanko mangrove forest in Nigeria. PAHs source diagnostic ratios of Flu/(Flu+Pyr) and Ant/(Ant+Phe) indicated that the PAHs have a pyrogenic origin which may have resulted from combustion of grass, wood, or coal.

Nganje et al. (2012) investigated the sources of PAHs in soil in the location of fuel-oil spillage from a tank farm distribution facility, Esuk Utan, Calabar municipality, Nigeria. The ratio of Phe/Ant, Flu/Pyr, Flu (Flu +Pyr) and BaA/ (BaA +Chry) revealed diverse sources of PAH in the area. The PAHs origins include fire wood burning from cooking, fuel spills, burning of motor tyres and vegetation, vehicle repairs and motor exhaust.

Inegite et al (2012) predicted sources of PAHs in Kolo Creek soil using diagnostic ratios of parent PAHs. The study revealed that in wet season, the PAHs were mainly of combustion origin, while in the dry season, it was a combination of petroleum and combustion sources. Yang et al. (2012) determined the sources of PAHs in agricultural soils from the Huanghuai plain, China. Principal component analysis and multiple linear regression suggested that low temperature combustion, coal combustion and traffic emissions could be the primary PAH contributors in soils from the Huanghuai plain, contributing about 46.7 %, 42.1 % and 11.2 % of PAHs respectively.

Kwon and Choi (2013) carried out source analysis of PAHs in industrial soils from South Korea. They employed diagnostic ratios and the positive matrix factorization (PMF) model. The diagnostic ratios suggested that the soil were contaminated by pyrogenic sources and traffic emission while the result of PMF identified four sources: gasoline and heavy oil

combustion (14%), diesel combustion (54%), coke oven (23%), and coal/biomass combustion (9%).

Xiao et al. (2014) estimated the potential sources of PAHs in forest soils from urban, semi-urban, and rural areas in the Pearl River Delta of Southern China. The diagnostic ratios indicated that the PAHs in the forest soil were majorly from traffic emissions, mixed sources and coal/wood burning in the urban, semi-urban and rural areas, respectively. Principal component analysis revealed that traffic release, coal burning and residential biomass burning were the three principal contributors to forest soil PAHs in the Pearl River Delta. Long-range transportation of PAHs though atmosphere from urban area might also contribute to the PAHs distribution in the forest soils of rural area.

2.12   Eco-toxicological and health risk assessment of exposure to PAHs

Risk assessment may be defined as the characterization of the potential adverse health effects of human exposures to environmental hazards or the process of predicting the possible effect of a chemical or physical agent on a specified ecological system under a specific circumstance (Markins and McBratney, 2001). Risk assessment is a multi-step procedure comprising data collection and evaluation of contaminants concentrations, identification of exposed populations, and identification of potential exposure routes and the estimation of contaminants intakes for each pathway for a range of scenarios, toxicity assessment and risk characterization (Ferguson, 1998; USEPA, 1998; USDOE, 2011).

The most important factors influencing health risks that arise from soil contamination are: land use, potential occupancy by children, bioavailability of contaminants, potential exposure pathways and state of the site surface (NEPC, 1999; Poggio et al., 2008). The use of soil affects the selection of the variables defining exposure situations, exposure frequency and exposure pathways.

Several tools have been used to assess health risk of contaminants in sois. These include BaP toxic equivalent factors (BaP-TEF) and BaP mutagenic equivalent factors (BaP-MEF) and excess cancer risk.

2.12.1 The use of BaP-TEF and BaP-MEF

Detailed toxicological studies has been carried out on Benzo(a)pyrene (BaP), which is the most toxic PAH while little information is available for most of the other PAHs. Many individual PAHs have been considered to be of equivalent toxicity as BaP in most risk assessments (Jung et al., 2010). This approach could lead to overestimation of cancer and mutagen potency of individual PAH because most PAH have considerable lower toxicity than BaP when analyzed in the same assay systems (Durant et al., 1996; 1999; Nisbet and LaGoy, 1992). Several approaches have been employed to get a more precise assessment of possible risk of exposure to a complex mixture of PAH using toxic equivalency factors based on BaP (Nisbet and LaGoy, 1992; Durant et al., 1996; 1999). One of such approaches is the carcinogenic equivalency factor (TEF) that can vary at either low or high dose settings. Mutagenicity of individual PAH relative to BaP has also been evaluated by utilizing the mutagenic equivalency factor (MEF) proposed by Durant et al. (1996; 1999). Mutagenic activity, while not as consistently related with cancer (Zeiger, 1998; Zeiger, 2001), may have associations for other non-cancerous adverse health effects, such as pulmonary diseases (Seagrave et al., 2002; Demarini et al., 2004). A TEF is an estimate of the relative toxicity of a chemical compared to a reference chemical. For a mixture of carcinogenic PAHs, benzo(a)pyrene is the reference chemical and was selected because its toxicity is well known. The toxicity equivalency factor for each carcinogenic PAH is an estimate of the relative toxicity of the carcinogenic PAH compound compared to benzo(a)pyrene. The application of benzo(a)pyrene (BaP)-toxic equivalent factor and BaP mutagenic equivalent factor to polycyclic aromatic hydrocarbons (PAH) concentrations can provide a more accurate risk assessment from environmental exposure to PAH.

2.12.2 Excess lifetime cancer risk (ELCR)

Potential carcinogenic effects that are considered by approximating the probability of cancer occurrence in a group of persons for a specific lifetime from expected intakes and chemical-specific dose-response data (i.e., slope factors). By multiplying the intake by the slope factor, the ELCR result is a possibility. The additional or extra risk of having cancer as a result of exposure to a toxic substance acquired over the lifetime of a person (http://www.opentoxipedia.org/index.php/Excess_Lifetime_Cancer_Risk). Excess cancer risk is calculated for the lifetime exposure, estimated as the incremental probability of an individual developing cancer over a lifetime as a result of total exposure to carcinogenic PAHs. Humans are exposed to PAHs through three major routes which are ingestion, inhalation and dermal contact (De Miguel et al., 2007). Excess cancer risk is calculated as the sum of the cancer risk from the three exposure routes.

Eco-toxicological and health risk assessment of PAHs exposures have been evaluated by many researchers. For instance, Peng et al. (2011) evaluated the human health risk associated with PAHs exposure in urban soils of Beijing. They found out that the incremental lifetime cancer risks (ILCRs) of' persons exposed to PAHs in the soils for adult were 1.77×10^{-6} and 2.48×10^{-5} under normal and extreme conditions respectively. For child, they were 8.87×10^{-7} and 6.72×10^{-6} under normal and extreme conditions respectively.

Olawoyin et al. (2012) evaluated human exposure risk to carcinogenic PAHs in the Niger Delta of Nigeria using the toxic equivalence factors (TEFs), mutagenic potency equivalent factors (MEFs) and the incremental lifetime cancer risk (ILCR). BaP-TEQ (mg/kg) for $\sum_{carc}^{soil}$ PAHs were determined as 98.65 ± 125.81 and varies from 68.20-953.84kg/kg while the MEQ (mg/kg) for $\sum_{carc}^{soil}$ 7PAHs were determined as 124.01 ± 163.37 and varied from 87.24-1 237.82 mg/kg. The BaP-TEQ (mg/kg) for $\sum_{carc}^{soil}$ 7PAHs were determined as

16.79±14.44 and varied from 5.55-52.69 mg/L, similarly the BaP-MEQ (mg/Kg) for $\sum_{total}^{H20}$PAHs were determined as 9.29 ± 8.15 and varied from 1.55- 2980mg/kg. The cumulative ILCR from the water and soil contaminations were determined as $1.13x10^{-4}$ and $6.42x10^{-4}$ respectively for children, while values of $1.09x10^{-4}$ and $6.19 xl0^{-4}$ were determined respectively for adult. Their study indicate contamination of environmental matrices in the region with high possibility of acute toxicity substantial enough to induce carcinogenicity and chronically affect the human health of residents with long-term exposures. Man et al. (2013) carried out a study to evaluate soils from 12 different land use types on human cancer risks and found out that cancer risk probabilities on humans due to ingestion and dermal exposure indicated a moderate potential for cancerous development.

Kumar et al. (2014) studied the distribution health risk of selected priority PAHs in residential street soils from an industrial city. Benzo(a)pyrene toxicity equivalency (BaPTEQ) for studied PAHs was estimated to range from $0.61 -197$ µg BaPTEQ kg^{-1} with the mean value of 46.78 ± 15.97 µg BaPTEQ kg^{-1}.

Kumar et al. (2015) estimated the toxicity equivalence and probabilistic health risk on lifetime daily intake of PAHs from urban soils. They found out that the BaP TEQ and index of additive cancer risk (IACR) were lower than guideline values of 0.6 mg kg^{-1} and <1, respectively. Also, estimated lifetime average daily intakes of PAHs via soil ingestion were lower than recommended dose. However, they found out that the ILCR for adults was within acceptable limits recommended by regulatory agencies, but may require action for children in Gwalior, India.

CHAPTER THREE

MATERIALS AND METHODS

3.1   Description of study area

The River Niger is the major river of West Africa, stretching approximately 4,180 km (2,600 miles). Its drainage basin is 2,117,700 km^2 (817,600 sq metre) in area. River Niger arises from Fouta Djallon highland in Guinea arriving in Nigeria through Kebbi State and flows through to the Atlantic Ocean (Olatunji, and Osibanjo, 2012). The study area is within the extent of the River Niger stretch traversing Asaba to Aboh area in the lower River Niger regime of Nigeria (Figure 1). The area lies between longitude 6.16^o to 6.43^o E and latitude 6.02^o to 6.43^o N. The study area has well defined dry and rainy seasons, and   a total rainfall of between 2,700 and 3,000 mm per year spread over the months of April to October. The maximum mean daily   temperature   ranged from 25 ^{o}C to 33 ^{o}C throughout the year. The mean relative humidity varies from 65 to 80%. The soil is hydromorphic and was characterized by rampant flooding and water logging which resulted from poor drainage, high soil bulk density and crusting, and improper urban settlement and human activities. Flooding is experienced at the peaks of the rainy season (July and September) (Ogbodo, 2011) every year and covers the floodplain.   A combination of heavy rain and sufficient sunshine along with adequate soil nutrients has created thick vegetation cover in the study area. The vegetation is made up of mangrove swamp forest, tall evergreen trees including pines with prolific undergrowth of entangled shrubs (Olatunji, and Osibanjo, 2012; Oyo-Ita *et al.,* 2011). The Niger River system sustains an extensive biological community, hosting diverse ecosystems. The upstream section of the study area (i.e. Asaba-Onitsha axis (AS1-AS5) is characterised by urbanization, industrial development and agricultural development. The mid-stream section (OK1-OK3) is a typical rural setting and the main activity in the area is farming. At the downstream section

(AB1-AB5), the major activity in these areas is canoeing and farming. There are clusters of oil wells, flow stations, pipelines, gas plant, independent power plant and multiple gas flaring points located few kilometres upstream of stations AB1-AB5. The approximate distance between the upstream sampling points and downstream sampling point is 102 km. The midstream sampling points were approximately 32 km from the upstream sampling points.
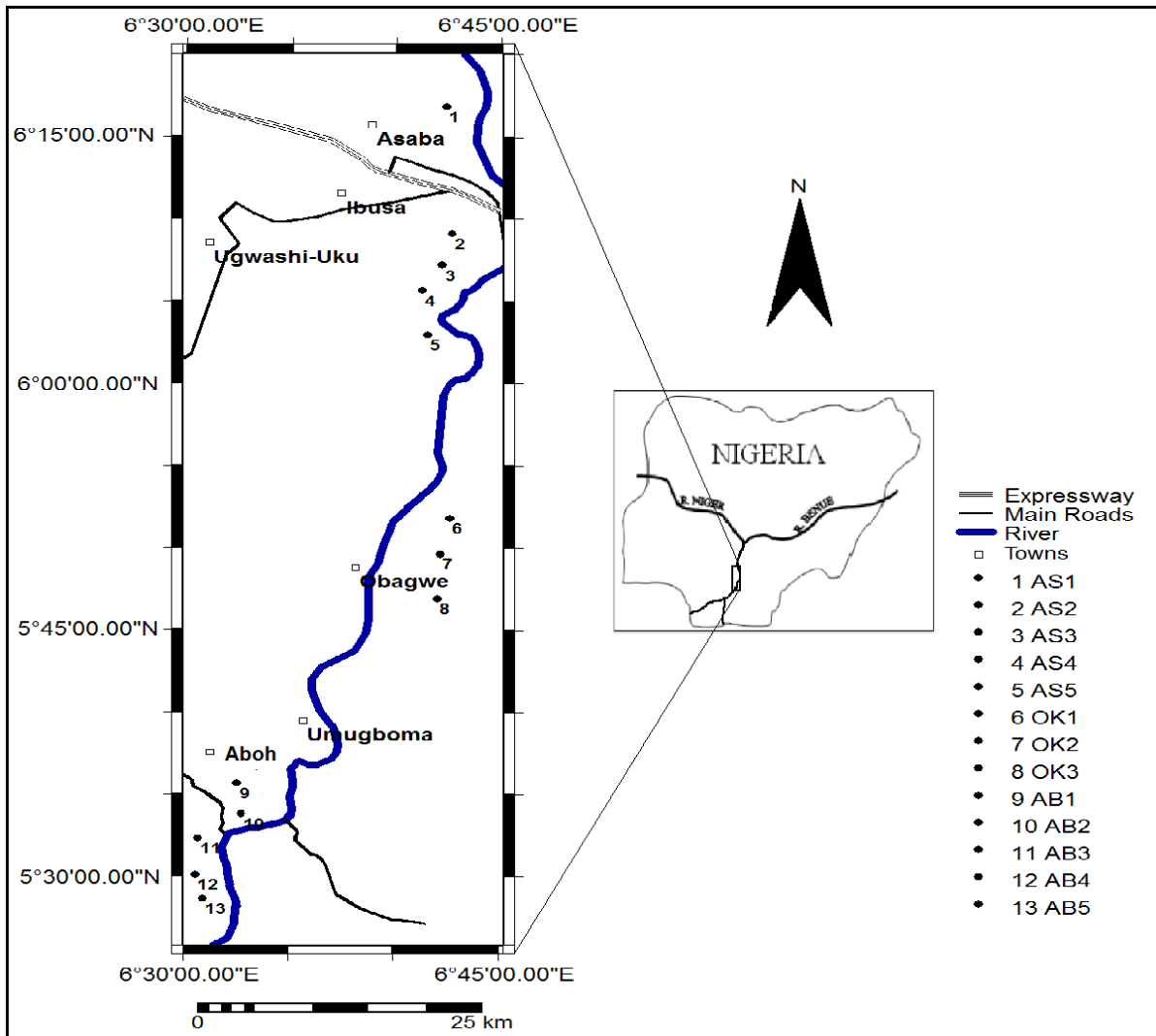
Figure 1: Map of study area

3.2   Sample Collection

Soil samples were collected three months after the Ladgo dam flood disaster of 2012 when the flood water has receded completely and a year after the major flooding. Soil samples were collected from 13 different locations designated as AS1-AS5, OK1-OK3 and AB1-AB5 along the floodplain of the River Niger. The soil samples were collected at 0-15 cm, 15-30 cm and 30-45 cm depths using stainless steel auger. Soil samples for metal analysis were stored in polythene bags while those for polycyclic aromatic hydrocarbons were stored in glass containers and kept in ice chest. Samples were labelled properly and transported back to the laboratory. In the laboratory, the soil samples were air dried in the dark, sieved through 2 mm mesh, and stored at -4 °C until analysis.

3.3   Determination of soil physicochemical characteristics

3.3.1   pH

The soil pH was determined in soil suspension (1:2 soil to water ratio) using a glass electrode pH meter (Abollino *et al.,* 2002). 10 g of soil was placed in beaker 20-ml of deionized water was added. The mixture was stirred and allow to stand for 15 minutes. Then, pH meter was placed into sample suspensions and read directly off display.

3.3.2   Conductivity

5 g of soil was placed in beaker or vial and 10-ml of deionized water was added. The mixture was stirred and allow to stand for 15 minutes. Then, conductivity probe was placed into sample suspensions and read directly off display while stirring the probe in the solution.

3.3.3   Total Organic Carbon

The wet oxidation digestion method of Walkley and Black (1934) as described by Radojevic and Bashkin (1999) was used. This method involves the quantification of the amount of oxidizable carbon as determined by reaction with excess dichromate and sulphuric acid. The

remaining unreacted dichromate is titrated with ferrous sulphate using 1, 10- phenanthroline as indicator.

Procedure: 0.5 g of air-dried, homogenised and sieved soil sample was weighed into a conical refluxing flask. 10 mL of standard $K_2Cr_2O_7$ (Sigma-Aldrich) solution was added and swirled to mix. 15 mL of concentrated H_2SO_4 (Sigma-Aldrich) was carefully added. The flask connected to a condenser and cooling water turned on with the open end of the condenser covered with a small beaker. Flask was placed in a hot plate and refluxed for 1 h. Thereafter, the solution was cooled and condenser rinsed with distilled water. Flask was disconnected from the condenser and 100 mL of water added. The solution was swirled to mix and 5 drops of Ferroin indicator was added. Thereafter, the sample solution was titrated with ferrous ammonium sulphate to the end point at which the colour changes from blue-green to violet-red. Also, a blank determination was carried out in the same way.

$$\text{Organic carbon (mg g}^{-1}) = \frac{18 \times \text{ C } \times \text{ V}}{M} \times \left(1 - \frac{V_1}{V_2}\right) \qquad (1)$$

Where; C is the concentration in mol/L of the dichromate solution (0.166M), V is the volume of dichromate solution used (10 mL), V_1 is the volume (mL) of titrant used up in the sample determination, V_2 is the volume (mL) of titrant used up in the blank determination respectively and M is the weight of sample used (g).Percent organic carbon was evaluated as;

$$\text{Organic carbon (\%)} = \frac{Organic\ carbon\ \text{(mg g}^{-1})}{10} \quad (2)$$

3.3.4   Particle size distribution

Particle size distribution was determined using the hydrometer method developed by Bouyoucos (1962). 100 g of soil sample was weighed into a 1000 mL plastic beaker. 75 mL of distilled water and 15 mL of H_2O_2 (Sigma-Aldrich) were added and gently stirred with a glass rod. 200 mL of distilled water and 100 mL sodium hexametaphosphate solutions were added

and the solution was stirred, covered and kept for 4 to 5 hrs. Thereafter, the solution was made up to 500 mL and stirred for 10 min. Then the whole content was quantitatively transferred to a suspension cylinder and made up to 1000 mL with distilled water. The cylinder was stoppered tightly and shaken several times to allow the soil particles to disperse completely. Then the stopper was removed and the hydrometer was immediately placed in the suspension. Hydrometer reading was recorded exactly 40 seconds after placement of hydrometer (S_1 and B_1). Thereafter, the cylinder was stoppered and inverted several times again to ensure complete dispersal of particles. Hydrometer was placed into suspension after two hours and the reading recorded (S_2 and B_2). Blank determination was simultaneously carried out and the room temperature in ^oF was also recorded. Particle size distribution was thus obtained using the expressions;

$$\% \text{ Silt} = \frac{(S_1 - B_1) + CF}{Weight\ of\ sample\ (g)} \times 100 \qquad (3)$$

Where,

Contamination factor (CF) = (Room temperature in ^oF – 68) × 0.2

S_1 and B_1 are hydrometer reading of sample and blank taken at 40 seconds

$$\% \text{ Clay} = \frac{(S_2 - B_2) + CF}{Weight\ of\ sample\ (g)} \times 100 \qquad (4)$$

S_2 and B_2 are hydrometer reading of sample and blank taken at 2hrs

% Sand = 100 – (Silt + Clay) $\qquad$ (5)

3.3.5 Determination of Cation Exchange Capacity (CEC)

Cation exchange capacity (CEC) of the soil samples was determined as the sum of basic cations extracted with neutral IM NH_4OAC (Sigma-Aldrich) and extractable acidity (Reeuwijk, 1995).The extractable Na^+, K^+, Mg^{2+} were determined by flame photometry and Ca^{2+} by Atomic absorption spectrometry.

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3.4 Determination of metals in soil

3.4.1 Samples digestion

0.5g of the soil sample was placed in digestion tube followed by addition of 15 mL of aqua regia (3:1 HCl:HNO$_3$) (Sigma-Aldrich) and was swirled to wet the sample and allowed to stand overnight. The next day, the tube was heated in a heating block of 50°C for 30 min and raise to temperature of 120 ^{o}C for 2 hr. The digest was made up dissolved with 0.25 mol/L HNO$_3$ and filtered through Whatman No. 1 filter paper and made up to 25 mL with 0.25 mol/L HNO$_3$ (Radojevic and Bashkin, 1999).

3.4.2 Analysis of samples for metals

The sample solutions were analyzed for Fe, Mn, Zn, Cu, Pb, Cd, Cr, Co, Al, Ba and Ni using inductively coupled plasma optical emission spectrophotometry (Perkin Elmer, 4300 D8 Watham Masechusett, USA).

3.5 Chemical Fractionation of metals in soils

In this study, the chemical fractionation of the metals was carried out using the three step sequential extraction procedure recommended by the Standards, Measurement and Testing (SM &T) programme of the European Commission, formerly known as the Community Bureau of Reference (BCR). The BCR three stage extraction procedure is as follows:

Step 1 (Exchangeable/acid soluble fraction)

For each sample, 1.0 g of soil was placed into 100 mL polypropylene centrifuge tube. 40 mL of 0.11 mol L^{-1} acetic acid (Sigma-Aldrich) was added to the centrifuge tube. The tube was stoppered and extracted by shaking for 16 hours (overnight) at room temperature. Thereafter, the extract was separated from the solid residue by centrifugation at 3000 rpm for 20 min. The supernatant solution was decanted into a polypropylene centrifuge tube, stoppered and stored in a refrigerator at 4 °C prior to analysis. The residue was washed with 20 mL of

distilled water, shaken for 15 min on an end-over-end shaker and then centrifuged for 20 min at 3000 rpm. The supernatant was decanted and discarded carefully leaving the residue.

Step 2 (reducible fraction - bound to Fe and Mn oxides)

40 mL of 0.5 mol L^{-1} hydroxylamine hydrochloride (Sigma-Aldrich) (adjusted to pH of 2.0 by addition of 2 mol L^{-1} HNO_3) was added to the residue from step 1 in the centrifuge tube. Again, the tube was stoppered and extracted by shaking for 16 hours (overnight) at room temperature. Thereafter, the extract was separated from the solid residue by centrifugation at 3000 rpm for 20 min. The supernatant liquid was decanted into a polypropylene centrifuge tube, stoppered and stored in a refrigerator at 4 °C prior to analysis. The residue was washed with 20 mL of distilled water, shaken for 15 min on an end-over-end shaker and then centrifuged for 20 min at 3000 rpm. The supernatant was decanted and discarded carefully leaving the residue.

Step 3 (oxidizable fraction - bound to organic matter and sulphides)

10 mL of 8.8 mol L^{-1} hydrogen peroxide (H_2O_2) (Sigma-Aldrich) (pH of 2-3) was added carefully, in small aliquots, to the residue from step 2 in the centrifuge tube. The tube was covered loosely and digested at room temperature for 1 h with occasional shaking. The digestion was continued at 85 ± 2 °C, with occasional manual shaking for the first half-hour (30 min) in a water bath and then the volume was reduced to less than 3 mL by further heating of the uncovered tube. Thereafter, 10 mL of hydrogen peroxide was further added to the tube, covered and heated again at 85 ± 2 °C and digested for 1 h with occasional shaking for the first half-hour (30 min). Then the cover was removed and the volume reduced to about 1 mL by further heating. After cooling, 50 mL of 1.0 mol L^{-1} ammonium acetate (adjusted to pH 2 by adding of concentrated HNO_3) was added to the residue and then extracted by extracted by mechanical shaking for 16 hours (overnight) at 22 ± 5 °C and a speed of 30 ± 10 rpm.

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Thereafter, the extract was separated from the solid residue by centrifugation at 3000 rpm for 20 min. The supernatant liquid was decanted into a polypropylene centrifuge tube, stoppered and stored in a refrigerator at 4 °C prior to analysis. The residue was washed with 20 mL of distilled water, shaken for 15 min on an end-over-end shaker and then centrifuged for 20 min at 3000 rpm. The supernatant was decanted and discarded carefully leaving the residue.

Step 4 (Residual fraction- strongly associated with the crystalline structures of the minerals)

This step was not part of the BCR procedure but was adopted as a measure of quality control checks. The residue from step 3 was digested with 10 mL of aqua regia. After cooling, the digests were centrifuged at 3000 rpm for 20 minutes and the supernatant liquid decanted into a polyethylene container. Then the container was stoppered and stored in a refrigerator at 4 °C prior to analysis.

The supernatants from each step were analysed for metal concentrations using inductively coupled plasma-optical emission spectrometer (Perkin Elmer, 4300 D8 Watham Masechusett, USA).

Calculation for the concentrations in each fraction was done using;

$$\text{Metal } (\mu g\ g^{-1}) = \frac{(\text{Instrument Reading} - \text{Blank} \times 20)}{0.5g}$$

3.6   Determination of polycyclic aromatic hydrocarbons (PAHs)

3.6.1   Extraction and Clean-up of PAHs from samples

The soil samples were prepared for analysis following the US EPA-3550C-ultrasonic extraction method (US EPA, 2007). A mass of 10.0 g of the soil samples was mixed with same amount of Na_2SO_4. The resulting material was extracted by ultrasonication with 50 mL of hexane/dichloromethane (DCM) (1:1 v/v) at 30 °C for 30 minutes. The contents were filtered and the process was repeated three times by sonication of the residue with a fresh mixture of acetone/dichloromethane each time. The extracts were evaporated to 1 mL by using a rotary

evaporator and purified by solid phase extractions with 2 g of aluminium oxide (5 % deactivated lower part). The PAHs were subsequently eluted with 15 mL of hexane, 15 mL hexane and dichloromethane (9:1) and 20 mL of hexane and dichloromethane (4:1). The eluted fractions were combined and evaporated to approximately 0.5 mL using stream of nitrogen gas.

3.6.2 Gas Chromatographic Analysis

The individual PAH was quantified using gas chromatography (Agilent 6890 Agilent Aundate USA) equipped mass spectrometry. Separation was effected on a HP5 (cross-linked PHME siloxane) column with (0.25 µm film thickness and dimensions of 0.25 mm x 30 m). The carrier gas was helium with a linear flow rate of 30 cm/s. The mass spectrometer was operated in electron impact mode (70 eV). The column temperature was programmed at a rate 25 ^{o}C/min from initial temperature of 60 ^{o}C to a temperature of 180 ^{o}C (1- min hold), then at 3 ^{o}C/min to 280 ^{o}C (30 min hold). The injector, transfer line and ion source temperature were 280, 250 and 250 ^{o}C respectively. The PAHs were monitored in selected ion monitoring (SIM) mode. The quantification was by the use of external calibrations which were obtained with PAH solutions at five concentration levels.

3.7 Quality Control/Assurance and Statistical Analysis

Quality control was assured by the use of blanks and spike recovery method. Reagent blank were analyzed with each batch of 5 samples. The acids used for digestion were of analytical grades. The spike recoveries for the various metals ranged from 92.6 to 104.3 %. Calibration standards for atomic absorption analysis were prepared by diluting a commercial Merck 1000 mg/L solutions of various metals with 0.25 M HNO$_3$ to closely matching the matrix of diluted digest.The r^2 values for the calibration lines for the metals were in the range of 0.9993 to 0.9999.

To evaluate the PAHs extraction efficiency, known concentrations of a standard PAH mixture were added to already analyzed samples and re-analyzed. The recoveries for the PAH compounds were in the range of 70.8 to 98.7%. The relative standard deviations for replicate analyses (n = 3) were less than 5%.

3.8   Statistical Analysis

One way Analysis of variance (ANOVA) was used to determine whether the concentrations and profiles of PAHs varied significantly among the various sites and depth with p-value less than 0.05 ($p<0.05$) considered to be statistically significant. The statistical calculations were performed with SPSS 11.5 version. Relationship between individual metals and PAHs was established by means of Pearson correlation coefficient.

3.9   Data Treatment

3.9.1   Contamination/pollution index

Assessment of soil for heavy metal pollution based on absolute metal content values provide inadequate information on the significance of the value obtained with the intrinsic soil feature and how the values are related to the maximum allowable limits for the metals (Iwegbue, 2014; Iwegbue *et al.,* 2010). The contamination/pollution index highlights the degree of contamination/pollution of a study site. The contamination/pollution index was computed as the ratio between metal effectively measured by chemical analysis to reference value. The contamination/pollution index was derived by employing the contamination/ pollution index as defined by Lacutusu (2000).

$$C/PI \quad = \quad \frac{Concentration\ of\ metal\ in\ soil}{Target\ value} \qquad (6)$$

In this study, the guideline values for metals as specified by the Department of Petroleum Resources of Nigeria were adopted as reference values (DPR, 2002). The conversion formula

used for the C/P index varies from one country to another because regulatory control limits vary from one country to another. C/P1> 1 refers to the pollution range while C/PI<1 define the contamination range. Metals in the environment may have synergistic, additive or antagonistic on one another. For this reason, the multiple pollution index (MPI) was derived from the addition of the C/PI values for the individual metals that were greater than 1. The computed C/P index and multiple pollution index (MPI) values were interpreted according to the scheme provided below. The categorization of degree of contamination/pollution based on this index is as follows: <0.1 = Very slight contamination; 0.10-0.25 = Slight contamination; 0.26-0.5=Moderate contamination; 0.51-0.75 = Severe contamination; 0.76-1.00 = Very severe contamination; 1.1-2.0 = Slight pollution. 2.1-4.0 = Moderate pollution; 4.1-8.0 = Severe pollution; 8.1-16.0 = Very severe pollution; >16.0 = Excessive pollution (Lacatusu, 2000).

3.9.2   Quantification of Enrichment Factor (EF)

The enrichment factor (EF), due to its universal formula, is a relatively simple and straightforward tool for measuring the extent of enrichment and for comparing the contamination levels of different environmental media (Agca and Ozdel 2014; Iwegbue, 2014). Heavy metals enrichment factor is used to distinguish between metal originating human activities and those of natural processes. Enrichment factor of metals in the soil was calculated following the equation of Reimann and De Caritat (2000).

$$\text{EF} = \frac{Cn \ (test \ element)}{Cn \ (Reference)} \quad \div \quad \frac{Bn \ (test \ element)}{Bn \ (Reference)} \qquad (7)$$

Where

Cn = Concentration of the test metal in the sample

Cn_{ref} = Concentration of the reference metal in the sample

Bn test element = background concentration of the test metal in crustal rock

Bn_{ref} background concentration of the reference metal in crustal rock (Reimann and De Caritat, 2000). In this case, Aluminium is chosen as the reference element because it is the most

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abundant element in the earth crust. The crustal abundance values for the respective metals (Turekian and Wedepohl, 1961) were used as background concentrations for the estimation of the enrichment factors. Five contamination categories are recognized on the basis of the enrichment factor (Suntherland, 2000; Loska and Wiechula, 2003). EF<2 =Deficiency to minimal enrichment. EF=2-5 = Moderate enrichment. FE=5-20 = Significant enrichment. EF=20-40 =Very high enrichment. EF>40 =extremely high enrichment.

3.9.3 Geoaccumulation index (Igeo)

The index of geoaccumulation enables the assessment of contamination by comparing the current and pre-industrial concentration in bottom sediment (Muller, 1969). It can also be applied to assessment of soil contamination. The geoaccumulation index is given by the equation:

$$\text{Igeo} = \text{Log } 2 \frac{C_n}{1.5B_n} \tag{8}$$

Where Cn is the measured concentration of the metal and Bn is the background concentration. In this case, the background concentration is the crustal abundance values of the respective metals (Turiekian and Wedepohl, 1961).The factor 1.5 is applied because of the possible variations in the background values due to lithological variations (Rogan *et al.,* 2010).The Muller index of geoaccumulation Igeo is divided into seven grades ranging from unpolluted to very seriously polluted. The interpretation for the geoaccumulation index is as follows: Igeo < 0 = practically unpolluted (class 1), 0-1 = unpolluted to moderately polluted (class 2), 1-2 = moderately polluted (class 3), 2-3 = moderately to strongly polluted (class 4), 3-4 = strongly polluted (class 5), 4-5 = strongly polluted to very polluted (class 6) and >5 = extremely polluted (class 7).

3.9.4 Pollution load index

Pollution load index was estimated using the equation;

$$\text{PLI} = \sqrt[n]{CF1 \times CF2 \times CF3 \times CF4 \times ... CFn} \qquad\qquad (9)$$

Where n = number of metals studied

CF = Contamination factor

$$\text{CF} = \frac{Cs}{Cn}$$

Where Cs and Cn are metal concentrations for samples and background respectively. Also, the background concentration used are the crustal abundance values of the respective metals (Turiekian and Wedepohl, 1961). PLI provides a simple but a comparative means of assessing site quality where a value of PLI <1 denotes perfection; PLI=1 present a baseline level of pollutant and PLI>1 indicate deteriorating site quality.

3.9.5 Ecological risk assessment metals in soils

The method of determining ecological risks of metals was originally introduced by Hakanson (1980). The index has been applied for ecological risks assessments of metals in dusts, sediments and soil (Saeedi *et al.,* 2012; Li *et al.,* 2013; Shi *et al.,* 2014). The potential ecological risk index is given by the equation.

$$\text{RI} = \Sigma\, \text{Er} \qquad\qquad (10)$$

Where Er = Tr $\times$ CF

$$\text{CF} = \frac{Cs}{Cn}$$

Where; Tr is the biological toxic factor of a single metal. Hekanson (1980) demonstrated Tr value for Cd, Cu, Pb, Cr, Zn, Ni, Co and Mn to be 30, 5, 5, 2, 1, 5, 2 and 1 respectively. CF is contamination factor, Cs and Cn are metal concentrations for samples and background respectively. Also, the background concentrations used are the crustal abundance values of the respective metals (Turiekian and Wedepohl, 1961). Er is the ecological risk of each metal and RI shows the ecological risk of multiple metals. The Er and RI have been classified into five and four categories depending on their values respectively. Er value <40 denotes low potential

ecological risk; ≥40<80 moderate potential ecological risk; ≥80<100 strong potential ecological risk; ≥100<320 very strong potential ecological risk and ≥320 extremely strong potential ecological risk. RI value <150 indicates low ecological risk; ≥150<300 moderate ecological risk; ≥300<600 strong ecological risk and ≥600 very strong ecological risk.

3.9.6 Human exposure and health risk assessment of metals

Humans can be exposed to heavy metals in agricultural soil through three pathways which are direct ingestion of soil, inhalation of particulates emitted from soil and dermal absorption of heavy metals through soil adhered to exposed skin (Shi *et al.,* 2014; Lai *et al.,* 2010). The non-carcinogenic and carcinogenic risk of these exposure pathways were considered in this study. The non-carcinogenic hazard risk (HI) for children and adults was calculated using equations (11) – (15) adapted from USDOE (2011) and USEPA (2011; 2001).

$$CDI_{ing\text{-}nc} = \frac{C \times IngR \times EF \times ED}{BW \times AT_{nc}} \times 10^{-6} \tag{11}$$

$$CDI_{inh\text{-}nc} = \frac{C \times EF \times ET \times ED}{PEF \times 24 \times AT_{nc}} \tag{12}$$

$$CDI_{dermal\text{-}nc} = \frac{C \times SA \times AF \times ABSd \times EF \times ED}{BW \times AT_{nc}} \times 10^{-6} \tag{13}$$

$$\text{Hazard Quotient (HQ)} = \frac{CDI_{nc}}{RfD} \tag{14}$$

$$\text{Hazard index (HI)} = \sum HQ = HQ_{ing} + HQ_{inh} + HQ_{dermal}$$

$$\text{Hazard index (HI)} = \frac{C\,DI_{ing}-nc}{RfD_{ing}} + \frac{CDI_{inh}-nc}{RfC_{inh}} + \frac{CDI_{dermal}-nc}{RdDermal} \tag{15}$$

The carcinogenic risk was calculated for the life time exposure, estimated as the incremental probability of an individual developing cancer over a lifetime as a result of total exposure to the potential carcinogens (Cd, Cr, Ni and Pb). The carcinogenic hazard risk (Total Risk) for children and adult was calculated using equation (16) - (23) adapted from USDOE (2011).

$$CDI_{ing}\text{-}ca \quad = \frac{C \times IngRadj \times EF}{ATca} \times 10^{-6} \tag{16}$$

$$IngR_{adj} = \frac{ED_{child} \times IngR_{child}}{BW_{child}} + \frac{(ED_{adult} - ED_{child})}{BW_{adult}} \times IngR_{adult} \tag{17}$$

$$CDI_{inh} - ca = \frac{C \times EF \times ET \times ED}{PEF \times 24 \times ATca} \times 10^3 \tag{18}$$

$$CDI_{dermal} - ca = \frac{C \times ABSd \times EF \times DFSadj}{ATca} \times 10^{-6} \tag{19}$$

$$DFS_{adj} = \frac{ED_{child} \times SA\,child \times AF\,child}{BW_{child}} + \frac{(ED_{adult} - ED_{child}) \times SAadult \times AF\,adult}{BW_{adult}} \tag{20}$$

$$Risk = CDI_{ca} \times CSF \tag{21}$$

$$Total\ Risk = Risk_{ing} + Risk_{inh} + Risk_{dermal} \tag{22}$$

$$Total\ Risk = CDI_{ing} - ca \times CSF_{ing} + CD_{inh}\text{-}ca \times IUR + \frac{CDI_{dermal} \times CSF_{ing}}{ABS_{GI}} \tag{23}$$

Where;

CDI_{ing}, CDI_{inh}, CDI_{dermal} are the chronic daily intake or dose contacted through ingestion, inhalation and dermal contact with soil respectively. RfD is the Reference dose, RfD_{ing} (Chronic oral reference dose), RfC_{inh} (chronic inhalation reference concentration), RfD_{dermal} (Chronic dermal reference dose = RfD_{ing} x ABS_{GI}) through the three exposure pathway respectively. CSF_{ing} is chronic oral slope factor via injection, IUR is the chronic inhalation unit risk, CSF_{dermal} is chronic dermal slope factor = CSF_{ing}/ABS_{GI} and C is the concentration of metals in soil. The definitions of symbols, used values of Nigerian-specific variables and parameters are shown in Tables 3.1 and 3.2.

Qualitative description of human health risk assessment followed that HQ value above 1 suggest level of concern. That is HQ $\leq$ 1 suggested unlikely adverse health effects whereas HQ > 1 suggests the probability of adverse health effects (Luo *et al.,* 2012). In general, the total cancer risk lower than 10^{-6} (a probability of 1 chance in 1,000,000 of an individual developing cancer) are considered to be negligible and cancer risks above 10^{-4} are considered unacceptable by most international regulatory agencies (Luo *et al.,* 2012, Guney *et al.,* 2010; USEPA, 1989). The value 10^{-6} is also considered the carcinogenic target risk (USEPA, 2011, Luo *et al.,* 2012).

Table 3.1: Values of variables for estimation of human health risk assessment

Parameters	Unit	Definition	Values		References
			Child	**Adult**	
C	µg/g	Metals concentration in soil			
ABS_d	-	Dermal absorption factor for metals	0.03	0.001	USEPA, 2011
ABS	-	Dermal absorption factor for PAH compounds	0.13	0.13	USEPA, 2011
AF	mg/cm^2	Soil to skin adherences factor	0.2	0.07	USEPA, 2011
BW	kg	Average body weight	15	60	Iwegbue et al. (2014)
ED	Year	Exposure duration	6	30	USEPA, 2001
EF	d/yr	Exposure frequency	313	313	USEPA, 2001
ET	h/d	Exposure time	8	8	USEPA, 1987
IngR	mg/d	Soil ingestion rate for receptor	200	100	USDOE, 2011
SA	cm^2/event	Skin surface area	2800	5700	USDOE, 2011
ATnc	d	Averaging time for non-carcinogenic	ED x 365		USDOE, 2011
ATca	d	Averaging time for carcinogenic	LT x 365		USDOE, 2011
DFS_{adj}	mg/yr/kg/d	Soil dermal contact for-age-adjusted	384		Equation (j)
$IngR_{adj}$	mg/yr/kg/d	Soil ingestion rate-age adjusted	120		Equation (g)
LT	Year	Lifetime	52 years		World Bank, 2014
PEF	m^3/kg	Soil to air particulate emission factor	1.36×10^9		USDOE, 2011

Table 3.2: Toxicological parameters of the investigated metals and PAHs used for health risk assessment

Element/PAHs	CSF_{ing} (mg/kg/d)	IUR (µg/m³)	RfD_{ing}	RfC_{inh}	ABS_{GI}
Cd		1.8×10^{-3}	1.0×10^{-3}	1.0×10^{-5}	0.025
Cr	5.0×10^{-3}	1.2×10^{-2}	3.0×10^{-3}	1.0×10^{-4}[*]	0.013
Ni		2.6×10^{-4}	2.0×10^{-2}	9.0×10^{-5}	0.04
Ba			$2.0 \ 10^{-1}$	5.0×10^{-4}[*]	
Al			1.0	$5.0 \ 10^{-4}$	
Fe			7.0×10^{-1}		1
Zn			3.0×10^{-1}	4.0×10^{-3}[**]	1
Co			3.0×10^{-4}	6.0×10^{-6}	1
Pb	8.5×10^{-3}	1.2×10^{-5}	3.5×10^{-3}	2.0×10^{-4}[**]	1
Mn			1.4×10^{-1}	5.0×10^{-5}[*]	1
Cu			4.0×10^{-1}	1.4×10^{-3}[*]	1
BaA	7.3×10^{-1}				1
Chry	7.3×10^{-3}				1
BbF	7.3×10^{-1}				1
BkF	7.3×10^{-2}				1
BaP	7.3				1
IndP	7.3×10^{-1}				1
DahA	7.3				1
Reference	USDOE, 2011	USDOE, 2011	USDOE, 2011	USDOE, 2011	USEPA, 2011

* USEPA (1997); ** MOEE, 2008

3.9.7   Assessment of health-risk from PAHs exposure

The risks of human from exposure to PAHs contaminated soils are evaluated using the BaPyr toxic equivalent factor (BaP$_{TEF}$), BaP mutagenic equivalent factor (BaP$_{MEF}$) and Incremental Life Cancer Risk models. These models have been used to evaluate the risks of PAHs in soils, dust and foods by several researchers (Thompson *et al.,* 1990; Nisbet and LaGoy, 1992; USEPA, 1993; Larsen and Larsen, 1998; Durant, 1996).

The BaP carcinogenic equivalent (BaP$_{TEQ}$) for the individual PAHs was calculated using the equation

$$BaP_{TEQ} = \sum C_i \times BaP_{TEF} \qquad\qquad (18)$$

Where BaP$_{TEF}$ is the cancer potency relative to BaP and C_i is the individual PAH concentration.

The BaP mutagenic equivalent (BaP$_{MEQ}$) for the individual PAHs was evaluated using the equation:

$$BaP_{MEQ} = \sum C_i \times BaP_{MEF} \qquad\qquad (19)$$

Where BaP$_{MEF}$ is the mutagenic potency relative to BaP and C_i is the individual PAH concentration.

The BaP toxic equivalency factors (BaP$_{TEFs}$) of the seven carcinogenic PAHs used are BaP (1), BaA (0.1), BbF (0.1), BkF (0.01), Chry (0.001), DahA (1) and IndP (0.1) (USEPA, 1993) while the BaP$_{MEFs}$ are BaP (1), BaA (0.082), BbF (0.25), BkF (0.11), Chry (0.017), DahA (0.29) and IndP (0.31) (Durant, 1996).

3.9.8   Incremental Lifetime Cancer Risk (ILCR) from PAHs

Exposure risk assessment was carried out by using the USEPA standard methods assuming the three major routes of exposure; ingestion, dermal and inhalation of vapour or dust-IDI (USEPA, 2009). The carcinogenic total risk was calculated from the summation of the individual risks through each route of exposure. The evaluation of the ILCR in terms of IDI

was carried out by using the parameters in Tables 3.1 and 3.2; and equation 20-22 (USEPA 1989; USEPA, 2009).

$$ILCR_{ing} = \frac{Csoil \times IngR \times EF \times ED \times CF \times SFO}{BW \times AT} \tag{20}$$

Where, $ILCR_{ing}$ is the incremental lifetime cancer risk via ingestion of soil particles; Csoil is the concentration of the pollutant in soil (mg/kg); IngR is the ingestion rate of soil (mg/day); EF is the exposure frequency (days/year); ED is the exposure duration (years); BW is the average body weight (kg); AT is the averaging time (days); CF is the conversion factor (1×10^{-6} kg/mg); SFO is the oral slope factor (mg/kg/day). The SFO values are 7.3×10^{-1}, 7.3×10^{-1}, 7.3×10^{-2}, 7.3, 7.3×10^{-3}, 7.3 and 7.3×10^{-1} for BaA, BbF, BkF, BaP, Chry, DBA and IndP respectively.

$$ILCR_{inh} = \frac{Csoil \times EF \times ED \times IUR}{PEF \times AT*} \tag{21}$$

Where $ILCR_{inh}$ is the incremental lifetime cancer risk via inhalation of soil particles; ET is the exposure time (h/day); IUR is the inhalation unit risk $(mg/m^3)^{-1}$; AT* is the averaging time (h); PEF is the particle emission factor $= 1.36 \times 10^9$ m^3/kg. PEF is the soil to air particulate emission factor (USEPA, 2001). The seven carcinogenic PAHs concentrations were used to conduct the cancer risk assessment (USEPA, 1993).

$$ILCR_{derm} = \frac{Csoil \times SA \times AF \times ABS \times EF \times ED \times CF \times SFO \times GIABS}{BW \times AT} \tag{22}$$

Where, $ILCR_{derm}$ is the incremental lifetime cancer risk via dermal contact of soil particles; SA is the surface area of the skin that contacts soil (cm^2/day); AF is the skin adherence factor for soil (mg/cm^2); ABS is the dermal absorption factor (chemical specific); GIABS is the gastrointestinal absorption factor. Qualitative descriptions of lifetime cancer risks are as follows: $\leq 10^{-6}$=very low; 10^{-6} to 10^{-4}= low; $>10^{-4}$ to 10^{-3}=moderate; $>10^{-3}$ to 10^{-1}= high and $\geq 10^{-1}$=very high (New York States Department of Health, 2007).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1   Physicochemical properties of soil

The results of some physicochemical characteristics of soils of the floodplain of the

lower reaches of River Niger are shown in Table 4.1.

Table 4.1: Result of some physicochemical properties of soil samples

	DEPTH (cm)	pH	EC (μʃ/cm)	TOC (%)	CEC Meq/100g	SAND (%)	SILT (%)	CLAY (%)	TEXTURE
						PARTICLE SIZE DISTRIBUTION			
AS1	0-15	6.03	18.0	1.08	3.18	1.0	57.0	45.0	Silt Clay
	15-30	5.07	18.2	1.00	2.55	2.0	60.0	48.0	Silt Clay
	30-45	4.72	19.2	0.60	3.11	1.0	55.0	52.0	Silt Clay
AS2	0-15	5.06	18.4	0.92	3.05	37.0	35.0	28.0	Clay Loam
	15-30	4.90	19.0	0.68	2.76	35.0	34.0	31.0	Clay Loam
	30-45	4.64	18.8	0.76	3.10	40.0	30.0	30.0	Clay Loam
AS3	0-15	6.49	17.9	1.12	3.00	47.0	17.0	36.0	Clay Loam
	15-30	6.68	18.2	1.00	2.54	45.0	19.0	36.0	Clay Loam
	30-45	7.08	18.4	0.92	2.02	43.0	20.0	37.0	Clay Loam
AS4	0-15	6.11	18.8	0.76	4.00	90.0	3.0	7.0	Sandy
	15-30	6.67	19.2	0.60	4.20	82.0	7.0	11.0	Sandy
	30-45	7.20	18.6	0.84	3.77	77.0	8.0	15.0	Sandy
AS5	0-15	8.40	19.0	0.68	2.84	80.0	2.0	18.0	Sandy
	15-30	8.23	18.8	0.76	3.45	70.0	13.0	17.0	Sandy
	30-45	8.68	19.4	0.52	2.97	78.0	12.0	10.0	Sandy
OK1	0-15	6.78	17.5	1.28	4.21	20.0	61.0	19.0	Silt
	15-30	5.06	18.7	0.80	3.95	1.0	96.0	3.0	Silt
	30-45	5.52	18.6	0.84	4.16	0.0	98.0	2.0	Silt
OK2	0-15	5.73	18.1	1.04	2.34	1.0	95.0	4.0	Silt
	15-30	5.54	17.9	1.12	2.66	19.0	70.0	11.0	Silt
	30-45	5.89	18.1	1.04	3.04	1.0	96.0	3.0	Silt
OK3	0-15	5.80	18.7	0.80	3.45	57.0	28.0	15.0	Loam
	15-30	6.20	18.9	0.72	3.51	50.0	30.0	20.0	Loam
	30-45	6.44	19.3	0.56	2.80	49.0	35.0	16.0	Loam
AB1	0-15	5.33	17.5	1.28	3.11	1.0	66.0	33.0	Silt Clay
	15-30	5.79	18.6	0.84	3.30	2.0	70.0	28.0	Silt Clay
	30-45	5.73	18.6	0.84	4.17	3.0	64.0	33.0	Silt Clay
AB2	0-15	5.63	16.9	1.52	4.03	1.0	68.0	31.0	Silt Clay
	15-30	5.22	17.7	1.20	3.81	2.0	65.0	33.0	Silt Clay
	30-45	5.79	18.3	0.96	4.16	0.0	71.0	28.0	Silt Clay
AB3	0-15	6.71	16.8	1.56	3.13	85.0	2.0	13.0	Sandy
	15-30	6.68	19.0	0.68	3.01	74.0	14.0	12.0	Sandy
	30-45	5.86	20.4	0.12	2.94	87.0	4.0	9.0	Sandy
AB4	0-15	5.09	9.70	4.39	3.26	1.0	58.0	41.0	Silt Clay
	15-30	5.30	18.2	1.00	4.32	1.0	60.0	39.0	Silt Clay
	30-45	5.12	18.4	0.92	3.21	0.0	57.0	42.0	Silt Clay
AB5	0-15	6.25	19.0	0.68	2.85	45.0	21.0	34.0	Clay Loam
	15-30	5.62	18.9	0.72	3.15	40.0	30.0	30.0	Clay Loam
	30-45	5.94	17.0	1.48	2.68	47.0	15.0	38.0	Clay Loam

4.1.1 pH Value

The pH of the soil ranged between 4.64 and 8.68. The pH values at all sites and depths except site AS5 indicated that the soils of the River Niger floodplain were acidic in nature. The pH increased with depth at all sites except sites AS1, AS2, OK1, AB3 and AB5 where the pH decreased with depth. Similar pH values have been reported for Niger Delta soils (Iwegbue *et al.,* 2006; Oviasogie and Ofomaja, 2007; Iwegbue *et al.,* 2009; Iwegbue *et al.,* 2012). Soil pH is very important when considering mobility because metal availability is relatively low when the pH is around 6.5 to 7. With exception of Mo, Se Cr and As, the mobility of most metals are reduced with increasing soil pH because of the precipitation as insoluble hydroxides, carbonates and organic complexes as well as increased adsorption to oxide surface (Iwegbue *et al.,* 2009). At high pH, ion hydrolysis (MoH^+) is favored, and the energy barrier that must be overcome when these ions approach the surface of soil particles is decreased (Yu *et al.,* 1997).

4.1.2 Electrical conductivity

The electrical conductivity (EC) of the studied soil ranged from 9.70 to 20.4 µS/cm. The highest EC was observed at site AB3 (30-45 cm) while the lowest was observed at site AB4 (0-15 cm). The EC values of all sites increased with depth except for sites AS4 and AB5. The EC obtained in this study were higher than those reported by Obasi *et al.* (2012), Badejo *et al.* (2013) and Idugboe *et al.* (2014). The high electrical conductivity of these soil profiles implies that there are appreciable amounts of metals in these soils.

4.1.3 Organic matter content

The organic matter content is one important factor that governs the distribution of hydrophobic pollutants in soils and sediments (King *et al.,* 2004). In the present study, the total organic carbon (TOC) contents of the soils ranged from 0.12% at site AB3 (0-15 cm) to 4.39% at site AB4 (0-15 cm). The TOC contents of these soils decreased with depths except for sites

AS4 and AB5.   In site OK2, higher content was observed at the 15-30 cm depth than the other layers. The TOC values of our sites were similar to the range reported for floodplain soils and sediments (Gocht *et al.,* 2001).

4.1.4   Cation Exchange Capacity

The cation exchange capacity (CEC) of the soils ranged from 2.02 to 4.32 meg/100g for all sites and depth with sites AB4 (15-30 cm depth) and AS3 (30-45 cm depth) having the highest and lowest values respectively. The cation exchange capacity is directly related to soil capacity of adsorbing heavy metals. The greater the CEC values, the more exchange site on the soil minerals will be available for metal retention (Iwegbue et al., 2009). Surface and subsurface soil samples of the same soil can exhibit different capacities of heavy metal adsorption, since the adsorption behavior depends on the combination of soil properties and the specific characteristics of the metal (Barry et al., 1995).

4.1.5   Particle size distribution

The percent fraction of sand in these soil profiles ranged from 0.0 to 90.0 %. The top soil of site AS4 have the highest sand fraction. Sites AS$, AS5, and AS3 are predominantly sandy in texture. The percent silt ranged from 2.0 to 98.0 %. Sites OK1 and OK2 were predominantly silt in texture. However, sites AS1, AB1, AB2 and AB4 also have higher silt content than other sites. The percent clay ranged from 2.0 to 52.0 % for all sites and depth. Clay content decreased with depth at all sites except sites AS1, AS2, AS3, AS4, AB4 and AB5. Increased clay minerals enhanced the retention of contaminants in soil and thereby decreasing contaminants mobility. The clay content in these soil profiles was low compared to sand and silt. Hence, there is reduced tendency for contaminants mobility in these soil profiles.

4.2   Metal concentrations in soil profiles three months after the major flooding

The concentration of metals in soil profiles of the study area three months after the major flooding are shown in Tables 4.2. The concentrations of metals in these sites and depth varied significantly ($p<0.05$). However, there was no regular trend in the distribution of these metals with respect to depths. Metals accumulation in deeper soils might be caused by mobility and soil texture. Du Laing *et al*. (2009) reported that the depth at which metal accumulate in soil profile varied from less than 5 cm below the surface in clayed organic soils to more than 1m in sandy soil in the intertidal marshes. Generally, the concentrations of metals in the downstream of the floodplain were higher than that of the midstream and upstream of the floodplain (Table 4.3). This may be due to discharges from oil and gas installations at few kilometres away from sites AB1-AB5. The concentrations of metals observed in the soil profiles of the study area in comparison with metal status of other floodplain soils around the world are displayed in Table 4.4.

Table 4.2: Metal concentrations (µg g^{-1}) in floodplain soils three months after the major flooding

Sites	Depth (cm)	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Ba	Al	Fe
AS1	0 - 15	2.0	4.5	10.9	8.2	180	4.8	28	1490	64.7	2650	4020
	15 - 30	0.6	1.9	12.2	11.2	96.5	6.2	13.8	91.4	124	10000	6750
	30 - 45	1.6	6.5	33.1	29.4	258	8.4	40.5	260	83.8	9490	15800
AS2	0 - 15	0.4	1.6	7.9	6.2	20.3	2.4	3.7	92.3	9.6	1340	3150
	15 - 30	0.5	1.3	11.1	4.4	56.0	2.1	8.2	48.5	10.7	1070	3960
	30 - 45	0.6	2.1	13.0	8.6	71.6	3.9	9.1	105	22.4	2570	5080
AS3	0 - 15	0.3	1.2	6.7	3.5	23.5	2.3	3.3	30.2	12.5	848	2430
	15 - 30	0.5	1.5	13.1	0.5	17.9	3.9	4.5	31.9	21.3	4380	4980
	30 - 45	0.7	4.9	19.2	10.0	156	7.9	3.0	58	76.4	9930	6300
AS4	0 - 15	0.9	8.0	44.7	10.9	340	19.5	7.1	83.4	127	5370	9390
	15 - 30	0.2	2.1	8.2	11.9	17.2	31.5	7.2	89.1	23.4	5240	1780
	30 - 45	0.3	1.0	0.8	1.5	5.1	1.1	1.1	18.7	18.1	2160	41
AS5	0 - 15	1.4	3.4	27.5	7.8	171	2.7	9.3	107	15.5	5200	13200
	15 - 30	1.0	2.8	27.7	6.9	128	2.9	3.8	37	16.2	4400	9770
	30 - 45	1.4	1.8	31.9	11.6	51.5	4.3	6.4	23.7	19.1	11100	14800
OK1	0 - 15	0.6	6.2	10.1	5.9	128	5.4	9.4	440	67.2	7260	4570
	15 - 30	1.2	6.0	25.7	7.2	239	6.2	7.6	306	59.9	4280	10600
	30 - 45	0.4	13.1	8.0	13.4	163	10.3	13.2	124	28.7	11300	4100
OK2	0 - 15	2.0	9.1	69.0	8.0	349	25.3	12.1	491	82.7	8450	17300
	15 - 30	1.8	1.6	43.6	10.8	343	12.3	7.2	57.5	89.1	14700	19200
	30 - 45	1.7	9.3	43.1	10.3	371	10.9	7.4	46.3	87.9	13200	18300
OK3	0 - 15	1.0	4.6	22.9	5.4	43.9	5.0	3.0	116	39.6	5170	9440
	15 - 30	0.5	2.3	8.9	3.7	43.3	2.5	2.8	94.4	12.3	1700	3520
	30 - 45	0.3	1.3	7.5	4.2	22.1	2.3	3.2	99.2	8	1060	2590
AB1	0 - 15	0.6	1.8	18.1	7.6	79.6	6.1	8.5	204	12.3	1170	3470
	15 - 30	0.3	1.6	10.7	8.0	42.5	2.6	6.0	170	11.3	982	2970
	30 - 45	1.3	6.6	28.0	6.2	215	7.0	4.6	45.5	50.7	6270	12600
AB2	0 - 15	0.2	7.1	39.0	12.8	195	8.8	15.7	135	99.5	11200	15600
	15 - 30	0.3	6.0	5.3	12.1	49.9	7.8	12.0	59.5	147	8010	2890
	30 - 45	2.7	11.8	61.0	14.8	443	15.2	12.2	46.0	7.9	20300	28000
AB3	0 - 15	1.9	9.2	45.1	12.6	364	11.7	12.0	76.2	117	11600	18300
	15 - 30	2.1	9.9	48.1	12.8	399	12.5	13.9	46.7	102	11000	21900
	30 - 45	2.0	9.8	46.8	12.8	431	10.9	12.1	42.1	90.9	12700	21200
AB4	0 - 15	1.3	7.0	31.6	8.7	240	7.8	6.3	311	57.4	8150	13800
	15 - 30	1.5	8.0	39.0	11.0	300	14.1	8.8	48	69.1	10500	16600
	30 - 45	1.1	5.7	26.0	6.5	232	6.0	5.2	31.2	51.0	5280	11200
AB5	0 - 15	2.8	14.4	66.9	19.9	790	16.3	12.4	96.7	0.4	24000	32200
	15 - 30	2.2	11.3	28.5	12.8	529	12.5	11.4	50.2	111	16000	23400
	30 – 45	2.2	11.8	47.8	15.4	529	26.3	14.8	58.0	144	1400	23200
	MIN	0.2	1.00	0.8	0.5	5.1	1.1	1.1	18.7	0.4	848	41
	MAX	2.8	14.4	69	29.4	790	31.5	40.5	1490	147	24000	32200
	MEAN	1.14	5.64	26.9	9.63	209	8.97	9.51	148	56.2	7473	11241
	DPRTV	0.8	20	100	36	-	35	85	140	200	-	-
	CAV	0.3	-	90	45	850	68	20	95	-	8.02*	4.7*

* (%), *DPRTV* Department of Petroleum Resources (2002) target values, *CAV* Crustal abundance value (Turekian and Wedepohl, 1961)

Table 4.3: Mean metal concentrations (µg g^{-1}) in floodplain soils three months after the major flooding

Depth (cm)	Sites	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Ba	Al	Fe
0-15 cm	Upstream (AS1-AS5)	1.00±0.71 (0.30-2.00)	3.74±2.73 (1.20-8.00)	19.5±16.4 (6.70-44.7)	7.32±2.72 (3.50-10.9)	142±132 (20.3-340)	6.34±7.43 (2.30-19.5)	10.3±10.3 (3.30-28.0)	361±632 (30.2-1490)	45.9±50.7 (9.60-127)	3082±2117 (848-5370)	6438±4668 (2430-13200)
	Midstream (OK1-OK3)	1.20±0.72 (0.60-2.00)	6.63±2.28 (4.60-9.10)	34.0±31.0 (10.1-69.0)	6.43±1.38 (5.40-8.00)	174±158 (43.9-349)	11.9±11.6 (5.00-25.3)	8.17±4.67 (3.00-12.1)	349±203 (116-491)	63.2±21.8 (39.6-82.7)	6960±1660 (5179-8450)	10437±6423 (4570-17300)
	Downstream (AB1-AB5)	1.36±1.04 (0.20-2.80)	7.90±4.54 (1.80-14.4)	40.1±18.0 (18.1-66.9)	12.3±4.83 (7.60-19.9)	334±275 (79.6-790)	10.1±4.00 (6.10-16.3)	11.0±3.65 (6.30-15.7)	165±95.2 (76.2-311)	57.3±51.5 (0.40-117)	11224±8275 (1170-24000)	16674±10338 (3470-32200)
15-30 cm	Upstream (AS1-AS5)	0.56±0.29 (0.20-1.00)	1.92±0.58 (1.30-2.80)	1.45±7.63 (8.20-27.7)	6.98±4.76 (0.50-11.9)	63.1±48.8 (17.2-128)	9.32±12.5 (2.10-31.5)	7.50±3.97 (3.80-13.8)	59.6±28.6 (31.9-91.4)	39.1±47.7 (10.7-124)	5018±3211 (1070-10000)	5448±3011 (1780-9770)
	Midstream (OK1-OK3)	1.17±0.65 (0.50-1.80)	3.30±2.36 (1.60-6.00)	26.1±17.4 (8.90-43.6)	7.23±3.55 (3.70-10.8)	208±152 (43.3-343)	7.00±4.95 (2.50-12.3)	5.87±2.66 (2.80-7.60)	153±134 (57.5-306)	53.8±38.8 (12.3-89.1)	6893±6883 (1700-14700)	11107±7852 (3520-19200)
	Downstream (AB1-AB5)	1.28±0.93 (0.30-2.20)	7.36±3.79 (1.60-11.3)	26.3±18.2 (26.3-18.2)	11.3±2.01 (8.00-12.8)	264±215 (42.5-529)	9.90±4.71 (2.60-14.1)	10.4±3.07 (6.00-13.9)	74.9±53.4 (46.7-170)	88.1±51.1 (11.3-147)	9298±5479 (982-16000)	13552±10020 (2890-23400)
30-45 cm	Upstream (AS1-AS5)	0.92±0.55 (0.30-1.60)	3.26±2.33 (1.00-6.50)	19.6±13.5 (0.80-33.1)	12.2±10.3 (1.50-29.4)	108±99.9 (5.10-258)	5.12±3.03 (1.10-8.40)	12.0±16.2 (1.00-40.5)	93.1±99.5 (18.7-260)	44.0±33.1 (18.1-83.8)	7050±4320 (2160-11100)	8404±6727 (41.0-15800)
	Midstream (OK1-OK3)	0.80±0.78 (0.30-1.70)	7.90±6.02 (1.30-13.1)	19.5±20.4 (7.50-43.1)	9.30±4.68 (4.20-13.4)	185±176 (22.1-371)	7.83±4.80 (2.30-10.9)	7.93±5.02 (3.20-13.2)	89.8±39.7 (46.3-124)	41.5±41.5 (8.00-87.9)	8520±6530 (1060-13200)	8330±8667 (2590-18300)
	Downstream (AB1-AB5)	1.86±0.66 (1.10-2.70)	9.14±2.87 (6.60-11.8)	41.9±14.7 (28.0-61.0)	11.1±4.48 (6.20-15.4)	370±139 (215-529)	13.08±8.23 (6.00-26.3)	9.79±4.59 (4.60-14.8)	44.6±9.59 (31.2-58.0)	68.9±51.2 (7.90-144)	9190±7420 (1400-20300)	19240±7159 (11200-28000)

Table 4.4: Concentrations of metals (mg kg⁻¹) in floodplain soils of River Niger and some other floodplains in the literature

Floodplain/ Country	Cd	Pb	Cr	Ni	Cu	Co	Zn	Ba	Mn	Fe	Al	Reference
River Niger Floodplain	0.2-2.8	1.1-40.5	0.8-69.0	1.1-26.3	0.5-29.4	1.0-14.4	18.7-1490	8.0-147	5.1-790	41-32200	848-24000	This Study
Odra River floodplain (Poland)	1.4-7.0	24.5-242	5.4-81	9.2-6.0			23.6-1006	-	-	-	-	Ibragimov et al. 2010
Bystrzyica River	<0.5-40.6	10-91	6-45	6-45	6-74	7-83	2-32	27-488	23-111	-	-	Bojakowska and Sokolowska, 1996
River Ona Floodplain (Ibadan, Nigeria)	0.0-0.01	33-40	0.21-1.21	-	4.57-17.87	-	3.09-263-50	-	7.9-34.6	86.2-181.0	-	Ande et al. 2014
River Meuse	5.6-14.0	157-326	-	-	62-116	705-1239	-	-	-	-	-	Albering et al. 1999
Rhine and Meuse floodplains (The Netherland)	-	70-490	-	-	30-130	-	170-1450	-	-	-	-	Middlekoop, 2000
River Nile floodplain (Sudan)	0.48-2.58	6.85-11.80	48.93-110.86	35.28-48.93	46.93-63.77	25.03-37.35	111.40-121.42	-	896.48-1337	54.21-72.42	-	Shumo et al. 2014
White Nile floodplain (Sudan)	1.97-2.02	10.03-12.46	41.45-85.19	0.29-36.23	29.59-37.29	16.03-20.51	67.45-72.15	-	571.25-632.19	34.08-42.79	-	Shumo et al. 2014
Blue Nile floodplain (Sudan)	0.97-1.51	4.19-7.91	43.63-82.76	19.67-48.16	45.21-51.10	25-34.36	67.19-101.17	-	911.75-1048.81	54.14-62.38	-	Shumo et al. 2014
Amik plain (Turkey)	0.02-0.65	0.60-20.94	-	46.6-3965.32	-	0.40-74.0	-	-	-	-	-	Karanlik et al. 2011
Cerrado Biome (State of Minas Gerais, Brazil)		Nd-50.3	43.6-145.6	7.0-17.3	30.6-88	-	5.0-36.3	9.0-35	-	-	-	Rosolen et al. 2015
Zarqa River Basin (Jordan)		61-112	62-120	66-100	33-61	35-71	78-140	-	-	-	-	Abderahman and Abu-Rukah, 2006
Faridpur floodplain (Bangladesh)	0.12-0.17	24.32-33.95	73.50-108.14	42.21-61.01	38.20-63.35	14.60-22.09	82.69-117.36	-	374.09-575.17	-	-	Ahsan et al. 2008
Dhamrai floodplain (Bangladesh)	0.11-0.22	23.22-26.61	45.60-84.38	43.80-47.94	29.61-33.71	15.41-17.26	78.88-125.87	-	471.09-655.24	-	-	Ahsan et al 2008
Bangladesh		14.3-31.0	61.0-176.0	14.0-134.0	8.7-65.7		27.8-138.0					Ali et al. 2003
Massawippi and Saint Francois rivers floodplain (Quebec, Canada)	<0.5-0.9	5.0-490	<2.0-55	<1.0-120	<2.0-46		38.0-310					Saint-Laurent et al.2013
Cross River floodplain (Nigeria)		21.39-22.60		10.40-22.38	14.09-22.61	5.09-11.52			33.60-42.92	-	-	Benson, 2006
River Nile floodplain (Egypt)	1.7	27.5		71.6	65		90.9		-	-	-	Shasheen et al. 2013
Elbe River floodplain (Germany)	7.9	100		66.6	168		861		-	-	-	Shasheen et al 2013
Penios (Greece)	1.5	21.5		232	29.7		4.30		-	-	-	Shasheen et al. 2013

Cadmium

The concentration of Cd in the soil profiles three months after the major flooding varied from 0.2 to 2.8 µg g^{-1}. The highest concentrations of Cd were found in soil profiles of AB5. The concentration of Cd decrease with increasing depth in sites AS1, AS4, AS5, OK1, OK2, OK3, AB4 and AB5 while Cd concentrations increased with depth in sites AS2, AS3, AB1, AB2 and AB3. The Department of Petroleum Resources of Nigeria (DPR) target value for Cd in soil is 0.8 mg kg^{-1} (DPR, 2002). The concentration of Cd in majority of these soil samples were above the DPR limit.

It has been noted that long-term and extensive use of land for agriculture with frequent application of agrochemicals is a major factor responsible for accumulation of metals such as Cd, Cu, Ni and Zn in agricultural soils (Zovko and Romic, 2011). Metals such as Cu, Cd, Pb and Zn can be mobilised during oxidation of anoxic or at low pH value in sediment through oxidation of sulphide phase and oxidation of organic matter (Charkhabi *et al*., 2008). A wide range of Cd concentrations have been reported for agricultural and floodplain soils. The concentrations of Cd found in the soils of River Niger floodplain were comparable to Cd concentrations found in the floodplain of Blue Nile and White Niger (Shumo *et al.,* 2014) but were higher than concentrations found in soils of agrarian floodplain Western Nigeria (Ande *et al*., 2014; Adeyeye, 2005). The concentrations of Cd observed in these sites were also higher than 0.04 to 0.24 mg kg^{-1} found in paddy soils of south eastern China (Wu and Zhang, 2010). Overesch *et al.* (2007) reported high concentrations of Cd in soils of the central Elbe River floodplain than concentrations found in these sites.

Cobalt

The cobalt content in these soils three months after the major flooding ranged from 1.0 to 14.4 µg g^{-1} with site AB5 (0-15 cm depth) having the highest concentration. In this study, there was no regular trend in the distribution of Co with respect to depth. The concentration of Co decreased with depth at sites AS4, AS5, OK3, AB4 and AB5 and increased with depth at

sites AS1, AS2, AS3, OK1, OK2 OK3, AB1, AB2 and AB3. The concentrations of Co in these sites were below 20 mg kg^{-1} specified by the Nigerian regulatory authority (DPR, 2002). The concentrations of Co in these sites were lower than Co concentration found in soils of the Haweja Canal in Iraq (Ali, 2007) and the alluvium of the Bystrzyca River (Bojakowska and Sokolowska, 1996) and floodplain soils of River Nile, Blue and White Nile (Shumo et al., 2014).

Chromium

In soil environment, chromium exist in oxidation states of +III and +VI which control its mobility and toxicity. Chromium (VI) adsorption decreases with increasing pH and Cr^{3+} adsorption increases with increasing pH (Iwegbue, 2014). On the other hand, Cr^{6+} is toxic to biological systems (Machender et al., 2011). The concentrations of Cr at these sites three months after the major flooding event ranged between 0.8 and 69.0 μg g^{-1} and the highest concentration was observed in the top soil of site OK2. In this study, the concentration of Cr decreased with depth at sites AS2, AS4, OK1, OK2, OK3, AB4 and AB5 while the concentration increased with depth at sites AS1, AS3, AS5, AB1, AB2 and AB3. The concentrations of Cr in these sites were below the 100 mg kg^{-1} maximum permissible limit for Cr in soil in Nigeria (DPR, 2002). The concentrations of Cr in these soil profiles were higher than concentrations found in floodplain soils in western Nigeria (Adeyeye, 2005; Ande et al., 2014) but were lower than Cr concentrations found in other wetland soils in other regions of the world (Overesch et al., 2007; Zhang et al., 2010; Bai et al., 2011; Rahman et al., 2012).

Copper

The concentration of Cu ranged from 0.5 to 29.4μg g^{-1}in the soil profiles. The highest concentrations of Cu was observed at the 30-45 cm depth of site AS1. The concentration of Cu increased with depth at all sites except sites AS4, OK3, AB1 AB4 and AB5. The Department of Petroleum Resources maximum allowed level of Cu in soil is 36 mg/kg. Copper

concentrations obtained in this study were below the permissible limit. The solubility of Cu and Zn is influenced by pH and redox conditions. For example, at pH between 5.4 and 6.5, Cu and Zn are more soluble under oxidizing conditions than reducing conditions (Bhattacharya *et al*., 2002). In this study, subsoil of sites AS1, AS3, AS4, OK2, OK3, AB2 and AB5 had pH value in this range, the solubility of Cu and Zn is unlikely in these sites. The concentrations of Cu in floodplain soils of river Niger were lower than Cu concentrations found in cultivated wetland in China (Bai *et al.,* 2010). The maximum copper concentrations in floodplain soils of river Rhine and Meuse in Netherland vary from 30 to 130 mg kg^{-1} (Middlelkoop, 2000).

Manganese

A high concentration of Mn in soil is of significance because of its high mobility. Manganese migrates easily and contaminates surface streams and groundwater. Its preferred oxidation states are +2, +3 and +4, while its oxidation and precipitation are more efficient at high pH and redox potential values. The concentrations of Mn in soil of this study ranged from 5.1 to 789.5 µg g^{-1}. The highest concentration of Mn in this sampling period was observed at 0–15 cm depth of site AB5. In terms of the distribution pattern, the concentration of Mn in the soil profiles increased with depth except at sites AS4, AS5, OK3, AB4 and AB5. There is no specified guideline value for Mn in soil by the Nigerian regulatory agencies, but the concentrations of Mn found in these sites were lower than the crustal abundance value of manganese (850 mg/kg). The concentrations of Mn observed in these sites were higher than concentrations of Mn found in agrarian wetland in Bangladesh (Ahsan *et al*., 2012) and those found in the floodplain utilsol of Cross River, Nigeria (Benson, 2006).

Nickel

The concentration of Ni found in the floodplain soils three months after the major flooding ranged between 1.1 and 31.5 µg g^{-1}. The soil profiles of OK2 and AB5 have higher concentration of Ni than other sites. The concentrations of Ni increased with depth at all sites

except sites AS4, OK2, OK3, AB3 and AB4. The concentrations of Ni found in these soil profiles were below the Nigerian regulatory limit of 35 mg kg^{-1} in soil (DPR, 2002). The concentrations of Ni in these samples were lower than Ni concentrations found in wetland soils of the Pearl River estuary, South China (Zhang et al., 2010; Bai et al., 2011), central Elbe River floodplain, Germany (Overesch et al., 2007), in River Nile, Blue and White Nile floodplain (Shumo et al., 2014), Odra River floodplain (Ibragimov et al., 2010) and floodplain soils from Egypt, Germany and Greece (Shasheen et al., 2013).

Lead

The concentrations of Pb ranged from 1.1 to 40.5 µg g^{-1} at all sites and depth. The highest concentrations of Pb were observed in the soil profile of site AS1. The concentration of Pb decreased with depth except at sites AS1, AS2, OK1, OK3, AB3 and AB5. The guideline value of Pb in soil in Nigeria is set at 85 mg/kg (DPR, 2002). The concentrations of Pb in these sites were below the DPR permissible limits. The concentrations of Pb found in these sites are comparable to Pb concentrations found in agrarian floodplain soils in the western part of Nigeria (Adeyeye, 2005; Ande et al., 2014) and that of River Nile, Blue and White Nile (Shumo et al., 2014).

Zinc

The concentrations of Zn in these soil profiles three months after the major flooding ranged from 18.7 to 1490µg g^{-1}. The highest concentration of Zn in these soil samples was observed at 0–15 cm depth of site AS1. Apart from AS1, the soil profiles of the midstream section (OK1-OK3) had higher concentrations of Zn than other sites. The guideline value of Zn in soil in Nigeria is set at 140 mg/kg (DPR, 2002). The concentrations of Zn found in 8 samples out of the 39 samples investigated were above the Nigerian regulatory control limit for Zn. In most sites, the concentrations of Zn decreased with increasing depth except at sites

AS2 and AS3. Wijnhoven et al. (2006) reported that manual turbation caused a fast decrease of the Zn content in the upper layer of 15 cm of the soil layer. It was especially zinc attached to colloid and organic that was redistributed from the top layer. Percolation process resulted in the attached zinc being drained to depths of more than 15 cm. Inundation was responsible for decrease in the zinc concentrations of the top layer. Zn concentrations in the range of 67.19 to 121.42 mg kg^{-1} have been reported in floodplain soils of the White Nile, Blue Nile and River Nile (Shumo *et al*., 2014). Ande *et al.* (2014) reported Zn concentrations of 3.09 to 263.50 mg kg^{-1} in soil profiles of agrarian floodplain in western Nigeria.

Barium

The concentration of Ba ranged from 8.0 to 147μg kg^{-1} in these soil profiles. The highest concentration of Ba was observed at 15–30 cm depth of site AB2. The concentrations of Ba in these sites were below the 200 mg/kg permissible limit of Ba in soils (DPR, 2002).

Aluminium

Aluminium is the second most abundant metal in these soil profiles. The concentration of Al ranged from 848 to 24000 µg g^{-1}. The highest concentration of Al was observed at 0-15 cm depth of site AB5. The concentration of Al increased with depth except at site AS4, OK3, AB4 and AB5. There is no specified guideline value for Al in soil by the Nigerian Regulatory Agency but the concentrations of Al at these sites were below the crustal abundance value of 8.02 %. The concentrations of Al in this study were lower than those concentrations reported by Shumo et al. (2014) for floodplain soils of River Nile, Blue Nile and White Nile.

Iron

Iron is the predominant metal in these soil profiles in terms of concentration. The concentration of Fe ranged from 41.0 to 32125 µg g^{-1}. The highest concentration of Fe was observed at 0-15 cm depth of site AB5. The concentration of Fe increased with depth except

at sites AS4, OK1, OK3, and AB4. Like Al, there is no specified guideline value for Fe in soil by the Nigerian Regulatory Agencies but the concentration of Fe at these sites were below the crustal abundance value of 4.7 %. The concentrations of Fe in these sites were lower than those concentrations reported for floodplain soils of River Nile, Blue Nile and White Nile (Shumo et al., 2014). However, Fe concentrations in these soils were comparable to those recorded in Kirki Region North East Greece (Nikolaidis et al., 2010).

4.3 Contamination/Pollution Index three months after the major flooding

In this study, the computed CPI and MPI values are shown in Table 4.5. The index values for Co, Cr, Cu, Ni, Pb and Ba were at the contamination range i.e. less than unity whereas Cd and Zn were at the pollution range (i.e. greater than unity) for some sites. The CPI values for Cd and Zn were within the slight pollution to moderate pollution range in 56% and 18% of the sites respectively. Only site AS1 (0-15 cm) had CPI in the 'very severe pollution' range for Zn. Multiple pollution index value for all sites and depth ranged from 1.19 to 13.1 with significant contribution from Cd and Zn.

Table 4.5: Contamination/pollution index of metals in soil three months after the major flooding

Sites	Depth (cm)	Cd	Co	Cr	Cu	Ni	Pb	Zn	Ba	MPI
AS1	0 - 15	2.44	0.23	0.11	0.23	0.14	0.33	10.7	0.32	13.1
	15 - 30	0.75	0.10	0.12	0.31	0.18	0.16	0.65	0.62	0
	30 - 45	2.00	0.32	0.33	0.82	0.24	0.48	1.86	0.42	3.86
AS2	0 - 15	0.50	0.08	0.08	0.17	0.07	0.04	0.66	0.05	0
	15 - 30	0.63	0.07	0.11	0.12	0.06	0.10	0.35	0.05	0
	30 - 45	0.75	0.10	0.13	0.24	0.11	0.11	0.75	0.11	0
AS3	0 - 15	0.38	0.06	0.07	0.10	0.06	0.04	0.22	0.06	0
	15 - 30	0.56	0.07	0.13	0.01	0.11	0.05	0.23	0.11	0
	30 - 45	0.81	0.25	0.19	0.28	0.23	0.04	0.41	0.38	0
AS4	0 - 15	1.13	0.40	0.45	0.30	0.56	0.08	0.60	0.63	1.13
	15 - 30	0.25	0.11	0.08	0.33	0.90	0.08	0.64	0.12	0
	30 - 45	0.31	0.05	0.01	0.04	0.03	0.01	0.13	0.09	0
AS5	0 - 15	1.69	0.17	0.27	0.22	0.08	0.11	0.77	0.08	1.69
	15 - 30	1.19	0.14	0.28	0.19	0.08	0.04	0.26	0.08	1.19
	30 - 45	1.69	0.09	0.32	0.32	0.12	0.08	0.17	0.10	1.69
OK1	0 - 15	0.75	0.31	0.10	0.16	0.15	0.11	3.14	0.34	3.14
	15 - 30	1.44	0.30	0.26	0.20	0.18	0.09	2.19	0.30	3.63
	30 - 45	0.50	0.65	0.08	0.37	0.29	0.16	0.88	0.14	0
OK2	0 - 15	2.44	0.45	0.69	0.22	0.72	0.14	3.51	0.41	5.94
	15 - 30	2.19	0.08	0.44	0.30	0.35	0.08	0.41	0.45	2.19
	30 - 45	2.13	0.46	0.43	0.28	0.31	0.09	0.33	0.44	2.13
OK3	0 - 15	1.19	0.23	0.23	0.15	0.14	0.04	0.83	0.20	1.19
	15 - 30	0.63	0.11	0.09	0.10	0.07	0.03	0.67	0.06	0
	30 - 45	0.31	0.06	0.08	0.12	0.07	0.04	0.71	0.04	0
AB1	0 - 15	0.69	0.09	0.18	0.21	0.17	0.10	1.46	0.06	1.46
	15 - 30	0.38	0.08	0.11	0.22	0.07	0.07	1.21	0.06	1.21
	30 - 45	1.56	0.33	0.28	0.17	0.20	0.05	0.33	0.25	1.56
AB2	0 - 15	0.21	0.35	0.39	0.36	0.25	0.18	0.96	0.50	0
	15 - 30	0.38	0.30	0.05	0.33	0.22	0.14	0.43	0.73	0
	30 - 45	3.31	0.59	0.61	0.41	0.43	0.14	0.33	0.04	3.31
AB3	0 - 15	2.38	0.46	0.45	0.35	0.33	0.14	0.54	0.59	2.38
	15 - 30	2.63	0.50	0.48	0.36	0.36	0.16	0.33	0.51	2.63
	30 - 45	2.44	0.49	0.47	0.36	0.31	0.14	0.30	0.45	2.44
AB4	0 - 15	1.63	0.35	0.32	0.24	0.22	0.07	2.22	0.29	3.85
	15 - 30	1.88	0.40	0.39	0.30	0.40	0.10	0.34	0.35	1.88
	30 - 45	1.31	0.29	0.26	0.18	0.17	0.06	0.22	0.26	1.31
AB5	0 - 15	3.50	0.72	0.67	0.55	0.46	0.15	0.69	0.002	3.50
	15 - 30	2.75	0.57	0.29	0.36	0.36	0.13	0.36	0.55	2.75
	30 – 45	2.69	0.59	0.48	0.43	0.75	0.17	0.41	0.72	2.69
	MIN	0.21	0.05	0.01	0.01	0.03	0.01	0.13	0.002	0.00
	MAX	3.50	0.72	0.69	0.82	0.90	0.48	10.7	0.73	13.1
	MEAN	1.39	0.28	0.27	0.27	0.26	0.11	1.06	0.28	1.8

4.4   Enrichment factors three months after the major flooding

The enrichment factor is a simple measure of geochemical trend and is used for making comparison between an area and overtime. The computed enrichment factors for the studied metals are shown in Table 4.6. Generally, EF value close to 1 can be considered a natural origin while values greater than 10 indicate non-crustal origin (Nolting et al., 1999). EF values less than 10 are not considered important because such enrichment may have resulted from the difference between the soil and reference used in the calculation (Pekay, 2006). The EF values for Cd ranged from 4.07 to 197 in these sites. The EF values of Cd were greater than 10 in all sites except for 30-45 cm and 0-15 cm depths of OK1 and AB1 respectively. The EF values of Cd suggest non-crustal sources. On the basis of EF categorization, 22, 10 and 4 of these soil samples had EF values for Cd   in the extremely very high enrichment (i.e. EF >40), very high enrichment and significant enrichment categories, respectively. The enrichment profiles of Cd in these sites indicated that Cd originated from anthropogenic sources. In the case of Zn, 19 out of the 38 samples investigated had EF values greater than 10 which indicate that Zn in these soil samples were from anthropogenic sources.

The enrichment factors for Fe, Cr, Cu, Ni, Mn and Ba were less than 10 in the majority of the samples investigated which indicate the source of these metals in the soil profiles were more of crustal origin. However, only the topsoil of site AB1 had EF values for Cr and Cu greater than 10 which suggest anthropogenic source.

Table 4.6: Enrichment factor of metals in soil three months after the major flooding

Sites	Depth (cm)	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Ba	Fe
AS1	0 - 15	197	7.18	3.67	5.49	6.42	2.14	42.4	476	3.38	2.59
	15 - 30	16.0	0.8	1.08	1.98	0.91	0.73	5.52	7.7	1.71	1.15
	30 - 45	45.1	2.87	3.1	5.51	2.56	1.04	17.1	23.2	1.22	2.82
AS2	0 - 15	79.6	4.87	5.2	8.16	1.43	2.11	11.0	5.98	0.98	4.00
	15 - 30	125	5.12	9.24	7.32	4.93	2.26	30.7	38.2	1.38	6.31
	30 - 45	62.5	3.37	4.52	5.98	2.63	1.77	14.2	34.7	1.2	3.38
AS3	0 - 15	94.6	5.98	7.04	7.26	2.62	3.13	15.4	30.1	2.03	4.89
	15 - 30	27.5	1.4	2.66	0.18	0.39	1.04	4.08	6.14	0.67	1.94
	30 - 45	17.5	2.08	1.72	1.8	1.48	0.94	1.21	4.93	1.06	1.08
AS4	0 - 15	44.8	6.29	7.41	3.62	5.96	4.27	5.3	13.1	3.26	2.99
	15 - 30	10.2	1.69	1.39	4.03	0.31	7.09	5.51	14.4	0.62	0.58
	30 - 45	30.9	1.85	0.33	1.2	0.22	0.6	1.95	7.3	1.16	0.03
AS5	0 - 15	69.3	2.76	4.7	2.67	3.09	0.61	7.16	17.4	0.41	4.34
	15 - 30	57.6	2.63	5.6	2.79	2.75	0.78	3.41	7.08	0.51	3.78
	30 - 45	32.4	0.68	2.55	1.85	0.44	0.45	2.3	1.79	0.24	2.27
OK1	0 - 15	22.1	3.58	1.24	1.44	1.67	0.88	5.17	51.2	1.28	1.08
	15 - 30	71.8	5.92	5.34	3.0	5.27	1.71	7.12	60.4	1.93	4.22
	30 - 45	9.46	4.87	0.63	2.11	1.36	1.07	4.68	9.23	0.35	0.62
OK2	0 - 15	61.7	4.52	7.27	1.69	3.89	3.53	5.72	49.0	1.35	3.49
	15 - 30	31.8	0.46	2.64	1.3	2.20	0.99	1.95	3.3	0.84	2.22
	30 - 45	34.4	2.95	2.9	1.38	2.64	0.97	2.24	2.95	0.92	2.36
OK3	0 - 15	49.2	3.72	3.95	1.86	0.80	1.14	2.33	19.0	1.06	3.12
	15 - 30	78.6	5.59	4.66	3.88	2.40	1.7	6.60	46.9	1.0	3.53
	30 - 45	63.3	5.0	6.33	7.0	1.97	2.57	12.0	79.3	1.05	4.18
AB1	0 - 15	126	6.51	13.8	11.5	6.43	6.16	29.2	148	1.45	5.07
	15 - 30	81.7	6.67	9.67	14.4	4.08	3.12	24.5	146	1.59	5.16
	30 - 45	53.3	4.41	3.97	1.75	3.24	1.32	2.94	6.13	1.12	3.44
AB2	0 - 15	4.07	2.66	3.11	2.04	1.64	0.92	5.62	10.2	1.23	2.38
	15 - 30	10.0	3.13	0.58	2.68	0.59	1.14	6.0	6.27	2.53	0.62
	30 - 45	34.9	2.45	2.68	1.3	2.06	0.88	2.4	1.91	0.05	2.36
AB3	0 - 15	43.6	3.34	3.45	1.92	2.95	1.19	4.12	5.53	1.39	2.69
	15 - 30	51.1	3.8	3.89	2.07	3.43	1.34	5.05	3.59	1.28	3.40
	30 - 45	50.0	3.25	3.28	1.79	3.2	1.01	3.8	2.79	0.99	2.84
AB4	0 - 15	42.6	3.63	3.46	1.89	2.77	1.12	3.1	32.23	0.97	2.90
	15 - 30	38.1	3.19	3.3	1.85	2.69	1.57	3.35	3.85	0.91	2.70
	30 - 45	53.2	4.56	4.39	2.20	4.15	1.34	3.91	4.99	1.34	3.62
AB5	0 - 15	31.3	2.53	2.49	1.48	3.11	0.8	2.07	3.41	0.003	2.29
	15 - 30	36.8	2.99	1.59	1.43	3.12	0.92	2.85	2.65	0.96	2.50
	30 – 45	29.7	2.57	2.20	1.42	2.58	1.60	3.05	2.53	1.03	2.05
	MIN	4.07	0.46	0.33	0.18	0.22	0.45	1.21	1.79	0.003	0.03
	MAX	197	7.18	13.8	14.4	6.43	7.09	42.4	476	3.38	6.31
	MEAN	51.8	3.64	4.03	3.42	2.68	1.74	8.13	35.6	1.20	2.8

4.5   Geoaccumulation index (I_{geo}) three months after the major flooding

The geoaccumulation index (I_{geo}) for the examined metals in these soils are displayed in Table 4.7. According to the defined *Igeo* classes, Co, Cr, Cu, Mn, Ni, Pb, Ba, Al and Fe fitted into *Igeo* class 1 which indicate that these soils were not polluted with these metals. The *Igeo* values for Cd indicate that 21%, 33% and 23% of the sites and depth fall into class 2, class 3 and class 4 respectively. The *Igeo* values for Zn indicate that only 0-15 cm depth of site AS1 was in the strongly polluted range of the *Igeo* class. Depth 15-30 cm of site AS1 and 0-15cm and 15-30 cm of site AB1 were in the range of unpolluted to moderately polluted while topsoil of sites OK1, OK2, AB4 and subsoil of site OK1 were in the moderately polluted range.

Table 4.7: Index of geoaccumulation of metals in soil

Sites	Depth (cm)	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Ba	Al	Fe
AS1	0 – 15	2.12	-2.66	-3.63	-3.05	-2.82	-4.41	-0.10	3.39	-3.75	-5.51	-4.13
	15 – 30	0.42	-3.91	-3.47	-2.60	-3.72	-4.04	-1.12	-0.64	-2.81	-3.59	-3.39
	30 – 45	1.83	-2.14	-2.03	-1.20	-2.31	-3.60	0.43	0.87	-3.38	-3.66	-2.17
AS2	0 – 15	-0.17	-4.20	-4.10	-3.46	-5.97	-5.41	-3.02	-0.63	-6.51	-6.48	-4.48
	15 - 30	0.15	-4.45	-3.60	-3.94	-4.51	-5.64	-1.87	-1.56	-6.35	-6.81	-4.15
	30 - 45	0.42	-3.80	-3.38	-2.97	-4.15	-4.73	-1.73	-0.44	-5.28	-5.55	-3.80
AS3	0 – 15	-0.59	-4.57	-4.33	-4.29	-5.76	-5.50	-3.21	-2.24	-6.13	-7.15	-4.86
	15 - 30	0.00	-4.30	-3.37	-7.23	-6.16	-4.73	-2.75	-2.16	-5.35	-4.78	-3.82
	30 - 45	0.53	-2.54	-2.81	-2.76	-3.03	-3.69	-3.32	-1.30	-3.51	-3.60	-3.48
AS4	0 – 15	1.00	-1.83	-1.60	-2.63	-1.91	-2.39	-2.08	-0.77	-2.78	-4.49	-2.91
	15 - 30	-1.17	-3.76	-4.05	-2.51	-6.21	-1.70	-2.06	-0.68	-5.22	-4.52	-5.31
	30 - 45	-0.85	-4.91	-7.40	-5.54	-7.98	-6.54	-4.84	-2.93	-5.59	-5.80	-10.8
AS5	0 – 15	1.59	-3.07	-2.30	-3.11	-2.90	-5.23	-1.69	-0.41	-5.82	-4.53	-2.41
	15 - 30	1.08	-3.37	-2.29	-3.29	-3.31	-5.14	-3.00	-1.95	-5.75	-4.77	-2.85
	30 - 45	1.59	-3.99	-2.08	-2.55	-4.63	-4.59	-2.23	-2.59	-5.51	-3.43	-2.25
OK1	0 – 15	0.42	-2.21	-3.74	-3.53	-3.31	-4.24	-1.68	1.63	-3.70	-4.05	-3.95
	15 - 30	1.35	-2.25	-2.40	-3.23	-2.41	-4.04	-1.98	1.10	-3.86	-4.81	-2.73
	30 - 45	-0.17	-1.13	-4.09	-2.33	-2.97	-3.31	-1.18	-0.21	-4.92	-3.41	-4.10
OK2	0 – 15	2.12	-1.66	-0.97	-3.08	-1.87	-2.01	-1.32	1.78	-3.40	-3.83	-2.03
	15 - 30	1.96	-4.16	-1.63	-2.65	-1.89	-3.05	-2.07	-1.31	-3.29	-3.03	-1.88
	30 - 45	1.92	-1.62	-1.65	-2.72	-1.78	-3.23	-2.02	-1.62	-3.31	-3.19	-1.95
OK3	0 – 15	1.08	-2.65	-2.56	-3.64	-4.86	-4.35	-3.32	-0.30	-4.46	-4.54	-2.90
	15 - 30	0.15	-3.66	-3.92	-4.19	-4.88	-5.38	-3.42	-0.59	-6.14	-6.15	-4.32
	30 - 45	-0.85	-4.51	-4.17	-4.02	-5.85	-5.47	-3.25	-0.52	-6.77	-6.83	-4.77
AB1	0 – 15	0.29	-3.99	-2.90	-3.16	-4.00	-4.06	-1.82	0.52	-6.15	-6.69	-4.35
	15 - 30	-0.59	-4.20	-3.66	-3.09	-4.91	-5.29	-2.32	0.25	-6.27	-6.94	-4.57
	30 - 45	1.47	-2.12	-2.27	-3.46	-2.57	-3.87	-2.71	-1.65	-4.10	-4.26	-2.48
AB2	0 – 15	-1.40	-2.02	-1.79	-2.4	-2.71	-3.54	-0.94	-0.08	-3.13	-3.43	-2.18
	15 - 30	-0.59	-2.26	-4.68	-2.49	-4.68	-3.72	-1.32	-1.26	-2.57	-3.91	-4.61
	30 - 45	2.56	-1.27	-1.15	-2.19	-1.53	-2.75	-1.30	-1.63	-6.79	-2.57	-1.33
AB3	0 – 15	2.08	-1.63	-1.58	-2.43	-1.81	-3.12	-1.33	-0.90	-2.89	-3.37	-1.94
	15 - 30	2.22	-1.53	-1.49	-2.4	-1.68	-3.03	-1.12	-1.61	-3.09	-3.45	-1.69
	30 - 45	2.12	-1.54	-1.53	-2.4	-1.57	-3.23	-1.32	-1.76	-3.26	-3.24	-1.74
AB4	0 – 15	1.53	-2.03	-2.10	-2.96	-2.41	-3.72	-2.25	1.13	-3.92	-3.88	-2.35
	15 - 30	1.74	-1.84	-1.79	-2.62	-2.09	-2.86	-1.77	-1.57	-3.66	-3.51	-2.08
	30 - 45	1.22	-2.32	-2.38	-3.38	-2.46	-4.09	-2.54	-2.19	-4.09	-4.51	-2.66
AB5	0 – 15	2.64	-0.99	-1.01	-1.76	-0.69	-2.65	-1.28	-0.56	-11.0	-2.33	-1.13
	15 - 30	2.29	-1.33	-2.24	-2.40	-1.27	-3.03	-1.40	-1.51	-2.98	-2.91	-1.59
	30 - 45	2.26	-1.27	-1.50	-2.13	-1.27	-1.96	-1.02	-1.30	-2.60	-2.64	-1.60
	MIN	-1.40	-4.91	-7.40	-7.23	-7.98	-6.54	-4.84	-2.93	-11.0	-7.15	-10.8
	MAX	2.64	-0.99	-0.97	-1.20	-0.69	-1.70	0.43	3.39	-2.57	-2.33	-1.13
	MEAN	0.92	-2.76	-2.76	-3.07	-3.35	-3.93	-1.98	-0.72	-4.62	-4.41	-3.22

4.6 Pollution load index three months after the major flooding

The computed pollution load indices are shown in Table 4.8. The pollution load index in this study ranged from 0.03 to 0.78 for all sites and depths. The highest and lowest PLI values were found at sites AB5 (0-15 cm depth) and AS4 (30-45 cm depth) respectively. The PLI of all sites and depths were less than 1, denoting perfection.

Table 4.8: Pollution load index of metals in soil three months after the major flooding

Sites	Depth (cm)	CFCd	CFCo	CFCr	CFCu	CFMn	CFNi	CFPb	CFZn	CFBa	CFAl	CFFe	PLI
AS1	0 - 15	6.50	0.24	0.12	0.18	0.21	0.07	1.40	15.7	0.11	0.03	0.09	0.32
	15 - 30	2.00	0.10	0.14	0.25	0.11	0.09	0.69	0.96	0.21	0.13	0.14	0.25
	30 - 45	5.33	0.34	0.37	0.65	0.30	0.12	2.03	2.74	0.14	0.12	0.33	0.51
AS2	0 - 15	1.33	0.08	0.09	0.14	0.02	0.04	0.19	0.97	0.02	0.02	0.07	0.09
	15 - 30	1.67	0.07	0.12	0.10	0.07	0.03	0.41	0.51	0.02	0.01	0.08	0.10
	30 - 45	2.00	0.11	0.14	0.19	0.08	0.06	0.45	1.11	0.04	0.03	0.11	0.16
AS3	0 - 15	1.00	0.06	0.07	0.08	0.03	0.03	0.16	0.32	0.02	0.01	0.05	0.07
	15 - 30	1.50	0.08	0.15	0.01	0.02	0.06	0.22	0.34	0.04	0.05	0.11	0.09
	30 - 45	2.17	0.26	0.21	0.22	0.18	0.12	0.15	0.61	0.13	0.12	0.13	0.24
AS4	0 - 15	3.00	0.42	0.50	0.24	0.40	0.29	0.36	0.88	0.22	0.07	0.20	0.37
	15 - 30	0.67	0.11	0.09	0.26	0.02	0.46	0.36	0.94	0.04	0.07	0.04	0.15
	30 - 45	0.83	0.05	0.01	0.03	0.01	0.02	0.05	0.20	0.03	0.03	0.00	0.03
AS5	0 - 15	4.50	0.18	0.31	0.17	0.20	0.04	0.47	1.13	0.03	0.06	0.28	0.31
	15 - 30	3.17	0.14	0.31	0.15	0.15	0.04	0.19	0.39	0.03	0.05	0.21	0.17
	30 - 45	4.50	0.09	0.35	0.26	0.06	0.06	0.32	0.25	0.03	0.14	0.32	0.20
OK1	0 - 15	2.00	0.32	0.11	0.13	0.15	0.08	0.47	4.63	0.12	0.09	0.10	0.25
	15 - 30	3.83	0.32	0.29	0.16	0.28	0.09	0.38	3.23	0.10	0.05	0.23	0.31
	30 - 45	1.33	0.69	0.09	0.30	0.19	0.15	0.66	1.30	0.05	0.14	0.09	0.34
OK2	0 - 15	6.50	0.48	0.77	0.18	0.41	0.37	0.60	5.17	0.14	0.11	0.37	0.54
	15 - 30	5.83	0.08	0.48	0.24	0.40	0.18	0.36	0.61	0.15	0.18	0.41	0.44
	30 - 45	5.67	0.49	0.48	0.23	0.44	0.16	0.37	0.49	0.15	0.16	0.39	0.40
OK3	0 - 15	3.17	0.24	0.25	0.12	0.05	0.07	0.15	1.22	0.07	0.06	0.20	0.20
	15 - 30	1.67	0.12	0.10	0.08	0.05	0.04	0.14	0.99	0.02	0.02	0.07	0.11
	30 - 45	0.83	0.07	0.08	0.09	0.03	0.03	0.16	1.04	0.01	0.01	0.06	0.08
AB1	0 - 15	1.83	0.09	0.20	0.17	0.09	0.09	0.43	2.15	0.02	0.01	0.07	0.16
	15 - 30	1.00	0.08	0.12	0.18	0.05	0.04	0.30	1.79	0.02	0.01	0.06	0.11
	30 - 45	4.17	0.34	0.31	0.14	0.25	0.10	0.23	0.48	0.09	0.08	0.27	0.26
AB2	0 - 15	0.57	0.37	0.43	0.28	0.23	0.13	0.78	1.42	0.17	0.14	0.33	0.36
	15 - 30	1.00	0.31	0.06	0.27	0.06	0.11	0.60	0.63	0.25	0.10	0.06	0.20
	30 - 45	8.83	0.62	0.68	0.33	0.52	0.22	0.61	0.48	0.01	0.25	0.60	0.63
AB3	0 - 15	6.33	0.48	0.50	0.28	0.43	0.17	0.60	0.80	0.20	0.15	0.39	0.46
	15 - 30	7.00	0.52	0.53	0.28	0.47	0.18	0.69	0.49	0.18	0.14	0.47	0.46
	30 - 45	6.50	0.52	0.52	0.28	0.51	0.16	0.60	0.44	0.16	0.16	0.45	0.44
AB4	0 - 15	4.33	0.37	0.35	0.19	0.28	0.11	0.32	3.27	0.10	0.10	0.29	0.36
	15 - 30	5.00	0.42	0.43	0.24	0.35	0.21	0.44	0.51	0.12	0.13	0.35	0.38
	30 - 45	3.50	0.30	0.29	0.14	0.27	0.09	0.26	0.33	0.09	0.07	0.24	0.24
AB5	0 - 15	9.33	0.76	0.74	0.44	0.93	0.24	0.62	1.02	0.00	0.30	0.68	0.78
	15 - 30	7.33	0.59	0.32	0.28	0.62	0.18	0.57	0.53	0.19	0.20	0.50	0.47
	30 - 45	7.17	0.62	0.53	0.34	0.62	0.39	0.74	0.61	0.25	0.24	0.49	0.58
	MIN	0.57	0.05	0.01	0.01	0.01	0.02	0.05	0.20	0.00	0.01	0.00	0.03
	MAX	9.33	0.76	0.77	0.65	0.93	0.46	2.03	15.7	0.25	0.30	0.68	0.78
	MEAN	3.72	0.30	0.30	0.21	0.24	0.13	0.48	1.56	0.10	0.10	0.24	0.30

4.7   Ecological risk assessment three months after the major flooding

The computed ecological risk of metals in the study sites are shown in Table 4.9. The potential ecological risk (Er) of Cr, Cu, Ni, Pb and Zn were in the low potential ecological risk category which indicated that these five metals have limited environmental impact in the study areas. The ER values of Cd in 21 out of 39 samples were greater than 80. There was higher potential ecological risk with soils of the downstream section of the floodplain than those of upstream and mid-stream sections of the floodplain. Similarly, the RI values ranged between 25.8 and 291 in these sites with 50% of the samples having RI values greater than 100. On the basis of RI values, these sites fall within the low ecological risk to moderate ecological risk categories with significant impact from Cd pollution.

Table 4.9: Ecological risk assessment of metals in soils three months after the major flooding

Sites	Depth (cm)	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	RI
AS1	0 - 15	195	0.47	0.24	0.91	0.21	0.35	7.00	15.7	220
	15 - 30	60.0	0.20	0.27	1.24	0.11	0.46	3.45	0.96	66.7
	30 - 45	160	0.68	0.73	3.26	0.30	0.62	10.1	2.74	178
AS2	0 - 15	40.0	0.16	0.17	0.68	0.02	0.18	0.93	0.97	43.1
	15 - 30	50.0	0.14	0.25	0.49	0.07	0.15	2.05	0.51	53.7
	30 - 45	60.0	0.22	0.29	0.96	0.08	0.28	2.26	1.11	65.2
AS3	0 - 15	30.0	0.13	0.15	0.38	0.03	0.17	0.81	0.32	32.0
	15 - 30	45.0	0.15	0.29	0.05	0.02	0.28	1.11	0.34	47.2
	30 - 45	65.0	0.52	0.43	1.11	0.18	0.58	0.75	0.61	69.2
AS4	0 - 15	90.0	0.84	0.99	1.21	0.40	1.43	1.78	0.88	97.5
	15 - 30	20.0	0.22	0.18	1.32	0.02	2.32	1.80	0.94	26.8
	30 - 45	25.0	0.10	0.02	0.16	0.01	0.08	0.26	0.20	25.8
AS5	0 - 15	135	0.36	0.61	0.87	0.20	0.20	2.33	1.13	141
	15 - 30	95.0	0.29	0.62	0.77	0.15	0.21	0.94	0.39	98.4
	30 - 45	135	0.19	0.71	1.28	0.06	0.31	1.60	0.25	140
OK1	0 - 15	60.0	0.65	0.22	0.65	0.15	0.40	2.34	4.63	69.0
	15 - 30	115	0.63	0.57	0.80	0.28	0.46	1.90	3.23	123
	30 - 45	40.0	1.37	0.18	1.49	0.19	0.76	3.30	1.30	48.6
OK2	0 - 15	195	0.95	1.53	0.89	0.41	1.86	3.01	5.17	209
	15 - 30	175	0.17	0.97	1.19	0.40	0.90	1.79	0.61	181
	30 - 45	170	0.97	0.96	1.14	0.44	0.80	1.85	0.49	177
OK3	0 - 15	95.0	0.48	0.51	0.60	0.05	0.37	0.75	1.22	99.0
	15 - 30	50.0	0.24	0.20	0.41	0.05	0.18	0.70	0.99	52.8
	30 - 45	25.0	0.13	0.17	0.46	0.03	0.17	0.79	1.04	27.8
AB1	0 - 15	55.0	0.19	0.40	0.84	0.09	0.45	2.13	2.15	61.3
	15 - 30	30.0	0.16	0.24	0.88	0.05	0.19	1.50	1.79	34.8
	30 - 45	125	0.69	0.62	0.68	0.25	0.51	1.15	0.48	129
AB2	0 - 15	17.0	0.74	0.87	1.42	0.23	0.64	3.91	1.42	26.2
	15 - 30	30.0	0.63	0.12	1.34	0.06	0.57	3.00	0.63	36.3
	30 - 45	265	1.24	1.35	1.64	0.52	1.12	3.04	0.48	274
AB3	0 - 15	190	0.97	1.00	1.39	0.43	0.86	2.99	0.80	198
	15 - 30	210	1.04	1.07	1.42	0.47	0.92	3.46	0.49	219
	30 - 45	195	1.03	1.04	1.42	0.51	0.80	3.01	0.44	203
AB4	0 - 15	130	0.74	0.70	0.96	0.28	0.57	1.58	3.27	138
	15 - 30	150	0.84	0.87	1.22	0.35	1.03	2.20	0.51	157
	30 - 45	105	0.60	0.58	0.72	0.27	0.44	1.29	0.33	109
AB5	0 - 15	280	1.51	1.49	2.21	0.93	1.19	3.09	1.02	291
	15 - 30	220	1.19	0.63	1.42	0.62	0.92	2.84	0.53	228
	30 - 45	215	1.24	1.06	1.71	0.62	1.93	3.69	0.61	225
	MIN	17.0	0.10	0.02	0.05	0.01	0.08	0.26	0.20	25.8
	MAX	280	1.51	1.53	3.26	0.93	2.32	10.1	15.7	291
	MEAN	111	0.59	0.60	1.07	0.24	0.66	2.37	1.56	118

4.8 **Human exposure and health risk assessment three months after the major flooding**

4.8.1 **Non-carcinogenic health risk three months after the major flooding**

The non-carcinogenic and carcinogenic risk calculated based on total metal concentration for children and adults are shown in Table 4.10. In Table 4.10, the mean values of the different exposure pathways showed that HQ is in the order of HQ_{ing} (0.67) >> HQ (0.025) $_{dermal}$ >> HQ_{inh} (0.0018) for children and HQ_{ing} (0.08) >>HQ_{dermal} (0.004) >> HQ_{inh} (0.0018) for adults. The computed hazard index (HI) for all sites and depth ranged from 0.08 to 1.82 with a mean of 0.69 for the case of children while the HI values ranged from 0.01 to 0.24 with a mean of 0.09 for adults scenario. The non-carcinogenic hazards were greater in children than adults. The HI values for the majority of the sites and depth were ≤ 1 for the adults and children scenarios except for sites OK2, AB3 and AB5 that had HI values greater than 1 for the children exposure. This suggested that there is a probability of health effects arising from metal contamination in these sites.

Table 4.10: Non-carcinogenic hazard exposure to metals in soil

Sites	Dpth (cm)	CHILD				ADULT			
		HQ_{Ing}	HQ_{Inh}	HQ_{Derm}	HI	HQ_{Ing}	HQ_{Inh}	HQ_{Derm}	HI
AS1	0 - 15	0.50	0.0013	0.013	0.52	0.06	0.0013	0.002	0.07
	15 - 30	0.42	0.0009	0.012	0.43	0.05	0.0009	0.002	0.06
	30 - 45	0.93	0.0023	0.031	0.97	0.12	0.0023	0.005	0.12
AS2	0 - 15	0.18	0.0003	0.007	0.19	0.02	0.0003	0.001	0.02
	15 - 30	0.21	0.0005	0.010	0.22	0.03	0.0005	0.002	0.03
	30 - 45	0.29	0.0007	0.012	0.30	0.04	0.0007	0.002	0.04
AS3	0 - 15	0.14	0.0003	0.006	0.15	0.02	0.0003	0.001	0.02
	15 - 30	0.26	0.0004	0.012	0.27	0.03	0.0004	0.002	0.04
	30 - 45	0.52	0.0013	0.018	0.54	0.07	0.0013	0.003	0.07
AS4	0 - 15	0.77	0.0024	0.040	0.82	0.10	0.0024	0.006	0.11
	15 - 30	0.25	0.0004	0.009	0.26	0.03	0.0004	0.001	0.03
	30 - 45	0.07	0.0001	0.001	0.08	0.01	0.0001	0.000	0.01
AS5	0 - 15	0.58	0.0016	0.025	0.60	0.07	0.0016	0.004	0.08
	15 - 30	0.46	0.0012	0.025	0.48	0.06	0.0012	0.004	0.06
	30 - 45	0.61	0.0012	0.029	0.64	0.08	0.0012	0.005	0.08
OK1	0 - 15	0.50	0.0011	0.010	0.51	0.06	0.0011	0.002	0.07
	15 - 30	0.63	0.0019	0.024	0.65	0.08	0.0019	0.004	0.08
	30 - 45	0.80	0.0014	0.009	0.81	0.10	0.0014	0.001	0.10
OK2	0 - 15	1.11	0.0030	0.062	1.18	0.14	0.0030	0.010	0.15
	15 - 30	0.80	0.0027	0.040	0.84	0.10	0.0027	0.006	0.11
	30 - 45	1.05	0.0030	0.040	1.10	0.13	0.0030	0.006	0.14
OK3	0 - 15	0.51	0.0009	0.021	0.53	0.06	0.0009	0.003	0.07
	15 - 30	0.22	0.0005	0.008	0.23	0.03	0.0005	0.001	0.03
	30 - 45	0.15	0.0003	0.007	0.16	0.02	0.0003	0.001	0.02
AB1	0 - 15	0.26	0.0007	0.016	0.28	0.03	0.0007	0.003	0.04
	15 - 30	0.20	0.0004	0.010	0.21	0.03	0.0004	0.002	0.03
	30 - 45	0.69	0.0019	0.026	0.72	0.09	0.0019	0.004	0.09
AB2	0 - 15	0.89	0.0020	0.034	0.92	0.11	0.0020	0.005	0.12
	15 - 30	0.45	0.0007	0.006	0.46	0.06	0.0007	0.001	0.06
	30 - 45	1.49	0.0040	0.057	1.55	0.19	0.0040	0.009	0.20
AB3	0 - 15	1.06	0.0030	0.042	1.11	0.13	0.0030	0.007	0.14
	15 - 30	1.16	0.0034	0.045	1.21	0.15	0.0034	0.007	0.16
	30 - 45	1.15	0.0035	0.044	1.20	0.15	0.0035	0.007	0.15
AB4	0 - 15	0.78	0.0021	0.029	0.81	0.10	0.0021	0.005	0.10
	15 - 30	0.93	0.0026	0.036	0.97	0.12	0.0026	0.006	0.12
	30 - 45	0.62	0.0019	0.024	0.64	0.08	0.0019	0.004	0.08
AB5	0 - 15	1.75	0.0058	0.062	1.82	0.22	0.0058	0.010	0.24
	15 - 30	1.23	0.0040	0.029	1.26	0.15	0.0040	0.005	0.16
	30 - 45	1.38	0.0041	0.046	1.42	0.17	0.0041	0.007	0.18
	MIN	0.07	0.0001	0.001	0.08	0.01	0.0001	0.000	0.01
	MAX	1.75	0.0058	0.062	1.82	0.22	0.0058	0.010	0.24
	MEAN	0.67	0.0018	0.025	0.69	0.08	0.0018	0.004	0.09

4.8.2 Carcinogenic health risk three months after the major flooding

The carcinogenic risk calculated based on total metal concentration for children and adults are shown in Table 4.11. The cancer risk via ingestion, inhalation and dermal contact ranged from 5.40×10^{-7} to 4.57×10^{-5}, 2.51×10^{-10} to 2.01×10^{-8} and 9.23×10^{-8} to 7.96×10^{-6} respectively for children and 8.11×10^{-7} to 6.85×10^{-5}, 1.26×10^{-12} to 1.01×10^{-10} and 1.85×10^{-7} to 1.59×10^{-5} respectively for adults (Table 4.11). The observed inhalation cancer risk was low compared to those of ingestion and dermal contact. The cancer risk via inhalation for adults was higher than the children scenario. This could be due to the longer exposure duration (ED) for adults. Cancer risk for the children case via ingestion and dermal contact were higher than for adults. This may be due to high physical contacts with soil and also with a smaller body weight (Olawoyin *et al.,* 2012). Thus, there is concern for possible adverse health effect on children.

The total cancer risks for all the sites and depths ranged from 2.25×10^{-7} to 2.16×10^{-6} with a mean value of 8.77×10^{-7} and 1.79×10^{-8} to 6.84×10^{-7} with a mean value of 3.16×10^{-7} for children and adults respectively. The total cancer risk values obtained in this study indicates potential cancer risk as the cancer risk were lower than the potentially acceptable carcinogenic target risk values of 10^{-6} set by USEPA (2011).

Table 4.11: Carcinogenic risk associated with metal exposure in soils

Sites	Depth (cm)	CHILD				ADULT			
		$RISK_{ING}$	$RISK_{INH}$	$RISK_{DERM}$	TOTAL CANCER RISK	$RISK_{ING}$	$RISK_{INH}$	$RISK_{DERM}$	TOTAL CANCER RISK
AS1	0 - 15	2.37E-07	1.90E-09	2.97E-07	5.35E-07	3.54E-07	1.01E-08	1.33E-08	3.77E-07
	15 - 30	1.44E-07	2.09E-09	3.22E-07	4.69E-07	2.16E-07	1.10E-08	1.44E-08	2.41E-07
	30 - 45	4.12E-07	5.64E-09	8.76E-07	1.29E-06	6.17E-07	2.98E-08	3.92E-08	6.86E-07
AS2	0 - 15	5.74E-08	1.35E-09	2.06E-07	2.64E-07	8.58E-08	7.12E-09	9.21E-09	1.02E-07
	15 - 30	1.01E-07	1.89E-09	2.91E-07	3.94E-07	1.51E-07	9.97E-09	1.30E-08	1.74E-07
	30 - 45	1.15E-07	2.21E-09	3.40E-07	4.58E-07	1.72E-07	1.17E-08	1.52E-08	1.99E-07
AS3	0 - 15	4.98E-08	1.14E-09	1.75E-07	2.25E-07	7.45E-08	6.04E-09	7.81E-09	8.83E-08
	15 - 30	8.39E-08	2.23E-09	3.40E-07	4.26E-07	1.26E-07	1.18E-08	1.52E-08	1.53E-07
	30 - 45	9.83E-08	3.27E-09	4.96E-07	5.98E-07	1.47E-07	1.73E-08	2.22E-08	1.87E-07
AS4	0 - 15	2.30E-07	7.60E-09	1.16E-06	1.39E-06	3.43E-07	4.02E-08	5.18E-08	4.35E-07
	15 - 30	8.27E-08	1.50E-09	2.15E-07	3.00E-07	1.24E-07	7.92E-09	9.65E-09	1.41E-07
	30 - 45	1.08E-08	1.46E-10	2.12E-08	3.22E-08	1.62E-08	7.73E-10	9.51E-10	1.79E-08
AS5	0 - 15	1.75E-07	4.67E-09	7.14E-07	8.94E-07	2.62E-07	2.47E-08	3.20E-08	3.19E-07
	15 - 30	1.38E-07	4.69E-09	7.16E-07	8.59E-07	2.07E-07	2.48E-08	3.21E-08	2.64E-07
	30 - 45	1.73E-07	5.41E-09	8.26E-07	1.00E-06	2.59E-07	2.86E-08	3.70E-08	3.24E-07
OK1	0 - 15	1.05E-07	1.73E-09	2.66E-07	3.73E-07	1.58E-07	9.16E-09	1.19E-08	1.79E-07
	15 - 30	1.56E-07	4.37E-09	6.67E-07	8.27E-07	2.34E-07	2.31E-08	2.98E-08	2.87E-07
	30 - 45	1.23E-07	1.39E-09	2.14E-07	3.38E-07	1.84E-07	7.37E-09	9.57E-09	2.01E-07
OK2	0 - 15	3.62E-07	1.17E-08	1.78E-06	2.16E-06	5.42E-07	6.20E-08	7.99E-08	6.84E-07
	15 - 30	2.26E-07	7.42E-09	1.13E-06	1.36E-06	3.38E-07	3.92E-08	5.05E-08	4.28E-07
	30 - 45	2.25E-07	7.32E-09	1.11E-06	1.35E-06	3.37E-07	3.87E-08	4.99E-08	4.25E-07
OK3	0 - 15	1.13E-07	3.89E-09	5.92E-07	7.09E-07	1.69E-07	2.06E-08	2.65E-08	2.16E-07
	15 - 30	5.53E-08	1.52E-09	2.31E-07	2.88E-07	8.26E-08	8.02E-09	1.03E-08	1.01E-07
	30 - 45	5.23E-08	1.28E-09	1.95E-07	2.49E-07	7.83E-08	6.75E-09	8.74E-09	9.38E-08
AB1	0 - 15	1.32E-07	3.08E-09	4.71E-07	6.06E-07	1.97E-07	1.63E-08	2.11E-08	2.34E-07
	15 - 30	8.45E-08	1.82E-09	2.79E-07	3.66E-07	1.26E-07	9.60E-09	1.25E-08	1.49E-07
	30 - 45	1.45E-07	4.76E-09	7.24E-07	8.74E-07	2.17E-07	2.52E-08	3.24E-08	2.74E-07
AB2	0 - 15	2.66E-07	6.59E-09	1.01E-06	1.29E-06	3.97E-07	3.48E-08	4.54E-08	4.78E-07
	15 - 30	1.04E-07	9.28E-10	1.43E-07	2.48E-07	1.55E-07	4.91E-09	6.42E-09	1.67E-07
	30 - 45	3.31E-07	1.04E-08	1.58E-06	1.92E-06	4.95E-07	5.48E-08	7.07E-08	6.20E-07
AB3	0 - 15	2.65E-07	7.67E-09	1.17E-06	1.44E-06	3.96E-07	4.05E-08	5.23E-08	4.89E-07
	15 - 30	2.90E-07	8.18E-09	1.25E-06	1.55E-06	4.34E-07	4.32E-08	5.59E-08	5.33E-07
	30 - 45	2.73E-07	7.95E-09	1.21E-06	1.49E-06	4.08E-07	4.20E-08	5.43E-08	5.04E-07
AB4	0 - 15	1.71E-07	5.37E-09	8.18E-07	9.94E-07	2.56E-07	2.84E-08	3.66E-08	3.21E-07
	15 - 30	2.18E-07	6.64E-09	1.01E-06	1.23E-06	3.26E-07	3.51E-08	4.52E-08	4.07E-07
	30 - 45	1.41E-07	4.42E-09	6.73E-07	8.18E-07	2.11E-07	2.34E-08	3.01E-08	2.64E-07
AB5	0 - 15	3.56E-07	1.14E-08	1.73E-06	2.10E-06	5.32E-07	6.01E-08	7.75E-08	6.70E-07
	15 - 30	1.94E-07	4.89E-09	7.41E-07	9.39E-07	2.90E-07	2.59E-08	3.32E-08	3.49E-07
	30 - 45	2.95E-07	8.18E-09	1.24E-06	1.54E-06	4.41E-07	4.33E-08	5.55E-08	5.40E-07
	LOWEST	1.08E-08	1.46E-10	2.12E-08	3.21E-08	1.62E-08	7.73E-10	9.51E-10	1.79E-08
	HIGHEST	4.12E-07	1.17E-08	1.78E-06	2.20E-06	6.17E-07	6.20E-08	7.99E-08	7.59E-07
	MEAN	1.74E-07	4.58E-09	6.98E-07	8.77E-07	2.60E-07	2.42E-08	3.13E-08	3.16E-07

**4.9	Correlation analysis three months after the major flooding**

To assess possible associations and co-contamination from similar sources among the data set, correlation analysis was performed on the concentrations of the individual metals in these soil samples at each site and depth. As shown in Table 4.12, the following metals, Cd, Co, Cr, Cu, Mn, Ni, Al and Fe, were positively correlated in all sites and depths, which suggested that they may have originated from a common anthropogenic source such as applications of agrochemicals, fertilizers, vehicular emissions and industrial discharges. The correlation patterns of these metals suggested that Cd, Co, Cr, Cu and Ni exist in the Fe, Mn, and Al oxides/hydroxides phases in these soils. Zinc showed strong positive correction with Pb and Ni at 0-15 cm and 30-45 cm depths respectively. The association of Zn and Pb in the topsoil indicates that these elements originated from vehicular emission. Barium showed positive correction with Ni at all depth (r=0.52-0.85), however, Ba also showed positive correlations with Co, Cr and Cu at 15-30 cm depth and Mn at 30-45 cm depth (Table 4.12). The association of Ba and Ni at all depths suggested emissions from the oil and gas industries. In this study, there was virtually no or weak correlation between the metal concentrations and soil physic-chemical characteristics such as pH, conductivity and total organic carbon contents. Weak or virtually no relationship have been found between metals and organic matter contents (Martin 1997; 2000; 2004; Taylor, 1996). The lack of significant correlation between metals and organic matter suggests that (i) metals can also be transported in coatings on quartz grains (sand) or in the form of ore grain (Leenaers and Rang, 1989; Lecce and Pavlowsky, 1997) which disturbs the negative grain size-metal relationship (Moore et al.,1989), (ii) migration of metals in the soil profiles (Hudson-Edward *et al.*, 1998; Ciezewski and Malik, 2004) due to leaching, mechanical turbation through farming activities or bioturbation which alters the relationship that exist in the fresh deposit (Thonon, 2006) and (iii) continuous input of fresh contamination, the presence of different sources and limited effect of physicochemical parameters on metals in the soil (Nam *et al*., 2008; Wu and Zhang, 2010;Yang *et al.*, 2012).

Table 4.12: Correlation among the metals and physicochemical properties in the soil

	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Ba	Al	Fe	pH	EC	TOC
0-15 cm depth														
Cd	1	0.70**	0.62*	0.58*	0.78**	0.48	0.43	0.32	0.00	0.62*	0.69*	0.21	0.04	-0.05
Co		1	0.86**	0.85**	0.93**	0.74**	0.27	-0.05	0.37	0.92**	0.89**	0.03	-0.06	0.06
Cr			1	0.74**	0.84**	0.87**	0.14	-0.2	0.34	0.76**	0.88**	0.01	0.03	-0.03
Cu				1	0.91**	0.51*	0.35	-0.13	0.17	0.89**	0.87**	0.02	0.04	-0.04
Mn					1	0.68*	0.29	-0.06	0.14	0.90**	0.90**	0.11	0.05	-0.05
Ni						1	0.14	-0.02	0.52*	0.50*	0.56*	-0.21	0.06	-0.06
Pb							1	0.81**	0.3	0.2	0.15	0.08	0.08	-0.08
Zn								1	0.14	-0.19	-0.25	-0.09	-0.05	0.05
Ba									1	0.09	0.09	-0.04	-0.15	0.15
Al										1	0.94**	0.1	-0.03	0.03
Fe											1	0.14	-0.04	0.04
pH												1	0.39	-0.39
EC													1	-1.00**
TOC														1
15-30 cm depth														
Cd	1	0.68*	0.90**	0.47	0.98**	0.16	0.38	-0.14	0.44	0.78**	1.00**	-0.01	0.06	-0.06
Co		1	0.47	0.54*	0.73**	0.21	0.56*	-0.02	0.53*	0.53*	0.66*	-0.09	0.15	-0.15
Cr			1	0.39	0.83**	0.17	0.24	-0.14	0.28	0.64*	0.91**	0.13	-0.03	0.03
Cu				1	0.55*	0.60*	0.74**	-0.07	0.72**	0.71**	0.50*	-0.19	-0.09	0.09
Mn					1	0.21	0.44	-0.07	0.50*	0.81**	0.98**	-0.12	0.05	-0.05
Ni						1	0.24	-0.11	0.17	0.39	0.18	0.09	0.21	-0.21
Pb							1	-0.1	0.85**	0.60*	0.4	-0.45	-0.18	0.18
Zn								1	-0.12	-0.33	-0.19	-0.33	0.13	-0.13
Ba									1	0.77**	0.47	-0.41	-0.52*	0.52*
Al										1	0.82**	-0.17	-0.33	0.33
Fe											1	-0.01	0.00	0.00
pH												1	0.35	-0.35
EC													1	-1.00**
TOC														1
30-45 cm depth														
Cd	1	0.63*	0.99**	0.55*	0.88**	0.73**	0.4	-0.05	0.46	0.84**	1.00**	-0.17	-0.15	0.15
Co		1	0.61*	0.46	0.83**	0.81**	0.34	0.07	0.34	0.81**	0.63*	-0.39	-0.33	0.33
Cr			1	0.49	0.88**	0.70**	0.32	-0.13	0.47	0.84**	0.99**	-0.12	-0.14	0.14
Cu				1	0.47	0.46	0.95**	0.73	0.38	0.54*	0.52*	-0.35	0.04	-0.04
Mn					1	0.88**	0.35	-0.05	0.65*	0.83**	0.88**	-0.36	-0.32	0.32
Ni						1	0.32	-0.01	0.62*	0.86**	0.73**	-0.22	-0.57*	0.57*
Pb							1	0.85**	0.32	0.31	0.37	-0.49	0.1	-0.1
Zn								1	0.07	-0.09	-0.09	-0.53*	0.16	-0.16
Ba									1	0.4	0.46	-0.17	-0.3	0.3
Al										1	0.85**	0.02	-0.35	0.35
Fe											1	-0.13	-0.15	0.15
pH												1	0.12	-0.12
EC													1	1.00**
TOC														1

*Pearson Correlation is significant at the 0.05 level (1 tailed)
** Pearson Correlation is significant at the 0.01 level (1 tailed)

4.10   Principal Component Analysis (PCA) three months after the major flooding

Principal component analysis was applied to the data sets to reduce the high dimensionality of variable space and also provide information on the relationships among the variables. Results of PCA application to all sites and depths are presented in Table 4.13 and Figures 2(a-c). As shown in Table 4.13, three principal components or groups of metals were extracted from the PCA of metals in the soils at 0-15 cm depth and accounted for 89.48 % of the variability of metals in the soils. Factor 1, was responsible for 59.55 % of the total variance and was dominated by Fe, Mn, Al, Co, Cu, Cr and Cd. These are mainly transition metals of the d-block in the belonging to the fourth period except for Al and Cd and characterised by similarities in chemical properties (Falkowaska and Falkowski, 2014) or suggest a common source. The major sources of these metals are anthropogenic activities and traffic emissions (Iwegbue, 2014; Tahmasbian *et al*., 2014). Factor 1 also suggests that these anthropogenic metals are associated with the Fe, Mn and Al oxides/hydroxides phase in these soils.   Factor 2 explains 18.29% of the total variance and was attributed mainly to Pb and Zn. These elements (Pb and Zn) are associated with traffic emissions. Factor 3 which explains 11.64 % of the total variance was dominated by Ba and Ni, which suggests emissions from the petroleum industries as a common source of these metals.   The use of drilling chemicals such as barite may be possible source of barium in these floodplain soils as indicated by its higher concentrations in the soil profiles of the downstream section of the floodplain where there is intense drilling activities by the oil and gas industries.

Table 4.13: PCA Factor loadings after Varimax with Kaiser Normalization rotation for metals in the soil

Metals	0-15 cm depth			15-30 cm depth			30-45 cm depth	
	Component			Component			Component	
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2
Cd	.757	.445		.972	.212		.935	.123
Co	.908		.349	.587	.529	-.141	.781	.178
Cr	.839		.442	.919		.128	.940	
Cu	.901		.104	.266	.850	.232	.441	.873
Mn	.964		.138	.924	.339		.959	.108
Ni	.579		.696		.435	.549	.882	.123
Pb	.204	.916	.134	.181	.894		.263	.951
Zn	-.160	.964		-.112		-.844	-.181	.964
Ba		.156	.931	.260	.865		.571	.200
Al	.952			.646	.582	.360	.924	
Fe	.968			.959	.251	.118	.944	
Variance %	**59.55**	**18.29**	**11.29**	**56.93**	**15.67**	**9.84**	**62.07**	**21.24**
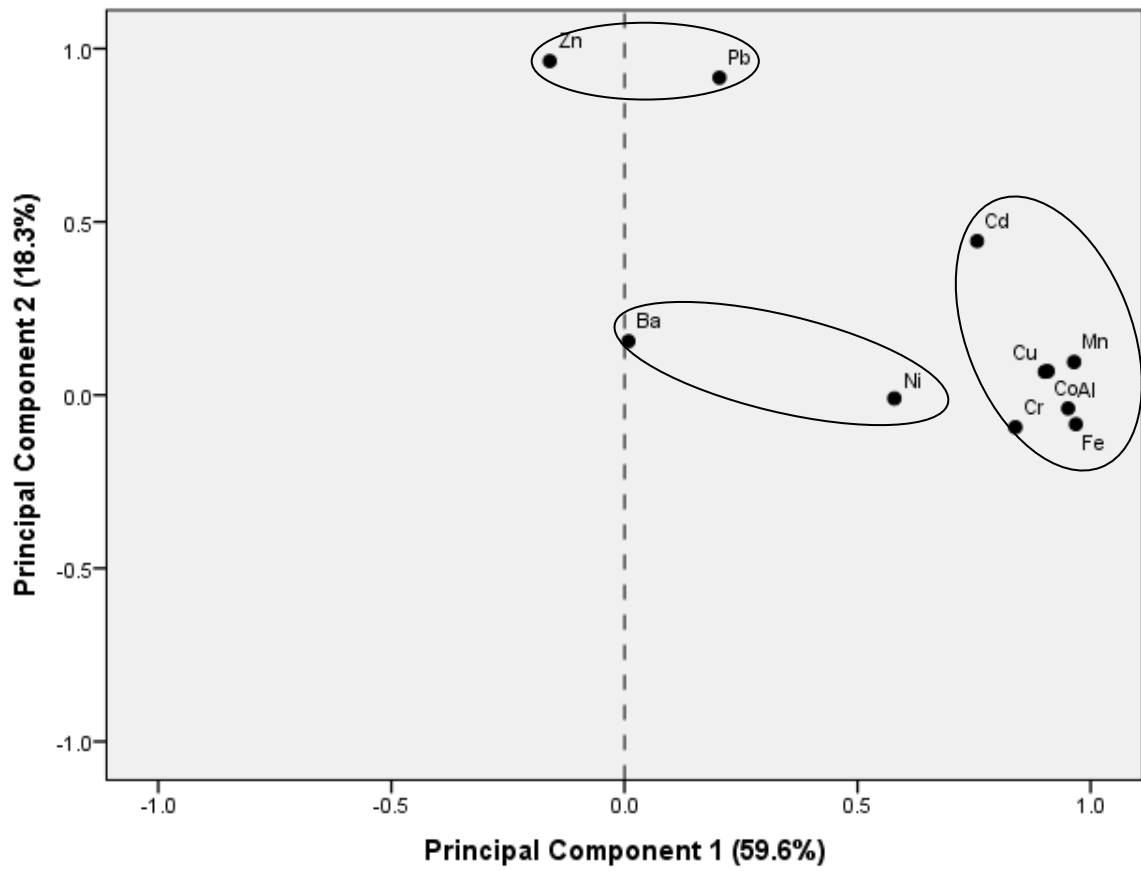
Figure 2a: The loading plot of PCA of heavy metals at depth 0-15 cm.
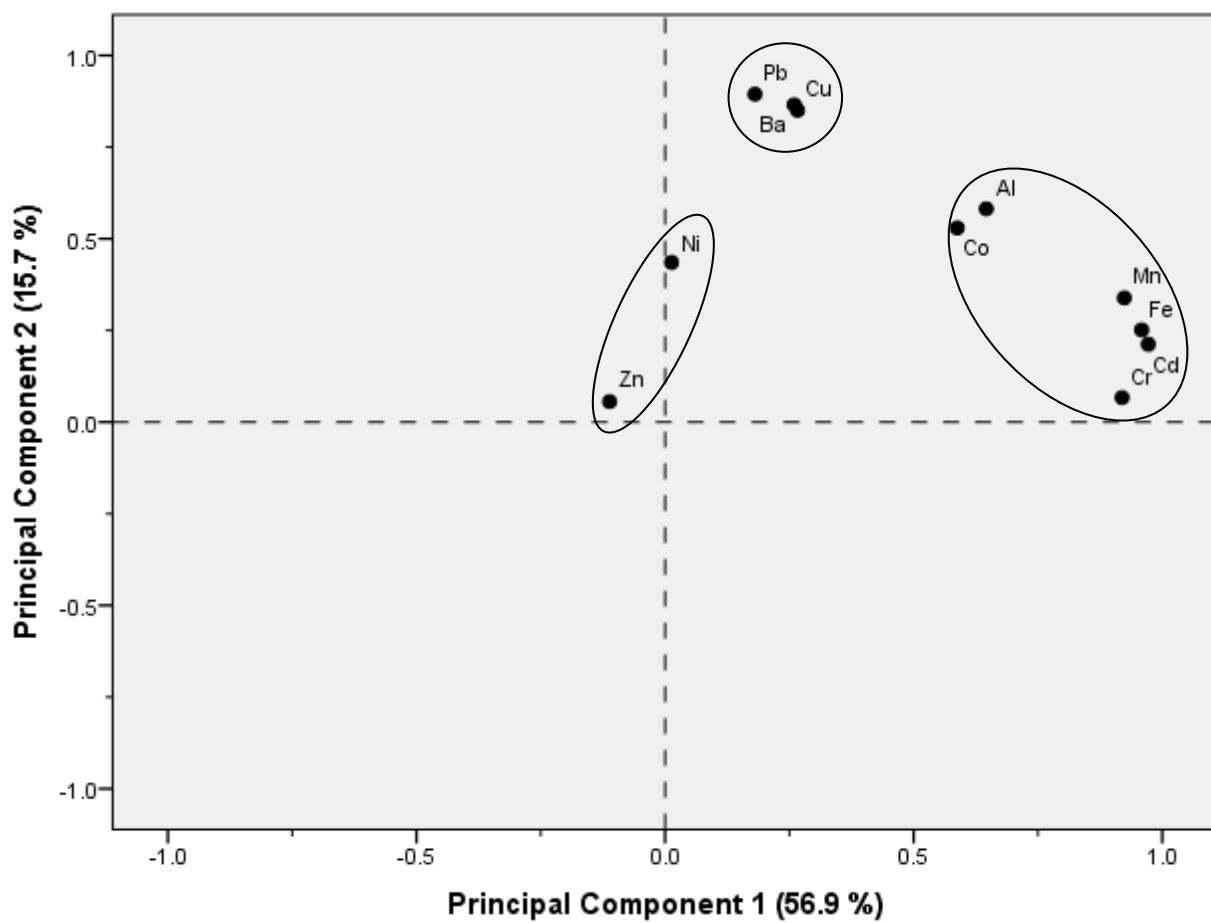
Figure 2b: The loading plot of PCA of heavy metals at depth 15-30 cm.
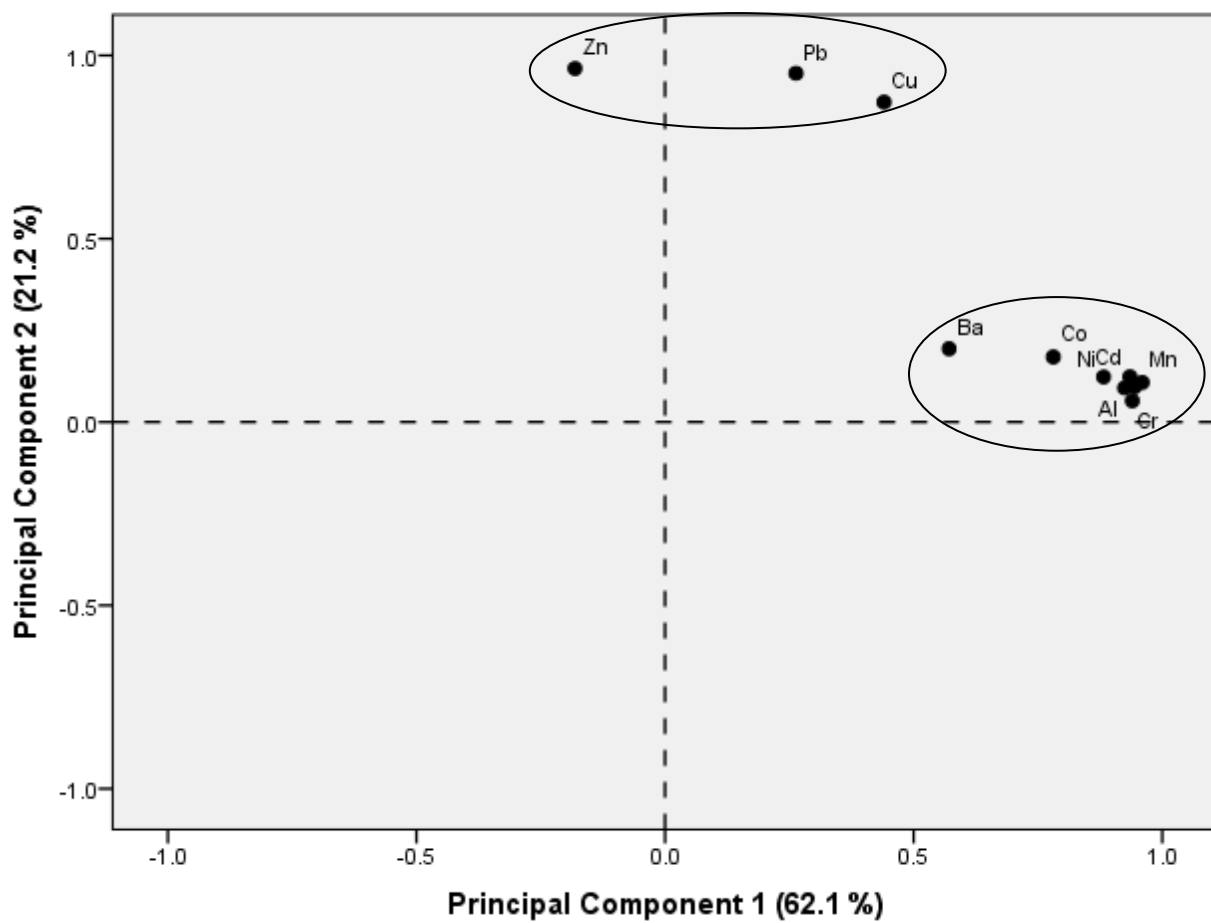
Figure 2c: The loading plot of PCA of heavy metals at depth 30-45 cm.

At 15-30 cm depth, three factors were also identified accounting for 82.44% of the variability in the data. Factor 1 explains 56.93% of the total variance and was characterised by positive loading of Cd, Fe, Mn, Cr, Al and Co. This indicates that these anthropogenic metals are associated with Fe, Mn and Al oxides/ hydroxide phase in this soil horizon. Iron (Fe), Mn and Al are metals that comes principally from natural sources, even though, Mn has anthropogenic sources which include the use organic manganese compound for improving the octane rating of unleaded fuel, the use of fertilizers, vanish and fungicides (Jumbe and Nandini, 2009; Iwegbue, 2014). Factor 2 accounts for 15.67% of the total variance. It was dominated by Pb, Ba and Cu. Factor 3 accounts for 9.84% of the total variance and was characterised by high loadings of Zn and Ni. Zinc and nickel have both traffic and agrochemical sources. The uses of organic manure, fertilizer and pesticides are possible sources of Zn and Ni in these soils in addition to Zn from the attrition of vehicular tyres and the use of lubricating oil containing zinc diphospate as additive, and Ni as an additive in burning fuel especially diesel (Iwegbue *et al*., 2013; Iwegbue, 2014).

At 30-45 cm depth, two component factors were identified accounting for 83.31% of variability of the metals in the soil. Factor 1 was responsible for 62.07% of the total variance. It was characterised by positive loading of Mn, Fe, Cr, Cd, Al, Ni, Co, Cu and Ba. Again, it suggested that existence in Fe, Mn and Al oxides and hydroxides phases are the possible retention mechanisms of these metals in these profiles. Factor 2 explains 21.24% of the total variance and was dominated by Zn, Pb and Cu. These are metals associated with industrial, agricultural and traffic emissions. For instance, Cu has been used in vehicular break systems and in Cu-brass automotive radiators while Zn comes from attrition of motor vehicle tyres as well as the use of lubricating oil which may contain zinc diphospate as additive (Iwegbue, 2014). Lead (Pb) comes from leaded fuel, although, the use of leaded fuel in Nigeria has reduced tremendously. Generally, the association of the majority of the studied metals with the Fe/Mn oxides in these soil profiles as suggested by the PCA results implies that decrease in pH and redox potentials as a result of fluctuating water table or flooding will lead to dissolution of

metals by dissolving the metal binding Fe/Mn oxides (Hesterberg, 1998; Thonon, 2006). Also, lower redox potential can lead to these metals to binding very insoluble sulphide thereby making these metals less mobile (Van Griethuysen *et al*., 2004, Thonon, 2006).

4.11   Chemical Fractionation of metals in the floodplain soils three months after the major flooding

The results for the concentrations of metals in different extraction phases are shown in Tables 14-22. The speciation patterns of these metals are also shown in Figures 3-11.

Cadmium

In these samples, the majority of Cd existed in the residual and Fe-Mn oxides/hydroxides phases. The percentage of Cd in the residual phase ranged between 7.5% and 95%. Cadmium was not found in the residual phase in the soils of 15-30 cm and 0-15 cm depth of sites AS3 and AB2 respectively. The dominance of Cd in residual fraction in floodplain soils have been reported in the literature (Shasheen *et al.*, 2013). The Fe-Mn oxides fraction (reducible phase) constituted 2.9% to 80% of the total Cd concentrations in these sites (Figure 3a-c). On average, the soil profile of OK3 had higher proportion of Cd in the Fe-Mn oxides phase than other sites. The significant amounts of Cd in the Fe-Mn oxides phase suggest anthropogenic origins. For instance, sites closer to industries and towns showed high levels of Cd in Fe-Mn oxides phase (site A3). In this study, 1.9% to 29.4% of the total Cd concentrations were found in the oxidizable phase. The exchangeable/acid soluble phase constituted 1.8 to 16% of the total concentrations of Cd in these soil profiles. The highest fraction of Cd in the exchangeable/acid soluble phase was observed at the 30-45 cm depth of site AS4. The similarity of the ionic radius of Ca (0.99A°) and Cd (0.97A°) favours the co-precipitation of Cd carbonates and its incorporation into calcite lattice to give solid solution of $Cd_\alpha Ca_{1-\alpha}CO_3$ (Ianni *et al.*, 2000; Korfali and Davies, 2004; Boughriet *et al*., 2007; Iwegbue *et al.*, 2009).

Table 4.14: Concentrations and percentages of cadmium in different extraction phases of the floodplain soils of the lower reaches of River Niger

Sites	Depth (cm)	CONCENTRATION ($\mu g\ g^{-1}$) F1	F2	F3	F4	SUM	TM	PERCENTAGE (%) F1	F2	F3	F4	RECOVERY (%)
AS1	0 - 15	0.04	0.2	0.2	1.56	2	1.95	2	10	10	78	102.6
	15 - 30	0.08	0.12	0.05	0.35	0.6	0.6	13.3	20	8.3	58.3	100
	30 - 45	0.04	0.24	0.05	1.27	1.6	1.6	2.5	15	3.1	79.4	100
AS2	0 - 15	0.04	0.04	0.14	0.22	0.44	0.4	9.1	9.1	31.8	50	110
	15 - 30	0.04	0.08	0.05	0.4	0.57	0.5	7	14	8.8	70.2	114
	30 - 45	ND	0.32	0.15	0.13	0.6	0.6	-	53.3	25	21.7	100
AS3	0 - 15	ND	0.04	0.09	0.23	0.36	0.3	-	11.1	25	63.9	120
	15 - 30	0.04	0.36	0.1	ND	0.5	0.45	8	72	20	-	111.1
	30 - 45	0.04	0.08	0.23	0.42	0.77	0.65	5.2	10.4	29.9	54.5	118.5
AS4	0 - 15	0.04	0.24	0.1	0.52	0.9	0.9	4.4	26.7	11.1	57.8	100
	15 - 30	ND	0.04	0.05	0.14	0.23	0.2	-	17.4	21.7	60.9	115
	30 - 45	0.04	0.16	0.05	ND	0.25	0.25	16	64	20	ND	100
AS5	0 - 15	0.04	0.56	0.05	0.75	1.4	1.35	2.9	40	3.6	53.6	103.7
	15 - 30	0.04	0.32	0.05	0.59	1	0.95	4	32	5	59	105.3
	30 - 45	0.04	0.48	0.05	0.83	1.4	1.35	2.9	34.3	3.6	59.3	103.7
OK1	0 - 15	0.04	0.28	0.05	0.23	0.6	0.6	6.7	46.7	8.3	38.3	100
	15 - 30	0.04	0.16	0.05	0.95	1.2	1.15	3.3	13.3	4.2	79.2	104.3
	30 - 45	0.04	0.28	0.05	0.03	0.4	0.4	10	70	12.5	7.5	100
OK2	0 - 15	0.04	0.04	ND	1.92	2	1.95	2	2	-	96	102.6
	15 - 30	0.04	0.04	0.05	1.67	1.8	1.75	2.2	2.2	2.8	92.8	102.9
	30 - 45	0.04	0.08	0.05	1.53	1.7	1.7	2.4	4.7	2.9	90	100
OK3	0 - 15	0.04	0.8	0.05	0.11	1	0.95	4	80	5	11	105.3
	15 - 30	0.04	0.16	0.05	0.25	0.5	0.5	8	32	10	50	100
	30 - 45	0.04	0.12	0.05	0.09	0.3	0.25	13.3	40	16.7	30	120
AB1	0 - 15	0.04	0.04	0.05	0.47	0.6	0.55	6.7	6.7	8.3	78.3	109.1
	15 - 30	0.04	0.08	0.05	0.13	0.3	0.3	13.3	26.7	16.7	43.3	100
	30 - 45	0.04	0.04	0.05	1.17	1.3	1.25	3.1	3.1	3.8	90	104
AB2	0 - 15	ND	0.12	0.05	ND	0.17	0.17	-	70.6	29.4	ND	100
	15 - 30	0.04	0.08	0.05	0.13	0.3	0.3	13.3	26.7	16.7	43.3	100
	30 - 45	0.24	0.08	0.05	2.33	2.7	2.65	8.9	3	1.9	86.3	101.9
AB3	0 - 15	0.08	0.08	0.05	1.69	1.9	1.9	4.2	4.2	2.6	88.9	100
	15 - 30	0.08	0.08	0.05	1.89	2.1	2.1	3.8	3.8	2.4	90	100
	30 - 45	0.04	0.08	0.05	1.83	2	1.95	2	4	2.5	91.5	102.6
AB4	0 - 15	0.04	ND	0.05	1.21	1.3	1.3	3.1	-	3.8	93.1	100
	15 - 30	0.04	0.08	0.05	1.33	1.5	1.5	2.7	5.3	3.3	88.7	100
	30 - 45	0.04	0.08	0.05	0.93	1.1	1.05	3.6	7.3	4.5	84.5	104.8
AB5	0 - 15	0.04	0.08	ND	2.68	2.8	2.8	1.4	2.9	-	95.7	100
	15 - 30	0.04	0.08	0.05	2.03	2.2	2.2	1.8	3.6	2.3	92.3	100
	30 - 45	0.04	0.08	0.05	2.03	2.2	2.15	1.8	3.6	2.3	92.3	102.3
	MIN	0.04	0.04	0.05	0.03	0.17	0.17	1.40	2.00	1.90	7.50	100
	MAX	0.24	0.80	0.23	2.68	2.80	2.80	16.0	80.0	31.8	96.0	120
	MEAN	0.05	0.17	0.07	0.95	1.14	1.11	5.68	23.5	10.5	67.2	104

F1 = Exchangeable fraction; F2 = Reducible fraction; F3 = Oxidizable fraction; F4 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil
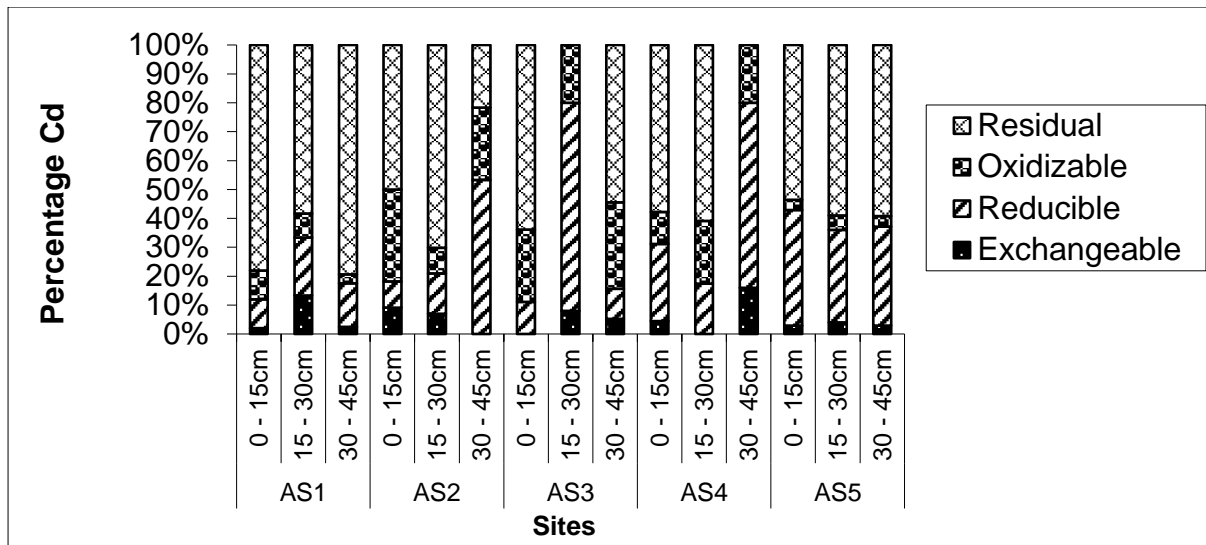
(3a)
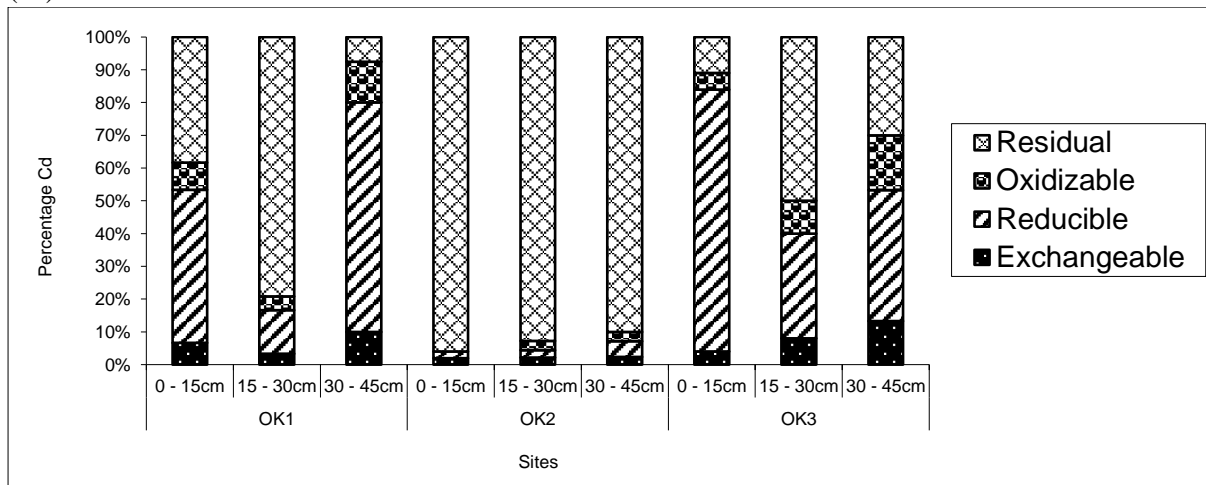
(3b)
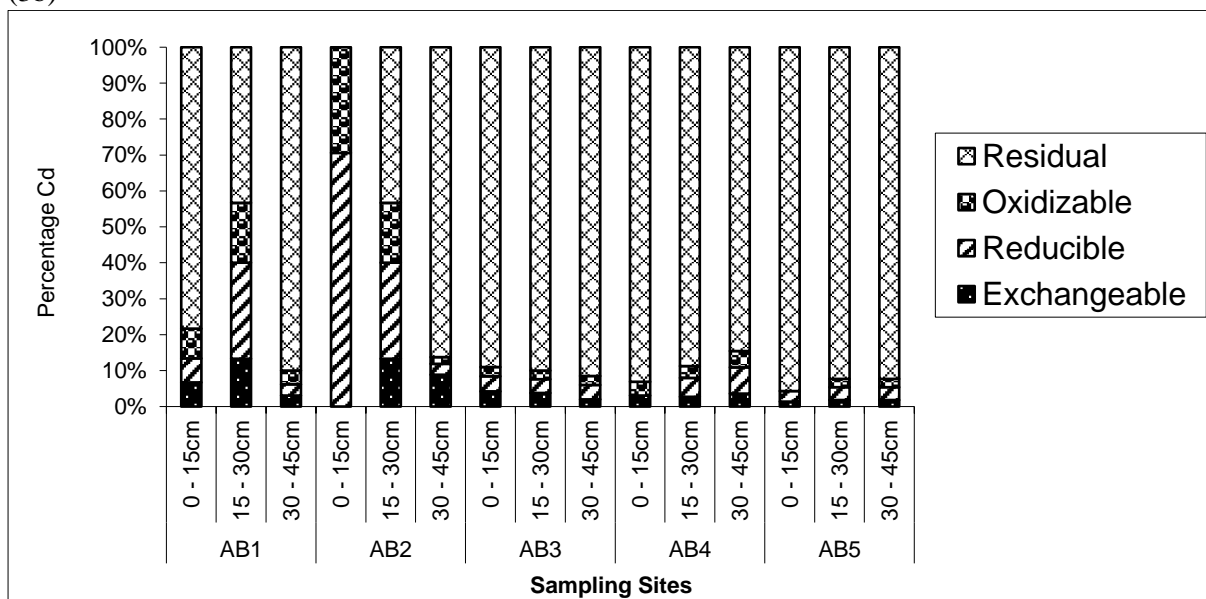
(3c)

Figure 3: Percentage of Cadmium in the various extraction phases as a function of total Cadmium content in the soils three months after the major flooding

Cobalt

The partition scheme of cobalt (Co) indicate its associated with all the extraction phases except for Fe-Mn oxide phase in some depth of site AB2 and AB5. The proportion of Co in the various extraction phases ranged 0.8 to 35.2%, 2.8 to 71.0%, 3.4 to 39.8% and 0.4 to 96.4% for exchangeable for exchangeable/acid soluble phase, reducible, oxidizable and residual phases respectively (Figure 4a-c). Overall, it should be noted that the residual and Fe-Mn oxides constitute major fractions for Co and relatively high percentages of Co (up to 39.8%) are found in the oxidizable phase in the soil profiles. The upstream section of the floodplain (AS1 to AS5) had higher proportion of Co in oxidizable phase than in the soil profiles of the mid and downstream section of the floodplain (Table 4.15).

Table 4.15: Concentrations and percentages of cobalt in different extraction phases of the floodplain soils of the lower reaches of River Niger

| Sites | Depth (cm) | CONCENTRATION (µg g⁻¹) | | | | | | PERCENTAGE (%) | | | | RECOVERY (%) |
		F1	F2	F3	F4	SUM	TM	F1	F2	F3	F4	
AS1	0 - 15	0.32	0.56	0.90	2.72	4.50	4.50	7.1	12.4	20.0	60.4	100
	15 - 30	0.24	0.64	0.65	0.37	1.90	1.90	12.6	33.7	34.2	19.5	100
	30 - 45	0.28	2.36	0.95	2.91	6.50	6.45	4.3	36.3	14.6	44.8	100.8
AS2	0 - 15	0.12	0.12	0.45	1.15	1.84	1.55	6.5	6.5	24.5	62.5	118.7
	15 - 30	0.12	0.08	0.45	0.72	1.37	1.30	8.8	5.8	32.8	52.6	105.4
	30 - 45	0.12	0.16	0.45	1.41	2.14	2.05	5.6	7.5	21.0	65.9	104.4
AS3	0 - 15	0.12	0.08	0.45	0.64	1.29	1.20	9.3	6.2	34.9	49.6	107.5
	15 - 30	0.12	0.08	0.45	0.86	1.51	1.45	7.9	5.3	29.8	57.0	104.1
	30 - 45	0.40	3.48	1.00	0.02	4.90	4.90	8.2	71	20.4	0.4	100
AS4	0 - 15	0.12	2.28	0.95	4.65	8.00	8.00	1.5	28.5	11.9	58.1	100
	15 - 30	0.12	0.15	0.45	1.51	2.23	2.10	5.4	6.7	20.2	67.7	106.2
	30 - 45	0.12	0.08	0.45	0.48	1.13	0.95	10.6	7.1	39.8	42.5	118.9
AS5	0 - 15	0.12	1.05	0.45	1.94	3.56	3.40	3.4	29.5	12.6	54.5	104.7
	15 - 30	0.12	0.53	0.45	1.65	2.75	2.75	4.4	19.3	16.4	60.0	100
	30 - 45	0.12	0.40	0.45	0.88	1.85	1.80	6.5	21.6	24.3	47.6	102.8
OK1	0 - 15	0.12	1.88	0.45	3.75	6.20	6.15	1.9	30.3	7.3	60.5	100.8
	15 - 30	0.12	4.12	0.45	1.31	6.00	6.00	2.0	68.7	7.5	21.8	100
	30 - 45	0.12	2.48	0.45	10.1	13.1	13.05	0.9	18.9	3.4	76.7	100.4
OK2	0 - 15	0.12	0.44	0.45	8.09	9.10	9.05	1.3	4.8	4.9	88.9	100.6
	15 - 30	0.56	0.48	0.55	ND	1.59	1.59	35.2	30.2	34.6	0.0	100
	30 - 45	0.12	0.68	0.40	8.10	9.30	9.25	1.3	7.3	4.3	87.1	100.5
OK3	0 - 15	0.12	0.48	0.40	3.60	4.60	4.55	2.6	10.4	8.7	78.3	101.1
	15 - 30	0.12	0.40	0.45	1.28	2.25	2.25	5.3	17.8	20.0	56.9	100
	30 - 45	ND	0.40	0.40	0.45	1.25	1.25	-	32.0	32.0	36.0	100
AB1	0 - 15	0.16	0.44	0.45	0.75	1.80	1.80	8.9	24.4	25.0	41.7	100
	15 - 30	0.08	0.44	0.45	0.63	1.60	1.55	5.0	27.5	28.1	39.4	103.2
	30 - 45	0.24	0.44	0.55	5.37	6.60	6.55	3.6	6.7	8.3	81.4	100.8
AB2	0 - 15	0.24	1.24	0.45	5.17	7.10	7.05	3.4	17.5	6.3	72.8	100.7
	15 - 30	1.08	ND	0.45	4.47	6.00	5.95	18.0	-	7.5	74.5	100.8
	30 - 45	0.24	ND	0.40	11.2	11.8	11.8	2.0	-	3.4	94.6	100
AB3	0 - 15	0.60	ND	0.40	8.20	9.20	9.20	6.5	-	4.3	89.1	100
	15 - 30	0.80	ND	0.45	8.65	9.90	9.90	8.1	-	4.5	87.4	100
	30 - 45	0.60	0.40	0.45	8.35	9.80	9.80	6.1	4.1	4.6	85.2	100
AB4	0 - 15	0.12	ND	0.45	6.43	7.00	7.00	1.7	-	6.4	91.9	100
	15 - 30	0.12	0.40	0.45	7.03	8.00	7.95	1.5	5.0	5.6	87.9	100.6
	30 - 45	0.12	0.40	0.40	4.78	5.70	5.70	2.1	7.0	7.0	83.9	100
AB5	0 - 15	0.12	0.40	ND	13.9	14.4	14.4	0.8	2.8	-	96.4	100.3
	15 - 30	0.12	0.40	0.45	10.3	11.3	11.3	1.1	3.5	4.0	91.4	100
	30 - 45	0.20	0.44	0.40	10.8	11.8	11.8	1.7	3.7	3.4	91.2	100
	MIN	0.08	0.08	0.40	0.02	1.13	0.95	0.80	2.80	3.40	0.00	100
	MAX	1.08	4.12	1.00	13.9	14.4	14.4	35.2	71.0	39.8	96.4	119
	MEAN	0.23	0.84	0.50	4.33	5.66	5.62	5.87	18.2	15.8	63.0	102

F1 = Exchangeable fraction; F2 = Reducible fraction; F3 = Oxidizable fraction; F4 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil
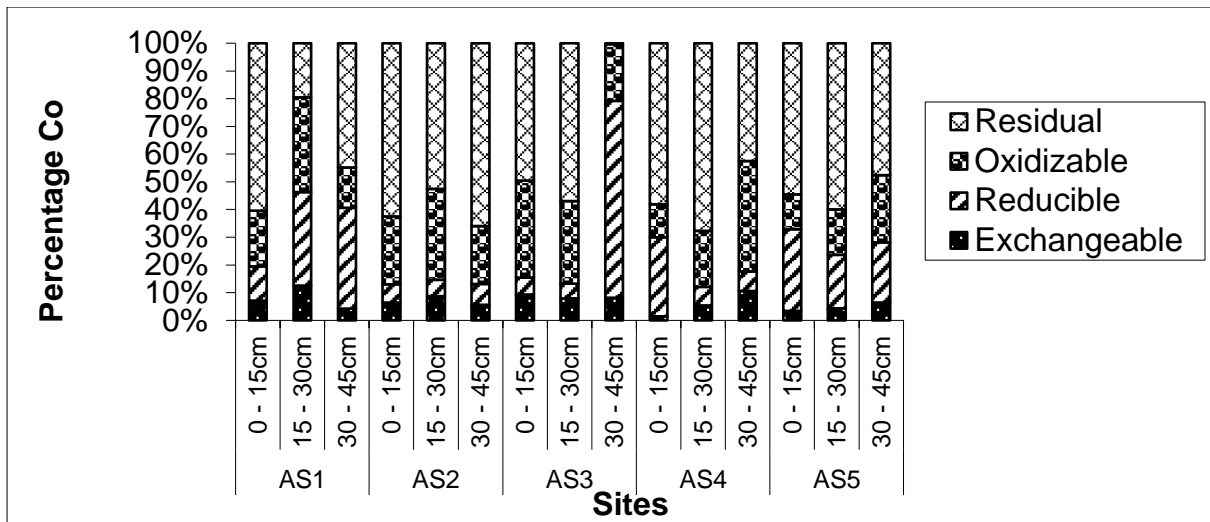
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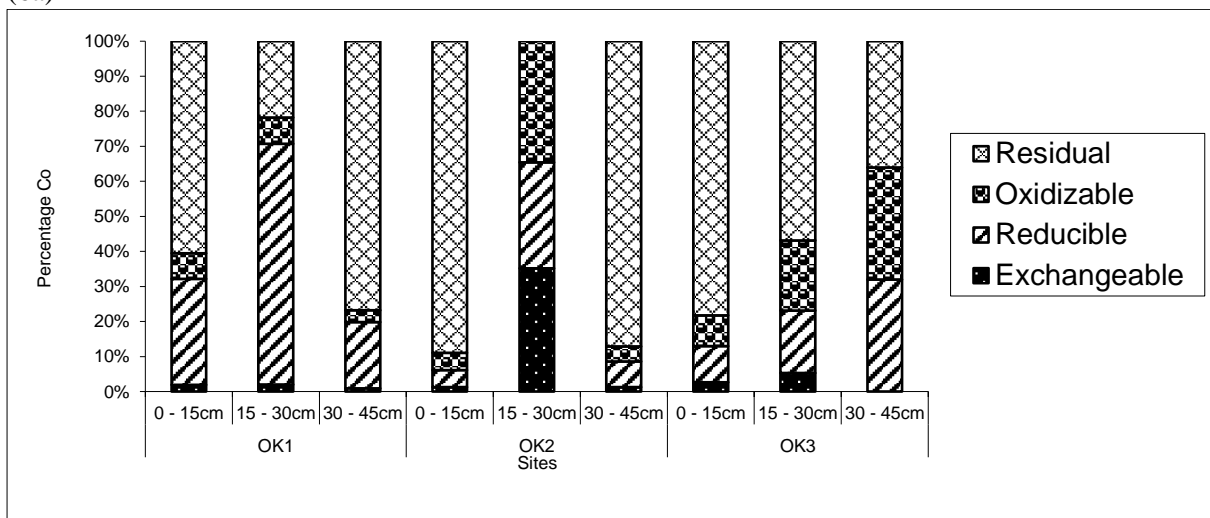
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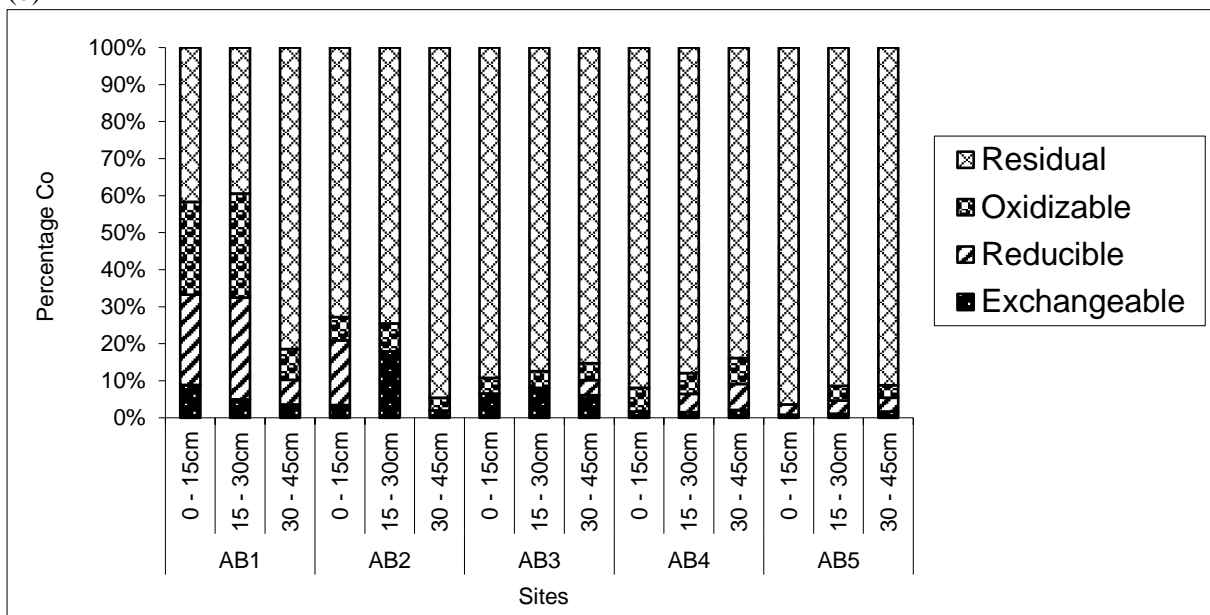
(c)

Figure 4: Percentage of Cobalt in the various extraction phases as a function of total Cobalt content in soils three months after the major flooding

Chromium

The residual fraction and reducible phase were the two important forms of chromium (Cr) in these soil profiles. The residual fractions consist of 29% to 100% of the total Cr in these sites (Figure 5a-c). The percentages of Cr in the residual phase were higher in the midstream and downstream of the floodplain than upstream section. The results indicate that Cr mainly existed in residual phase because the series of reactions in soils favours the transformation of Cr into insoluble hydroxides precipitates which stayed in the residue (Li *et al*., 2011). The Fe-Mn oxides phase constituted 0.1% to 48% of Cr in these soil profiles. No Cr was found in Fe-Mn oxides phase in the soil profiles of sites AB3, AB4 and AB5 (Table 4.16). Chromium was only found in the oxidizable phase in soils collected within upstream section of the floodplain. The fraction of Cr in the oxidizable phase was approximately 4.5% to 28.0% of the total Cr. The occurrence of Cr in the oxidizable phase results from the formation of stable organic matter at existing physicochemical properties of these sites (Kotokyl *et al.*, 2003). The exchangeable and acid soluble phase in soil profiles consist of 0.7 to 18.1% of the total Cr in some sites. However, Cr was not found in exchangeable and acid soluble phase in majority of the sites which indicates that Cr is not mobile in these soil profiles.

Table 4.16: Concentrations and percentages of chromium in different extraction phases of the floodplain soils of the lower reaches of River Niger

Sites	Depth (cm)	CONCENTRATION (µg g⁻¹)						PERCENTAGE (%)				RECOVERY (%)
		F1	F2	F3	F4	SUM	TM	F1	F2	F3	F4	
AS1	0 - 15	0.48	1.48	1.95	6.99	10.9	10.9	4.4	13.6	17.9	64.1	100
	15 - 30	0.64	1.68	1.35	8.53	12.2	12.2	5.2	13.8	11.1	69.9	100
	30 - 45	0.40	3.52	4.05	25.1	33.1	33.1	1.2	10.6	12.2	75.9	100
AS2	0 - 15	0.40	0.48	0.36	6.77	8.01	7.85	5.0	6.0	4.5	84.5	102
	15 - 30	0.65	3.00	4.96	3.29	11.9	11.1	5.5	25.2	41.7	27.6	107.2
	30 - 45	0.92	3.24	4.05	5.19	13.4	13.0	6.9	24.2	30.2	38.7	103.1
AS3	0 - 15	0.32	1.36	2.15	3.25	7.08	6.70	4.5	19.2	30.4	45.9	105.7
	15 - 30	0.32	5.16	3.30	4.32	13.1	13.1	2.4	39.4	25.2	33.0	100
	30 - 45	0.24	2.96	5.75	10.3	19.2	19.2	1.3	15.4	29.9	53.4	100
AS4	0 - 15	ND	4.04	4.90	35.8	44.7	44.7	-	9.0	11.0	80.0	100
	15 - 30	ND	3.52	2.30	2.38	8.20	8.15	-	42.9	28.0	29.0	100.6
	30 - 45	ND	0.37	ND	0.58	0.95	0.80	-	38.9	-	61.1	118.8
AS5	0 - 15	ND	7.92	ND	19.6	27.5	27.5	-	28.8	-	71.2	100
	15 - 30	ND	5.36	ND	22.3	27.7	27.7	-	19.4	-	80.6	100
	30 - 45	ND	6.56	ND	25.3	31.9	31.9	-	20.6	-	79.4	100
OK1	0 - 15	ND	4.04	ND	6.06	10.1	10.1	-	40.0	-	60.0	100
	15 - 30	ND	3.52	ND	22.2	25.7	25.7	-	13.7	-	86.3	100
	30 - 45	ND	3.84	ND	4.16	8.00	7.95	-	48.0	-	52.0	100.6
OK2	0 - 15	ND	1.24	ND	67.8	69.0	69.0	-	1.8	-	98.2	100
	15 - 30	ND	0.48	ND	43.12	43.6	43.6	-	1.1	-	98.9	100
	30 - 45	ND	1.52	ND	41.6	43.1	43.1	-	3.5	-	96.5	100
OK3	0 - 15	ND	1.48	ND	21.4	22.9	22.9	-	6.5	-	93.5	100
	15 - 30	ND	2.68	ND	6.22	8.90	8.90	-	30.1	-	69.9	100
	30 - 45	ND	2.32	ND	5.18	7.50	7.50	-	30.9	-	69.1	100
AB1	0 - 15	ND	1.72	ND	16.4	18.1	18.1	-	9.5	-	90.5	100
	15 - 30	ND	1.6	ND	9.10	10.7	10.7	-	15.0	-	85.0	101
	30 - 45	0.44	1.44	ND	26.1	28.0	28.0	1.6	5.1	-	93.3	100
AB2	0 - 15	0.28	2.08	ND	36.6	39.0	39.0	0.7	5.3	-	93.9	100
	15 - 30	0.96	0.16	ND	4.18	5.30	5.25	18.1	3.0	-	78.9	101
	30 - 45	0.44	0.04	ND	60.5	61.0	61.0	0.7	0.1	-	99.2	100
AB3	0 - 15	ND	ND	ND	45.1	45.1	45.1	-	-	-	100.0	100
	15 - 30	0.92	ND	ND	47.2	48.1	48.1	1.9	-	-	98.1	100
	30 - 45	0.52	ND	ND	46.3	46.8	46.8	1.1	-	-	98.9	100
AB4	0 - 15	ND	ND	ND	31.6	31.6	31.6	-	-	-	100	100
	15 - 30	ND	ND	ND	39.0	39.0	39.0	-	-	-	100	100
	30 - 45	ND	ND	ND	26.0	26.0	26.0	-	-	-	100	100
AB5	0 - 15	ND	ND	ND	66.9	66.9	66.9	-	-	-	100	100
	15 - 30	ND	ND	ND	28.5	28.5	28.5	-	-	-	100	100
	30 - 45	1.32	ND	ND	46.5	47.8	47.8	2.8	-	-	97.2	100
	MIN	ND	0.04	0.36	0.58	0.95	0.80	0.0	0.10	4.50	27.6	100
	MAX	1.32	7.92	5.75	67.8	69.0	69.0	18.1	48.0	41.7	100	119
	MEAN	0.54	2.63	3.19	23.8	26.9	26.9	3.72	18.0	22.0	78.3	101

F1 = Exchangeable fraction; F2 = Reducible fraction; F3 = Oxidizable fraction; F4 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil
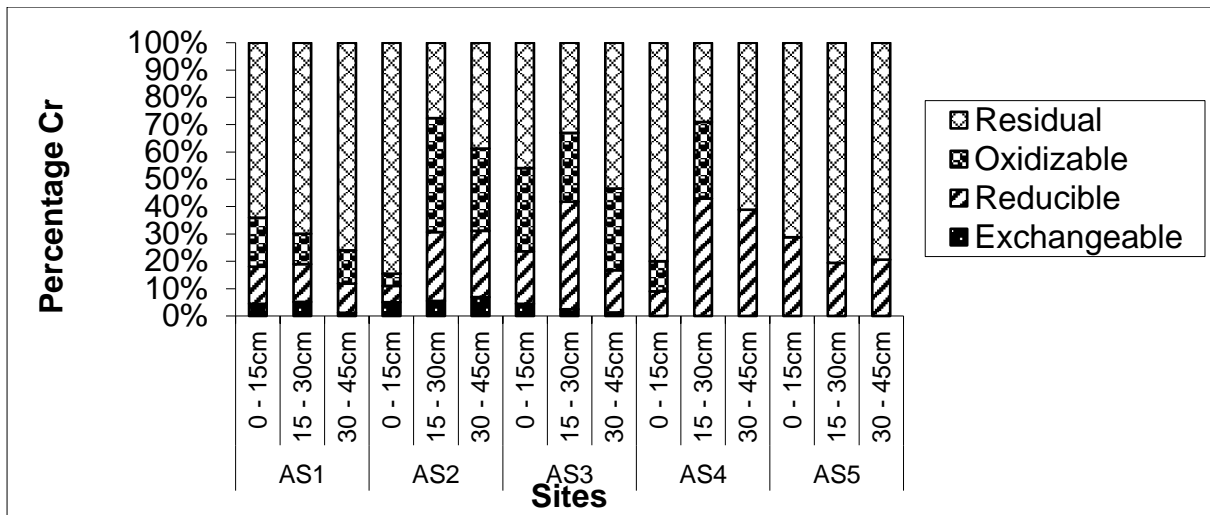
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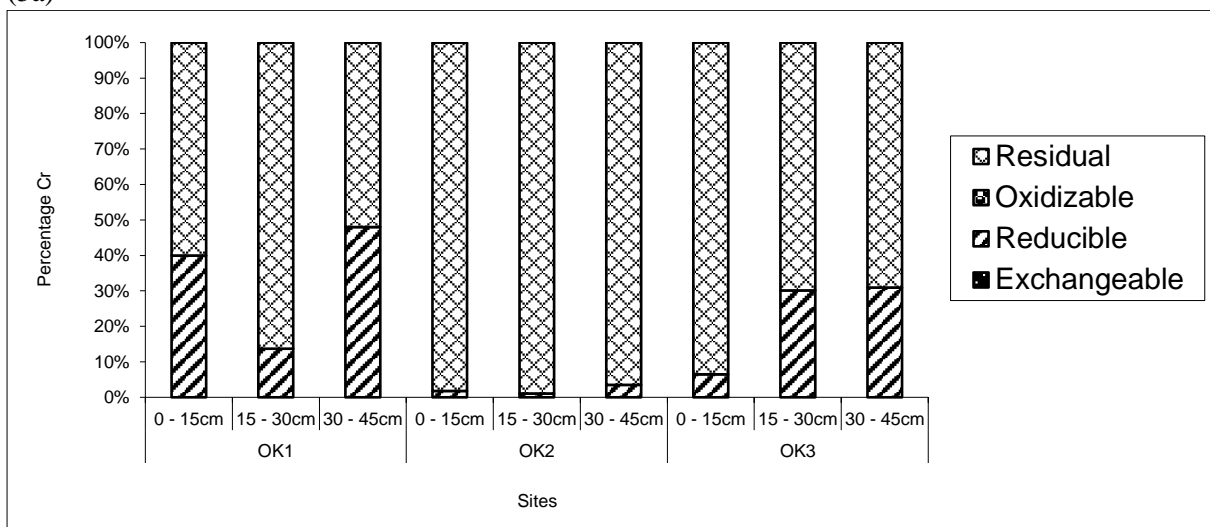
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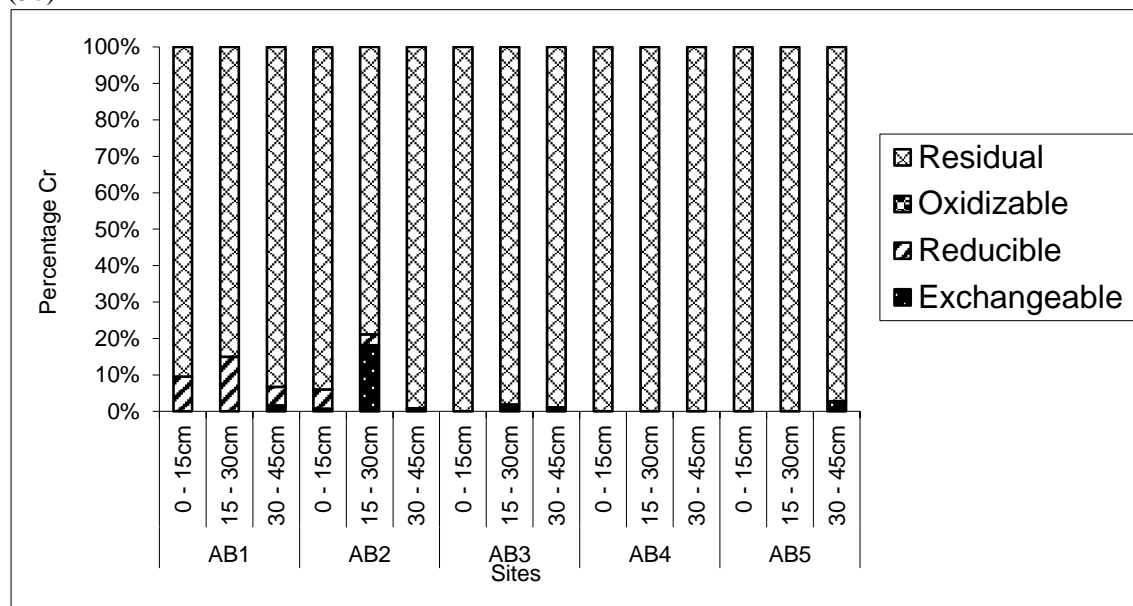
(5c)

Figure 5: Percentage of Chromium in the various extraction phases as a function of total Chromium content in soils three months after the major flooding

Copper

The fractionation patterns of Cu in these soil profiles were similar to that of Cr. The proportion of Cu in various extraction phases ranged from 2.7 to 19.8%, 3.0 to 82%, 7.6 to 25.0% and 17.8 to 100% for exchangeable/acid soluble, reducible, oxidizable and residual phases respectively (Figure 6a-c). The high percentage of Cu in the residual phase may be related to the fact that Cu is easily chemisorbed on or incorporated in clay minerals. It was surprising that Cu was not found in the oxidizable in the majority of these sites despite the known affinity of Cu for the oxidizable as a result of formation of stable Cu-organic matter complex (Iwegbue, 2007; Iwegbue *et al*., 2009; Ashraf *et al*., 2012). Cu was found in the exchangeable/acid soluble phases in some sites in the upstream (AS1-AS5) and downstream (AB1-AB5) sections of the floodplain (Table 4.17). The similarity in the speciation patterns and inter elemental correlation of Cu and Cr (r=0.75) suggests chemical similarity and common sources.

Table 4.17: Concentrations and percentages of copper in different extraction phases of the floodplain soils of the lower reaches of River Niger

Sites	Depth (cm)	CONCENTRATION (µg g⁻¹)						PERCENTAGE (%)				
		F1	F2	F3	F4	SUM	TM	F1	F2	F3	F4	RECOVERY
AS1	0 - 15	0.72	1.36	1.55	4.57	8.2	8.15	8.8	16.6	18.9	55.7	100.6
	15 - 30	1.04	1.24	1.25	7.67	11.2	11.2	9.3	11.1	11.2	68.5	100.4
	30 - 45	0.8	1.76	2.3	24.5	29.4	29.4	2.7	6.00	7.8	83.5	100.2
AS2	0 - 15	1.28	3.32	ND	1.88	6.48	6.15	19.8	51.2	-	29	105.4
	15 - 30	0.26	0.39	ND	4.2	4.85	4.4	5.4	8.00	-	86.6	110.2
	30 - 45	1.2	2.3	2.22	3.3	9.02	8.6	13.3	25.5	24.6	36.6	104.9
AS3	0 - 15	0.68	1.13	0.44	1.8	4.05	3.45	16.8	27.9	10.9	44.4	117.4
	15 - 30	ND	0.21	ND	0.29	0.5	0.45	-	42.0	-	58	111.1
	30 - 45	0.8	3.24	2.5	3.46	10	10	8.00	32.4	25	34.6	100
AS4	0 - 15	ND	2.16	1.35	7.39	10.9	10.9	-	19.8	12.4	67.8	100
	15 - 30	ND	2.2	0.9	8.8	11.9	11.9	-	18.5	7.6	73.9	100.4
	30 - 45	ND	0.4	ND	1.32	1.72	1.45	-	23.3	-	76.7	118.6
AS5	0 - 15	ND	3.96	ND	3.84	7.8	7.8	-	50.8	-	49.2	100
	15 - 30	ND	3.56	ND	3.34	6.9	6.9	-	51.6	-	48.4	100
	30 - 45	ND	4.04	ND	7.56	11.6	11.6	-	34.8	-	65.2	100.4
OK1	0 - 15	ND	3.00	ND	2.9	5.9	5.85	-	50.8	-	49.2	100.9
	15 - 30	ND	3.44	ND	3.76	7.2	7.2	-	47.8	-	52.2	100
	30 - 45	ND	6.16	ND	7.24	13.4	13.4	-	46	-	54	100
OK2	0 - 15	ND	1.6	ND	6.4	8.00	8.00	-	20	-	80	100
	15 - 30	ND	0.32	ND	10.5	10.8	10.8	-	3.00	-	97	100.5
	30 - 45	ND	1.44	ND	8.86	10.3	10.3	-	14	-	86	100.5
OK3	0 - 15	ND	2.4	ND	3.00	5.4	5.4	-	44.4	-	55.6	100
	15 - 30	ND	3.04	ND	0.66	3.7	3.7	-	82.2	-	17.8	100
	30 - 45	ND	2.44	ND	1.76	4.2	4.15	-	58.1	-	41.9	101.2
AB1	0 - 15	ND	1.68	ND	5.92	7.6	7.55	-	22.1	-	77.9	100.7
	15 - 30	ND	1.76	ND	6.24	8.00	7.95	-	22.0	-	78	100.6
	30 - 45	1.00	1.56	ND	3.64	6.2	6.15	16.1	25.2	-	58.7	100.8
AB2	0 - 15	0.68	1.56	ND	10.6	12.8	12.8	5.3	12.2	-	82.5	100
	15 - 30	0.8	ND	ND	11.3	12.1	12.1	6.6	-	-	93.4	100.4
	30 - 45	0.92	ND	ND	13.9	14.8	14.8	6.2	-	-	93.8	100
AB3	0 - 15	0.24	ND	ND	12.4	12.6	12.6	1.9	-	-	98.1	100.4
	15 - 30	1.04	ND	ND	11.8	12.8	12.8	8.1	-	-	91.9	100
	30 - 45	1.04	ND	ND	11.8	12.8	12.8	8.1	-	-	91.9	100
AB4	0 - 15	ND	ND	ND	8.7	8.7	8.65	-	-	-	100	100.6
	15 - 30	ND	ND	ND	11	11	11.0	-	-	-	100	100.5
	30 - 45	ND	ND	ND	6.5	6.5	6.5	-	-	-	100	100
AB5	0 - 15	ND	ND	ND	19.9	19.9	19.9	-	-	-	100	100
	15 - 30	ND	ND	ND	12.8	12.8	12.8	-	-	-	100	100
	30 - 45	0.72	ND	ND	14.7	15.4	15.4	4.7	-	-	95.3	100
	MIN	0.24	0.21	0.44	0.29	0.50	0.45	1.90	3.00	7.60	17.80	100
	MAX	1.28	6.16	2.50	24.5	29.4	29.4	19.8	82.2	25.0	100	119
	MEAN	0.83	2.20	1.56	7.44	9.68	9.60	8.82	31.0	14.8	71.1	102

F1 = Exchangeable fraction; F2 = Reducible fraction; F3 = Oxidizable fraction; F4 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil
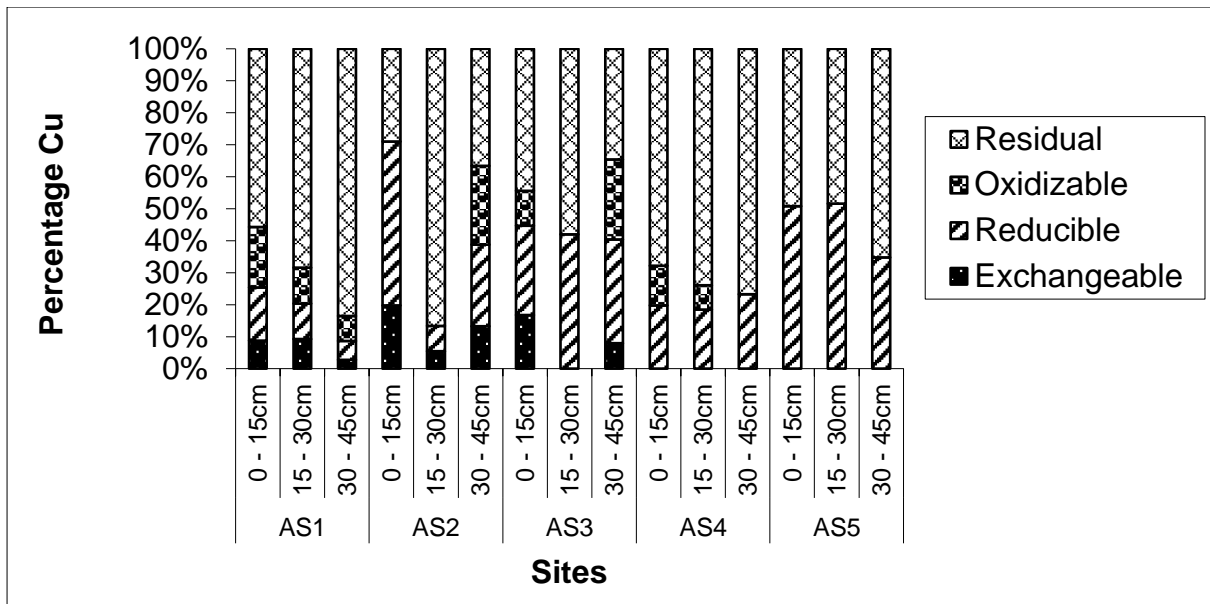
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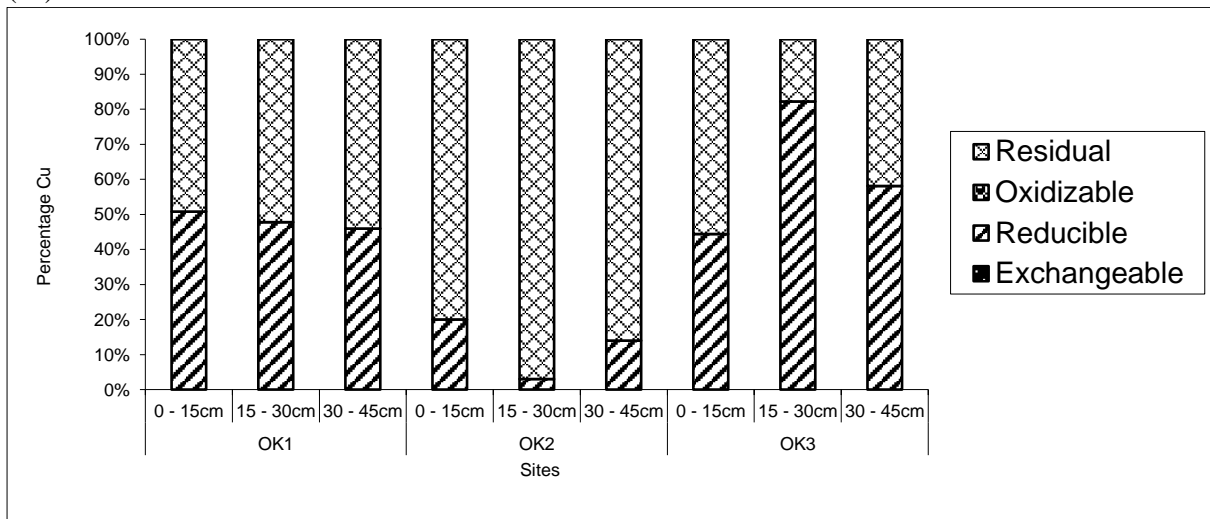
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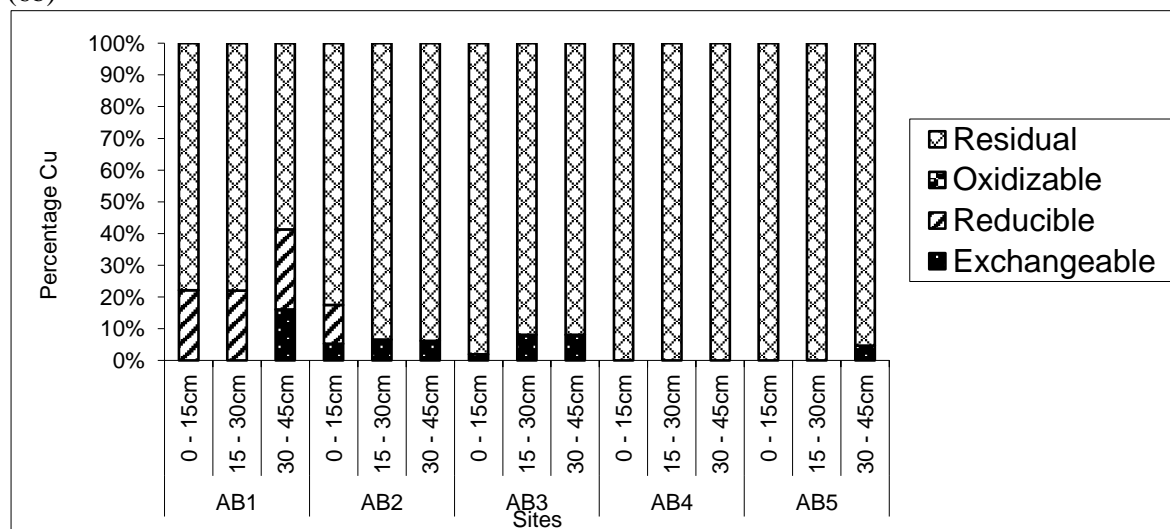
(6c)

Figure 6: Percentage of Copper in the various extraction phases as a function of total Copper content in soils three months after the major flooding

Manganese

The residual (16% to 99.8%) and Fe-Mn oxides (0.1 to 86.3%) phases are the dominant phases of Mn in these soil profiles (Figure 7a-c). Manganese was only found in the oxidizable phase in soil profiles of the upstream section of the floodplain (AS1 to AS5) (Table 4.18). The proportions of Mn in oxidization phase in these sites were up to 41.4%. High proportions of Mn in reducible phase is consistent with the reduction of Mn oxides by hydroxylamine chloride and the specificity of this dissolution with respect to ferric oxide (Herondez-Moreno *et al.*, 2007; Teixera *et al.*, 2010; Iwegbue, 2011). The proportions of Mn in the exchangeable/acid soluble were low in the majority of these sites especially in mid and downstream reaches of the floodplain even though the soil profiles of AS2 and AS3 had significant proportion of Mn in exchangeable and acid soluble phase (up to 24.8%). This is probably related to the known close association of Mn with carbonates. In this phase, weakly sorbed Mn retained on soil surface by relatively weak electrostatic interactions may be released by ion exchange processes and dissociation of Mn-carbonate phase. The significant proportions of Mn in the oxidizable and Fe-Mn oxides phases imply that changes in soil conditions such as pH and redox potential may result in significant remobilization of Mn.

Table 4.18: Concentrations and percentages of Manganese in different extraction phases of the floodplain soils of the lower reaches of River Niger

| Sites	Depth (cm)	CONCENTRATION (µg g⁻¹)						PERCENTAGE (%)				
		F1	F2	F3	F4	SUM	TM	F1	F2	F3	F4	RECOVERY
AS1	0 - 15	16.5	13.6	3.7	146	180	180	9.2	7.5	2.1	81.3	100
	15 - 30	16.1	15.4	2.55	62.4	96.5	96.5	16.7	16	2.6	64.7	100.1
	30 - 45	20.1	105	9.55	123	258	258	7.8	40.7	3.7	47.8	100
AS2	0 - 15	4.67	4.9	4.23	9.7	23.5	20.3	19.9	20.9	18	41.3	115.8
	15 - 30	7.08	10.5	16.3	24.4	58.2	56	12.2	18	28	41.9	103.9
	30 - 45	18.1	12.5	20.9	21.53	73	71.6	24.8	17.1	28.6	29.5	102
AS3	0 - 15	4.2	4.56	6.34	9.98	25.1	23.5	16.7	18.2	25.3	39.8	106.7
	15 - 30	1.45	3.37	2.33	12.35	19.5	17.9	7.4	17.3	11.9	63.3	108.9
	30 - 45	35.3	42.7	22.0	58.4	158	155.7	22.3	27	13.9	36.9	101.7
AS4	0 - 15	0.16	91.7	11.5	236	340	339	0.1	27	3.4	69.5	100
	15 - 30	0.12	5.47	7.95	5.66	19.2	17.2	0.6	28.5	41.4	29.5	111.6
	30 - 45	0.12	2.72	ND	3.01	5.85	5.05	2.1	46.5	-	51.5	115.8
AS5	0 - 15	0.12	44.4	ND	134	179	170	0.1	24.9	-	75.1	104.7
	15 - 30	0.16	51.2	ND	80.1	132	128	0.1	39	-	60.9	102.5
	30 - 45	0.12	21.2	ND	32.9	54.2	51.5	0.2	39.1	-	60.7	105.3
OK1	0 - 15	0.12	92.4	ND	35.7	128	128	0.1	72	-	27.9	100
	15 - 30	0.12	116	ND	123	239	239	0.1	48.5	-	51.4	100
	30 - 45	0.12	135	ND	27.2	163	163	0.1	83.2	-	16.7	100
OK2	0 - 15	0.12	2.96	ND	345	349	348	0.03	0.8	-	99.1	100
	15 - 30	0.12	11.4	ND	332	343	343	0.03	3.3	-	96.6	100
	30 - 45	0.12	15.6	ND	355	371	371	0.03	4.2	-	95.7	100
OK3	0 - 15	0.16	4.56	ND	39.2	43.9	43.9	0.4	10.4	-	89.2	100.1
	15 - 30	0.12	18.1	ND	26.5	44.7	43.3	0.3	40.5	-	59.2	103.2
	30 - 45	0.16	19.1	ND	2.86	22.1	22.1	0.7	86.3	-	12.9	100
AB1	0 - 15	0.12	2.04	ND	77.4	79.6	79.6	0.2	2.6	-	97.3	100.1
	15 - 30	0.12	1.92	ND	40.5	42.5	42.5	0.3	4.5	-	95.2	100.1
	30 - 45	1.68	1.8	ND	212	215	215	0.8	0.8	-	98.4	100
AB2	0 - 15	1.08	49.2	ND	145	195	195	0.6	25.2	-	74.2	100
	15 - 30	0.8	5.28	ND	46.2	52.3	49.9	1.5	10.1	-	88.4	104.7
	30 - 45	5.72	2.48	ND	434	443	442	1.3	0.6	-	98.1	100
AB3	0 - 15	21.3	2.12	ND	340	364	364	5.9	0.6	-	93.6	100
	15 - 30	48.0	1.48	ND	350	399	399	12	0.4	-	87.6	100
	30 - 45	44.7	0.96	ND	385	431	431	10.4	0.2	-	89.4	100
AB4	0 - 15	0.16	ND	ND	239	240	240	0.1	-	-	99.9	100
	15 - 30	0.12	0.84	ND	299	300	300	0.04	0.3	-	99.7	100
	30 - 45	0.12	1.00	ND	231	232	232	0.1	0.4	-	99.5	100
AB5	0 - 15	0.16	1.16	ND	788	790	790	0.02	0.1	-	99.8	100
	15 - 30	0.16	1.4	ND	527	529	529	0.03	0.3	-	99.7	100
	30 - 45	5.6	1.92	ND	521	529	529	1.1	0.4	-	98.6	100
	MIN	0.12	0.84	2.33	2.86	5.85	5.05	0.02	0.10	2.10	12.9	100
	MAX	48.0	135	22.0	788	790	790	24.8	86.3	41.4	100	116
	MEAN	6.55	24.2	9.75	176	209	208	4.52	20.6	16.3	70.8	102

F1 = Exchangeable fraction; F2 = Reducible fraction; F3 = Oxidizable fraction; F4 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil
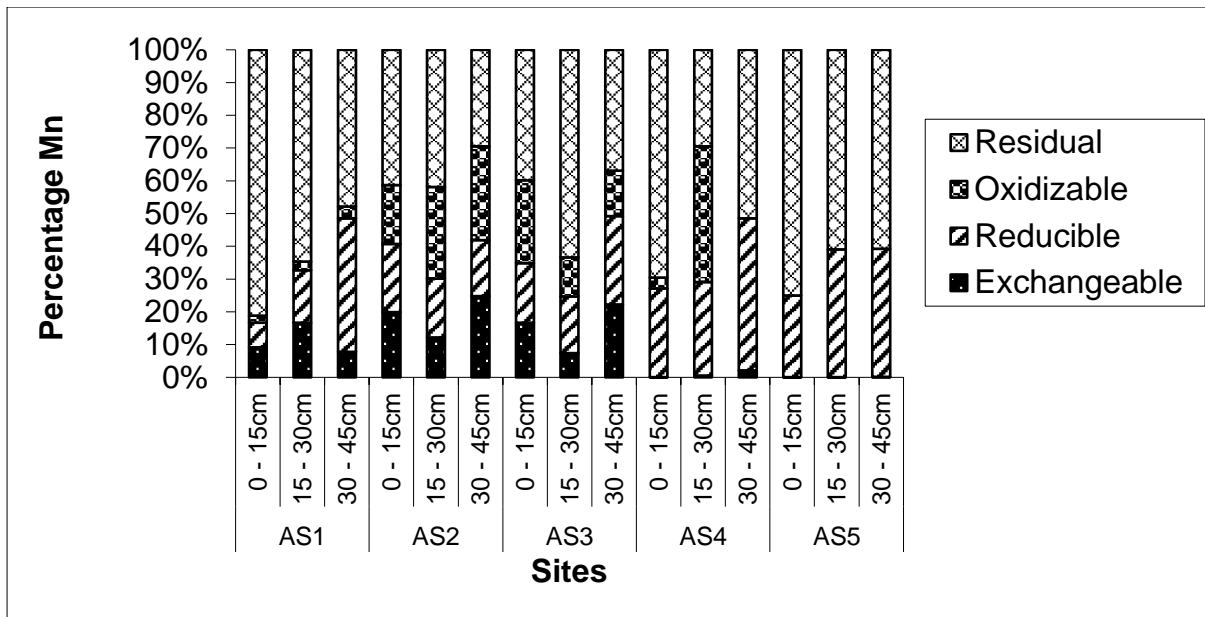
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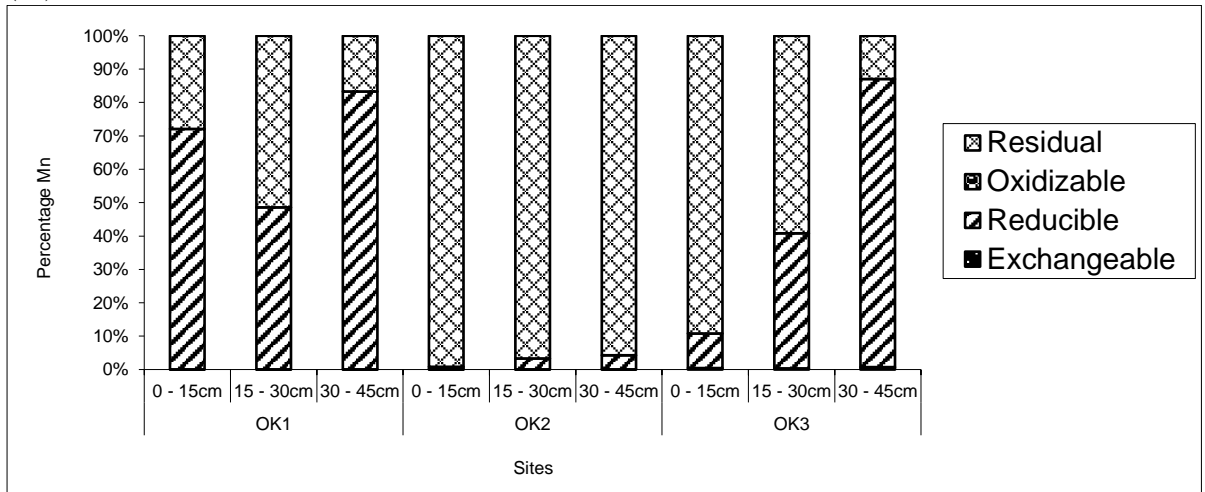
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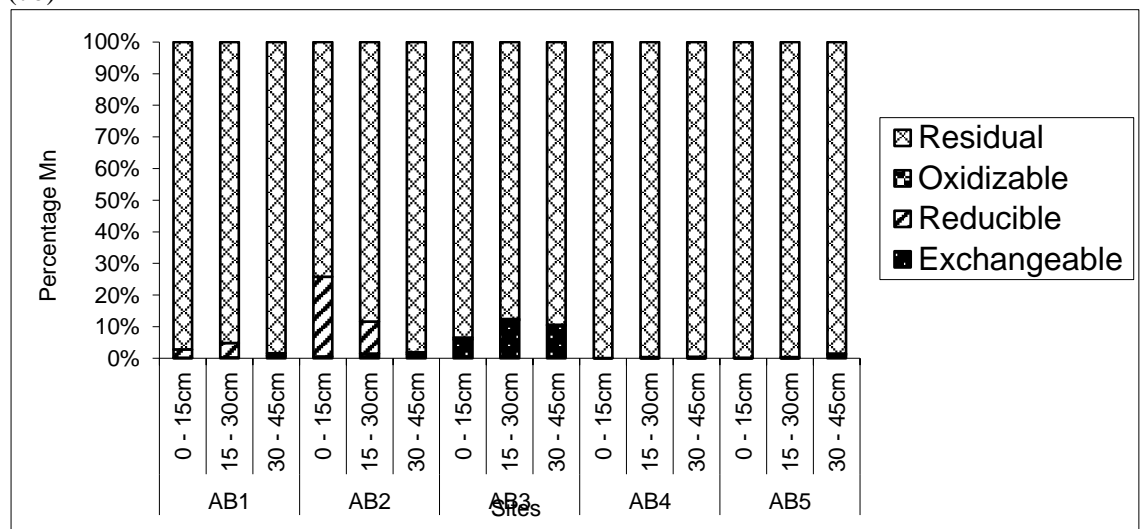
(7c)

Figure 7: Percentage of Manganese in the various extraction phases as a function of total Manganese content in soils three months after the major flooding

Nickel

The speciation profiles of Ni showed that the major portions were bound to the residual (11.5-94.8%) and Fe-Mn oxides (2.0 to 72.3%) phases (Figure 8a-c). The high proportion of Ni in the residual phase is associated with its detrital nature which allows its occlusion by silicate during soil weathering (Iwegbue *et al.*, 2009b). However, the high proportions of Ni in residual phase suggested that Ni is largely influenced by parent materials (Turner and Maynard, 2003; Moral *et al.*, 2005). The affinity of Ni for the reducible phase suggested that adsorption by Mn oxide controls Ni concentration in the soil. Based on crystal field theory, substitution of Ni^{2+} for surface Mn in mixed valence Mn oxide may be adsorption mechanism for Ni in these soils (Iwegbue *et al.*, 2009). The proportions of Ni in the oxidizable phase (2.0 to 29.1%) were higher than that in the exchangeable/acid soluble phase (1.2 to 29%) (Table 4.19). Nickel usually occurs in organically bound form; which under acid and neutral conditions enhances its mobility and bioavailability (Machender *et al.*, 2011). The high proportion Ni in the exchangeable/acid soluble phase in soil profiles of site AS3 indicates that Ni mobile in this site than other sites. The association of Ni in different extraction fractions followed the order Residual > Fe-Mn > Oxidizable > Exchangeable/acid soluble phase.

Table 4.19: Concentrations and percentages of Nickel in different extraction phases of the floodplain soils of the lower reaches of River Niger

| Sites	Depth (cm)	CONCENTRATION (μg g⁻¹)						PERCENTAGE (%)				
		F1	F2	F3	F4	SUM	TM	F1	F2	F3	F4	RECOVERY
AS1	0 - 15	0.44	0.76	1.2	2.4	4.8	4.8	9.2	15.8	25	50	100
	15 - 30	0.44	0.68	0.9	4.18	6.2	6.2	7.1	11	14.5	67.4	100
	30 - 45	0.84	1.08	2.2	4.28	8.4	8.4	10	12.9	26.2	51	100
AS2	0 - 15	0.24	0.81	0.55	1.05	2.65	2.4	9.1	30.6	20.8	39.6	110.4
	15 - 30	0.24	0.7	0.55	0.96	2.45	2.05	9.8	28.6	22.4	39.2	119.5
	30 - 45	0.24	1.64	0.5	1.67	4.05	3.85	5.9	40.5	12.3	41.2	105.2
AS3	0 - 15	0.24	0.64	0.55	0.95	2.38	2.25	10.1	26.9	23.1	39.9	105.8
	15 - 30	1.16	1.28	1.00	0.46	3.9	3.85	29.7	32.8	25.6	11.8	101.3
	30 - 45	0.96	1.2	2.3	3.44	7.9	7.9	12.2	15.2	29.1	43.5	100
AS4	0 - 15	0.24	1.08	1.25	16.9	19.5	19.5	1.2	5.5	6.4	86.8	100.3
	15 - 30	0.2	1.12	0.95	29.23	31.5	31.5	0.6	3.6	3	92.8	100
	30 - 45	ND	0.5	0.5	0.13	1.13	1.1	-	44.2	44.2	11.5	102.7
AS5	0 - 15	0.2	1.96	0.55	ND	2.71	2.71	7.4	72.3	20.3	-	100
	15 - 30	0.24	1.56	0.6	0.5	2.9	2.9	8.3	53.8	20.7	17.2	100
	30 - 45	0.2	1.76	0.5	1.84	4.3	4.25	4.7	40.9	11.6	42.8	101.2
OK1	0 - 15	0.24	1.16	0.5	3.5	5.4	5.4	4.4	21.5	9.3	64.8	100
	15 - 30	0.24	1.68	0.5	3.78	6.2	6.2	3.9	27.1	8.1	61	100
	30 - 45	0.24	1.28	0.5	8.28	10.3	10.3	2.3	12.4	4.9	80.4	100
OK2	0 - 15	0.24	0.64	0.5	23.9	25.3	25.3	0.9	2.5	2.0	94.5	100
	15 - 30	0.24	0.56	0.55	11.0	12.3	12.3	2.0	4.6	4.5	89	100
	30 - 45	0.24	0.72	0.5	9.44	10.9	10.9	2.2	6.6	4.6	86.6	100.5
OK3	0 - 15	0.24	0.72	0.5	3.54	5.0	5.0	4.8	14.4	10	70.8	100
	15 - 30	0.24	1.36	0.5	0.4	2.5	2.45	9.6	54.4	20	16	102
	30 - 45	0.24	1.00	0.55	0.51	2.3	2.3	10.4	43.5	23.9	22.2	100
AB1	0 - 15	0.24	0.64	0.5	4.72	6.1	6.1	3.9	10.5	8.2	77.4	100
	15 - 30	0.24	0.64	0.5	1.22	2.6	2.6	9.2	24.6	19.2	46.9	100
	30 - 45	0.44	0.64	0.6	5.32	7.0	7.0	6.3	9.1	8.6	76	100
AB2	0 - 15	0.44	0.72	0.5	7.14	8.8	8.75	5	8.2	5.7	81.1	100.6
	15 - 30	0.64	0.52	0.55	6.09	7.8	7.75	8.2	6.7	7.1	78.1	100.6
	30 - 45	0.48	0.56	0.55	13.6	15.2	15.2	3.2	3.7	3.6	89.5	100
AB3	0 - 15	0.56	0.52	0.5	10.1	11.7	11.7	4.8	4.4	4.3	86.5	100
	15 - 30	1.08	0.52	0.55	10.4	12.5	12.5	8.6	4.2	4.4	82.8	100.4
	30 - 45	1.56	0.52	0.5	8.32	10.9	10.9	14.3	4.8	4.6	76.3	100.5
AB4	0 - 15	0.24	ND	0.55	7.01	7.8	7.75	3.1	-	7.1	89.9	100.6
	15 - 30	0.28	0.52	0.55	12.75	14.1	14.1	2.0	3.7	3.9	90.4	100.4
	30 - 45	0.28	0.36	0.55	4.81	6.0	6.0	4.7	6.0	9.2	80.2	100
AB5	0 - 15	0.28	0.56	ND	15.5	16.3	16.3	1.7	3.4	-	94.8	100.3
	15 - 30	0.2	0.52	0.6	11.2	12.5	12.5	1.6	4.2	4.8	89.4	100.4
	30 - 45	0.32	0.52	0.55	24.9	26.3	26.3	1.2	2.0	2.1	94.7	100.2
	MIN	0.20	0.36	0.50	0.13	1.13	1.10	0.60	2.00	2.00	11.5	100
	MAX	1.6	2.0	2.3	29.2	31.5	31.5	29.7	72.3	44.2	94.8	120
	MEAN	0.40	0.9	0.69	7.2	9.0	8.9	6.41	18.9	12.8	64.6	101

F1 = Exchangeable fraction; F2 = Reducible fraction; F3 = Oxidizable fraction; F4 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil
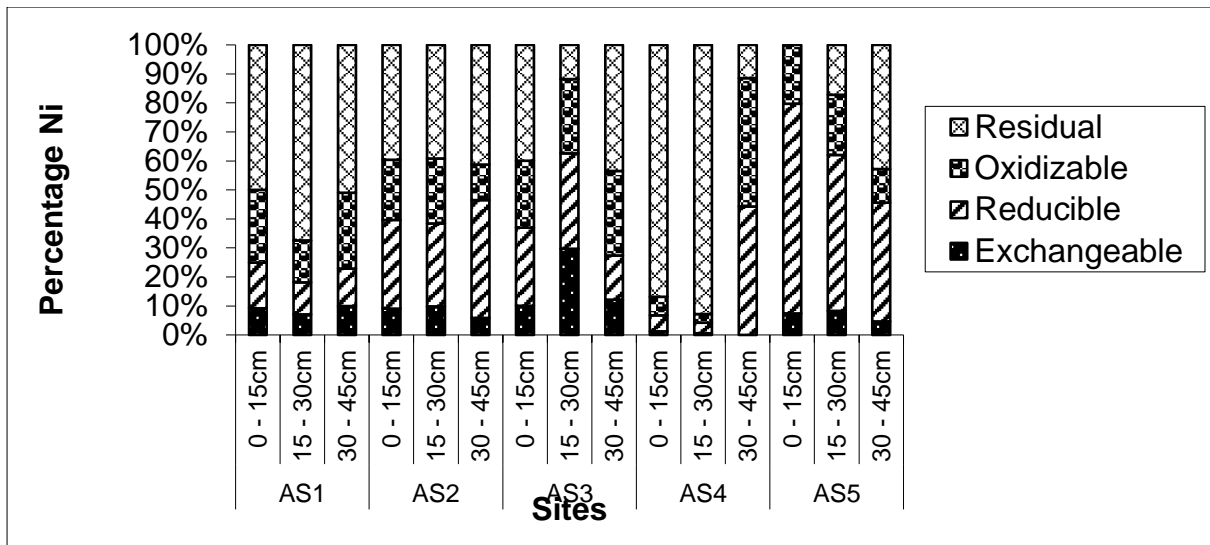
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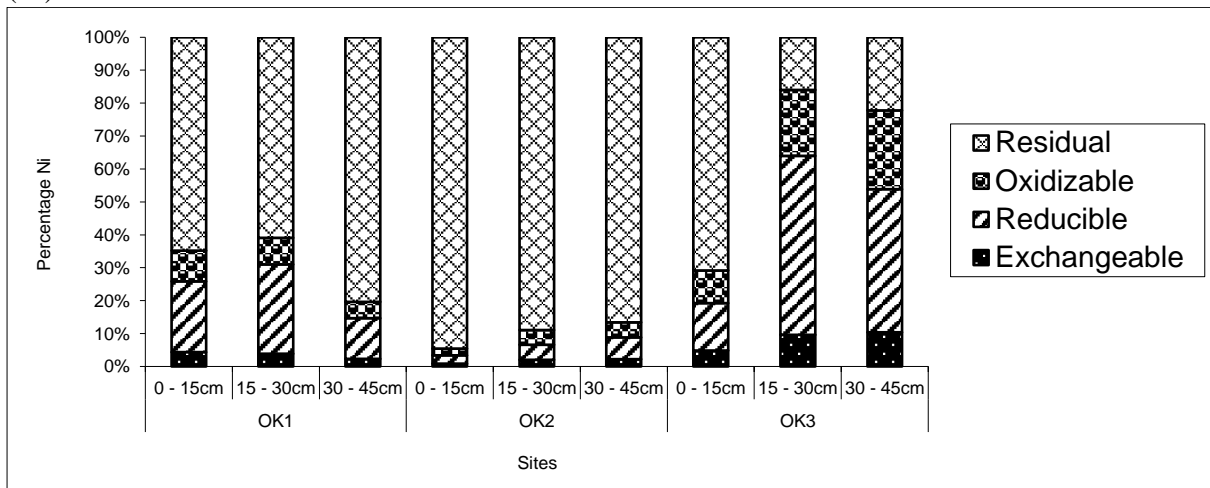
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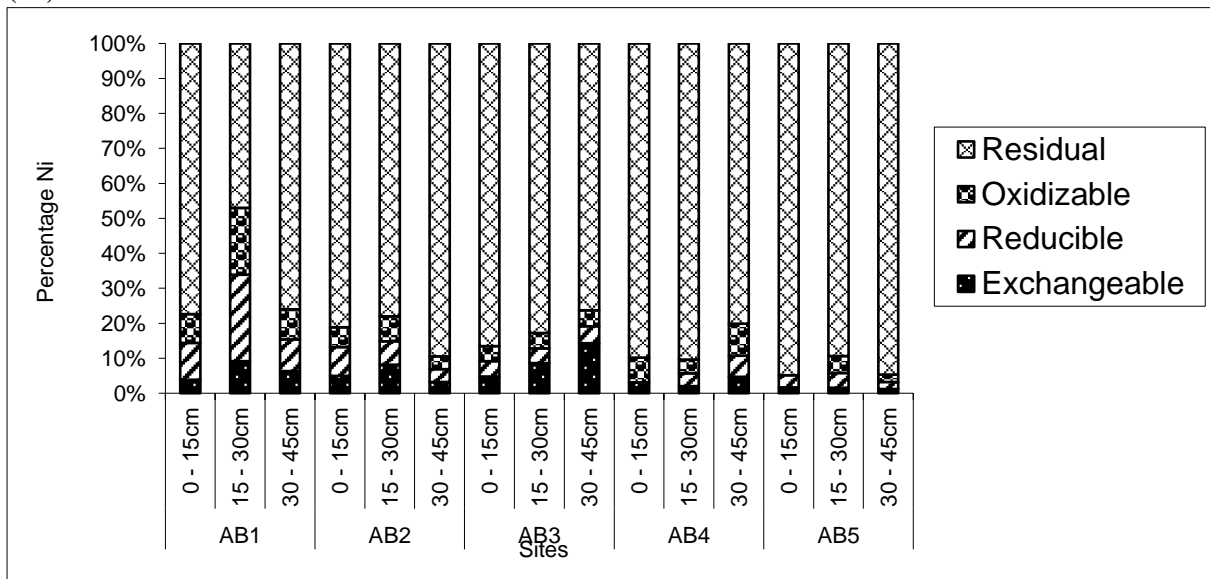
(8c)

Figure 8: Percentage of Nickel in the various extraction phases as a function of total Nickel content in soils three months after the major flooding

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Lead

The residual and Fe-Mn oxides phases were the two important forms of Pb in these soils. The residual and Fe-Mn oxides phases constituted 11 to 98% and 2.0 to 76% of the total Pb in these soil profiles respectively (Figure 9a-c). The association of Pb with Fe-Mn oxides phase is likely due to the formation of stable surface complexes (Lopez-Sanchez, 1996; Jones and Turkie, 1996; Iwegbue *et al.*, 2009b) and the known ability of amorphous Fe–Mn oxides to scavenge Pb from solution. It has been noted that of anoxic conditions may results in a rapid desorption of Pb and Cu adsorbed to sulphides. Thus, a proportion of Pb in the reducible phase is a hazard for the floodplain because Fe and Mn species can be reduced into the pore waters during early diagenesis by microbially mediated redox reactions. Dissolution will also release Pb associated with oxide phases to the pore water possibly to the overlying water column during flooding (Sarkar *et al.*, 2014). The associated of Pb with the reducible form and residual phase have been reported in the literature (Iwegbue *et al.*, 2009b; Rodriguez *et al.*, 2009; Davutluoglu *et al.*, 2010; Acosta *et al.*, 2011). The oxidizable phase Pb constituted up to 39.6% of the total Pb in the soil profiles. Shaheen *et al.* (2013) found 57% of the total Pb in the oxidizable in the floodplain soil of Elbe River, Germany. Despite reported affinity for Pb for organic matter Pb was not detected in the organic bound phase in the majority of the sites and depth (Table 4.20).The oxidizable phase Pb was found at sites AS1, AS2 and AS3. The exchangeable/carbonate bound phase consist of 0.3% to 30.9% of the total Pb concentration. In this study, the proportion of Pb in the readily available phase is greater than 20% in 39% of the samples which implied that Pb is mobile and bioavailable in these soil profiles.

Table 4.20: Concentrations and percentages of Lead in different extraction phases of the floodplain soils of the lower reaches of River Niger

Sites	Depth (cm)	CONCENTRATION (µg g⁻¹)						PERCENTAGE (%)				
		F1	F2	F3	F4	SUM	TM	F1	F2	F3	F4	RECOVERY
AS1	0 - 15	2.64	2.64	1.8	20.9	28	28	9.4	9.4	6.4	74.7	100
	15 - 30	3.00	3.8	0.35	6.65	13.8	13.8	21.7	27.5	2.5	48.2	100
	30 - 45	2.4	4.04	0.95	33.1	40.5	40.5	5.9	10	2.3	81.8	100
AS2	0 - 15	ND	1.1	1.65	1.2	3.95	3.7	-	27.8	41.8	30.4	106.8
	15 - 30	0.92	2.96	2.22	3.55	9.65	8.2	9.5	30.7	23.0	36.8	117.7
	30 - 45	1.48	3.47	1.45	3.85	10.3	9.05	14.4	33.9	14.1	37.6	113.3
AS3	0 - 15	1.16	1.05	0.3	1.24	3.75	3.25	30.9	28	8.00	33.1	115.4
	15 - 30	ND	1.65	0.75	2.08	4.48	4.45	-	36.8	16.7	46.4	100.7
	30 - 45	0.92	0.78	0.55	1.33	3.58	3.00	25.7	21.8	15.4	37.2	119.3
AS4	0 - 15	1.52	4.8	ND	0.78	7.1	7.1	21.4	67.6	-	11	100
	15 - 30	ND	3.12	2.85	1.23	7.2	7.2	-	43.3	39.6	17.1	100
	30 - 45	0.28	0.31	ND	0.64	1.23	1.05	22.8	25.2	-	52	117.1
AS5	0 - 15	1.24	3.2	ND	5.76	10.2	9.3	12.2	31.4	-	56.5	109.7
	15 - 30	1.16	1.31	ND	1.56	4.03	3.75	28.8	32.5	-	38.7	107.5
	30 - 45	ND	3.04	ND	3.61	6.65	6.4	-	45.7	-	54.3	103.9
OK1	0 - 15	1.36	3.56	ND	5.23	10.2	9.35	13.4	35.1	-	51.5	108.6
	15 - 30	ND	5.84	0.6	1.16	7.6	7.6	-	76.8	7.9	15.3	100
	30 - 45	ND	5.28	ND	8.27	13.55	13.2	-	39	-	61	102.7
OK2	0 - 15	ND	5.88	ND	6.22	12.1	12.1	-	48.6	-	51.4	100
	15 - 30	ND	1.52	ND	5.68	7.2	7.15	-	21.1	-	78.9	100.7
	30 - 45	0.6	3.76	0.75	2.29	7.4	7.4	8.1	50.8	10.1	30.9	100
OK3	0 - 15	ND	1.67	ND	1.78	3.45	3.0	-	48.4	-	51.6	115
	15 - 30	ND	1.04	ND	1.89	2.93	2.8	-	35.5	-	64.5	104.6
	30 - 45	0.88	0.91	0.55	1.02	3.36	3.15	26.2	27.1	16.4	30.4	106.7
AB1	0 - 15	0.52	3.8	ND	4.18	8.5	8.5	6.1	44.7	-	49.2	100
	15 - 30	0.44	1.04	ND	4.52	6.0	6.0	7.3	17.3	-	75.3	100
	30 - 45	1.37	1.34	ND	2.04	4.75	4.6	28.8	28.2	-	42.9	103.3
AB2	0 - 15	ND	3.88	ND	11.8	15.7	15.7	-	24.7	-	75.3	100
	15 - 30	0.04	0.56	ND	11.4	12.0	12.0	0.3	4.7	-	95	100
	30 - 45	3.36	ND	0.25	8.59	12.2	12.2	27.5	-	2	70.4	100
AB3	0 - 15	2.76	1.64	ND	7.6	12.0	12.0	23.0	13.7	-	63.3	100.4
	15 - 30	ND	0.28	ND	13.6	13.9	13.9	-	2	-	98	100.4
	30 - 45	1.6	2.64	ND	7.86	12.1	12.1	13.2	21.8	-	65	100.4
AB4	0 - 15	1.56	ND	ND	4.74	6.3	6.3	24.8	-	-	75.2	100
	15 - 30	0.92	1.56	ND	6.32	8.8	8.8	10.5	17.7	-	71.8	100
	30 - 45	ND	1.56	ND	3.64	5.2	5.15	-	30.0	-	70.0	101
AB5	0 - 15	0.16	0.8	ND	11.4	12.4	12.4	1.3	6.5	-	92.3	100.4
	15 - 30	1.44	ND	ND	9.96	11.4	11.4	12.6	-	-	87.4	100.4
	30 - 45	1.16	0.52	ND	13.1	14.8	14.8	7.8	3.5	-	88.6	100.3
	MIN	0.04	0.28	0.25	0.64	1.23	1.05	0.30	2.00	2.00	11.0	100
	MAX	3.4	5.9	2.9	33.1	40.5	40.5	30.9	76.8	41.8	98.0	119
	MEAN	1.34	2.4	1.07	6.2	9.7	9.5	15.9	29.7	14.7	56.7	104

F1 = Exchangeable fraction; F2 = Reducible fraction; F3 = Oxidizable fraction; F4 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil
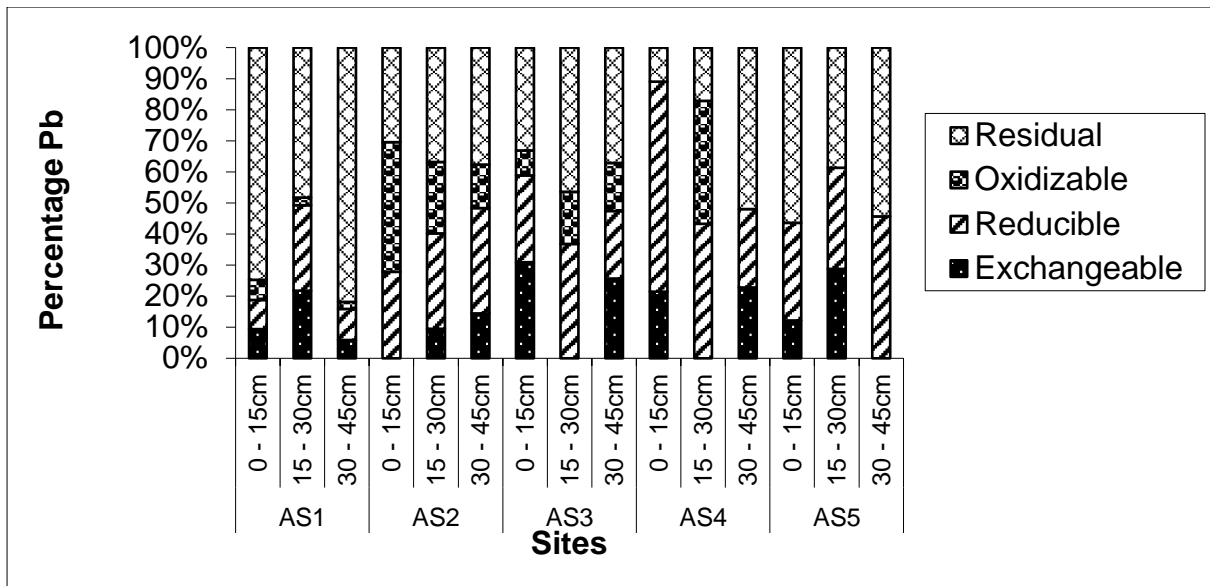
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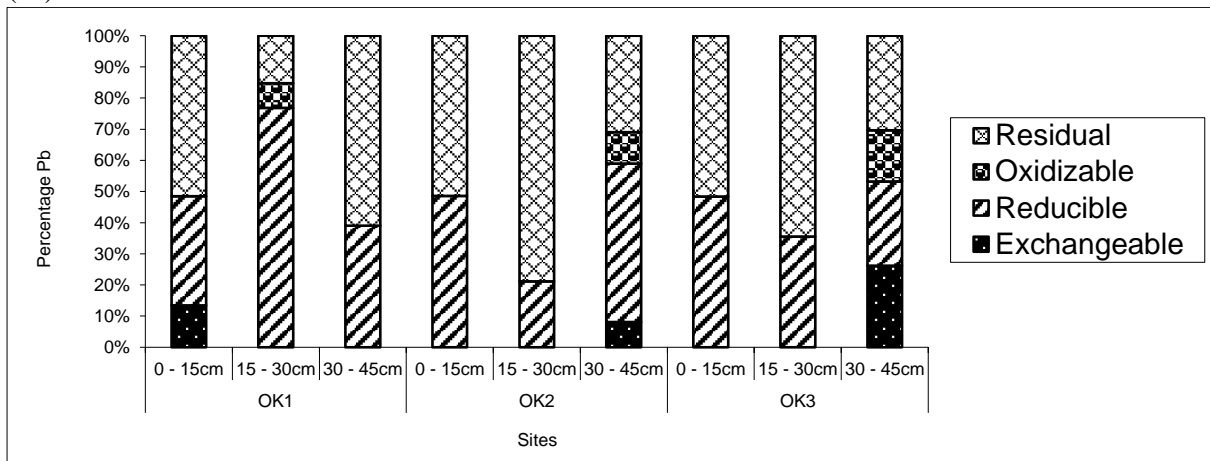
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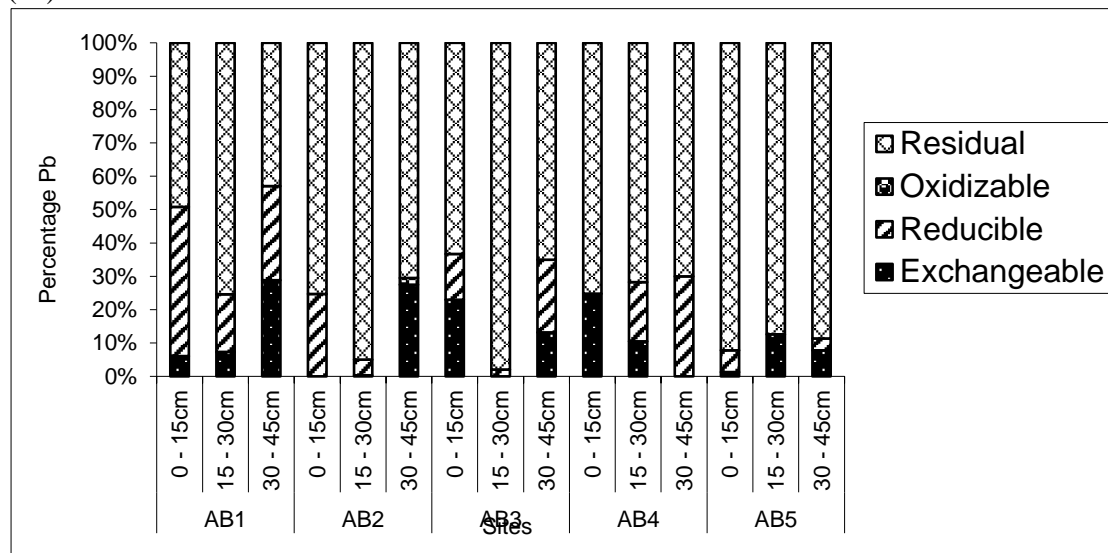
(9c)

Figure 9: Percentage of Lead in the various extraction phases as a function of total Lead content in soils three months after the major flooding

Zinc

The proportions of Zn in the exchangeable/acid soluble, reducible, oxidizable and residual fractions were in the range of 0.3 to 46.5%, 0.6 to 75%, 0.01 to 26.7% and 2.1 to 100% respectively (Figure 10a-c). The residual and reducible phases were the dominant form of zinc in these soil profiles. The dominance of Zn in the residual and Fe-Mn oxides phases have been reported in the literature (Ashraf *et al*., 2012; Iwegbue, 2011; Shasheen *et al*., 2013). The dominance of Zn in the residual phase indicates that Zn existed mainly as stable silicate mineral (Li *et al*., 2011). A significant proportion of Zn (up to 75%) was associated with Fe–Mn oxides phase, due to the high stability constants of Zn oxides. Iron oxides can adsorb considerable amounts of Zn and these oxides may also occlude Zn in the lattice structures. The association of Zn with Fe-Mn oxides/hydroxides phase have been reported in the literature (Kotokyl *et al.*, 2003; Zauyah *et al.*, 2004; Broghriet *et al.*, 2007; Acosta *et al.*, 2011). Zinc was not found in the exchangeable/acid soluble and oxidizable phases in greater than 54% of these samples For instance, Zn was not found in the exchangeable/acid soluble phase in site AS1 to AB1 and AB4 while significant proportions of Zn were found in the exchangeable/acid soluble phase in some sites e.g. AS2, AB2 and AB2. The occurrence of Zn in the oxidizable phase was restricted to the soil profiles of the upstream section of the floodplain (Table 4.21) while little or virtually no zinc was found in the oxidizable phase in the soil profiles of mid and downstream sections of the floodplain. The association of Zn with oxidizable phase is due to the formation of zinc-organic matter complex.

Table 4.21: Concentrations and percentages of Zinc in different extraction phases of the floodplain soils of the lower reaches of River Niger

| Sites	Depth (cm)	CONCENTRATION (µg g⁻¹)						PERCENTAGE (%)				
		F1	F2	F3	F4	SUM	TM	F1	F2	F3	F4	RECOVERY
AS1	0 - 15	129	8.68	8.6	1344	1491	1491	8.6	0.6	0.6	90.2	100
	15 - 30	24.9	20.6	13.0	34.1	92.6	91.4	26.9	22.3	14	36.8	101
	30 - 45	24.4	12.0	18.0	206	260	260	9.4	4.6	6.9	79.1	100
AS2	0 - 15	54.6	19.8	15.9	1.92	92.3	92.3	59.2	21.5	17.2	2.1	100
	15 - 30	12.4	11.1	13.0	12.1	48.5	48.5	25.5	22.8	26.7	25	100
	30 - 45	6.56	12.2	10.1	76.5	105	105	6.2	11.6	9.6	72.6	100
AS3	0 - 15	6.12	9.56	4.35	12.3	32.3	30.2	18.9	29.6	13.5	38	107
	15 - 30	6.8	8.4	6.95	9.75	31.9	31.9	21.3	26.3	21.8	30.6	100
	30 - 45	3.4	4.96	15.3	34.3	58.0	58.0	5.9	8.6	26.4	59.2	100
AS4	0 - 15	ND	63.3	13.6	6.57	83.4	83.4	-	75.9	16.2	7.9	100
	15 - 30	ND	9.16	4.6	75.3	89.1	89.1	-	10.3	5.2	84.6	100
	30 - 45	ND	8.52	4.8	5.38	18.7	18.7	-	45.6	25.7	28.8	100
AS5	0 - 15	ND	21.4	ND	86.0	107	107	-	19.9	-	80.1	100
	15 - 30	ND	12.9	ND	23.5	37	37.0	-	34.9	-	63.5	100
	30 - 45	ND	11.7	ND	12.0	23.7	23.7	-	49.3	-	50.7	100
OK1	0 - 15	ND	88.5	0.05	352	440	440	-	20.1	0.01	79.9	100
	15 - 30	ND	25.3	ND	281	306	306	-	8.3	-	91.7	100
	30 - 45	ND	55.9	ND	67.7	124	124	-	45.2	-	54.8	100
OK2	0 - 15	ND	6.52	0.05	484	491	491	-	1.3	0.01	98.7	100
	15 - 30	ND	3.0	0.1	54.4	57.5	57.5	-	5.2	0.2	94.6	100
	30 - 45	ND	8.04	ND	38.3	46.3	46.3	-	17.4	-	82.6	100
OK3	0 - 15	ND	4.88	ND	111	116	116	-	4.2	-	95.8	100
	15 - 30	ND	20.5	0.05	73.8	94.4	94.4	-	21.7	0.1	78.2	100
	30 - 45	ND	14.7	ND	84.5	99.2	99.2	-	14.8	-	85.2	100
AB1	0 - 15	ND	5.6	ND	199	204	204	-	2.7	-	97.3	100
	15 - 30	ND	5.68	ND	164	170	170	-	3.3	-	96.7	100
	30 - 45	17.5	3.6	ND	26.1	47.2	45.5	37.1	7.6	-	55.3	104
AB2	0 - 15	12.1	33.2	ND	89.3	135	135	9	24.7	-	66.3	100
	15 - 30	28.0	1.36	ND	30.8	60.2	59.5	46.5	2.3	-	51.3	101
	30 - 45	5.16	0.96	ND	39.9	46.0	46.0	11.2	2.1	-	86.7	100
AB3	0 - 15	23.8	1.0	ND	52.7	77.5	76.2	30.7	1.3	-	68	102
	15 - 30	19.4	0.8	ND	27.1	47.2	46.7	41	1.7	-	57.3	101
	30 - 45	19.4	0.76	0.05	21.9	42.1	42.1	46	1.8	0.1	52.1	100
AB4	0 - 15	ND	ND	ND	311	311	311	-	-	-	100	100
	15 - 30	ND	0.88	ND	47.1	48.0	48.0	-	1.8	-	98.2	100
	30 - 45	ND	1.2	ND	30.0	31.2	31.2	-	3.8	-	96.2	100
AB5	0 - 15	0.28	1.4	ND	95.0	96.7	96.7	0.3	1.4	-	98.3	100
	15 - 30	ND	1.24	ND	49.0	50.2	50.2	-	2.5	-	97.5	100
	30 - 45	3.36	1.16	ND	60.2	64.7	58.0	5.2	1.8	-	93	112
	MIN	0.28	0.76	0.05	1.92	18.7	18.7	0.30	0.60	0.01	2.10	100
	MAX	129	88.5	18.0	1344	1491	1491	59.2	75.9	26.7	100	112
	MEAN	22.0	13.7	7.6	121	148	148	22.7	15.3	10.8	69.9	101

F1 = Exchangeable fraction; F2 = Reducible fraction; F3 = Oxidizable fraction; F4 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil
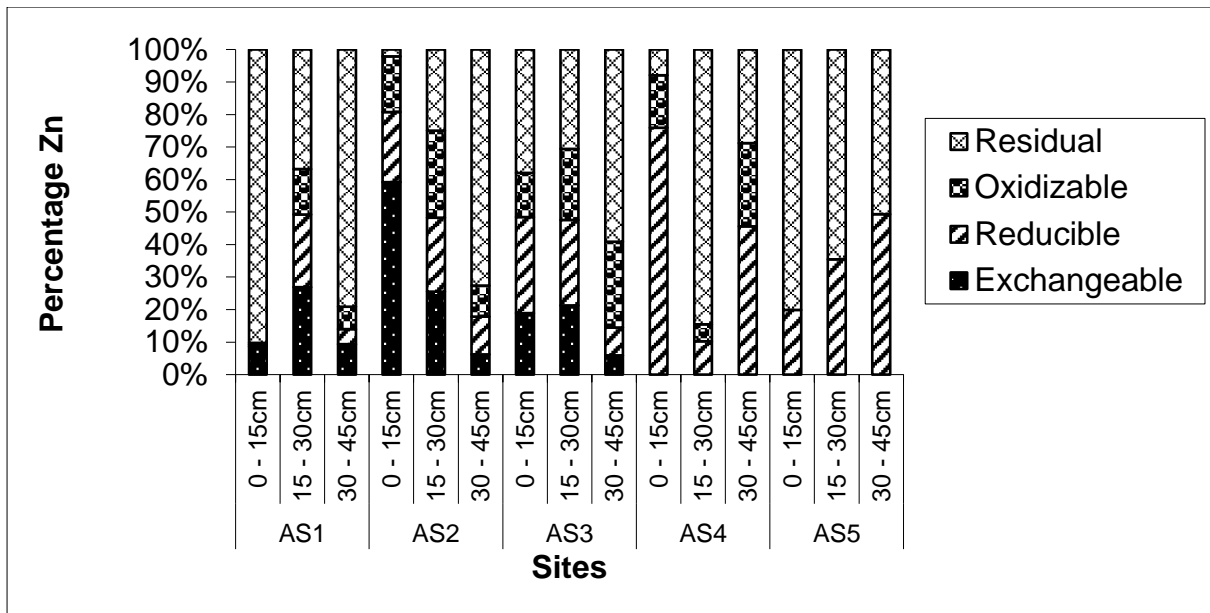
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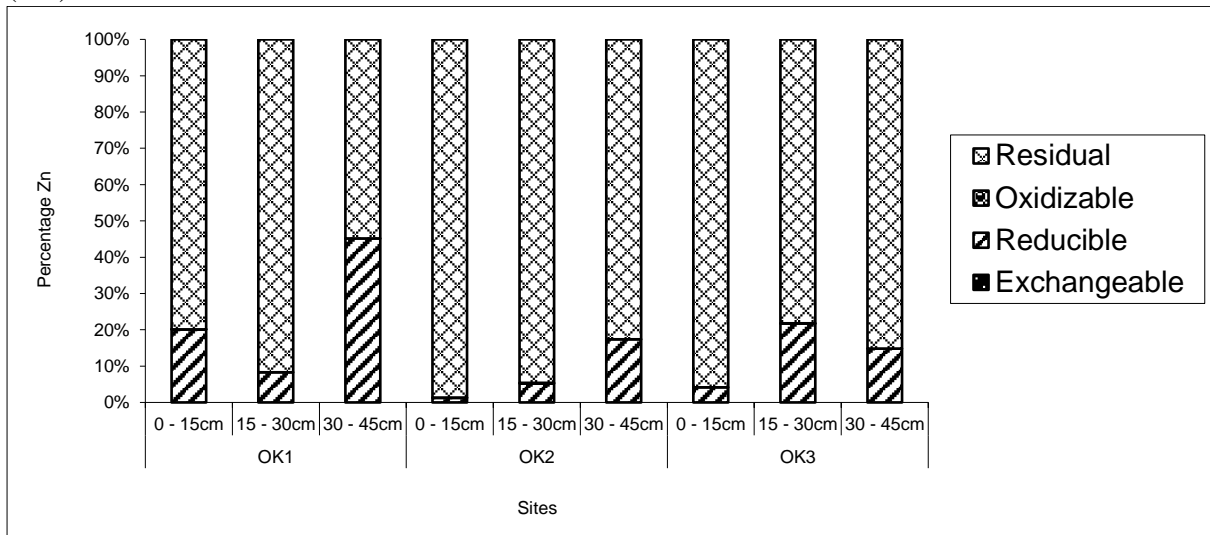
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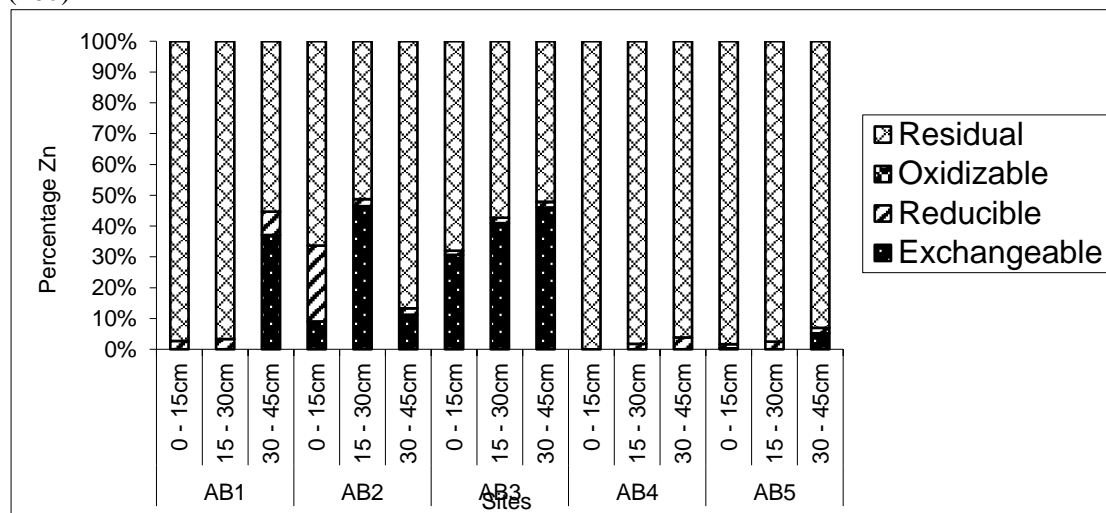
(10c)

Figure 10: Percentage of Zinc in the various extraction phases as a function of total Zinc content in soils three months after the major flooding

Barium

The residual (3.0 to 100%) and Fe-Mn oxides (0.4 to 98.3%) were the dominant form of barium in these soil profiles. The percentage of total of Mn in the oxidizable and exchangeable/acid soluble phases ranged from 0.3 to 38.4% and 3.2% to 85.0% respectively (Figure 11a-c). Although, Ba was not detected in the exchangeable/acid soluble phase in site AS4 to AB1 as well as AB4 and AB5 while significant proportion of Ba was found in the exchangeable phase in sites AS1 to AS3 and AB2 to AB3 (Table 4.22). Barium was found only the reducible phase in the 0-15 cm depth of AB5.

Table 4.22: Concentrations and percentages of Barium in different extraction phases of the floodplain soils of the lower reaches of River Niger

| Sites	Depth (cm)	CONCENTRATION (μg g⁻¹)						PERCENTAGE (%)				
		F1	F2	F3	F4	SUM	TM	F1	F2	F3	F4	RECOVERY
AS1	0 - 15	23.0	2.08	1.95	37.7	64.7	64.7	35.5	3.2	3.0	58.3	100
	15 - 30	16.3	2.16	2.05	104	124	124	13.1	1.7	1.7	83.5	100
	30 - 45	28.9	13.7	24.9	16.4	83.8	83.8	34.5	16.3	29.7	19.5	100
AS2	0 - 15	2.38	2.67	2.53	3.76	11.3	9.55	21.0	23.5	22.3	33.2	119
	15 - 30	2.05	2.24	3.06	3.73	11.1	10.7	18.5	20.2	27.6	33.7	104
	30 - 45	4.7	2.56	3.97	13.4	24.6	22.4	19.1	10.4	16.1	54.4	110
AS3	0 - 15	1.85	4.65	1.32	5.41	13.2	12.5	14	35.1	10.0	40.9	106
	15 - 30	3.68	6.76	8.4	3.05	21.9	21.3	16.8	30.9	38.4	13.9	103
	30 - 45	33.4	30.0	6.15	6.81	76.4	76.4	43.7	39.3	8.0	8.9	100
AS4	0 - 15	ND	13.2	5.4	108	127	126	-	10.5	4.3	85.3	100
	15 - 30	ND	18.6	4.1	0.7	23.4	23.4	-	79.5	17.5	3.0	100
	30 - 45	ND	7.68	3.1	7.74	18.5	18.1	-	41.5	16.7	41.8	102
AS5	0 - 15	ND	4.43	0.5	11.2	16.1	15.5	-	27.5	3.1	69.4	104
	15 - 30	ND	6.45	ND	10	16.5	16.2	-	39.2	-	60.8	102
	30 - 45	ND	8.78	0.5	9.96	19.2	19.1	-	45.6	2.6	51.8	101
OK1	0 - 15	ND	23.7	0.5	43.0	67.2	67.2	-	35.2	0.7	64.0	100
	15 - 30	ND	49.1	0.5	10.3	59.9	59.9	-	82	0.8	17.2	100
	30 - 45	ND	28.2	0.5	ND	28.7	28.7	-	98.3	1.7	-	100
OK2	0 - 15	ND	1.44	0.5	80.8	82.7	82.7	-	1.7	0.6	97.7	100
	15 - 30	ND	0.8	0.5	87.8	89.1	89.1	-	0.9	0.6	98.5	100
	30 - 45	ND	3.04	0.5	84.4	87.9	87.9	-	3.5	0.6	96.0	100
OK3	0 - 15	ND	1.84	0.5	37.3	39.6	39.6	-	4.6	1.3	94.1	100
	15 - 30	ND	5.08	0.5	6.87	12.5	12.3	-	40.8	4.0	55.2	101
	30 - 45	ND	3.41	0.5	4.32	8.23	8.0	-	41.4	6.1	52.5	103
AB1	0 - 15	ND	4.32	0.5	7.48	12.3	12.3	-	35.1	4.1	60.8	100
	15 - 30	ND	4.24	0.5	6.56	11.3	11.3	-	37.5	4.4	58.1	100
	30 - 45	7.64	4.6	0.5	38.0	50.7	50.7	15.1	9.1	1.0	74.9	100
AB2	0 - 15	7.68	3.8	0.5	87.5	99.5	99.5	7.7	3.8	0.5	88.0	100
	15 - 30	7.84	0.96	0.5	137	147	146	5.4	0.7	0.3	93.7	100
	30 - 45	6.68	0.68	0.5	ND	7.86	7.86	85	8.7	6.4	-	100
AB3	0 - 15	19.8	0.52	0.5	96.4	117	117	16.9	0.4	0.4	82.3	100
	15 - 30	34.5	0.48	0.5	66.6	102	102	33.8	0.5	0.5	65.3	100
	30 - 45	56.2	0.44	0.5	33.8	90.9	90.9	61.8	0.5	0.6	37.1	100
AB4	0 - 15	ND	ND	0.5	56.9	57.4	57.4	-		0.9	99.1	100
	15 - 30	ND	0.48	0.5	68.1	69.1	69.1	-	0.7	0.7	98.6	100
	30 - 45	ND	0.56	0.5	49.9	51	51	-	1.1	1.0	97.9	100
AB5	0 - 15	ND	0.44	ND	ND	0.44	0.44	-	100		-	100
	15 - 30	ND	0.6	0.5	109	111	111	-	0.5	0.5	99	100
	30 - 45	4.6	0.52	0.5	138	144	144	3.2	0.4	0.3	96.1	100
	MIN	1.85	0.44	0.50	0.70	0.44	0.44	3.20	0.40	0.30	3.0	100
	MAX	56.2	49.1	24.9	138	147	146	85.0	100	38.4	99.1	119
	MEAN	15.4	7.0	2.15	44.2	56.4	56.1	26.2	24.5	6.50	63.5	101

F1 = Exchangeable fraction; F2 = Reducible fraction; F3 = Oxidizable fraction; F4 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil
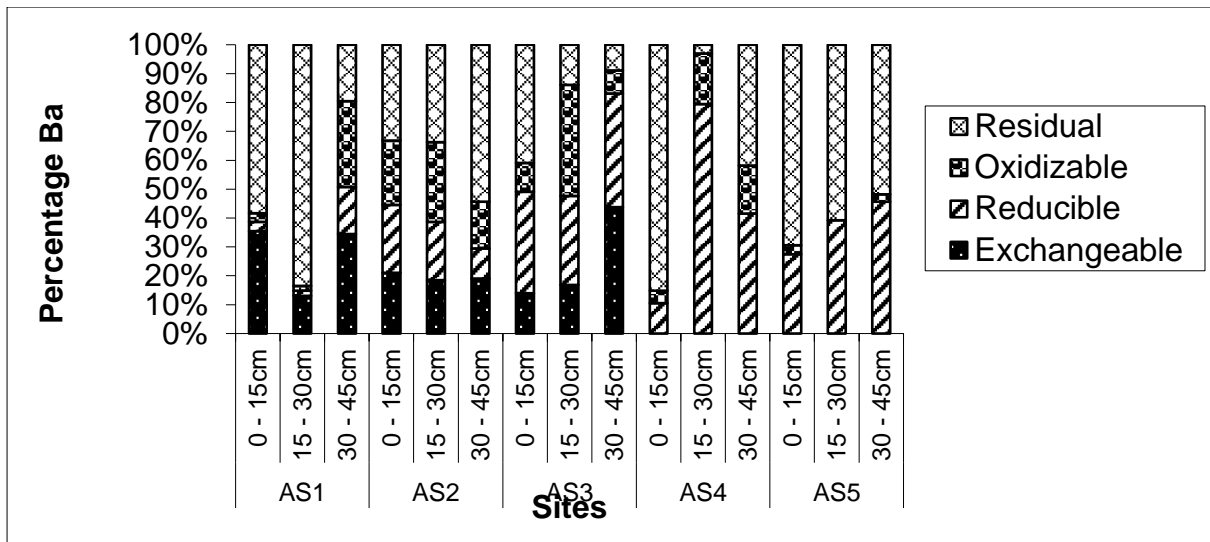
(11a)
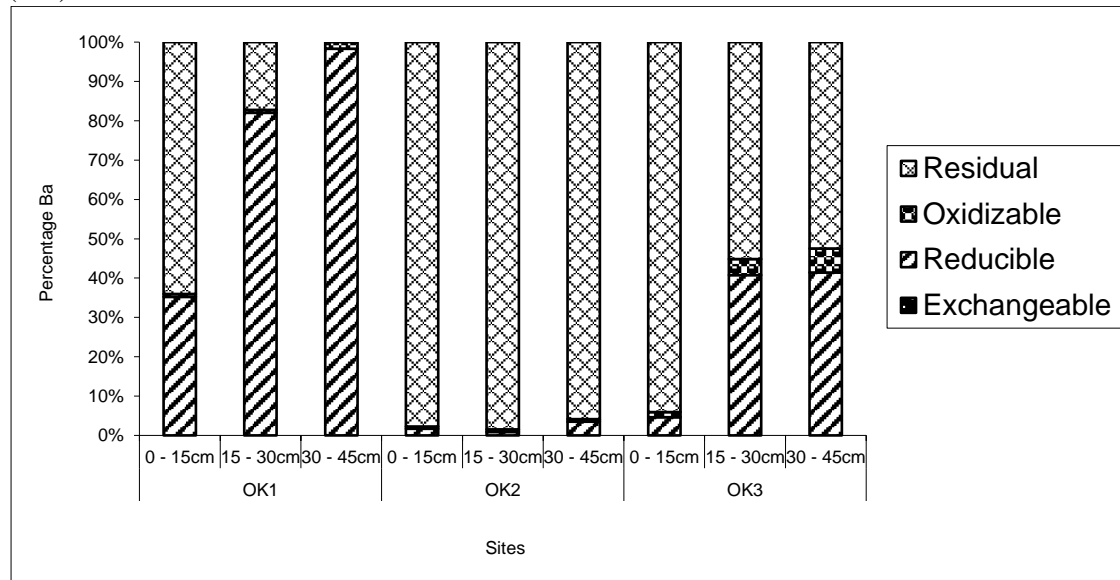
(11b)
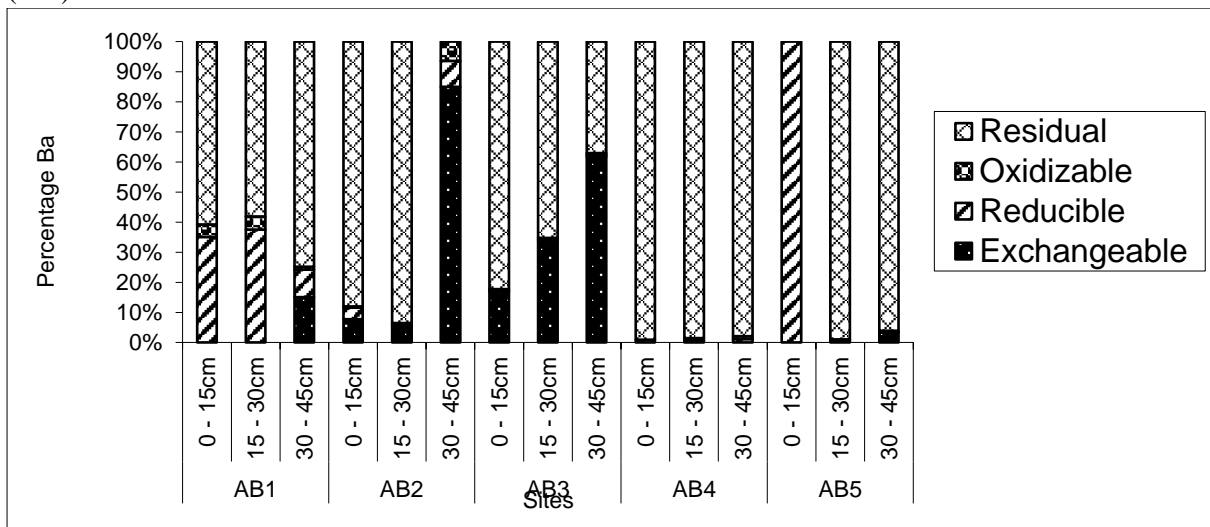
(11c)

Figure 11: Percentage of Barium in the various extraction phases as a function of total Barium content in soils three months after the major flooding

4.12   Mobility of metals in the soil three months after the major flooding

The mobility of metal in the soil profile may be assessed on the basis of the relative content of the readily available fraction or the basis of the relative contents of potentially available fractions. The mobility factor equation described by several investigators (Salbu *et al*., 1998; Kabala and Singh, 2001; Iwegbue, 2007; 2011) was based on the sum of relative contents of the easily available fraction i.e. water soluble + exchangeable + carbonate bound fractions in a 5 or 6 steps sequential extraction schemes. However, it is also necessary to evaluate the proportion of metals that may be potentially available which included those in the exchangeable/water soluble + carbonate bound+ Fe-Mn oxides+ organically bound fractions**.** In this case, we distinguished between the mobility of metals at the prevailing physicochemical and environmental conditions of the soil and the sum that may be potentially available when the environmental and physicochemical characteristics of the soils as indicated in Table 4.23. The potentially available fractions are of prime importance in floodplain soils whose pH and redox conditions are greatly influenced by flooding events. The potential mobility of the metals followed the order Pb>Ba>Cd>Ni>Co>Zn>Mn>Cu>Cr. The proportions of metals in the readily available or mobile fraction were greater than 20% in less than 36% of the samples while the proportions in the potentially mobile or available metals in the majority of these sites and depth were greater than 20% (Table 4.23) which indicates that changes in the physicochemical conditions as a result of   flooding may lead to significant remobilization of these aforementioned metals.

Table 4.23: Percentages of metals in the readily available and potentially available fractions in floodplain soils three months after the major flooding.

Sites	Depth (cm)	Readily mobile fraction									Potential mobile fraction								
		Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Ba	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Ba
AS1	0 – 15	2	7.1	4.4	8.8	9.2	9.2	9.4	8.6	35.5	22	39.5	35.9	44.3	18.8	50	25.2	9.8	41.7
	15 – 30	13.3	12.6	5.2	9.3	16.7	7.1	21.7	26.9	13.1	41.6	80.5	30.1	31.6	35.3	32.6	51.7	63.2	16.5
	30 – 45	2.5	4.3	1.2	2.7	7.8	10	5.9	9.4	34.5	20.6	55.2	24	16.5	52.2	49.1	18.2	20.9	80.5
AS2	0 – 15	9.1	6.5	5	19.8	19.9	9.1	-	59.2	21	50	37.5	15.5	71	58.8	60.5	69.6	97.9	66.8
	15 – 30	7	8.8	5.5	5.4	12.2	9.8	9.5	25.5	18.5	29.8	47.4	72.4	13.4	58.2	60.8	63.2	75	66.3
	30 – 45	-	5.6	6.9	13.3	24.8	5.9	14.4	6.2	19.1	78.3	34.1	61.3	63.4	70.5	58.7	62.4	27.4	45.6
AS3	0 – 15	-	9.3	4.5	16.8	16.7	10.1	30.9	18.9	14	36.1	50.4	54.1	55.6	60.2	60.1	66.9	62	59.1
	15 – 30	8	7.9	2.4	-	7.4	29.7	-	21.3	16.8	100	43	67	42	36.6	88.1	53.5	69.4	86.1
	30 – 45	5.2	8.2	1.3	8	22.3	12.2	25.7	5.9	43.7	45.5	99.6	46.6	65.4	63.2	56.5	62.9	40.9	91
AS4	0 – 15	4.4	1.5	-	-	0.1	1.2	21.4	-	-	42.2	41.9	20	32.2	30.5	13.1	89	92.1	14.8
	15 – 30	-	5.4	-	-	0.6	0.6	-	-	-	39.1	32.3	70.9	26.1	70.5	7.2	82.9	15.5	97
	30 – 45	16	10.6	-	-	2.1	-	22.8	-	-	100	57.5	38.9	23.3	48.6	88.4	48	71.3	58.2
AS5	0 – 15	2.9	3.4	-	-	0.1	7.4	12.2	-	-	46.5	45.5	28.8	50.8	25	100	43.6	19.9	30.6
	15 – 30	4	4.4	-	-	0.1	8.3	28.8	-	-	41	40.1	19.4	51.6	39.1	82.8	61.3	34.9	39.2
	30 – 45	2.9	6.5	-	-	0.2	4.7	-	-	-	40.8	52.4	20.6	34.8	39.3	57.2	45.7	49.3	48.2
OK1	0 – 15	6.7	1.9	-	-	0.1	4.4	13.4	-	-	61.7	39.5	40	50.8	72.1	35.2	48.5	20.11	35.9
	15 – 30	3.3	2	-	-	0.1	3.9	-	-	-	20.8	78.2	13.7	47.8	48.6	39.1	84.7	8.3	82.8
	30 – 45	10	0.9	-	-	0.1	2.3	-	-	-	92.5	23.2	48	46	83.3	19.6	39	45.2	100
OK2	0 – 15	2	1.3	-	-	0.03	0.9	-	-	-	4	11	1.8	20	0.83	5.4	48.6	1.31	2.3
	15 – 30	2.2	35.2	-	-	0.03	2	-	-	-	7.2	100	1.1	3	3.33	11.1	21.1	5.4	1.5
	30 – 45	2.4	1.3	-	-	0.03	2.2	8.1	-	-	10	12.9	3.5	14	4.23	13.4	69	17.4	4.1
OK3	0 – 15	4	2.6	-	-	0.4	4.8	-	-	-	89	21.7	6.5	44.4	10.8	29.2	48.4	4.2	5.9
	15 – 30	8	5.3	-	-	0.3	9.6	-	-	-	50	43.1	30.1	82.2	40.8	84	35.5	21.8	44.8
	30 – 45	13.3	-	-	-	0.7	10.4	26.2	-	-	70	64	30.9	58.1	87	77.8	69.7	14.8	47.5
AB1	0 – 15	6.7	8.9	-	-	0.2	3.9	6.1	-	-	21.7	58.3	9.5	22.1	2.8	22.6	50.8	2.7	39.2
	15 – 30	13.3	5	-	-	0.3	9.2	7.3	-	-	56.7	60.6	15	22	4.8	53	24.6	3.3	41.9
	30 – 45	3.1	3.6	1.6	16.1	0.8	6.3	28.8	37.1	15.1	10	18.6	6.7	41.3	1.6	24	57	44.7	25.2
AB2	0 – 15	-	3.4	0.7	5.3	0.6	5	-	9	7.7	100	27.2	6	17.5	25.8	18.9	24.7	33.7	12
	15 – 30	13.3	18	18.1	6.6	1.5	8.2	0.3	46.5	5.4	56.7	25.5	21.1	6.6	11.6	22	5	48.8	6.4
	30 – 45	8.9	2	0.7	6.2	1.3	3.2	27.5	11.2	85	13.8	5.4	0.8	6.2	1.9	10.5	29.5	13.3	100
AB3	0 – 15	4.2	6.5	0	1.9	5.9	4.8	23	30.7	16.9	11	10.8	0	1.9	6.5	13.5	36.7	32	17.7
	15 – 30	3.8	8.1	1.9	8.1	12	8.6	-	41	33.8	10	12.6	1.9	8.1	12.4	17.2	2	42.7	34.8
	30 – 45	2	6.1	1.1	8.1	10.4	14.3	13.2	46	61.8	8.5	14.8	1.1	8.1	10.6	23.7	35	47.9	62.9
AB4	0 – 15	3.1	1.7	-	-	0.1	3.1	24.8	-	-	6.9	8.1	0	0	0.1	10.2	24.8	0	0.9
	15 – 30	2.7	1.5	-	-	0.04	2	10.5	-	-	11.3	12.1	0	0	0.34	9.6	28.2	1.8	1.4
	30 – 45	3.6	2.1	-	-	0.1	4.7	-	-	-	15.4	16.1	0	0	0.5	19.9	30	3.8	2.1
AB5	0 – 15	1.4	0.8	-	-	0.02	1.7	1.3	0.3	-	4.3	3.6	0	0	0.12	5.1	7.8	1.7	100
	15 – 30	1.8	1.1	-	-	0.03	1.6	12.6	-	-	7.7	8.6	0	0	0.33	10.6	12.6	2.5	1
	30 – 45	1.8	1.7	2.8	4.7	1.1	1.2	7.8	5.2	3.2	7.7	8.8	2.8	4.7	1.5	5.3	11.3	7	3.9

4.13   PAHs Concentration in soils three months after the major flooding

The results for the determination of $\sum$16 PAHs in floodplain soils are displayed in Table 4.24. The concentration of the Σ16 PAHs ranged from 1470.3 to 8338.5 µg kg^{-1}, 2067 to 10651.4 µg kg^{-1}and 811.8 to 6588.1 µg kg^{-1} for 0-15 cm, 15-30 cm and 30-45 cm depths respectively. The concentrations of PAHs in these soils varied significantly ($p<0.05$) with respect to sites and depths. The results indicated that there was no regular trend in the concentrations of PAHs with respect to depth of the soil profile. For example, at the following sites AS1, AS4, AS5, OK1, OK3, AB2, AB4 and AB5, the PAHs concentrations decreased with depth while at sites AS2, AS3, OK2, AB1 and AB3, the PAHs concentrations increased with increasing depth of the profile. However, at sites AS1, AS2 and AB3 the middle layer (15-30 cm) had higher concentrations of PAHs than the other layers. The variations in the concentrations of PAHs may be related to the length of time for which the soil had been contaminated and the volatility of the PAHs. The soils of the downstream sections of the floodplain had higher concentrations of the $\sum$16 PAHs than the upper sections of the floodplain (Table 4.25). The high concentrations of PAHs in the downstream section of the flood plain may be associated with the gas flaring and related oil exploration activities in this section of the flood plain. The concentrations of $\sum$16 PAHs in this study in comparison with levels reported for soils in the literature are presented in Table 4.26. The concentrations of $\sum$16 PAHs in these sites were comparable to PAHs concentration reported for soils of the Rhine River floodplain (Pies *et al.,* 2007), and with the range reported for agricultural soils (Chen *et al.,* 2005; Morello *et al.,* 2008; Yang *et al.,* 2012). Although, the concentrations of $\sum$16 PAHs were much higher than previously reported in soils in the Niger Delta (Olajire *et al.,* 2005; Sojinu *et al.,* 2010).

Table 4.24: Concentrations (µg kg^{-1}) of PAHs in soils three months after the major flooding

	DEPTH (cm)	Acy	Ace	Flu	Phen	Ant	Flt	Pyr	BaA	Chry	BbF	BkF	BaP	IndP	DahA	BghiP	Total	3R	4R	5R	6R	∑PAH$_{7c}$
AS1	0-15	ND	48.9	27.6	ND	ND	ND	ND	3071.2	24.4	63	ND	2030.6	ND	ND	ND	5265.7	76.5	3095.6	2093.6	ND	5189.2
	15-30	1088	ND	1036.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2124.9	2124.9	ND	ND	ND	ND
	30-45	ND	61.7	ND	ND	ND	ND	ND	743.6	3.6	0.7	2.2	ND	ND	ND	ND	811.8	61.7	747.2	2.9	ND	750.1
AS2	0-15	ND	2090.2	ND	ND	ND	ND	ND	54.3	89.8	1076.4	2027.8	ND	ND	ND	ND	5338.5	2090.2	144.1	3104.2	ND	3248.3
	15-30	ND	ND	ND	ND	ND	ND	ND	ND	2077	33.1	33	ND	ND	ND	ND	2143.1	ND	2077	66.1	ND	2143.1
	30-45	ND	ND	39.4	ND	ND	ND	104.9	ND	ND	ND	ND	ND	ND	ND	ND	1144.4	39.4	104.9	ND	ND	ND
AS3	0-15	82	2520.1	241.5	50	203	49.5	19.7	94.1	25	88	71.5	39.1	2098.5	41.2	36.5	5659.6	3096.4	188.3	239.8	2135	2457.4
	15-30	ND	116.9	13.3	62.8	35.2	119.5	34	70.2	3116.8	105.8	ND	4065.2	ND	ND	ND	7739.6	228.2	3340.5	4171	ND	7358
	30-45	ND	44.4	ND	ND	ND	ND	3032.6	107.9	51	118.4	ND	63.1	ND	ND	ND	3417.4	44.4	3191.5	181.5	ND	340.4
AS4	0-15	51.5	88.7	63.1	25.4	38.3	ND	1039.2	ND	35.2	85.6	ND	43.2	ND	ND	ND	1470.3	267	1074.4	128.8	ND	164
	15-30	ND	ND	ND	ND	ND	ND	ND	62.2	39.8	4038.6	33.8	ND	ND	ND	ND	4273.8	ND	102	4072.4	ND	4174.4
	30-45	ND	ND	ND	ND	ND	ND	ND	ND	49.5	27.8	2033.7	ND	ND	ND	ND	2110.9	ND	49.5	2061.5	ND	2111
AS5	0-15	ND	ND	1087.7	210.8	80.1	132	132	ND	78	114.8	ND	53.4	ND	ND	53.7	1942.7	1378.6	342	168.2	53.7	246.2
	15-30	84.5	11	79.8	2036.4	65.6	38	26.2	23.7	88.4	54.3	ND	2054.3	ND	ND	ND	4562.2	2277.3	176.3	2108.6	ND	2220.7
	30-45	44.4	62.3	44.3	ND	ND	ND	ND	2052.6	27.9	46.5	ND	53.1	25.5	ND	ND	2356.7	151	2080.5	99.6	25.5	2205.6
OK1	0-15	ND	ND	ND	ND	ND	ND	ND	2054	34.4	25.4	1032.7	ND	ND	ND	ND	3146.5	ND	2088.4	1058.1	ND	3146.5
	15-30	ND	ND	ND	ND	ND	ND	ND	ND	1083.2	51.8	933	ND	ND	ND	ND	2067	ND	1083.2	984.8	ND	2068
	30-45	ND	845.9	25.5	ND	ND	ND	ND	7.5	44.8	27.4	18.8	ND	ND	ND	ND	970	871.4	52.3	46.2	ND	98.5
OK2	0-15	888	ND	1036.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1924.9	1924.9	ND	ND	ND	ND
	15-30	ND	74.1	ND	ND	ND	ND	ND	67.6	940.2	ND	1103.4	ND	ND	ND	ND	2185.3	74.1	1007.8	1103.4	ND	2111.2
	30-45	2046.3	49.4	29.7	ND	ND	ND	ND	93.3	34.2	2043	303.3	ND	ND	ND	ND	4599.1	2125.4	127.5	2346.3	ND	2473.8
OK3	0-15	1063.2	88.2	2044.1	ND	ND	ND	ND	82.8	2042.4	169	36.9	62.9	1048.2	ND	ND	6637.7	3195.5	2125.2	268.8	1048.2	3442.2
	15-30	44.4	62.3	44.3	ND	ND	ND	ND	1050	27.9	99.4	ND	53.1	1025.5	ND	ND	2407	151	1077.9	152.5	1025.5	2255.9
	30-45	6.2	7.7	5.5	ND	ND	ND	ND	51.4	34.6	95.6	ND	749.5	ND	ND	ND	950.4	19.4	86	845.1	ND	931.1
AB1	0-15	44.4	62.3	2044.3	ND	ND	ND	ND	50	27.9	465.2	ND	1053.1	25.5	ND	ND	3772.7	2151	77.9	1518.3	25.5	1621.7
	15-30	ND	ND	5032.3	95.6	ND	58.5	52.9	33.9	4141.5	102.1	ND	1069.1	ND	ND	65.4	10651.4	5127.9	4286.8	1171.2	65.4	5346.6
	30-45	44.9	32	36.8	3057.9	45.8	101.4	2199	36.6	1033.7	ND	ND	ND	ND	ND	ND	6588.1	3217.4	3370.7	ND	ND	1070.3
AB2	0-15	ND	90.2	ND	ND	ND	ND	ND	2054.9	89.8	6076.4	27.8	ND	ND	ND	ND	8338.5	90.2	2144.1	6104.2	ND	8248.3
	15-30	1086.2	3136.1	98.6	26.2	28.1	31.2	46.1	1063.6	28.3	408.4	63.4	118.6	56	ND	ND	6190.8	4375.2	1169.2	590.4	56	1738.3
	30-45	ND	ND	ND	35.8	ND	1025	37.8	122.7	95	2103.2	35.8	66.6	42.7	129.5	936.4	4630.6	35.8	1280.6	2335.1	979.1	2595.5
AB3	0-15	35.6	6.8	43.4	ND	ND	ND	48.6	88.2	2034.5	173.1	ND	999.6	24.6	ND	ND	3454.4	85.8	2171.3	1172.7	24.6	3320
	15-30	ND	13.7	30.7	22.4	931	2037	66.9	17.1	16.5	ND	ND	ND	ND	ND	ND	3134.8	997.7	2137.1	ND	ND	33.6
	30-45	ND	ND	ND	ND	3006	63.7	64	1029.5	1023.3	ND	ND	ND	ND	ND	ND	5186	3005.5	2180.5	ND	ND	2052.8
AB4	0-15	ND	ND	ND	ND	51.8	ND	4025.9	51.3	27.8	42.2	140.2	1096.9	47.7	23.7	155.7	5663.2	51.8	4105	1303	203.4	1429.8
	15-30	ND	ND	ND	ND	ND	ND	32.5	2045.7	39.8	84.9	38.2	5.7	39.9	10.8	68.8	2366.2	ND	2118	139.6	108.7	2265
	30-45	ND	ND	ND	ND	ND	3032	28.7	52.6	6	22	1005.8	10.9	30.8	28.1	52.6	4269.4	ND	3119.1	1066.8	83.4	1156.2
AB5	0-15	55.4	102.9	90.2	ND	25.3	26.4	51	2071.9	28.5	80.5	ND	27.4	44.5	ND	ND	2603.9	273.8	2177.8	107.9	44.5	2252.8
	15-30	ND	11.7	13.3	6.3	35.2	11.9	34	70.2	1011.7	105.8	ND	965.3	ND	ND	ND	2265.4	66.5	1127.8	1071.1	ND	2153
	30-45	ND	ND	ND	ND	55.1	1047	122.2	24.1	28.6	ND	ND	ND	ND	ND	ND	1277.4	55.1	1222.3	ND	ND	52.7

Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phen), Anthracene (Ant), Fluoranthene (Flt), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chry), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(1,2,3-cd)perylene (IndP), Dibenzo(a,h)anthracene (DahA) and Benzo(ghi)perylene (BghiP), R= Rings

Table 4.25: Mean concentrations (µg kg^{-1}) of PAHs in soils three months after the major flooding

DEPTH (cm)	Upstream			Midstream			Downstream		
	0-15	15-30	30-45	0-15	15-30	30-45	0-15	15-30	30-45
Nap	ND	ND	ND	ND	ND	ND	ND	ND	ND
	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acy	66.8±21.6	586.3±709.6	44.4±0.0	975.6±123.9	44.4±0.0	1026.3±1442.6	45.1±9.9	1086.2±0.0	44.9±0.0
	(ND-82)	(ND-1088)	(ND-44.4)	(ND-1063.2)	(ND-44.4)	(ND-2046.3)	(ND-55.4)	(ND-1086.2)	(ND-44.9)
Ace	1187.0±1303.1	64.0±74.9	56.1±10.2	88.2±0.0	68.2±8.3	301.0±472.4	65.6±42.7	1053.8±1803.3	32.0±0.0
	(ND-2520.1)	(ND-116.9)	(ND-62.3)	(ND-88.2)	(ND-74.1)	(7.7-845.9)	(ND-102.9)	(ND-3136.1)	(ND-32.0)
Flu	355.0±497.4	376.7±572.7	41.9±3.5	1540.5±712.2	44.3±0.0	20.2±12.9	726.0±1141.9	1293.7±2492.7	36.8±0.0
	(ND-1087.7)	(ND-1036.9)	(ND-44.3)	(ND-2044.1)	(ND-44.3)	(5.5-29.7)	(ND-2044.3)	(ND-5032.3)	(ND-36.8)
Phen	95.4±100.7	1049.6±1395.5	ND	ND	ND	ND	ND	37.6±39.6	1546.9±2136.9
	(ND-210.8)	(ND-2036.4)	ND	ND	ND	ND	ND	(ND-95.6)	(ND-3057.9)
Ant	107.1±85.6	50.4±21.5	ND	ND	ND	ND	38.6±18.7	331.4±519.3	1035.6±1706.4
	(ND-203.0)	(ND-65.6)	ND	ND	ND	ND	(ND-51.8)	(ND-931.0)	(ND-3006)
Flt	90.8±58.3	78.8±57.6	ND	ND	ND	ND	26.4±0.0	534.7±1001.7	1053.8±1204.3
	(ND-132)	(ND-119.5)	ND	ND	ND	ND	(ND-26.4)		(63.7-3032)
Pyr	397.0±559	30.1±5.5	1568.8±2070.2	ND	ND	ND	1375.2±2295.6	46.5±14.2	490.3±955.9
	(ND-1039.2)	(ND-34.0)	(ND-3032.6)	ND	ND	ND	(ND-4025.9)	(32.5-66.9)	(28.7-2199)
BaA	1073.2±1730.4	52.0±24.9	968.0±991.6	1068.4±1393.8	558.8±694.7	50.7±42.9	863.1±1095.5	646.1±899.3	253.1±435.7
	(ND-3071.2)	(ND-70.2)	(ND-2052.6)	(ND-2054.0)	(ND-1050.0)	(7.5-93.3)	(50.0-2071.9)	(17.1-2045.7)	(24.1-1029.5)
Chry	50.5±31.1	1330.5±1522.8	33.0±22.3	1038.4±1419.9	683.8±572.5	37.9±6.0	441.7±890.8	1047.6±1781.2	437.3±540.7
	(24.4-78.0)	(ND-3116.8)	(ND-51.0)	(ND-2042.4)	(27.2-1083.2)	(34.2-44.8)	(27.8-2034.5)	(16.5-4141.5)	(6.0-1033.7)
BbF	285.6±442.5	1058.0±1987.3	48.4±50.3	97.2±101.5	75.6±33.7	722.0±1144.5	1367.5±2637.6	175.3±155.7	1062.6±1471.6
	(63.0-1076.4)	(ND-4038.6)	(ND-118.4)	(ND-169.0)	(ND-99.4)	(27.4-2043.0)	(42.2-6076.4)	(ND-408.4)	(ND-2103.2)
BkF	1049.7±1383.3	33.4±0.6	1018.0±1436.5	534.8±704.1	1018.2±120.5	161.1±201.2	84.0±79.5	50.8±17.8	520.8±685.9
	(ND-2027.8)	(ND-33.8)	(ND-2033.7)	(ND-1032.7)	(ND-1103.4)	(ND-303.3)	(ND-140.2)	(ND-63.4)	(ND-1005.8)
BaP	541.6±992.7	3059.8±1421.9	58.1±7.1	62.9±0.0	53.1±0.0	749.5±0.0	794.3±512.8	539.7±554.9	38.8±39.4
	(ND-2030.6)	(ND-4065.2)	(ND-63.1)	(ND-62.9)	(ND-53.1)	(ND-749.5)	(ND-1096.9)	(ND-1069.1)	(ND-66.6)
IndP	2098.5±0.0	ND	25.5±0.0	1048.2±0.0	1025.5±0.0	ND	35.6±12.2	48.0±11.4	36.8±8.4
	(ND-2098.5)	ND	(ND-25.5)	(ND-1048.2)	(ND-1025.5)	ND	(ND-47.7)	(ND-56.0)	(ND-42.7)
DahA	41.2±0.0	ND	ND	ND	ND	ND	23.7±0.0	10.8±0.0	78.8±71.7
	(ND-41.2)	ND	ND	ND	ND	ND	(ND-23.7)	(ND-10.8)	(ND-129.5)
BghiP	45.1±12.2	ND	ND	ND	ND	ND	155.7±0.0	67.1±2.4	494.5±624.9
	(ND-53.7)	ND	ND	ND	ND	ND	(ND-155.7)	(ND-68.8)	(ND-936.4)
Total	3935.4±2046.9	4168.7±2302.0	1968.2±1035.3	3903.0±2445.8	2219.8±2100.9	2173.2±2100.9	4766.5±2288.5	4921.7±3578.4	4390.3±1951.0
	(1470.3-5659.6)	(2124.9-7739.6)	(811.8-3417.4)	(1924.9-6637.7)	(2067.0-2407.0)	(950.4-4599.1)	(2603.9-8338.5)	(2366.2-10651.4)	(1277.4-6588.1)
3R	1381.7±1263.8	1543.5±1141.6	74.1±52.1	2560.2±898.4	112.6±1059.4	1005.4±1059.4	530.5±910.0	2641.8±2484.7	1578.5±1772.3
	(76.5-3096.4)	(ND-2277.3)	(ND-151.0)	(ND-3195.5)	(ND-151.0)	(19.4-2125.4)	(51.8-2151.0)	(ND-5127.9)	(ND-3217.4
4R	968.9±1246.7	1424.0±1571.0	1234.7±1365.9	2106.8±26.0	1056.3±37.7	88.6±37.7	2135.2±1424.4	2167.8±1281.8	2234.6±1001.4
	(144.1-3095.6)	(ND-3340.5)	(49.5-3191.5)	(ND-2125.2)	(1007.8-1083.2)	(52.3-127.5)	(77.9-4105.0)	(1127.8-4286.8)	(1222.3-3370.7)
5R	1146.9±1373.4	2604.5±1940.6	586.4±986.1	663.5±558.1	746.9±1167.8	1079.2±1167.8	2041.2±2335.5	743.1±475.5	1701.0±896.8
	(128.8-3104.2)	(ND-4072.4)	(ND-2061.5)	(ND-1058.1)	(152.5-1103.4)	(46.2-2346.3)	(107.9-6104.2)	(139.6-1171.2)	(ND-2335.1)
6R	1094.4±1471.7	ND	25.5±0.0	1048.2±0.0	1025.5±0.0	ND	74.5±86.4	76.7±28.1	531.3±633.4
	(ND-2135)	ND	(ND-25.5)	(ND-1048.2)	(ND-1025.5)	ND	(ND-203.4)	(ND-108.7)	(ND-979.1)
∑PAH7c	2261.0±2123.9	3974.1±2443.9	1351.8±947	3294.4±209.1	2145.0±98.4	1167.8±1205.2	3374.5±2822.6	2307.3±1920.7	1385.5±979.5
	(164-5189.2)	(ND-4174.4)	(ND-2205.6)	(ND-3442.2)	(2068.0-2255.9)	(98.5-2473.8)	(1429.8-8248.3)	(33.6-5346.6)	(52.7-2595.5)

Table 4.26: Comparison of PAH in urban soil with different soils from areas worldwide.

Location	Soil type	Concentration ranged (μgkg^{-1})	Reference
Nigeria (River Niger)	Floodplain	811.8-10651.4	This study[a]
Estonia	Rural, urban and Industrial soils	50-22,200	Trapido (1999)
China (Hong Kong)	Rural and urban soils	30-170	Zhang *et al.* (2006)
Switzerland	Pasture grassland and urban soils	50-600	Bucheli *et al.* (2004)
Germany (Rhine River)	Alluvial soils	20-3600	Gocht *et al.* (2001)
China (Beijing)	Rural and suburban soils	20-3900	Mai *et al.* (2005)
China (Huanghuai plain)	Agricultural soils	15.7-1247.6	Yang *et al.* (2012)
America (Miami Florida)	Urban soils	251-2364	Banger *et al.* (2010)
Korea (Ansan City)	Industrial soils	109.93-178.92	Imran *et al.* (2006)
Nigeria (Niger Delta)	Soil vicinity oil installation	24-120	Sojinu *et al.* (2010)
Spain (Sevilla)	Agriculture and urban soils	89.5-4004.2	Morello *et al.* (2008)
Nigeria (Niger Delta)	Urban soils	182-433	Olajire *et al.* (2005)
India (Kuruksheta)	Urban Roadside soils	16.1- 2538.0	Kumar *et al.*(2012)
Nigeria(Lagos)	Mangrove fresh soil	65.5 188.0	Sojinu *et al.*(2012)
United kingdom	Urban soil	2700 $\pm$ 500	Meharg *et al.* (1998)
China (Beijing)	Urban soil	467-5470	Li *et al.* (2006)
Germany (Mosel and Saar River)	Floodplain	100-81500	Pies *et al.* (2007)
Canada	Floodplain	0.016-12.0	Sartori *et al.* (2010)
China (Guangzhou)	Vegetable soils	42-3077	Chen *et al.* (2005)

The high concentrations of PAHs in soils of the floodplain could be associated with the flooding events in which wastes containing polycyclic aromatic hydrocarbons were carried by the flood from dumpsites, industries, oil installations among others into the River Niger and consequently transferred into the floodplains. However, Nganje *et al.* (2012) reported $\sum$16 PAHs concentrations in the ranged of 0.02 to 97,954 µg kg^{-1} in soils in the vicinity of fuel-oil spillage from a tank farm distribution facility, Esuk Utan, Calabar municipality, Nigeria. Edwards (1983) reported that the typical endogenous PAHs in soils are in the range of 1-10 µg kg^{-1}, and most of them are derived from oil seeps, bitumen, coal, plant debris, forest and prairie fires (Yunker *et al.,* 2002). The concentrations of PAHs in these sites were higher than the background value (Edwards, 1983). A good correlation has been shown between PAH concentration and TOC for highly contaminated soils (Wilcke, 2000; Agarwal *et al.,* 2009). However, a few studies also reported the presence of poor correlation (Zhang *et al.,* 2006; Jian *et al.,* 2009; Yang *et al.,* 2012). In this study, there was no significant relationship between $\sum$16 PAHs concentration and TOC ($R^2 = 0.0467$). The lack of significant relationship between PAHs and soil physicochemical parameters indicates continuous input of fresh contamination or the presence of different sources (Nam *et al.,* 2003; Yang *et al.,* 2012).

According to Malizewkwa-Kordybach (1996) classification, soil with PAH concentrations less than 200 µg kg^{-1} (not contaminated); 200-600 µg kg^{-1} (weakly contaminated); 600-1000 (contaminated) and greater than 1,000 µg kg^{-1} (heavily contaminated). Based on the above classification, the concentrations of PAH observed in these sites were within the heavily contaminated category. The concentrations of $\sum$16 PAHs in these soils were higher than the PAHs target value of 1000 µg kg^{-1} set by the Dutch Government.

4.14   Occurrence and profiles of PAHs in the soil three months after the major flooding

The occurrence patterns and profiles of PAHs in these soils are shown in Figure 12 (a-c). The occurrence patterns and profiles varied with sites and depths. In these soil profiles, the distribution patterns of PAHs followed the order $4 > 5 > 3 > 6 > 2$. The four and five ring PAHs were the dominant PAH compounds in the soil profiles. In this study, the PAHs with 4-6 rings comprised the majority of PAHs in the soil samples (72.3 % on average) while PAHs with 2-3 rings only accounted for 25.4 % of $\sum 16$ PAHs on average. This could be due to the higher biodegradation rate of soil bacterial in utilizing low ring than high ring PAHs as source of energy (Li *et al.,* 2010). The concentrations of 2-ring PAH compound (naphthalene) were below the limit of quantification in all sites and depths. This could be due to its weak association with organic matter, thus increasing its losses by volatilization (Li *et al.,* 2010). Another reason for dominance of HMW PAH is due to the volatility and K_{ow}, the LMW PAHs might have a higher proportion in the air-phase than the HMW PAH (Augusto *et al.,* 2009) and would be subject to longer distance "multiple-hop" transport to more remote areas from the emission source. The HMW PAHs are more likely associated with air-borne particulate that undergo single-hoop transport behaviour committing more of the HMW PAH to accumulate in soil close to emission sources, thereby leading to the high soil concentration in these sites(Nam *et al.,* 2008; Wang *et al.,* 2007).
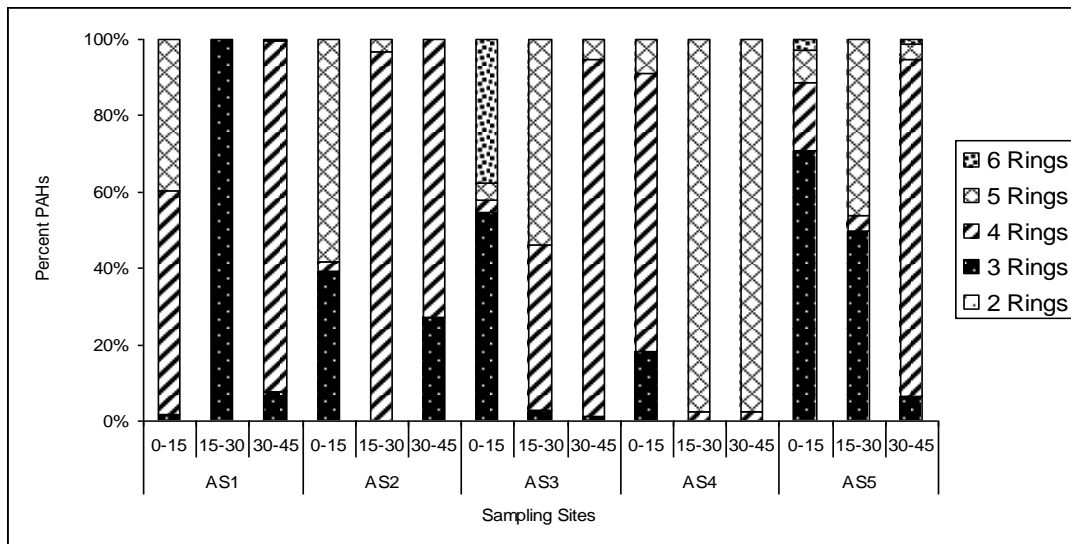
(12a)
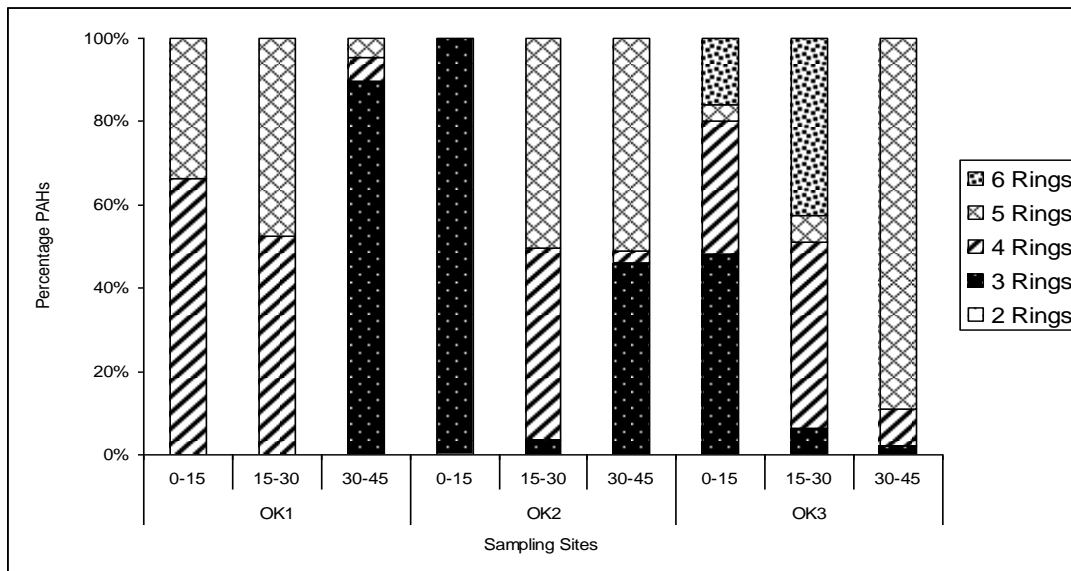
(12b)
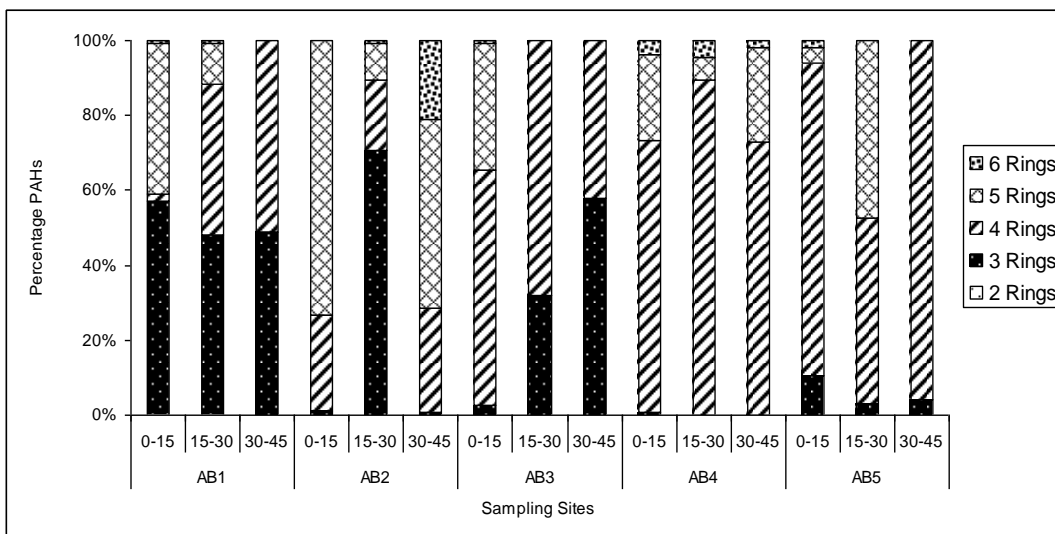
(12c)

Figure 12: PAHs profiles in floodplain soils three months after the major flooding

The concentration of Σ3-ring PAHs (Acy + Ace + Flu + Phe + Ant) ranged from 51.8 to 3195.5 µg kg^{-1}, 66.5 to 5127.9 µg kg^{-1} and 19.4 to 3217.4 µg kg^{-1} for 0-15 cm, 15-30 cm and 30-45 cm respectively. The 3-ring PAHs constituted 0.9 to 100 %, 2.9 to 100 % and 0.8 to 89.8 % of the Σ16 PAHs at 0-15 cm, 15-30 cm and 30-45 cm depth respectively. The concentrations of the 3-ring PAHs showed a decrease with respect to depth in all sites except for sites OK1, OK2, AB1 and AB3. Fluorene (Flu) was the dominant 3-ring PAH compound in these sites in terms of concentrations and frequency of occurrence. Higher concentrations of the 3-ring PAHs were at the 0-15 cm soil depth of sites AS3, AS5, OK2, OK3 and AB1; 15-30 cm depth of sites AS1, AS5 and AB2 and 30-45 cm depth of sites OK1 and AB3 than 4-,5- and 6-ring PAHs.

The concentrations of Σ4-ringed PAHs (Flt + Pyr+ BaA + Chry) ranged from 77.9 to 4105 µg kg^{-1}, 102 to 4286.8 µg kg^{-1} and 49.5 to 3370.7 µg kg^{-1} for 0-15 cm, 15-30 cm and 30-45 cm respectively. The 4-ring PAHs constituted 2.1 to 83.6%, 2.4 to 96.9% and 2.3 to 95.7 % of the Σ16 PAHs in the 0-15 cm, 15-30 cm and 30-45 cm depth respectively. The concentration of the 4-ringed PAHs decreased with depth except at sites AS3, AS5, AB1 and AB3. Chrysene (Chry) was the dominant 4-ring PAHs, in terms of concentration and frequency of occurrence.

The concentration of Σ5-ring PAHs (BbF + BkF + BaP + DahA) in all sites and depth ranged from 2.9 to 6104.2 µg kg^{-1}. The 5-ringed PAH constituted 3.1 to 97.7 % of the Σ16 PAHs in these soil profiles. The 5-ring PAHs decreased with depth in all sites except AS4, OK2 and OK3. Benzo(b)fluoranthene (BbF) was the dominant 5-ring PAH compound in terms of concentration and frequency of occurrence. Benzo(a)pyrene (BaP) was detected in 50% of the soil samples at concentrations in the range of 5.7 to 4065.2 µg kg^{-1}.

The concentration of Σ6-ring PAHs (IndP + BghiP) ranged from 24.6 to 2135 µg kg^{-1}, 56 to 1025.5 µg kg^{-1} and 25.5 to 979.1 µg kg^{-1} for 0-15 cm, 15-30 cm and 30-45 cm which

constituted 0.7 to 37.7%, 0.6 to 42.6% and 1.1 to 21.1% of the $\Sigma16$ PAHs respectively. The concentrations of the 6-ring PAHs showed a decrease with the increasing depth of the soil profile except at site AS2. Indeno (1,2,3-cd)perylene (IndP) was the most abundant 6-ring PAH compound in these soils in terms of concentration and frequency of occurrence.

4.15 Health Risk Assessment of PAHs in soil three months after the major flooding

In this study, the summation of the 7 carcinogenic PAHs concentrations ($\sum PAH_{7c}$) ranged from not detected to 8248.3 $\mu g\ kg^{-1}$ in all site and depths. The carcinogenic PAHs constituted 4.1 to 98.9 % of the total PAHs in these sites. The BaP_{TEQ} and BaP_{MEQ} concentrations calculated for $\sum PAH_{7c}$ are presented in Table 4.27. The concentrations of BaP_{TEQ} and BaP_{MEQ} ranged from below detection limit to 4086 $\mu g\ kg^{-1}$ and below detection limit to 4150 $\mu g\ kg^{-1}$ respectively for all sites and depth. The BaP_{TEQ} and BaP_{MEQ} concentrations obtained in this study were found to be higher than levels reported in the literature (Orecchio, 2010; Olawoyin *et al.,* 2012; Yang *et al.,* 2012). The following PAH compounds: BaA, BbF and BaP have significant impact on the BaP_{TEQ} and BaP_{MEQ} values. In this study, the BaP_{TEQ} in 72 % of the soil samples were higher than the Dutch target value of 33 $\mu g\ kg^{-1}$ (Netherlands Ministry of Housing and Environment, 1994) while the BaP_{TEQ} in 54 % of the soil samples were higher than the Method B clean-up level of 137 $\mu g\ kg^{-1}$ (Washington State Department of Ecology, 2007).

Table 4.27: BaP$_{TEQ}$ and BaP$_{MEQ}$ concentrations (µg kg^{-1}) for the floodplain soils three months after major flooding

	DEPTH (cm)	BaA	Chry	BbF	BkF	BaP	IndP	DahA	BaP$_{TEQ}$	BaA	Chry	BbF	BkF	BaP	IndP	DahA	BaP$_{MEQ}$
AS1	0-15	307	0.02	6.3	ND	2031	ND	ND	2344	252	0.41	15.8	ND	2031	ND	ND	2299
	15-30	ND	ND	ND	ND	ND	ND	ND	0	ND	ND	ND	ND	ND	ND	ND	0
	30-45	74.4	0	0.07	0.02	ND	ND	ND	74.5	61.0	0.06	0.18	0.24	ND	ND	ND	61.5
AS2	0-15	5.43	0.09	108	20.3	ND	ND	ND	133	4.45	1.53	269	223	ND	ND	ND	498
	15-30	ND	2.08	3.31	0.33	ND	ND	ND	5.7	ND	35.3	8.28	3.63	ND	ND	ND	47.2
	30-45	ND	ND	ND	ND	ND	ND	ND	0	ND	ND	ND	ND	ND	ND	ND	0
AS3	0-15	9.41	0.03	8.8	0.72	39.1	210	41.2	309	7.72	0.43	22	7.87	39.1	651	12.0	740
	15-30	7.02	3.12	10.6	ND	4065	ND	ND	4086	5.76	53.0	26.5	ND	4065	ND	ND	4150
	30-45	10.8	0.05	11.8	ND	63.1	ND	ND	86	8.85	0.87	29.6	ND	63.1	ND	ND	102
AS4	0-15	ND	0.04	8.56	ND	43.2	ND	ND	52	ND	0.6	21.4	ND	43.2	ND	ND	65.2
	15-30	6.22	0.04	404	0.34	ND	ND	ND	410	5.1	0.68	1010	3.72	ND	ND	ND	1019
	30-45	ND	0.05	2.78	20.3	ND	ND	ND	23	ND	0.84	6.95	224	ND	ND	ND	232
AS5	0-15	ND	0.08	11.5	ND	53.4	ND	ND	65	ND	1.33	28.7	ND	53.4	ND	ND	83
	15-30	2.37	0.09	5.43	ND	2054	ND	ND	2062	1.94	1.5	13.58	ND	2054	ND	ND	2071
	30-45	205	0.03	4.65	ND	53.1	2.55	ND	266	168	0.47	11.6	ND	53.1	7.91	ND	241
OK1	0-15	205	0.03	2.54	10.3	ND	ND	ND	218	168	0.58	6.35	114	ND	ND	ND	289
	15-30	ND	1.08	5.18	9.33	ND	ND	ND	16	ND	18.4	13.0	103	ND	ND	ND	134
	30-45	0.75	0.04	2.74	0.19	ND	ND	ND	4	0.62	0.76	6.85	2.07	ND	ND	ND	10.3
OK2	0-15	ND	ND	ND	ND	ND	ND	ND	0	ND	ND	ND	ND	ND	ND	ND	0
	15-30	6.76	0.94	ND	11.0	ND	ND	ND	19	5.54	16.0	ND	121	ND	ND	ND	143
	30-45	9.33	0.03	204	3.03	ND	ND	ND	217	7.65	0.58	511	33	ND	ND	ND	552
OK3	0-15	8.28	2.04	16.9	0.37	62.9	105	ND	195	6.79	34.7	42.3	4.06	62.9	325	ND	476
	15-30	105	0.03	9.94	ND	53.1	103	ND	271	86.1	0.47	24.9	ND	53.1	317.91	ND	482
	30-45	5.14	0.03	9.56	ND	750	ND	ND	764	4.21	0.59	23.9	ND	750	ND	ND	778
AB1	0-15	5.00	0.03	46.5	ND	1053	2.55	ND	1107	4.1	0.47	116	ND	1053	7.91	ND	1182
	15-30	3.39	4.14	10.2	ND	1069	ND	ND	1087	2.78	70.4	26	ND	1069	ND	ND	1168
	30-45	3.66	1.03	ND	ND	ND	ND	ND	4.7	3.0	17.6	ND	ND	ND	ND	ND	20.6
AB2	0-15	205	0.09	608	0.28	ND	ND	ND	813	168	1.53	1519	3.06	ND	ND	ND	1692
	15-30	106	0.03	40.8	0.63	119	5.6	ND	272	87.2	0.48	102	6.97	119	17.4	ND	333
	30-45	12.3	0.1	210	0.36	66.6	4.27	130	423	10.1	1.62	526	3.94	66.6	13.2	37.6	659
AB3	0-15	8.82	2.03	17.3	ND	1000	2.46	ND	1030	7.23	34.6	43.3	ND	1000	7.63	ND	1092
	15-30	1.71	0.02	ND	ND	ND	ND	ND	1.7	1.4	0.28	ND	ND	ND	ND	ND	1.68
	30-45	103	1.02	ND	ND	ND	ND	ND	104	84.4	17.4	ND	ND	ND	ND	ND	102
AB4	0-15	5.13	0.03	4.22	1.4	1097	4.77	23.7	1136	4.21	0.47	10.6	15.4	1097	14.8	6.87	1149
	15-30	205	0.04	8.49	0.38	5.7	3.99	10.8	234	168	0.68	21.2	4.2	5.7	12.37	3.13	215
	30-45	5.26	0.01	2.2	10.1	10.9	3.08	28.1	60	4.31	0.1	5.5	111	10.9	9.55	8.15	149
AB5	0-15	207	0.03	8.05	ND	27.4	4.45	ND	247	170	0.48	20.1	ND	27.4	13.8	ND	232
	15-30	7.02	1.01	10.6	ND	965	ND	ND	984	5.76	17.2	26.5	ND	965	ND	ND	1015
	30-45	2.41	0.03	ND	ND	ND	ND	ND	2.4	1.98	0.49	ND	ND	ND	ND	ND	2.46

4.16   Incremental Lifetime Cancer Risk (ILCR) three months after the major flooding

The computed ILCR values for adults and children are shown in Table 4.28. The ILCR levels of the soils three months after the major flooding via soil ingestion, inhalation and dermal contacts ranged from 2.00×10^{-5} to 3.94×10^{-2}, 4.99×10^{-14} to 1.10×10^{-10} and 6.05×10^{-6} to 1.43×10^{-3} respectively for children and 1.04×10^{-5} to 2.46×10^{-2}, 2.50×10^{-13} to 5.48×10^{-10} and 5.38×10^{-6} to 1.27×10^{-2}, respectively for adults. The observed inhalation cancer risks for PAHs were low when compared with other exposure routes (ingestion and dermal contact). However, total cancer risk ranged from 2.61×10^{-5} to 5.37×10^{-2} with a mean of 6.45×10^{-3} and 1.58×10^{-5} to 3.73×10^{-2} with a mean of 4.48×10^{-3} for children and adults respectively. The ILCR values obtained indicates that there are 6450 and 4480 chances in a million population to develop the risk of cancer for children and adults respectively considering samples of soils three months after major flooding event.

Table 4.28: Incremental Life Cancer Risk due to PAHs exposure in the floodplain soil

	DEPTH (cm)	CHILD				ADULT			
		ILCRIng	ILCRInh	ILCRDerm	Total Cancer Risk	ILCRIng	ILCRInh	ILCRDerm	Total Cancer Risk
AS1	0-15	2.26E-02	6.24E-11	8.21E-03	3.08E-02	1.41E-02	3.12E-10	7.31E-03	2.14E-02
	15-30	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	30-45	7.20E-04	1.99E-12	2.61E-04	9.81E-04	4.48E-04	9.94E-12	2.32E-04	6.80E-04
AS2	0-15	1.29E-03	8.43E-12	4.68E-04	1.76E-03	8.03E-04	4.22E-11	4.16E-04	1.22E-03
	15-30	6.00E-05	7.29E-13	2.00E-05	8.00E-05	3.44E-05	3.64E-12	1.78E-05	5.22E-05
	30-45	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
AS3	0-15	2.98E-03	8.51E-12	1.08E-03	4.06E-03	1.86E-03	4.25E-11	9.63E-04	2.82E-03
	15-30	3.94E-02	1.10E-10	1.43E-02	5.37E-02	2.46E-02	5.48E-10	1.27E-02	3.73E-02
	30-45	8.30E-04	2.30E-12	3.01E-04	1.13E-03	5.16E-04	1.15E-11	2.67E-04	7.83E-04
AS4	0-15	5.00E-04	1.39E-12	1.81E-04	6.81E-04	3.12E-04	6.94E-12	1.61E-04	4.73E-04
	15-30	3.96E-03	1.10E-11	1.44E-03	5.40E-03	2.47E-03	5.51E-11	1.28E-03	3.75E-03
	30-45	2.20E-04	5.50E-12	8.12E-05	3.01E-04	1.39E-04	2.75E-11	7.22E-05	2.11E-04
AS5	0-15	6.30E-04	1.75E-12	2.28E-04	8.58E-04	3.91E-04	8.74E-12	2.02E-04	5.93E-04
	15-30	1.99E-02	5.49E-11	7.23E-03	2.71E-02	1.24E-02	2.75E-10	6.43E-03	1.88E-02
	30-45	2.56E-03	7.08E-12	9.31E-04	3.49E-03	1.60E-03	3.54E-11	8.28E-04	2.43E-03
OK1	0-15	2.10E-03	8.29E-12	7.65E-04	2.87E-03	1.31E-03	4.15E-11	6.80E-04	1.99E-03
	15-30	1.50E-04	2.91E-12	5.46E-05	2.05E-04	9.38E-05	1.45E-11	4.86E-05	1.42E-04
	30-45	4.00E-05	1.55E-13	1.30E-05	5.30E-05	2.24E-05	7.74E-13	1.16E-05	3.40E-05
OK2	0-15	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	15-30	1.80E-04	3.37E-12	6.56E-05	2.46E-04	1.13E-04	1.68E-11	5.84E-05	1.71E-04
	30-45	2.09E-03	6.50E-12	7.59E-04	2.85E-03	1.30E-03	3.25E-11	6.75E-04	1.98E-03
OK3	0-15	1.88E-03	5.78E-12	6.84E-04	2.56E-03	1.18E-03	2.89E-11	6.09E-04	1.79E-03
	15-30	2.61E-03	7.21E-12	9.48E-04	3.56E-03	1.63E-03	3.61E-11	8.44E-04	2.47E-03
	30-45	7.36E-03	2.04E-11	2.68E-03	1.00E-02	4.60E-03	1.02E-10	2.38E-03	6.98E-03
AB1	0-15	1.07E-02	2.95E-11	3.88E-03	1.46E-02	6.66E-03	1.47E-10	3.45E-03	1.01E-02
	15-30	1.05E-02	2.99E-11	3.81E-03	1.43E-02	6.54E-03	1.50E-10	3.39E-03	9.93E-03
	30-45	5.00E-05	3.73E-13	1.64E-05	6.64E-05	2.82E-05	1.86E-12	1.46E-05	4.28E-05
AB2	0-15	7.84E-03	2.17E-11	2.85E-03	1.07E-02	4.89E-03	1.09E-10	2.54E-03	7.43E-03
	15-30	2.62E-03	7.40E-12	9.53E-04	3.57E-03	1.64E-03	3.70E-11	8.48E-04	2.49E-03
	30-45	4.08E-03	1.17E-11	1.48E-03	5.56E-03	2.55E-03	5.85E-11	1.32E-03	3.87E-03
AB3	0-15	9.93E-03	2.79E-11	3.61E-03	1.35E-02	6.20E-03	1.40E-10	3.21E-03	9.41E-03
	15-30	2.00E-05	4.99E-14	6.05E-06	2.61E-05	1.04E-05	2.50E-13	5.38E-06	1.58E-05
	30-45	1.00E-03	3.01E-12	3.64E-04	1.36E-03	6.25E-04	1.51E-11	3.24E-04	9.49E-04
AB4	0-15	1.10E-02	3.06E-11	3.98E-03	1.50E-02	6.83E-03	1.53E-10	3.54E-03	1.04E-02
	15-30	2.25E-03	6.36E-12	8.20E-04	3.07E-03	1.41E-03	3.18E-11	7.29E-04	2.14E-03
	30-45	5.70E-04	4.07E-12	2.09E-04	7.79E-04	3.59E-04	2.03E-11	1.86E-04	5.45E-04
AB5	0-15	2.38E-03	6.59E-12	8.66E-04	3.25E-03	1.49E-03	3.29E-11	7.70E-04	2.26E-03
	15-30	9.48E-03	2.64E-11	3.45E-03	1.29E-02	5.92E-03	1.32E-10	3.07E-03	8.99E-03
	30-45	2.00E-05	7.18E-14	8.54E-06	2.85E-05	1.47E-05	3.59E-13	7.60E-06	2.23E-05
	HIGHEST	3.94E-02	1.10E-10	1.43E-02	5.37E-02	2.46E-02	5.48E-10	1.27E-02	3.73E-02
	LOWEST	2.00E-05	4.99E-14	6.05E-06	2.61E-05	1.04E-05	2.50E-13	5.38E-06	1.58E-05
	MEAN	4.73E-03	1.37E-11	1.72E-03	6.45E-03	2.95E-03	6.87E-11	1.53E-03	4.48E-03

The chances of cancer risk for children cases via ingestion and dermal contact were found to be higher than for adults. This raise concern for possible adverse health effects on children. Polycyclic aromatic hydrocarbons (PAHs) carcinogen sensitivity in children are higher, making them the most susceptible group due to high physical contact with soil and dust from peer play times and a smaller body weight (Olawoyin *et al.,* 2012). The cancer risk via inhalation for adults was higher than that of children. This could be due to the longer exposure duration (ED) for adults. The results obtained for cancer risk assessment in this study are comparable to previous studies of health risk from PAHs exposure in soil from Niger Delta of Nigeria (Olawoyin *et al.,* 2012), contaminated soils from Hong Kong (Man *et al.,* 2013) and soils from metropolitan areas in China (Peng *et al.,* 2011; Wang *et al.,* 2011).

The risk based action levels set by USEPA (2010b) for exposure scenarios are based on a potentially acceptable value of 10^{-6} as the target excess cancer risk (one in million have the chance of developing cancer). Risk management and remediation plans are necessary for sites with cancer risk levels exceeding 10^{-6}. Comparing the results obtained in this study with the potentially acceptable value (10^{-6}), the potential risks for children and adults cases were greater than the standard value of potentially acceptable risk in the soil samples, signifying a high potential human carcinogenic risk in the study area.

4.17   PAH Interrelationships three months after the major flooding

The results of PAH interrelationship are shown in Table 4.30. It is known that when two compounds have a common source, there is more likely to be a correlation between their concentrations (Essumang *et al.,* 2009; Gilbert *et al.,* 2006)

At 0.01 levels, significant positive correlations were observed between individual PAHs. Flt/Phen (0.964), Flt/Ant (0.997) and BghiP/DahA (0.987) have the highest PAH interrelationships at the 0-15 cm, 15-30 cm and 30-45 cm depth respectively while strong

positive correlation was observed between the following pairs; IndP/Ant (0.758), DahA/Ant (0.862), DahA/IndP (0.748), BghiP/Pyr (0.890) at 0-15 cm depth; DahA/BaA (0.801) at 15-30 cm depth; DahA/IndP (0.804) and BghiP/IndP (0.735) at 30-45 cm depth.

At 0.05 levels, significant positive correlations were also observed between individual PAHs with IndP/Ace, BghiP/DahA and BghiP/BbF recording the highest correlation coefficients of 0.640, 0.697 and 0.683 at 0-15 cm, 15-30 cm and 30-45 cm depths respectively. Other pairs that also showed strong positive correlation at the 0-15 cm depth were Flu/Ace (0.617), Ant/Acy (0.609), Flt/Ant (0.567), BkF/Ace (0.505), DahA/Ace (0.602) and BghiP/DahA (0.584). At the 15-30 cm depth, Ace/Acy (0.668), Pyr/Ant (0.587), Pyr/Flt (0.588), Chry/Flu (0.651), BaP/Chry (0.518), BghiP/Flu (0.625) and BghiP/BaA (0.500) were positively correlated while at 30-45 cm depth, Pyr/Phen (0.538), Chry/Phen (0.679), Chry/Ant (0.681), BbF/Acy (0.661), IndP/Flt (0.619) and DahA/BbF (0.657) were positively correlated.

Table 4.29: Correlation analysis of PAHs three months after the major flooding

	pH	EC	TOC	CEC	Acy	Ace	Flu	Phen	Ant	Flt	Pyr	BaA	Chry	BbF	BkF	BaP	IndP	DahA	BghiP
0-15 cm depth																			
pH	1.000	0.388	-0.388	-0.052	-0.166	-0.147	0.001	0.804**	0.344	0.805**	-0.314	0.031	0.078	-0.231	-0.245	-0.196	0.065	-0.062	-0.046
EC		1.000	-1.000	-0.084	0.207	0.149	0.248	0.231	-0.046	0.250	-0.895	0.124	0.068	-0.035	0.062	-0.390	0.114	-0.439	-0.845
TOC			1.000	0.084	-0.207	-0.149	-0.248	-0.232	0.046	-0.251	0.895**	-0.123	-0.068	0.035	-0.062	0.390	-0.114	0.439	0.844**
CEC				1.000	-0.279	-0.187	-0.286	-0.224	-0.190	-0.330	0.091	0.327	0.031	0.407	0.142	-0.114	-0.097	-0.136	-0.117
Acy					1.000	-0.151	0.617*	-0.172	-0.192	-0.183	-0.175	-0.297	0.455	-0.171	-0.202	-0.270	0.270	-0.140	-0.203
Ace						1.000	-0.211	0.027	0.609*	0.118	-0.168	-0.251	-0.171	-0.014	0.505*	-0.272	0.640*	0.602*	-0.010
Flu							1.000	0.175	-0.118	0.144	-0.240	-0.422	0.298	-0.187	-0.289	-0.053	0.175	-0.197	-0.142
Phen								1.000	0.472	0.964**	-0.078	-0.265	-0.154	-0.133	-0.165	-0.226	0.074	0.071	0.247
Ant									1.000	0.567*	0.130	-0.286	-0.238	-0.195	-0.193	-0.206	0.758**	0.862**	0.396
Flt										1.000	-0.128	-0.187	-0.177	-0.151	-0.182	-0.256	0.185	0.173	0.245
Pyr											1.000	-0.241	-0.158	-0.142	-0.098	0.260	-0.132	0.407	0.890**
BaA												1.000	-0.261	0.303	-0.022	0.281	-0.247	-0.254	-0.287
Chry													1.000	-0.106	-0.159	0.066	0.195	-0.183	-0.191
BbF														1.000	0.019	-0.203	-0.142	-0.149	-0.163
BkF															1.000	-0.258	-0.144	-0.113	-0.120
BaP																1.000	-0.226	0.006	0.207
IndP																	1.000	0.748	0.065
DahA																		1.000	0.584*
BghiP																			1.000
15-30 cm depth																			
pH	1.000	0.354	-0.354	0.030	-0.321	-0.212	-0.087	0.743**	0.295	0.266	0.249	-0.221	-0.108	0.224	-0.302	0.535*	0.069	-0.197	-0.179
EC		1.000	-1.000	0.149	-0.565	-0.564	-0.028	0.144	0.276	0.264	-0.108	-0.358	-0.021	0.364	-0.295	-0.102	0.178	-0.230	-0.157
TOC			1.000	-0.149	0.565*	0.564*	0.028	-0.144	-0.276	-0.264	0.108	0.358	0.021	-0.364	0.295	0.102	-0.178	0.230	0.157
CEC				1.000	-0.099	0.218	-0.085	0.051	-0.161	-0.173	0.019	0.571*	-0.373	0.462	-0.024	-0.342	0.124	0.487	0.360
Acy					1.000	0.668*	0.018	-0.073	-0.127	-0.136	0.004	0.131	-0.334	-0.084	-0.175	-0.200	-0.067	-0.132	-0.194
Ace						1.000	-0.094	-0.083	-0.069	-0.080	0.295	0.337	-0.198	-0.003	-0.077	-0.105	-0.019	-0.092	-0.135
Flu							1.000	-0.048	-0.116	-0.081	0.332	-0.176	0.651*	-0.104	-0.169	0.077	-0.105	-0.105	0.625*
Phen								1.000	-0.019	-0.069	0.080	-0.162	-0.154	-0.100	-0.149	0.383	-0.101	-0.093	-0.100
Ant									1.000	0.997**	0.587*	-0.167	-0.216	-0.120	-0.159	-0.105	-0.107	-0.099	-0.146
Flt										1.000	0.588*	-0.167	-0.172	-0.117	-0.152	-0.102	-0.103	-0.095	-0.117
Pyr											1.000	0.123	0.210	-0.249	-0.418	0.287	-0.263	0.125	0.370
BaA												1.000	-0.360	-0.092	-0.187	-0.244	0.383	0.801**	0.500*
Chry													1.000	-0.210	-0.003	0.518*	-0.230	-0.206	0.350
BbF														1.000	-0.129	-0.154	-0.083	-0.084	-0.120
BkF															1.000	-0.256	-0.144	-0.104	-0.176
BaP																1.000	-0.160	-0.158	-0.043
IndP																	1.000	-0.049	-0.103
DahA																		1.000	0.697*
BghiP																			1.000
30-45 cm depth																			
pH	1.000	0.121	-0.121	-0.233	-0.029	-0.109	0.141	-0.087	-0.053	-0.278	0.171	0.528*	-0.078	-0.057	0.168	0.174	0.140	-0.124	-0.084
EC		1.000	-1.000	-0.032	-0.221	-0.023	0.082	-0.040	0.630*	-0.358	-0.132	0.584*	0.432	-0.276	-0.122	0.223	-0.059	-0.174	-0.158
TOC			1.000	0.032	0.221	0.023	-0.082	0.040	-0.630	0.358	0.132	-0.584	-0.432	0.276	0.122	-0.223	0.059	0.174	0.158

	CEC	Acy	Ace	Flu	Phen	Ant	Flt	Pyr	BaA	Chry	BbF	BkF	BaP	IndP	DahA	BghiP
CEC	1.000	-0.087	0.398	0.225	0.435	-0.138	0.049	-0.225	-0.210	0.239	0.227	0.220	-0.226	0.270	0.419	0.425
Acy		1.000	-0.049	0.282	-0.065	-0.090	-0.145	-0.123	-0.104	-0.111	0.661*	0.015	-0.107	-0.150	-0.106	-0.093
Ace			1.000	0.234	-0.070	-0.114	-0.183	-0.099	-0.105	-0.125	-0.117	-0.155	-0.120	-0.166	-0.134	-0.117
Flu				1.000	0.378	-0.231	-0.367	0.034	0.268	0.095	0.009	-0.291	-0.150	-0.078	-0.281	-0.246
Phen					1.000	-0.071	-0.102	0.538*	-0.148	0.679*	-0.127	-0.132	-0.106	-0.145	-0.090	-0.077
Ant						1.000	-0.115	-0.105	0.340	0.681*	-0.140	-0.135	-0.110	-0.159	-0.105	-0.091
Flt							1.000	-0.172	-0.215	-0.170	0.050	0.270	-0.130	0.619	0.406	0.264
Pyr								1.000	-0.191	0.329	-0.164	-0.201	-0.087	-0.227	-0.145	-0.127
BaA									1.000	0.134	-0.166	-0.237	-0.101	0.242	-0.133	-0.112
Chry										1.000	-0.161	-0.190	-0.151	-0.203	-0.105	-0.082
BbF											1.000	-0.072	-0.055	0.419	0.657*	0.683*
BkF												1.000	-0.157	0.061	-0.032	-0.092
BaP													1.000	-0.072	-0.028	-0.014
IndP														1.000	0.804**	0.735**
DahA															1.000	0.987**
BghiP																1.000

*Pearson Correlation is significant at the 0.05 level (1 tailed)

** Pearson Correlation is significant at the 0.01 level (1 tailed)

Naphthalene (Nap), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phen), Anthracene (Ant), Fluoranthene (Flt), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chry), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(1,2,3-cd)perylene (IndP), Dibenzo(a,h)anthracene (DahA) and Benzo(ghi)perylene (BghiP).

4.18   Source estimates from diagnostic ratios of PAHs three months after the major flooding

The ratios of specific PAH compounds have been used to distinguished natural and anthropogenic sources (Soclo *et al.,* 2000; Kavouras *et al.,* 2001; Yunker *et al.,* 2002; Doong and Lin, 2004; Essumang *et al.,* 2009; Wang *et al.,* 2011; Semlali *et al.,* 2012). Based on the PAH isomer pair ratio measurement compiled by Yunker *et al.,* (2002), Flt/(Flt + Pyr) < 0.4 implies petroleum origins, 0.4–0.5 implies petroleum combustion and >0.5 implies combustion origins of coal and biomass; Ant/(Ant + Phen) ratio < 0.10 are seen in petroleum input whereas value > 0.1 are characteristic of combustion process; BaA (Chry + BaA) ratio < 0.2 indicates petroleum, 0.2 – 0.35 petroleum combustion and > 0.35 indicates combustion of coal and biomass and IndP/(IndP + BghiP) ratio < 0.2 were from petroleum origin input, between 0.2 and 0.5 were from petroleum combustion and > 0.5 were typical of combustion of coal, wood and grassed matter. In this study, the Flt/(Flt + Pyr), Ant/(Ant + Phen), BaA/(Chry + BaA), IndP/(IndP + BghiP), LMW/HMW ratios ranged from 0.04 to 0.99, 0.01 to 1.0, 0.01 to 1.0, 0.04 to 0.98 and 0.01 to 8.85 respectively (Table 4.31) which indicate that the sources of PAHs in these floodplains were due to fossil fuel, combustion of wood and traffic emissions. The corresponding cross plot of the isomer ratios corroborate these facts (Figures 13-15).

Table 4.30: Source ratios of PAHs in floodplain soils at different depths

	AS1	AS2	AS3	AS4	AS5	OK1	OK2	OK3	AB1	AB2	AB3	AB4	AB5
0-15 cm													
Phen/Ant	0.00	0.00	0.25	0.66	2.63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Flt/(Ft+Pyr)	0.00	0.00	0.72	0.00	0.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.34
Ant/(Ant+Phen)	0.00	0.00	0.80	0.60	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BaP/BghiP	0.00	0.00	1.07	0.00	0.99	0.00	0.00	0.00	0.00	0.00	0.00	7.04	0.00
BaA/(BaA+Chry)	0.99	0.38	0.79	0.00	0.00	0.98	0.00	0.04	0.64	0.96	0.04	0.65	0.99
IndP/(IndP+BghiP)	0.00	0.00	0.98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.00
Fluo/Pyr	0.00	0.00	2.51	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.52
LMW/HMW	0.01	0.64	1.21	0.22	2.44	0.00	0.00	0.93	1.33	0.01	0.03	0.03	0.12
15-30 cm													
Phen/Ant	0.00	0.00	1.78	0.00	31.04	0.00	0.00	0.00	0.00	0.93	0.02	0.00	0.18
Flt/(Flt+Pyr)	0.00	0.00	0.78	0.00	0.59	0.00	0.00	0.00	0.53	0.40	0.97	0.00	0.26
Ant/(Ant+Phen)	0.00	0.00	0.36	0.00	0.03	0.00	0.00	0.00	0.00	0.52	0.98	0.00	0.85
BaP/BghiP	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	16.35	0.00	0.00	0.08	0.00
BaA/(BaA+Chry)	0.00	0.00	0.02	0.61	0.21	0.00	0.07	0.97	0.01	0.97	0.51	0.98	0.06
IndP/(IndP+BghiP)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.37	0.00
Fluo/Pyr	0.00	0.00	3.51	0.00	1.45	0.00	0.00	0.00	1.11	0.68	30.44	0.00	0.35
LMW/HMW	0.00	0.00	0.03	0.00	1.00	0.00	0.04	0.07	0.93	2.41	0.47	0.00	0.03
30-45 cm													
Phen/Ant	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	66.77	0.00	0.00	0.00	0.00
Flt/(Flt+Pyr)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.96	0.50	0.99	0.90
Ant/(Ant+Phen)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	1.00	0.00	1.00
BaP/BghiP	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.21	0.00
BaA/(BaA+Chry)	1.00	0.00	0.68	0.00	0.99	0.14	0.73	0.60	0.03	0.56	0.50	0.90	0.46
IndP/(IndP+BghiP)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.37	0.00
Fluo/Pyr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	27.12	1.00	105.64	8.57
LMW/HMW	0.08	0.38	0.01	0.00	0.07	8.85	0.86	0.02	0.95	0.01	1.38	0.00	0.05
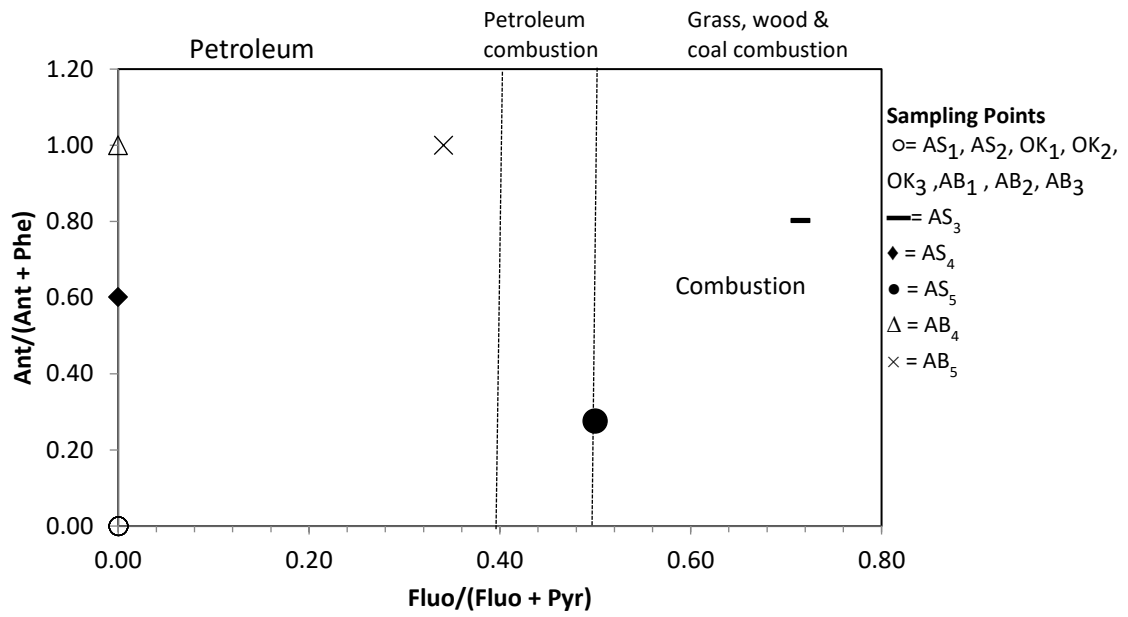
(a)
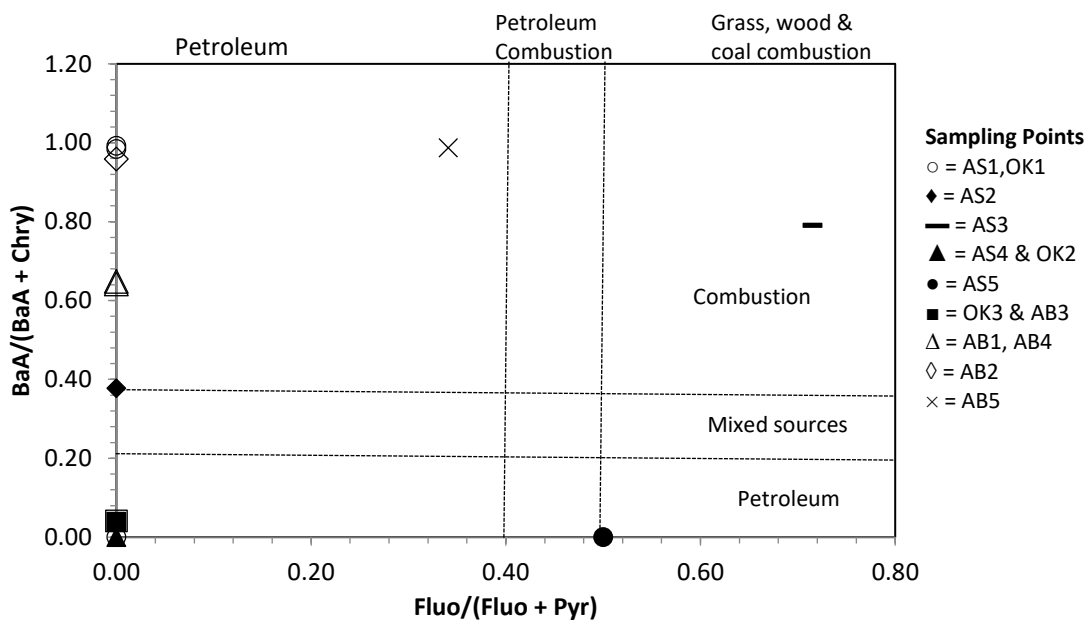
(b)
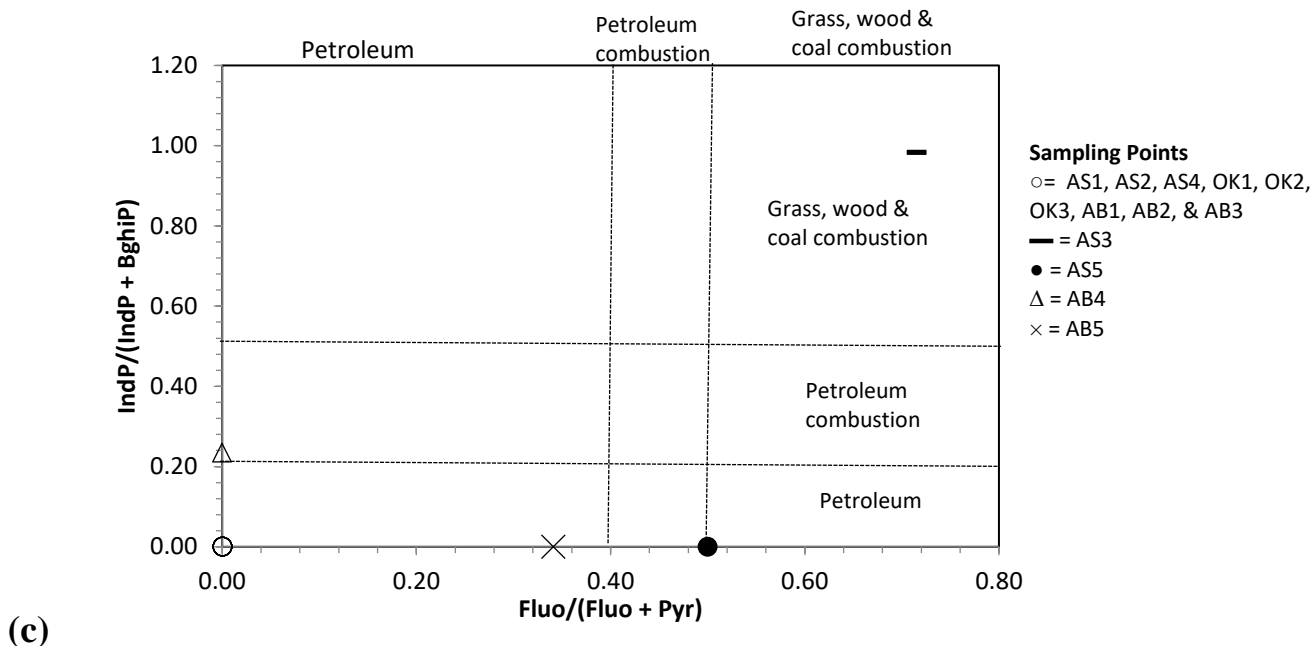
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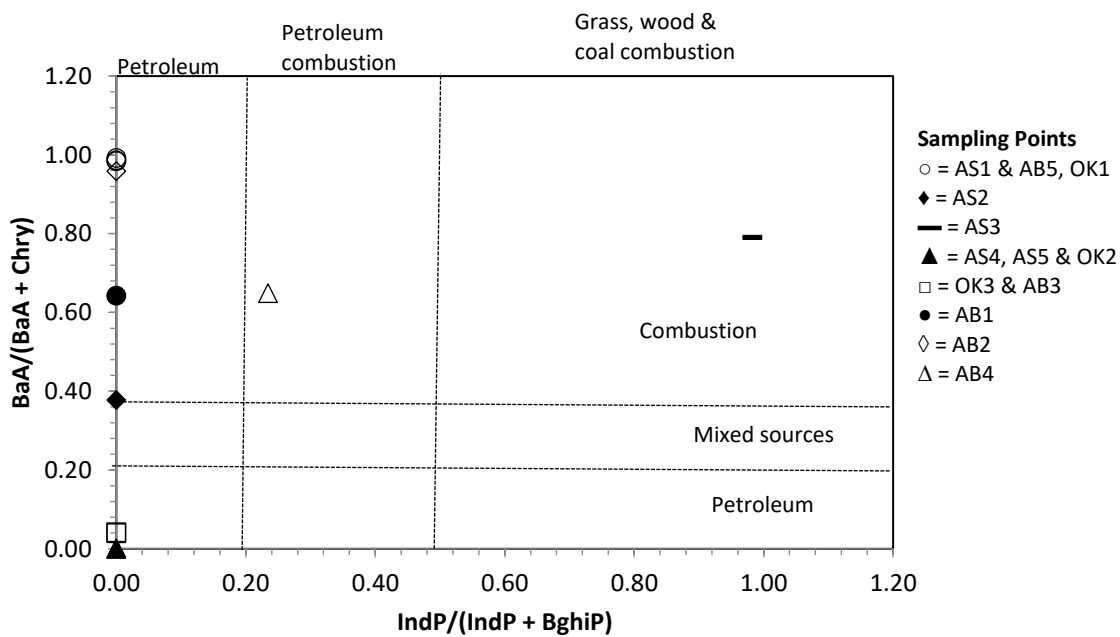
(d)

Figure 13: Plots of PAH isomer pair ratios for source identification at 0-15 cm depth: (a) Ant/(Ant + Phen) versus Flt/(Flt + Pyr); (b) BaA/(BaA + Chry) versus Fluo/(Fluo + Pyr); (c) IndP/(IndP + BghiP) versus Flt/(Flt + Pyr); (d) BaA/(BaA + Chry) versus IndP/(IndP + BghiP)
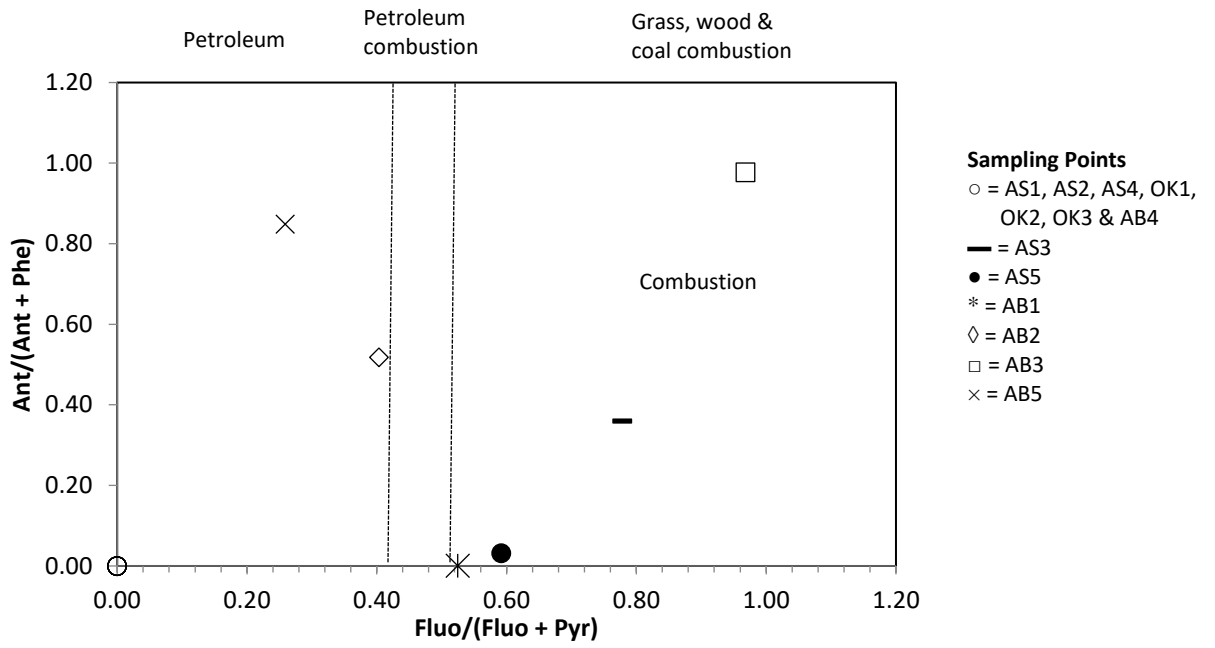
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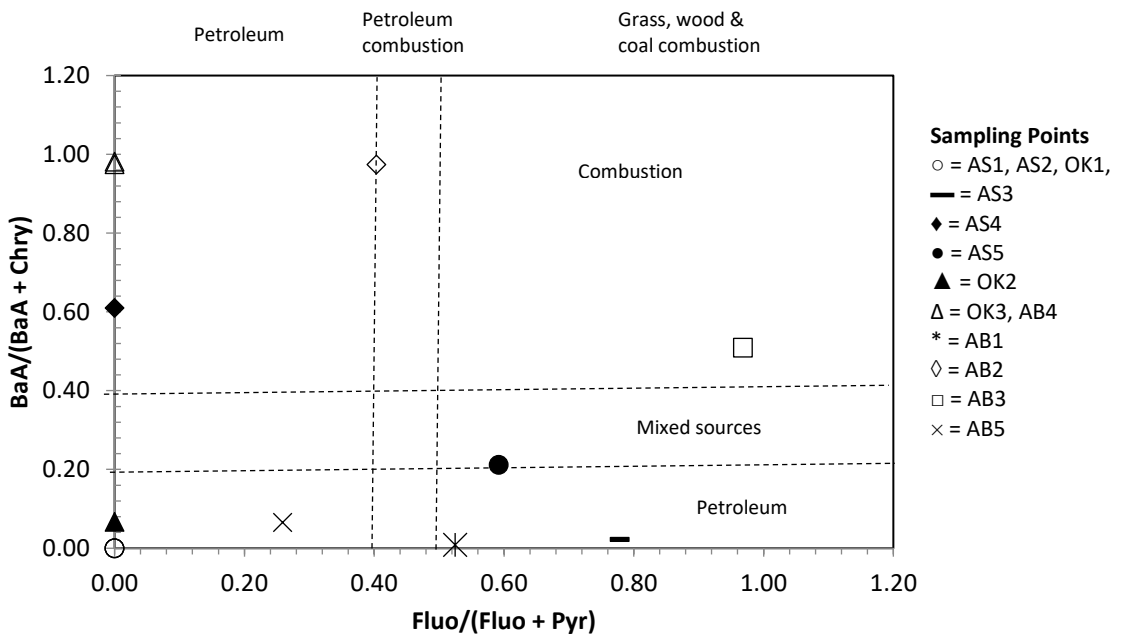
(b)
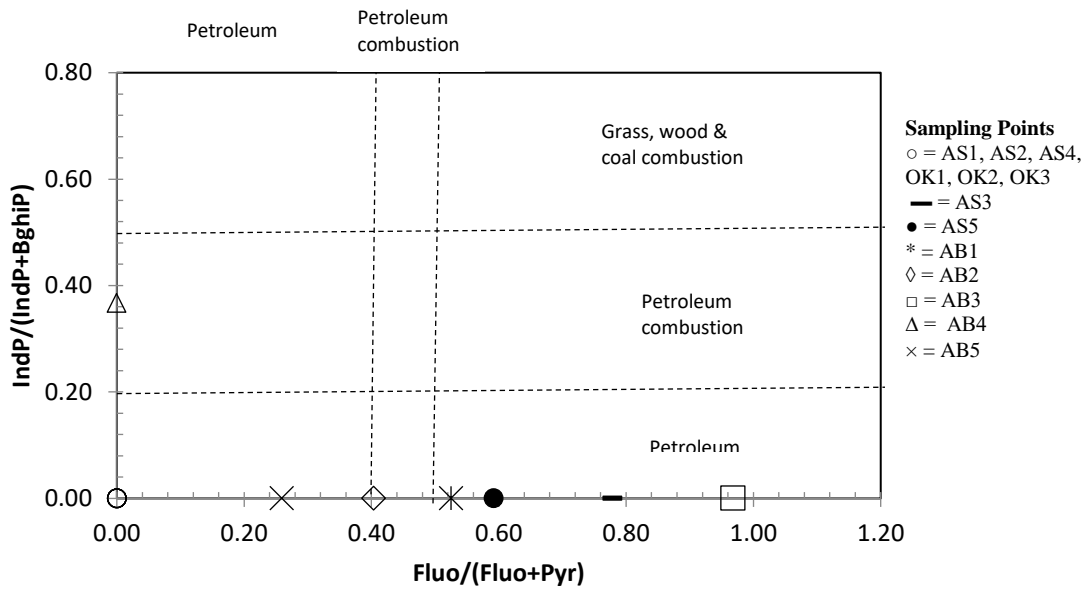
(c)
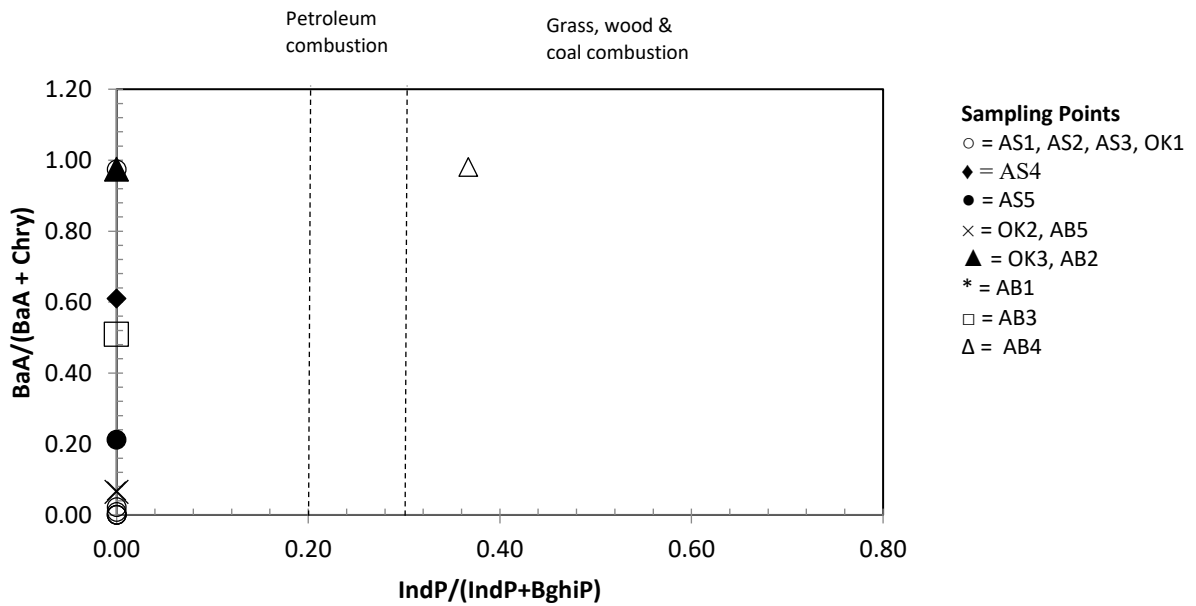
(d)

Figure 14: Plots of PAH isomer pair ratios for source identification at 15-30 cm depth: (a) Ant/(Ant + Phen) versus Flt/(Flt + Pyr); (b) BaA/(BaA + Chry) versus Fluo/(Fluo + Pyr); (c) IndP/(IndP + BghiP) versus Flt/(Flt + Pyr); (d) BaA/(BaA + Chry) versus IndP/(IndP + BghiP)
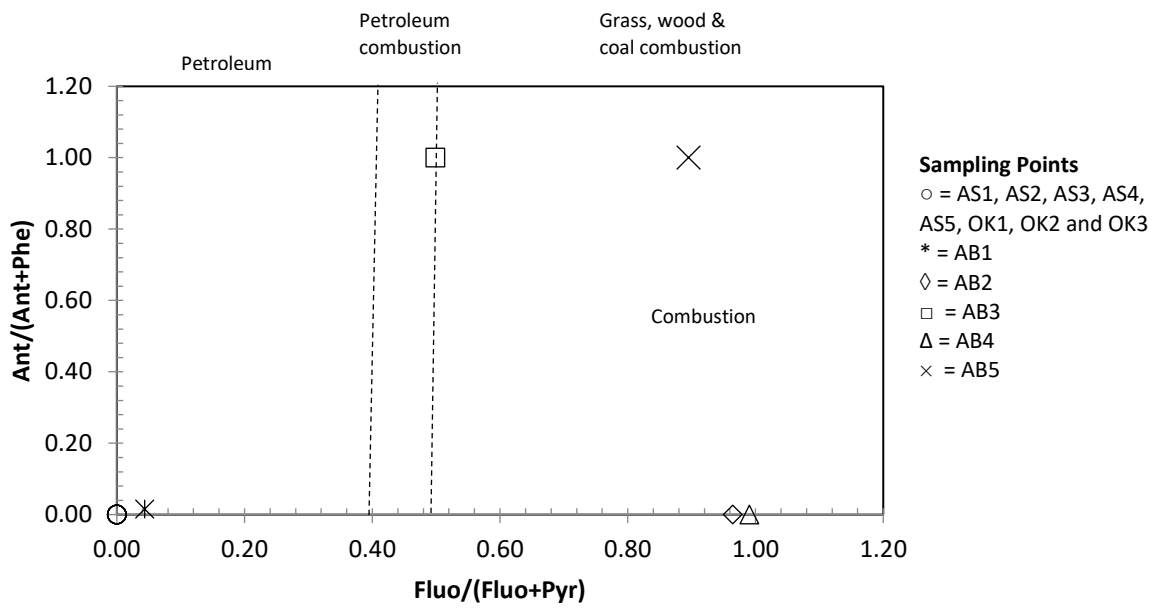
(a)
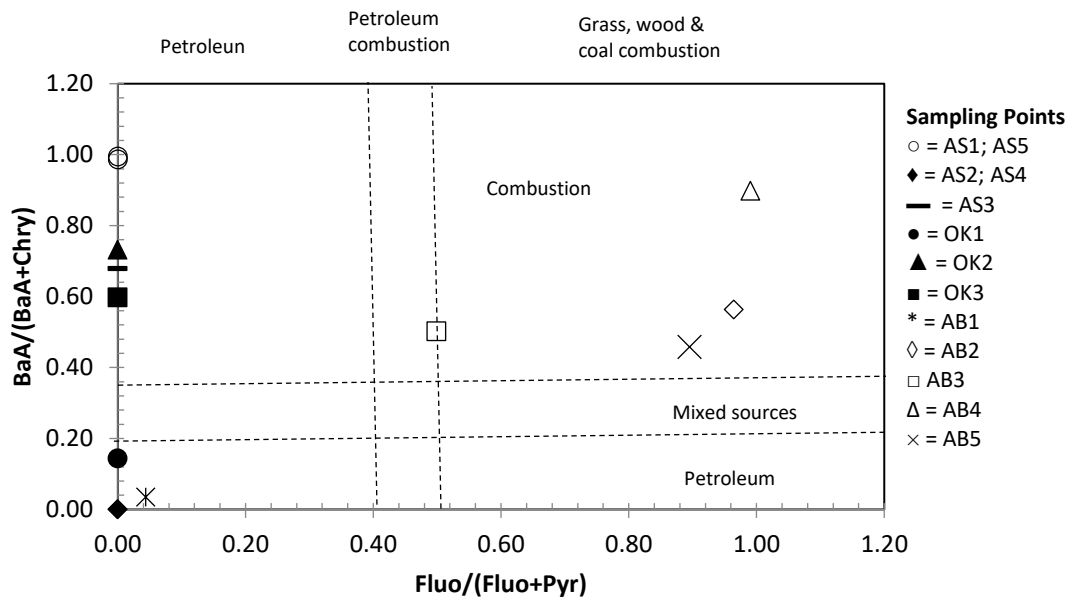
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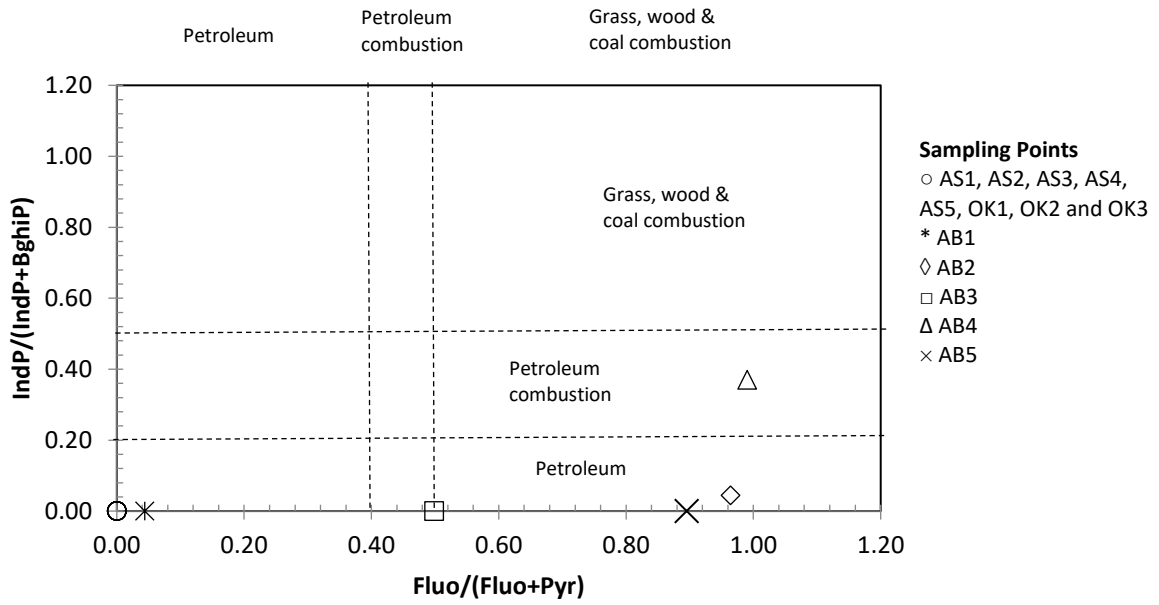
(c)
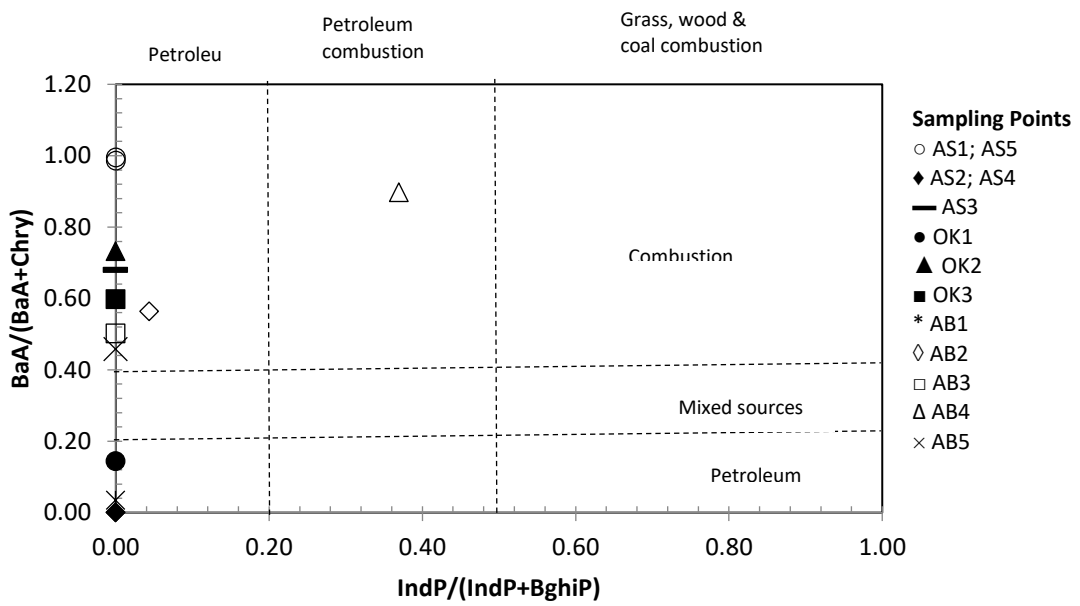
(d)

Figure 15: Plots of PAH isomer pair ratios for source identification at 30-45 cm depth: (a) Ant/(Ant + Phen) versus Flt/(Flt + Pyr); (b) BaA/(BaA + Chry) versus Fluo/(Fluo + Pyr); (c) IndP/(IndP + BghiP) versus Flt/(Flt + Pyr); (d) BaA/(BaA + Chry) versus IndP/(IndP + BghiP)

4.19   Source estimates from principal component analysis (PCA) three months after the major flooding

Principal component analysis (PCA) has been used as a tool to identify pollution sources (Guo *et al.,* 2003; Nava-Martinez *et al.,* 2011; Garcia-Flores *et al.,* 2013). The purpose of PCA is to represent the total variability of the original PAH data with a minimum number of factors. By critically evaluating the factor loadings, an estimate of the chemical source responsible for each factor can be made (Larsen and Baker, 2003; Liu *et al.,* 2009). The results of PCA for PAHs in the soils are presented in Table 4.32 and Figures 16 (a-c).

For 0–15cm depth, three factors were identified which accounts for 59.04% of the variability in the data. Factor 1 which explains 26.2 % of the total variance was characterized by high loadings of Ant, IndP and DahA and moderate loadings of Ace, Phen and Flt. Ant is a product of wood and coke combustion (Jenkins *et al.,* 1996; Yunker *et al.,* 2002) while IndP and DahA are characteristic emission from traffic sources (Fraser *et al.,* 1997; Simcik *et al.,* 1999; Yang *et al.,* 2012). Ace and Phen are products of wood combustion (Jenkins *et al.,* 1996) while Flt is a product of coal combustion (Larsen and Baker, 2003). Thus, Factor 1 indicated that the combustion of fossil fuels, grass, and wood were the major sources of PAHs in these soils. Factor 2 accounted for 17.89% of the total variance, and was characterized by high loadings in Acy and Flu and moderate loadings of Chry. Acy and Flu are products from low temperature pyrogenic processes such as wood combustion (Yang *et al.,* 2012; Jenkins *et al.,* 1996). Chry on the other hand is a product of diesel and natural gas combustion (Khalili *et al.,* 1995). Consequently, Factor 2 indicates that wood, diesel and natural gas combustion are the sources of PAHs. Factor 3 which explained 14.9% of total variance is characterized by high loadings of Pyr and BghiP and moderate loading of BaP. Pyr and BaP are markers for coal combustions (Larsen and Baker, 2003) while BghiP is a marker for traffic emissions (Simcik *et al.,* 1999). Thus from Factor 3, the source of PAHs is attributed to coal combustion.

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Table 4.31: PCA Factor loadings after Varimax with Kaiser Normalization Rotation for PAHs in floodplain soils three months after the major flooding

PAHs	0-15 cm depth			15-30 cm depth			30-45 cm depth		
	Component			Component			Component		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
Acy		.776		-.436					.748
Ace	.660	-.403	-.449	-.427					
Flu		.838		.681		.328		.396	.603
Phen	.538							.781	
Ant	.945				.917			.371	-.507
Flt	.615				.914		.496	-.337	-.375
Pyr			.853		.845			.553	
BaA	-.500	-.454		-.485		.829			
Chry		.619		.904				.851	-.357
BbF		-.316					.710		.584
BkF		-.466	-.426		-.379			-.480	
BaP	-.338		.558	.606					
IndP	.778			-.331			.853		
DahA	.797					.829	.974		
BghiP	.399		.820	.374		.877	.945		
Variance %	**26.21**	**17.89**	**14.94**	**18.74**	**17.64**	**16.91**	**24.90**	**14.40**	**13.00**
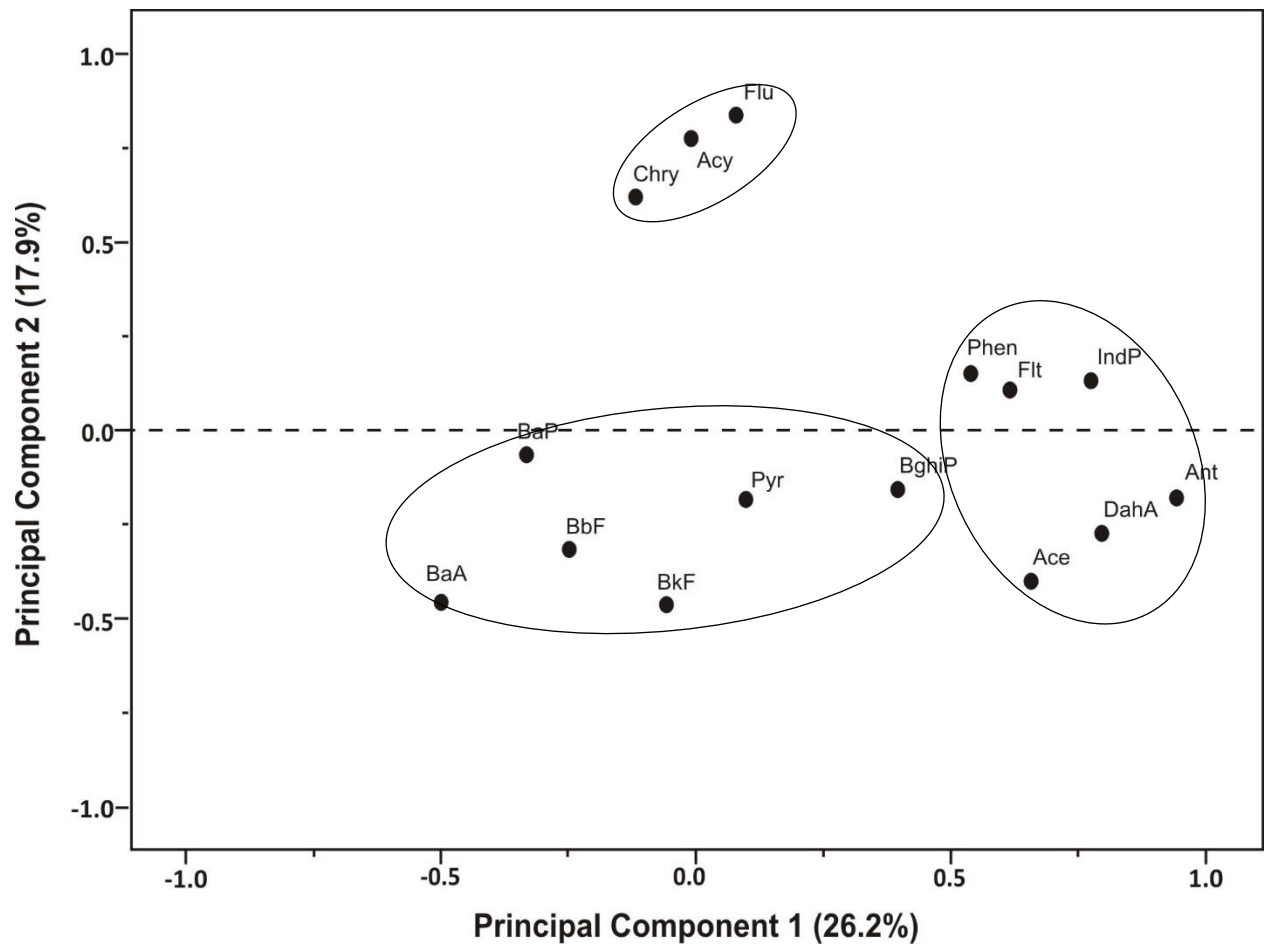
(16a)
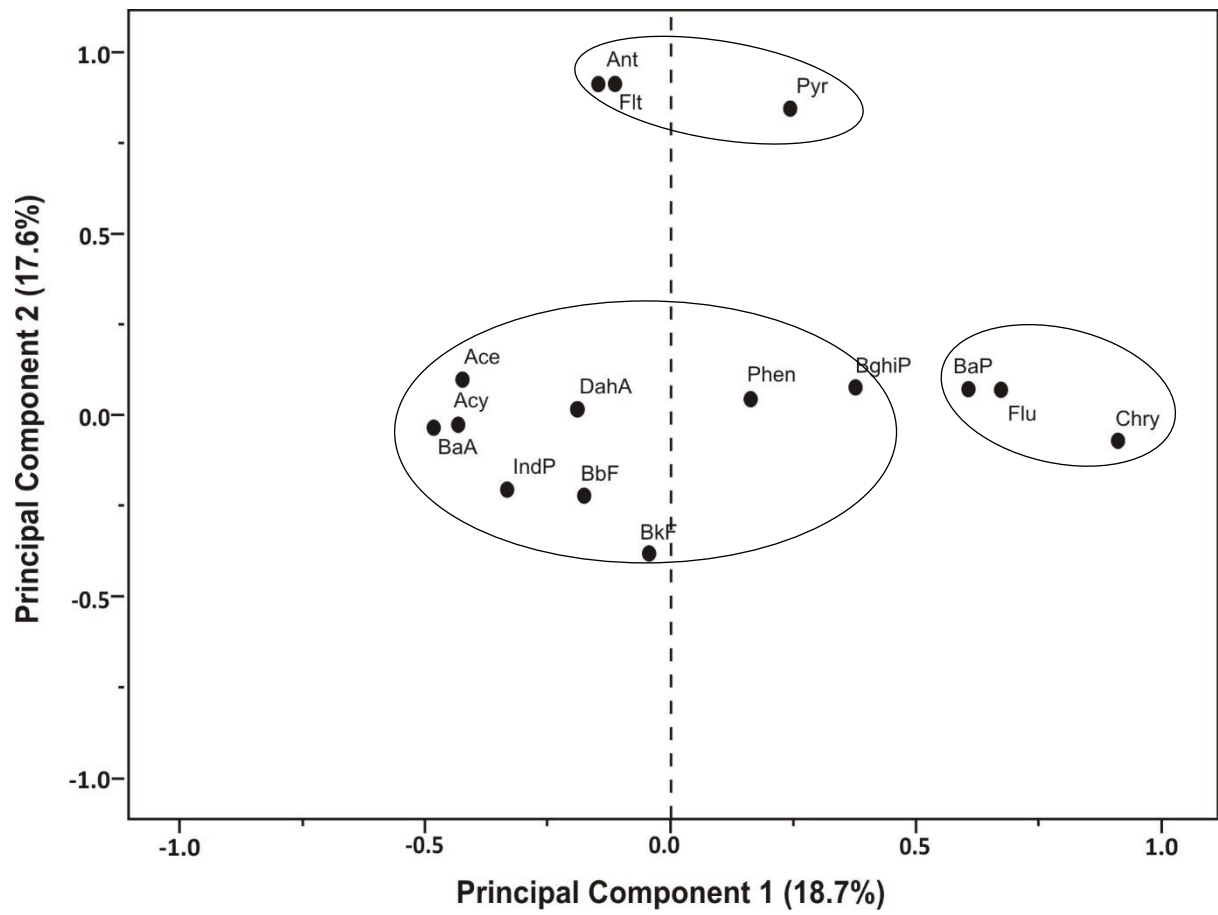
(16b)
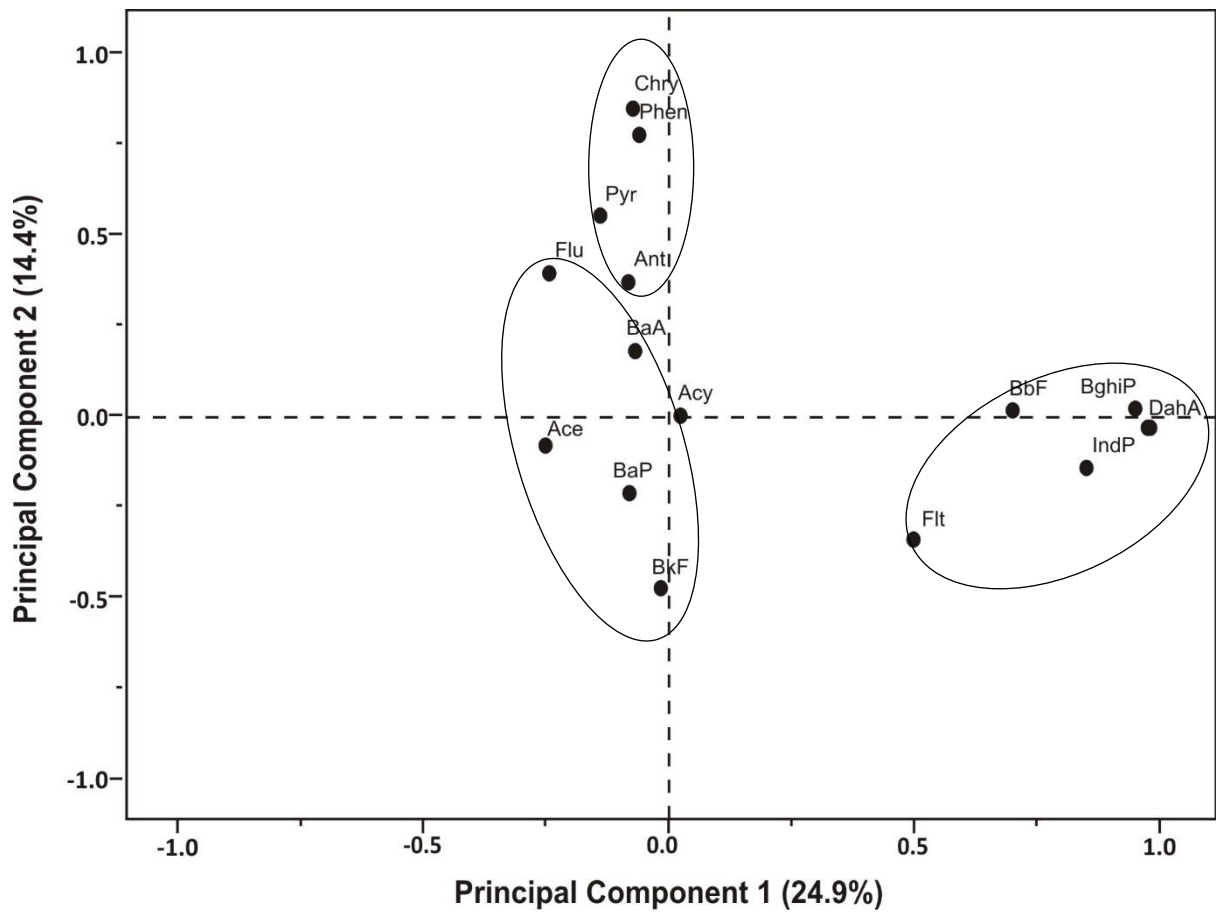
(16c)

Figure 16: The loading plot of PCA of PAHs of the floodplain soils three months after the major flooding.

For 15–30 cm depth, three component factors were also identified accounting for 53.2% of the variability in the data at this depth. Factor 1 explains 18.7% of the total variance and was characterized by high loading of Chry and moderate loading of Flu and BaP. Chry often resulted from the combustions of both diesel and natural gas (Khalili *et al.,* 1995; Yang *et al.,* 2012). Flu is an important indicator of coal combustion (Larsen and Baker, 2003). Therefore, Factor 1 indicates that fossil fuels combustion was the major source of PAHs. Factor 2 explains 17.6 % of the total variance. This factor was characterized by high loading of Ant, Flt and Pyr. These are products of wood, and coal combustion (Jenkins *et al.,* 1996; Larsen and Baker, 2003; Yang *et al.,* 2012). Thus factor 2 also showed that fossil fuel combustion was the major source of PAHs in these sites and depth. Factor 3 accounts for 16.91% of the total variance and was characterized by high loadings of BaA, DahA and BghiP. BaA is usually a marker for diesel combustion (Khalili *et al.,* 1995) and DahA and BghiP are the characteristic emission from traffic sources (Simcik *et al.,* 1999; Fraser *et al.,* 1997). Therefore, Factor 3 indicated that diesel combustion and traffic emissions are the sources of PAHs.

For 30 – 45 cm depth, three component factors were again identified accounting for 52.3% of the variability in the data at this depth. The first factor explained 24.9% of the total variances and was characterized by high loadings of IndP, DahA and BghiP and moderate loadings of BbF. IndP, DahA and BghiP are the characteristic emissions from traffic sources (Yang *et al.,* 2012; Simcik *et al.,* 1999; Fraser et al, 1997) while BbF is a component of fossil fuel associated with their combustion (Yang *et al.,* 2012; Kavouras *et al.,* 2001). Consequently, PC1 reflected that traffic emission is the major source of PAHs. The second factor is responsible for 14.4 % of the total variances and was characterized by high loadings of Phen and Chry and moderate loading of Pyr. Phen, Chry and Pyr are typical markers for coal and coke combustion (Yang *et al.,* 2012; Larsen and Baker, 2003; Yunker *et al.,* 2002). Thus, PC2 indicated that coal (fossil fuels) combustion was the major source of PAHs. The third factor

account for 13.0 % of the total variances and was characterized by moderate loadings of Acy, Flu and BbF. Acy is a typical product of low temperature pyrogenic processes such as wood combustion (Jenkins *et al.,* 1996). Flu and BbF are markers for coke oven and fossil fuels combustion, respectively (Yanker *et al.,* 2002; Kavouras *et al.,* 2001; Yang *et al.,* 2012). Therefore, PC3 indicated that combustion of grass, wood and coal were the major sources of PAHs in these soil profiles.

4.20 Distribution and Changes in metal concentrations in the floodplain soils a year after the major flooding

The concentration of metals in soil profiles of the study area a year after the major flooding are shown in Tables 4.33. The concentrations of metals in these sites and depth also varied significantly ($p<0.05$) a year after the major flooding. There was also no regular trend in the distribution of these metals with respect to depths. Again, the concentrations of metals in the downstream of the floodplain were higher than that of the midstream and upstream of the floodplain (Table 4.34). The changes in the concentrations of metals three months after the major flooding and a year after the major flooding are shown in Table 4.35.

Table 4.32: Metal concentrations (µg g^{-1}) of metals in soils a year after the major flooding

Sites	Depth (cm)	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Ba	Al	Fe
AS1	0 - 15	0.2	1.4	1.6	1.1	7.0	8.7	1.4	19.6	46.2	1905	57
	15 - 30	1.4	2.4	30.4	10.5	32.6	12.8	9.5	25.9	58.0	9875	119
	30 - 45	0.2	1.5	1.2	0.9	20.3	1.9	1.5	10.3	75.9	100	82
AS2	0 - 15	1.4	6.3	32.5	6.8	264	8.7	5.3	63.7	57.7	4926	11140
	15 - 30	2.4	11.4	47.8	11.8	577	12.8	14.6	62.6	112	9380	20455
	30 - 45	1.0	4.6	22.2	4.0	152	0.7	4.0	84.3	36.9	4373	33050
AS3	0 - 15	0.6	1.7	11.7	3.5	31.6	3.0	4.1	65.7	14.0	3748	4046
	15 - 30	0.8	1.7	16.7	4.9	19.3	3.1	5.9	56.2	14.1	5020	6030
	30 - 45	0.2	0.5	5.9	4.3	1.1	0.7	1.0	0.1	0.3	3926	3491
AS4	0 - 15	1.7	12.5	36.4	17.0	299	10	20.1	91.4	126	11420	14310
	15 - 30	0.6	5.7	9.9	11.9	89	6.3	11.4	57.9	120	8340	4117
	30 - 45	2.7	10.7	52.7	13.3	351	12.7	14.4	68.4	102	12280	22770
AS5	0 - 15	0.8	2.8	15.6	6.5	72.9	3.9	8.4	58.0	37.1	3068	5390
	15 - 30	0.9	3.1	20.4	15.5	84.9	5.5	24.1	89.9	50.6	4041	7630
	30 - 45	0.6	2.1	11.1	4.2	40.8	3.3	6.7	34.0	24.3	2008	3606
OK1	0 - 15	1.6	7.0	37.1	9.5	137	9.4	11.4	70.4	79.4	7735	12810
	15 - 30	1.7	7.8	32.9	5.7	152	3.4	9.8	51.6	67.5	6440	14105
	30 - 45	1.1	9.5	19.9	8.3	233	6.4	9.5	53.1	117	7325	8295
OK2	0 - 15	8.5	4.2	18.4	3.5	134	5.9	7.1	59.2	34.7	3533	6815
	15 - 30	0.3	2.9	4.2	3.1	66.9	3.5	1.6	51.3	24.9	1765	563
	30 - 45	0.7	2.9	11.2	4.1	68.3	3.6	3.6	30.4	49.6	1787	4375
OK3	0 - 15	0.6	2.3	14.4	5.8	35.6	7.3	4.2	74.5	33.1	5095	4144
	15 - 30	0.5	1.8	11.3	3.6	21.5	7.7	2.4	54.0	19.3	2605	2552
	30 - 45	0.4	1.3	7.6	2.2	17.6	2.4	2.2	32.1	12.8	1079	1902
AB1	0 - 15	0.2	1.3	1.3	1.1	5.2	2.3	2.1	21.0	48.1	1982	47
	15 - 30	0.2	6.0	1.1	2.2	108	4.6	5.1	38.7	112	1559	109
	30 - 45	2.0	9.9	43.4	9.7	443	16.0	9.7	37.3	88.4	10320	18350
AB2	0 - 15	2.7	10.8	59.7	18.4	337	15.9	18.7	1141	151	18045	24090
	15 - 30	0.2	0.5	19.1	13.4	1.1	0.6	0.7	0.1	0.3	17555	24225
	30 - 45	2.9	11.5	69.4	20.6	413	20.4	15.5	69.1	161	20905	24195
AB3	0 - 15	2.5	11.7	57.6	15.9	394	15.2	11.3	60.6	130	14785	21735
	15 - 30	3.0	15.5	79.3	21.3	617	21	18.5	55.0	177	26770	29925
	30 - 45	3.2	17.4	83.2	21.4	674	23.1	17.4	52.8	140	27270	32190
AB4	0 - 15	0.8	4.8	22.6	6.7	151	6.6	5.2	46.1	40.4	5030	7975
	15 - 30	0.5	4.1	109	9.3	79.6	93.6	3.1	20.9	20.8	1531	4692
	30 - 45	1.2	6.8	31.2	9.5	273	8.2	9.3	40.6	62.9	5140	11675
AB5	0 - 15	2.1	11.1	47.8	13.6	591	14.7	10.9	49.4	119	8690	19310
	15 - 30	2.1	11.3	53.5	13.7	466	13.3	12.8	43.4	123	10785	20865
	30 - 45	1.3	6.1	32.2	9.3	219	8.1	8.1	28.9	65.0	6020	13095
	MIN	0.2	0.5	1.1	0.9	1.1	0.6	0.7	0.1	0.3	100.0	47.0
	MAX	8.5	17.4	109	21.4	674	93.6	24.1	1141	177	27270	33050
	MEAN	1.4	6.1	30.3	8.9	197	10.4	8.5	76.1	70.6	7645.2	11393.1
	DPRTV	0.8	20	100	36	-	35	85	140	200	-	-
	CAV	0.3	-	90	45	850	68	20	95	-	8.02*	4.7*

* (%), *DPRTV* Department of Petroleum Resources (2002) target values, *CAV* Crustal abundance value (Turekian and Wedepohl, 1961)

Table 4.33: Mean metal concentrations (µg g^{-1}) in floodplain soils a year after the major flooding

Depth (cm)	Sites	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Ba	Al	Fe
0-15 cm	Upstream	0.94±0.61	4.94±4.65	19.6±14.6	6.98±6.07	135±136	6.86±3.17	7.86±7.29	59.7±25.8	56.2±42.1	5013±3745	6989±5703
	(AS1-AS5)	(0.2-1.7)	(1.4-12.5)	(1.6-36.4)	(1.1-17.0)	(7.0-299)	(3.0-10.0)	(1.4-20.1)	(19.6-91.4)	(14.0-126)	(1905-11420)	(57.0-14310)
	Midstream	3.57±4.30	4.50±2.36	23.3±12.1	6.27±3.03	102±57.7	7.53±1.76	7.57±3.62	68.0±7.92	49.1±26.3	5454±2124	7923±4438
	(OK1-OK3)	(0.6-8.5)	(2.3-7.0)	(14.4-37.1)	(3.5-9.5)	(35.6-137)	(5.9-9.4)	(4.2-11.4)	(59.2-74.5)	(33.1-79.4)	(3533-7735)	(4144-12810)
	Downstream	1.66±1.10	7.94±4.64	37.8±25.2	11.1±7.11	296±226	10.9±6.13	9.64±6.38	264±490	97.7±50.2	9706±6669	14631±10233
	(AB1-AB5)	(0.2-2.7)	(1.3-11.7)	(1.3-59.7)	(1.1-18.4)	(5.2-591))	(2.4-15.9)	(2.1-18.7)	(21.0-1141)	(40.4-151)	(1982-18045)	(47.0-24090)
15-30 cm	Upstream	1.22±0.72	4.86±3.96	25.0±14.7	10.9±3.84	161±235	8.10±4.45	13.1±6.91	58.5±22.8	70.9±44.4	7331±2639	7670±7678
	(AS1-AS5)	(0.6-2.4)	(1.7-11.4)	(9.9-47.8)	(4.9-15.5)	(19.3-577)	(3.1-12.8)	(5.9-24.1)	(25.9-89.9)	(14.1-120)	(4041-9875)	(119-20455)
	Midstream	0.83±0.76	4.17±3.19	16.1±14.9	4.13±1.38	80.0±66.1	4.87±2.45	4.60±4.52	52.3±1.48	37.2±26.4	3603±2492	5740±7312
	(OK1-OK3)	(0.3-1.7)	(1.8-7.8)	(4.2-32.9)	(3.1-5.7)	(21.5-151.7)	(3.4-7.7)	(1.6-9.8)	(51.3-54.0)	(19.3-67.5)	(1765-6440)	(563-14105)
	Downstream	1.20±1.28	7.48±5.94	52.4±43.8	12.0±6.98	254±270	26.6±38.3	8.04±7.40	31.6±21.5	86.6±74.0	11640±10822	15963±12900
	(AB1-AB5)	(0.2-3.0)	(0.5-15.5)	(1.1-109)	(2.2-21.3)	(1.1-617)	(0.6-93.6)	(0.7-18.5)	(0.1-55.0)	(0.3-177)	(1531-26770)	(109-29925)
30-45 cm	Upstream	0.94±1.04	3.88±4.10	18.6±20.6	5.34±4.67	113±145	3.86±5.06	5.52±5.46	39.4±36.3	47.9±40.9	4537±4649	12600±14510
	(AS1-AS5)	(0.2-2.7)	(0.5-10.7)	(1.2-52.7)	(0.9-13.3)	(1.1-351)	(0.7-12.7)	(1.0-14.4)	(0.1-68.4)	(0.3-102)	(100-12280)	(82-33050)
	Midstream	0.73±0.35	4.57±4.35	12.9±6.32	4.87±3.12	106±112	4.13±2.05	5.10±3.87	38.5±12.6	59.9±53.0	3397±3420	4857±3224
	(OK1-OK3)	(0.4-1.1)	(1.3-9.5)	(7.6-19.9)	(2.2-8.3)	(17.6-233)	(2.4-6.4)	(2.2-9.5)	(30.4-53.1)	(12.8-117.3)	(1079-7325)	(1902-8295)
	Downstream	2.12±0.91	10.3±4.52	51.9±23.3	14.1±6.31	404±178	15.2±6.88	12.0±4.16	45.7±15.6	103±44.6	13931±9740	19901±8454
	(AB1-AB5)	(1.2-3.2)	(6.1-17.4)	(31.2-83.2)	(9.3-21.4)	(219-674)	(8.2-23.1)	(8.1-17.4)	(28.9-69.1)	(62.9-161)	(5140-27270)	(11675-32190)

Table 4.34: Changes in metal concentrations (µg g^{-1}) in the soils during the two sampling periods

Sites	Depth (cm)	Cd FSP	Cd SSP	Cd % change	Co FSP	Co SSP	Co % change	Cr FSP	Cr SSP	Cr % change	Cu FSP	Cu SSP	Cu % change	Mn FSP	Mn SSP	Mn % change	Ni FSP	Ni SSP	Ni % change
AS1	0 - 15	2	0.2	-900	4.5	1.4	-221	10.9	1.6	-581	8.2	1.1	-645	180	7	-2473	4.8	8.7	44.8
	15 - 30	0.6	1.4	57.1	1.9	2.4	20.8	12.2	30.4	59.9	11.2	10.5	-6.7	96.5	32.6	-196	6.2	12.8	51.6
	30 - 45	1.6	0.2	-700	6.5	1.5	-333	33.1	1.2	-2658	29.4	0.9	-3167	258	20.3	-1170	8.4	1.9	-342
	MEAN	**1.4**	**0.6**	**-514**	**4.3**	**1.8**	**-178**	**18.7**	**11.1**	**-1060**	**16.3**	**4.2**	**-1273**	**178**	**20.0**	**-1280**	**6.5**	**7.8**	**-81.9**
AS2	0 - 15	0.4	1.4	71.4	1.6	6.3	74.6	7.9	32.5	75.7	6.2	6.8	8.8	20.3	264	92.3	2.4	8.7	72.4
	15 - 30	0.5	2.4	79.2	1.3	11.4	88.6	11.1	47.8	76.8	4.4	11.8	62.7	56	577	90.3	2.1	12.8	83.6
	30 - 45	0.6	1	40.0	2.1	4.6	54.3	13	22.2	41.4	8.6	4	-115	71.6	152.3	53.0	3.9	0.7	-457
	MEAN	**0.5**	**1.6**	**63.5**	**1.7**	**7.4**	**72.5**	**10.7**	**34.2**	**64.6**	**6.4**	**7.5**	**-14.5**	**49.3**	**331**	**78.5**	**2.8**	**7.4**	**-100**
AS3	0 - 15	0.3	0.6	50.0	1.2	1.7	29.4	6.7	11.7	42.7	3.5	3.5	0.0	23.5	31.6	25.6	2.3	3	23.3
	15 - 30	0.5	0.8	37.5	1.5	1.7	11.8	13.1	16.7	21.6	0.5	4.9	89.8	17.9	19.3	7.3	3.9	3.1	-25.8
	30 - 45	0.7	0.2	-250	4.9	0.5	-880	19.2	5.9	-225	10	4.3	-133	156	1.1	-14055	7.9	0.7	-1029
	MEAN	**0.5**	**0.5**	**-54.2**	**2.5**	**1.3**	**-280**	**13.0**	**11.4**	**-53.7**	**4.7**	**4.2**	**-14.3**	**65.7**	**17.3**	**-4674**	**4.7**	**2.3**	**-344**
AS4	0 - 15	0.9	1.7	47.1	8	12.5	36.0	44.7	36.4	-22.8	10.9	17	35.9	340	299.1	-13.5	19.5	10	-95.0
	15 - 30	0.2	0.6	66.7	2.1	5.7	63.2	8.2	9.9	17.2	11.9	11.9	0.0	17.2	89	80.7	31.5	6.3	-400
	30 - 45	0.3	2.7	88.9	1	10.7	90.7	0.8	52.7	98.5	1.5	13.3	88.7	5.1	351	98.5	1.1	12.7	91.3
	MEAN	**0.5**	**1.7**	**67.5**	**3.7**	**9.6**	**63.3**	**17.9**	**33.0**	**31.0**	**8.1**	**14.1**	**41.5**	**121**	**246**	**55.2**	**17.4**	**9.7**	**-135**
AS5	0 - 15	1.4	0.8	-75.0	3.4	2.8	-21.4	27.5	15.6	-76.3	7.8	6.5	-20.0	171	72.9	-134	2.7	3.9	30.8
	15 - 30	1	0.9	-11.1	2.8	3.1	9.7	27.7	20.4	-35.8	6.9	15.5	55.5	128	84.9	-51.1	2.9	5.5	47.3
	30 - 45	1.4	0.6	-133	1.8	2.1	14.3	31.9	11.1	-187	11.6	4.2	-176	51.5	40.8	-26.2	4.3	3.3	-30.3
	MEAN	**1.3**	**0.8**	**-73.1**	**2.7**	**2.7**	**0.8**	**29.0**	**15.7**	**-99.8**	**8.8**	**8.7**	**-46.9**	**117**	**66.2**	**-70.4**	**3.3**	**4.2**	**15.9**
OK1	0 - 15	0.6	1.6	62.5	6.2	7	11.4	10.1	37.1	72.8	5.9	9.5	37.9	128	137	6.4	5.4	9.4	42.6
	15 - 30	1.2	1.7	29.4	6	7.8	23.1	25.7	32.9	21.9	7.2	5.7	-26.3	239	151.7	-57.7	6.2	3.4	-82.4
	30 - 45	0.4	1.1	63.6	13.1	9.5	-37.9	8	19.9	59.8	13.4	8.3	-61.4	163	232.7	30.0	10.3	6.4	-60.9
	MEAN	**0.7**	**1.5**	**51.8**	**8.4**	**8.1**	**-1.1**	**14.6**	**30.0**	**51.5**	**8.8**	**7.8**	**-16.6**	**177**	**174**	**-7.1**	**7.3**	**6.4**	**-33.6**
OK2	0 - 15	2	8.5	76.5	9.1	4.2	-117	69	18.4	-275	8	3.5	-129	349	134.1	-160	25.3	5.9	-329
	15 - 30	1.8	0.3	-500	1.6	2.9	44.8	43.6	4.2	-938	10.8	3.1	-248	343	66.9	-413	12.3	3.5	-251
	30 - 45	1.7	0.7	-143	9.3	2.9	-221	43.1	11.2	-285	10.3	4.1	-151	371	68.3	-443	10.9	3.6	-203
	MEAN	**1.8**	**3.2**	**-189**	**6.7**	**3.3**	**-97.5**	**51.9**	**11.3**	**-499**	**9.7**	**3.6**	**-176**	**354**	**89.8**	**-339**	**16.2**	**4.3**	**-261**
OK3	0 - 15	1	0.6	-66.7	4.6	2.3	-100	22.9	14.4	-59.0	5.4	5.8	6.9	43.9	35.6	-23.3	5	7.3	31.5
	15 - 30	0.5	0.5	0.0	2.3	1.8	-27.8	8.9	11.3	21.2	3.7	3.6	-2.8	43.3	21.5	-101	2.5	7.7	67.5
	30 - 45	0.3	0.4	25.0	1.3	1.3	0.0	7.5	7.6	1.3	4.2	2.2	-90.9	22.1	17.6	-25.6	2.3	2.4	4.2
	MEAN	**0.6**	**0.5**	**-13.9**	**2.7**	**1.8**	**-42.6**	**13.1**	**11.1**	**-12.2**	**4.4**	**3.9**	**-28.9**	**36.4**	**24.9**	**-50.1**	**3.3**	**5.8**	**34.4**
AB1	0 - 15	0.6	0.2	-200	1.8	1.3	-38.5	18.1	1.3	-1292	7.6	1.1	-591	79.6	5.2	-1431	6.1	2.3	-165
	15 - 30	0.3	0.2	-50.0	1.6	6	73.3	10.7	1.1	-873	8	2.2	-264	42.5	107.6	60.5	2.6	4.6	43.5
	30 - 45	1.3	2	35.0	6.6	9.9	33.3	28	43.4	35.5	6.2	9.7	36.1	215	443	51.4	7	16	56.3
	MEAN	**0.7**	**0.8**	**-71.7**	**3.3**	**5.7**	**22.7**	**18.9**	**15.3**	**-710**	**7.3**	**4.3**	**-273**	**113**	**185**	**-440**	**5.2**	**7.6**	**-21.8**
AB2	0 - 15	0.2	2.7	92.6	7.1	10.8	34.3	39	59.7	34.7	12.8	18.4	30.4	195	337.4	42.3	8.8	15.9	44.7
	15 - 30	0.3	0.2	-50.0	6	0.5	-1100	5.3	19.1	72.3	12.1	13.4	9.7	49.9	1.1	-4436	7.8	0.6	-1200
	30 - 45	2.7	2.9	6.9	11.8	11.5	-2.6	61	69.4	12.1	14.8	20.6	28.2	443	412.6	-7.2	15.2	20.4	25.5
	MEAN	**1.1**	**1.9**	**16.5**	**8.3**	**7.6**	**-356**	**35.1**	**49.4**	**39.7**	**13.2**	**17.5**	**22.8**	**229**	**250**	**-1467**	**10.6**	**12.3**	**-377**
AB3	0 - 15	1.9	2.5	24.0	9.2	11.7	21.4	45.1	57.6	21.7	12.6	15.9	20.8	364	394.2	7.7	11.7	15.2	23.0
	15 - 30	2.1	3	30.0	9.9	15.5	36.1	48.1	79.3	39.3	12.8	21.3	39.9	399	616.5	35.2	12.5	21	40.5
	30 - 45	2	3.2	37.5	9.8	17.4	43.7	46.8	83.2	43.8	12.8	21.4	40.2	431	674	36.1	10.9	23.1	52.8
	MEAN	**2.0**	**2.9**	**30.5**	**9.6**	**14.9**	**33.7**	**46.7**	**73.4**	**34.9**	**12.7**	**19.5**	**33.6**	**398**	**562**	**26.3**	**11.7**	**19.8**	**38.8**
AB4	0 - 15	1.3	0.8	-62.5	7	4.8	-45.8	31.6	22.6	-39.8	8.7	6.7	-29.9	240	151.3	-58.4	7.8	6.6	-18.2
	15 - 30	1.5	0.5	-200	8	4.1	-95.1	39	108.9	64.2	11	9.3	-18.3	300	79.6	-277	14.1	93.6	84.9
	30 - 45	1.1	1.2	8.3	5.7	6.8	16.2	26	31.2	16.7	6.5	9.5	31.6	232	272.9	14.9	6	8.2	26.8
	MEAN	**1.3**	**0.8**	**-84.7**	**6.9**	**5.2**	**-41.6**	**32.2**	**54.2**	**13.7**	**8.7**	**8.5**	**-5.5**	**257**	**168**	**-107**	**9.3**	**36.1**	**31.2**
AB5	0 - 15	2.8	2.1	-33.3	14.4	11.1	-29.7	66.9	47.8	-40.0	19.9	13.6	-46.3	790	590.5	-33.7	16.3	14.7	-10.9
	15 - 30	2.2	2.1	-4.8	11.3	11.3	0.0	28.5	53.5	46.7	12.8	13.7	6.6	529	466.1	-13.4	12.5	13.3	6.0
	30 - 45	2.2	1.3	-69.2	11.8	6.1	-93.4	47.8	32.2	-48.4	15.4	9.3	-65.6	529	218.6	-142	26.3	8.1	-225
	MEAN	**2.4**	**1.8**	**-35.8**	**12.5**	**9.5**	**-41.1**	**47.7**	**44.5**	**-13.9**	**16.0**	**12.2**	**-35.1**	**616**	**425**	**-63.0**	**18.4**	**12.0**	**-76.5**
	MEAN*	**1.14**	**1.43**	**-62.0**	**5.64**	**6.07**	**-65.0**	**26.9**	**30.3**	**-170**	**9.63**	**8.93**	**-137**	**208**	**197**	**-641**	**8.97**	**10.4**	**-101**

Table 4.35 Cont'd

Sites	Depth (cm)	Pb FSP	Pb SSP	Pb % change	Zn FSP	Zn SSP	Zn % change	Ba FSP	Ba SSP	Ba % change	Al FSP	Al SSP	Al % change	Fe FSP	Fe SSP	Fe % change
AS1	0 - 15	28	1.4	-1900	1491	19.6	-7505	64.7	46.2	-40.0	2646	1905	-38.9	4023	57	-6958
	15 - 30	13.8	9.5	-45.3	91.4	25.9	-253	124	58	-114	10025	9875	-1.5	6745	119	-5568
	30 - 45	40.5	1.5	-2600	260	10.3	-2426	83.8	75.9	-10.4	9490	100	-9390	15710	82	-19059
	MEAN	**27.4**	**4.1**	**-1515**	**614**	**18.6**	**-3395**	**90.9**	**60.0**	**-54.9**	**7387**	**3960**	**-3143**	**8826**	**86.0**	**-10528**
AS2	0 - 15	3.7	5.3	30.2	92.3	63.7	-44.9	9.6	57.7	83.4	1344	4926	72.7	3150	11140	71.7
	15 - 30	8.2	14.6	43.8	48.5	62.6	22.5	10.7	111.5	90.4	1071	9380	88.6	3961	20455	80.6
	30 - 45	9.1	4	-128	105.4	84.3	-25.0	22.4	36.9	39.3	2565	4373	41.3	5075	33050	84.6
	MEAN	**7.0**	**8.0**	**-17.8**	**82.1**	**70.2**	**-15.8**	**14.2**	**68.7**	**71.0**	**1660**	**6226**	**67.5**	**4062**	**21548**	**79.0**
AS3	0 - 15	3.3	4.1	19.5	30.2	65.7	54.0	12.5	14	10.7	848	3748	77.4	2431	4046	39.9
	15 - 30	4.5	5.9	23.7	31.9	56.2	43.2	21.3	14.1	-51.1	4378	5020	12.8	4980	6030	17.4
	30 - 45	3.0	1.0	-200	58	0.1	-57900	76.4	0.3	-25367	9925	3926	-153	6305	3491	-80.6
	MEAN	**3.6**	**3.7**	**-52.3**	**40.0**	**40.7**	**-19268**	**36.7**	**9.5**	**-8469**	**5050**	**4231**	**-20.9**	**4572**	**4522**	**-7.8**
AS4	0 - 15	7.1	20.1	64.7	83.4	91.4	8.8	127	126	-0.6	5370	11420	53.0	9395	14310	34.3
	15 - 30	7.2	11.4	36.8	89.1	57.9	-53.9	23.4	120	80.5	5240	8340	37.2	1782	4117	56.7
	30 - 45	1.1	14.4	92.4	18.7	68.4	72.7	18.1	102	82.3	2163	12280	82.4	41	22770	99.8
	MEAN	**5.1**	**15.3**	**64.6**	**63.7**	**72.6**	**9.2**	**56.0**	**116**	**54.1**	**4258**	**10680**	**57.5**	**3739**	**13732**	**63.6**
AS5	0 - 15	9.3	8.4	-10.7	107.4	58	-85.2	15.5	37.1	58.2	5205	3068	-69.7	13225	5390	-145
	15 - 30	3.8	24.1	84.2	37	89.9	58.8	16.2	50.6	68.0	4407	4041	-9.1	9770	7630	-28.0
	30 - 45	6.4	6.7	4.5	23.7	34	30.3	19.1	24.3	21.4	11145	2008	-455	14805	3606	-311
	MEAN	**6.5**	**13.1**	**26.0**	**56.0**	**60.6**	**1.3**	**16.9**	**37.3**	**49.2**	**6919**	**3039**	**-178**	**12600**	**5542**	**-161**
OK1	0 - 15	9.4	11.4	17.5	440.1	70.4	-525	67.2	79.4	15.4	7255	7735	6.2	4573	12810	64.3
	15 - 30	7.6	9.8	22.4	306.4	51.6	-494	59.9	67.5	11.3	4281	6440	33.5	10595	14105	24.9
	30 - 45	13.2	9.5	-38.9	123.6	53.1	-133	28.7	117	75.5	11305	7325	-54.3	4101	8295	50.6
	MEAN	**10.1**	**10.2**	**0.3**	**290**	**58.4**	**-384**	**51.9**	**88.1**	**34.1**	**7614**	**7167**	**-5**	**6423**	**11737**	**46.6**
OK2	0 - 15	12.1	7.1	-70.4	490.9	59.2	-729	82.7	34.7	-138	8450	3533	-139	17275	6815	-153
	15 - 30	7.2	1.6	-350	57.5	51.3	-12.1	89.1	24.9	-258	14725	1765	-734	19165	563	-3304
	30 - 45	7.4	3.6	-106	46.3	30.4	-52.3	87.9	49.6	-77.2	13225	1787	-640	18260	4375	-317
	MEAN	**8.9**	**4.1**	**-175**	**198**	**47.0**	**-265**	**86.6**	**36.4**	**-158**	**12133**	**2362**	**-505**	**18233**	**3918**	**-1258**
OK3	0 - 15	3.0	4.2	28.6	116	74.5	-55.7	39.6	33.1	-19.6	5165	5095	-1.4	9440	4144	-128
	15 - 30	2.8	2.4	-16.7	94.4	54	-74.8	12.3	19.3	36.3	1701	2605	34.7	3522	2552	-38.0
	30 - 45	3.2	2.2	-45.5	99.2	32.1	-209	8	12.8	37.5	1056	1079	2.1	2588	1902	-36.1
	MEAN	**3.0**	**2.9**	**-11.2**	**103**	**53.5**	**-113**	**20.0**	**21.7**	**18.0**	**2641**	**2926**	**11.8**	**5183**	**2866**	**-67.3**
AB1	0 - 15	8.5	2.1	-305	204.1	21	-872	12.3	48.1	74.4	1167	1982	41.1	3468	47	-7279
	15 - 30	6.0	5.1	-17.6	169.7	38.7	-339	11.3	112	89.9	982	1559	37.0	2968	109	-2623
	30 - 45	4.6	9.7	52.6	45.5	37.3	-22.0	50.7	88.4	42.6	6270	10320	39.2	12630	18350	31.2
	MEAN	**6.4**	**5.6**	**-89.9**	**140**	**32.3**	**-411**	**24.8**	**82.7**	**69.0**	**2806**	**4620**	**39.1**	**6355**	**6169**	**-3290**
AB2	0 - 15	15.7	18.7	16.0	134.6	1140.5	88.2	99.5	151	34.0	11175	18045	38.1	15605	24090	35.2
	15 - 30	12.0	0.7	-1614	59.5	0.1	-59400	146.5	0.3	-48733	8015	17555	54.3	2889	24225	88.1
	30 - 45	12.2	15.5	21.3	46	69.1	33.4	7.9	161	95.1	20290	20905	2.9	28020	24195	-15.8
	MEAN	**13.3**	**11.6**	**-526**	**80.0**	**403**	**-19759**	**84.6**	**104**	**-16201**	**13160**	**18835**	**31.8**	**15505**	**24170**	**35.8**
AB3	0 - 15	12.0	11.3	-6.2	76.2	60.6	-25.7	117	130	10.0	11640	14785	21.3	18325	21735	15.7
	15 - 30	13.9	18.5	24.9	46.7	55	15.1	102	177	42.3	10995	26770	58.9	21885	29925	26.9
	30 - 45	12.1	17.4	30.5	42.1	52.8	20.3	90.9	140	35.1	12720	27270	53.4	21165	32190	34.2
	MEAN	**12.7**	**15.7**	**16.4**	**55.0**	**56.1**	**3.2**	**103**	**149**	**29.1**	**11785**	**22942**	**44.5**	**20458**	**27950**	**25.6**
AB4	0 - 15	6.3	5.2	-21.2	311	46.1	-575	57.4	40.4	-42.1	8150	5030	-62.0	13845	7975	-73.6
	15 - 30	8.8	3.1	-184	48	20.9	-130	69.1	20.8	-232	10535	1531	-588	16645	4692	-255
	30 - 45	5.2	9.3	44.1	31.2	40.6	23.2	51	62.9	18.9	5275	5140	-2.6	11195	11675	4.1
	MEAN	**6.8**	**5.9**	**-53.6**	**130**	**35.9**	**-227**	**59.2**	**41.4**	**-85.1**	**7987**	**3900**	**-218**	**13895**	**8114**	**-108**
AB5	0 - 15	12.4	10.9	-13.8	96.7	49.4	-95.7	0.4	119	99.7	23955	8690	-176	32125	19310	-66.4
	15 - 30	11.4	12.8	10.9	50.2	43.4	-15.7	111	123	10.5	15975	10785	-48.1	23395	20865	-12.1
	30 - 45	14.8	8.1	-82.7	58	28.9	-101	144	65	-121	19365	6020	-222	23235	13095	-77.4
	MEAN	**12.9**	**10.6**	**-28.5**	**68.3**	**40.6**	**-70.7**	**84.8**	**102**	**-3.6**	**19765**	**8498**	**-148**	**26252**	**17757**	**-52.0**
	MEAN*	**9.5**	**8.5**	**-182**	**148**	**76.1**	**-3376**	**56.2**	**70.6**	**-1896**	**7936**	**7645**	**-305**	**11239**	**11393**	**-1171**

Cadmium

The concentration of Cd varied from 0.2 to 8.5 µg g^{-1} a year after the major flooding. The highest concentration of Cd (8.5 µg g^{-1}) was recorded in topsoil of site OK2. The concentration of Cd decreased with increasing depth in sites AS2, AS3, AS5, OK1, OK2, OK3 and AB5 and increased with increasing depth in sites AS4, AB1, AB2 AB3 and AB4 a year after the major flooding. The mean change in concentration of Cd in these soil profiles showed a decrease of 62 % between the two sampling periods (Table 4.35). However, there was higher increase of 63.5, 67.5 and 51.8 % at sites AS2, AS4 and OK1 respectively while higher decreased of 514, 54.2, 73.1, 189, 71.7 and 84.7 % was observed at sites AS1, AS3, AS5, OK2, AB1 and AB4.

Cobalt

Cobalt content in these soils a year after the major flooding event varied from 0.5 to 17.4 µg g^{-1} with site AB3 (30-45 cm depth) having the highest concentration. A year after the major flooding event, there was a slight variation in the distribution of Co as Co content increased with depth at site AB4 and decreased with depth at sites AS2, AB3 and OK2. The concentration of Co showed a mean decreased of 65 % within the two sampling period (Table 4.35). The mean change in the concentration of Co decreased at all sites except sites AS2, AS4, AS5, AB1 and AB3. The concentration of Co increased at sites AS2 and AS4 up to 72.5 and 63.3 % respectively while very high decrease was observed at sites AS1, AS3, OK3 and AB2.

Chromium

A year after the major flooding, the concentration of Cr at these sites ranged between 1.1 to 108.9 µg g^{-1} and the highest concentration was observed at the 15-30 cm depth of site AB4. The concentration of Cr decreased with depth at sites AS4 and AB4 then increased

with depth at sites AS1, AS3 and AS5. The mean change in the concentration of Cr after the major flooding and a year later showed a decreased as high as 170 % (Table 4.35). There was increased in Cr concentration at sites AS2, AS4, OK1, AB2, AB3 and AB4. Higher increased was observed at sites AS2 (64.7 %) and OK1 (51.5 %) while very high decreased was observed at sites AS1, AS5, OK2 and AB1.

Copper

The concentration of Cu ranged from 0.9 to 21.4 μg g^{-1}a year after the major flooding event and the highest concentration of Cu was observed at the 30-45 cm depth of site AB3. The concentration of Cu decreased with depth at sites AS1, AS2, AS5, and AB2 and increased with depth at sites OK2, AB1, AB4 and AB5 during this period. The change in the concentration of Cu showed a mean decrease of 137 % within the two sampling period (Table 4.35). There was decreased in all sites except site AS4, AB2 and AB3 which have increased not more than 45 %. Decreased in mean change in concentration of Cu as high as 1273, 176, and 273 % was observed at sites AS1, OK2 and AB1.

Manganese

A year after the major flooding event, the concentration of Mn in the soil varied from 1.1 to 674.0 μg g^{-1} and the highest concentration of Mn was observed at 30-45 cm depth of site AB4. However, the distribution pattern changed slightly a year after the major flooding as the concentration of Mn decreased with depth at sites AS2, AS3 and OK2 and increased with depth at sites AS4 and AB5. The changes in manganese concentration in these soil profiles showed a very high decreased of 641 % (Table 4.35). Very high decreased in Mn concentration was observed in all sites except AS2 and AS4 were there was increased of up to 78.5 and 55.2 %.

Nickel

The concentrations of Ni ranged from 0.6 to 93.6 µg g^{-1}. The soil profiles of AB2 and AB3 have higher concentrations of Ni a year after the major flooding. The concentration of Ni decreased with depth except at sites AS4, AB1, AB2, AB3 and AB4. The mean concentration of Ni showed a decreased of 101 % in all sites and depth (Table 4.35). The result showed that the mean change in concentration of Ni decreased at all sites except sites AS5, OK3, AB3 and AB4. The highest decreased was observed at site AB2 while the highest increased was observed at site AB3.

Lead

The concentration of Pb ranged from 0.7 to 24.1 µg g^{-1}. The highest concentrations of Pb were observed in the soil profile of sites AS4, AB2, and AB3 a year after the flooding. The concentration of Pb decreased with depth except at sites AS1, AB1, AB3 and AB4. The mean change in the concentration of Pb showed a decreased of 182 % (Table 4.35). Very high decreased in Pb concentration was observed at sites AS1, OK2 and AB2 while increased of up to 64.6 % was observed at site AS4.

Zinc

After a year, the concentration of Zn ranged from 0.1 to 1141 µg g^{-1}. The highest concentration of Zn in these soil samples a year after the flooding was observed at the topsoil of site AB2. The highest change in the concentration of metals in these soil profiles was observed in Zn. The mean change in the concentration of Zn in these soil profiles showed a decreased of 3376 % (Table 4.35). The result showed that the mean change in Zn concentration decreased greatly at all sites except sites AS4, AS5 and AB3 that recorded very little increase in concentration. The highest and lowest Zn concentration decreased were observed at sites Ab2 and AS2.

Barium

The concentrations of Ba in the soil profiles a year after the major flooding event ranged from 0.3 to 177.0µg kg^{-1}. The highest concentration of Ba was observed at 15-30 cm depth of site AB3. There is no significant difference between the concentrations of Ba observed in the two sampling period. The concentration of Ba showed a mean decreased of 1896 % in all sites and depth within the two sampling periods (Table 4.35). However, there was an increased ranging from 18.0 % at site OK3 to 71.0 % at site AS2. The highest and lowest Ba concentrations decreased were observed at sites AB2 and AB5 respectively.

Aluminium

The concentrations of Al ranged from 100 to 27270 µg g^{-1} a year after major flooding. There was a change in the distribution pattern as the concentration of Al decreased with depth at sites AS3, AS5, OK2 and OK3 while the concentration of Al increased with depth at sites AS4 and AB4. Also, the concentration of Al showed a mean decreased of 305 % within the two sampling period (Table 4.35). Very high decreased was observed at sites AS1, AS5, OK2, AB4 and AB5 while higher increased was observed at sites AS2 and AS4.

Iron

The concentration of Fe ranged from 47.0 to 33050 µg g^{-1} a year after the major flooding. The highest concentration of Fe was observed at 30-45 cm depth of site AB2. The concentration of Fe increased with depth except at sites AS3, AS5, OK1, OK2, OK3 and AB5. The mean change in the concentration of Fe showed a decreased of 1171 % (Table 4.35). There was a decreased in Fe concentration at all sites except AS2, AS4, OK1, AB2 and AB3 with increased change in Fe concentration ranging from 25.6 to 79.0 %.

4.21   Contamination/Pollution index of metals a year after major flooding

The computed CPI and MPI values a year after the major flooding are shown in Table 4.35. The CPI a year after are similar to that obtain three months after the major flooding as the index values for Co, Cr, Cu, Ni, Pb and Ba were also at the contamination range i.e. less than unity whereas that of Cd and Zn were at the pollution range (i.e. greater than unity) for some sites.

Table 4.35: Contamination/Pollution index of metals a year after major flooding

Sites	Depth (cm)	Cd	Co	Cr	Cu	Ni	Pb	Zn	Ba	MPI
AS1	0 - 15	0.25	0.07	0.02	0.03	0.24	0.02	0.14	0.23	
	15 - 30	1.69	0.12	0.30	0.29	0.35	0.11	0.18	0.29	1.69
	30 - 45	0.19	0.08	0.01	0.02	0.05	0.02	0.07	0.38	
AS2	0 - 15	1.69	0.31	0.33	0.19	0.24	0.06	0.45	0.29	1.69
	15 - 30	3.00	0.57	0.48	0.33	0.35	0.17	0.45	0.56	3.00
	30 - 45	1.25	0.23	0.22	0.11	0.02	0.05	0.60	0.18	1.25
AS3	0 - 15	0.69	0.08	0.12	0.10	0.08	0.05	0.47	0.07	
	15 - 30	0.94	0.08	0.17	0.14	0.09	0.07	0.40	0.07	
	30 - 45	0.25	0.03	0.06	0.12	0.02	0.01	0.00	0.00	
AS4	0 - 15	2.13	0.62	0.36	0.47	0.28	0.24	0.65	0.63	2.13
	15 - 30	0.69	0.29	0.10	0.33	0.18	0.13	0.41	0.60	
	30 - 45	3.31	0.53	0.53	0.37	0.35	0.17	0.49	0.51	
AS5	0 - 15	0.94	0.14	0.16	0.18	0.11	0.10	0.41	0.19	
	15 - 30	1.13	0.16	0.20	0.43	0.15	0.28	0.64	0.25	1.13
	30 - 45	0.69	0.11	0.11	0.12	0.09	0.08	0.24	0.12	
OK1	0 - 15	1.94	0.35	0.37	0.26	0.26	0.13	0.50	0.40	1.94
	15 - 30	2.13	0.39	0.33	0.16	0.09	0.12	0.37	0.34	2.13
	30 - 45	1.31	0.48	0.20	0.23	0.18	0.11	0.38	0.59	1.31
OK2	0 - 15	10.6	0.21	0.18	0.10	0.16	0.08	0.42	0.17	10.6
	15 - 30	0.31	0.14	0.04	0.09	0.10	0.02	0.37	0.12	
	30 - 45	0.81	0.14	0.11	0.11	0.10	0.04	0.22	0.25	
OK3	0 - 15	0.69	0.12	0.14	0.16	0.20	0.05	0.53	0.17	
	15 - 30	0.56	0.09	0.11	0.10	0.21	0.03	0.39	0.10	
	30 - 45	0.44	0.07	0.08	0.06	0.07	0.03	0.23	0.06	
AB1	0 - 15	0.25	0.07	0.01	0.03	0.06	0.02	0.15	0.24	
	15 - 30	0.19	0.30	0.01	0.06	0.13	0.06	0.28	0.56	
	30 - 45	2.44	0.50	0.43	0.27	0.44	0.11	0.27	0.44	2.44
AB2	0 - 15	3.31	0.54	0.60	0.51	0.44	0.22	8.15	0.75	3.31
	15 - 30	0.25	0.03	0.19	0.37	0.02	0.01	0.00	0.00	
	30 - 45	3.56	0.58	0.69	0.57	0.57	0.18	0.49	0.80	3.56
AB3	0 - 15	3.06	0.58	0.58	0.44	0.42	0.13	0.43	0.65	3.06
	15 - 30	3.75	0.77	0.79	0.59	0.58	0.22	0.39	0.88	3.75
	30 - 45	3.94	0.87	0.83	0.59	0.64	0.20	0.38	0.70	3.94
AB4	0 - 15	1.00	0.24	0.23	0.19	0.18	0.06	0.33	0.20	1.00
	15 - 30	0.63	0.21	1.09	0.26	2.60	0.04	0.15	0.10	1.09
	30 - 45	1.50	0.34	0.31	0.26	0.23	0.11	0.29	0.31	1.50
AB5	0 - 15	2.56	0.56	0.48	0.38	0.41	0.13	0.35	0.59	2.56
	15 - 30	2.63	0.57	0.53	0.38	0.37	0.15	0.31	0.62	2.63
	30 - 45	1.56	0.30	0.32	0.26	0.23	0.10	0.21	0.32	1.56
	MIN	0.19	0.03	0.01	0.02	0.02	0.01	0.00	0.00	1.00
	MAX	10.6	0.87	1.09	0.59	2.60	0.28	8.15	0.88	10.6
	MEAN	1.75	0.30	0.30	0.25	0.29	0.10	0.54	0.35	2.60

4.22   Enrichment factor a year after the major flooding

The enrichment factor of these soil profiles a year after the major flooding are shown in Table 4.36. The EF values for Cd a year after the major flooding ranged from 3.05 to 643.26 in these sites. The EF values of Cd were greater than 10 in all sites except for 15-30 cm depth of site AB2. The EF values of 22, 14 and 2 of these soil samples were in the extremely very high enrichment (i.e. EF >40), very high enrichment and significant enrichment categories, respectively. The EF values of Cd suggest non-crustal sources. The enrichment factors for Fe, Cr, Cu, Ni, Mn and Ba were less than 10 in the majority of the samples investigated in this study a year after the major flooding which indicate the source of these metals in the soil profiles were of crustal origin. A year after the major flooding, 30-45 cm depth of site AS1 had EF values for Co, Cr, Cu, Mn, Ni, Pb and Ba greater than 10 which suggest anthropogenic source. Also, 15-30 cm depth of site AB4 had EF values for Co, Cr, Cu and Ni greater than 10 which again suggest anthropogenic source.

Table 4.36: Enrichment factor of metals a year after major flooding

Sites	Depth (cm)	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Ba	Fe
AS1	0 - 15	28.1	2.99	0.73	0.98	0.34	5.36	2.84	8.69	3.35	0.05
	15 - 30	36.6	1.03	2.74	1.89	0.31	1.52	3.86	2.21	0.81	0.02
	30 - 45	401	63.4	10.3	15.2	19.2	21.8	60.2	87.0	105	1.39
AS2	0 - 15	73.3	5.36	5.88	2.46	5.06	2.07	4.31	10.9	1.62	3.86
	15 - 30	68.4	5.11	4.54	2.23	5.80	1.60	6.24	5.63	1.64	3.72
	30 - 45	61.1	4.44	4.51	1.61	3.29	0.18	3.62	16.3	1.17	12.9
AS3	0 - 15	39.2	1.86	2.78	1.64	0.80	0.93	4.39	14.8	0.51	1.84
	15 - 30	39.9	1.39	2.96	1.74	0.36	0.73	4.71	9.45	0.39	2.05
	30 - 45	13.6	0.54	1.33	1.93	0.03	0.20	0.97	0.01	0.01	1.52
AS4	0 - 15	39.8	4.60	2.84	2.65	2.47	1.03	7.06	6.75	1.52	2.14
	15 - 30	17.6	2.88	1.05	2.53	1.01	0.89	5.48	5.86	1.99	0.84
	30 - 45	57.7	3.66	3.82	1.93	2.70	1.21	4.69	4.70	1.15	3.16
AS5	0 - 15	65.4	3.78	4.53	3.78	2.24	1.48	10.9	16.0	1.67	3.00
	15 - 30	59.6	3.24	4.50	6.81	1.98	1.61	23.9	18.8	1.73	3.22
	30 - 45	73.2	4.41	4.90	3.73	1.91	1.91	13.3	14.3	1.67	3.06
OK1	0 - 15	53.6	3.82	4.27	2.19	1.67	1.43	5.91	7.68	1.42	2.83
	15 - 30	70.6	5.11	4.55	1.58	2.22	0.62	6.10	6.76	1.45	3.74
	30 - 45	38.3	5.47	2.41	2.02	3.00	1.03	5.20	6.12	2.21	1.93
OK2	0 - 15	643	5.02	4.63	1.74	3.58	1.95	8.00	14.2	1.36	3.29
	15 - 30	37.9	6.82	2.12	3.13	3.58	2.31	3.52	24.5	1.95	0.54
	30 - 45	97.2	6.73	5.59	4.09	3.60	2.34	7.97	14.4	3.84	4.18
OK3	0 - 15	28.9	1.91	2.52	2.03	0.66	1.69	3.27	12.3	0.9	1.39
	15 - 30	46.2	2.84	3.85	2.46	0.78	3.46	3.62	17.5	1.02	1.67
	30 - 45	86.7	5.09	6.24	3.55	1.53	2.57	8.18	25.1	1.63	3.01
AB1	0 - 15	27.0	2.77	0.56	0.94	0.25	1.34	4.25	8.93	3.35	0.04
	15 - 30	25.7	16.1	0.63	2.52	6.51	3.48	13.12	20.9	9.89	0.12
	30 - 45	50.5	4.05	3.74	1.67	4.05	1.83	3.77	3.05	1.18	3.03
AB2	0 - 15	39.3	2.53	2.95	1.81	1.76	1.04	4.14	53.4	1.16	2.28
	15 - 30	3.05	0.12	0.97	1.36	0.01	0.04	0.16	0.00	0.00	2.35
	30 - 45	36.5	2.32	2.96	1.75	1.86	1.15	2.96	2.79	1.06	1.97
AB3	0 - 15	44.3	3.33	3.47	1.92	2.52	1.21	3.06	3.46	1.22	2.51
	15 - 30	30.0	2.44	2.64	1.42	2.17	0.93	2.76	1.73	0.91	1.91
	30 - 45	30.9	2.69	2.72	1.40	2.33	1.00	2.55	1.63	0.71	2.01
AB4	0 - 15	42.5	4.03	3.99	2.37	2.84	1.55	4.15	7.73	1.11	2.71
	15 - 30	87.3	11.3	63.4	10.8	4.90	72.1	7.99	11.5	1.88	5.23
	30 - 45	62.4	5.54	5.40	3.28	5.01	1.88	7.22	6.66	1.69	3.88
AB5	0 - 15	63.1	5.39	4.90	2.78	6.41	2.00	5.03	4.8	1.89	3.79
	15 - 30	52.1	4.42	4.42	2.26	4.08	1.45	4.74	3.40	1.58	3.30
	30 - 45	55.5	4.24	4.77	2.75	3.43	1.59	5.4	4.05	1.49	3.71
	MIN	3.05	0.12	0.56	0.94	0.01	0.04	0.16	0.00	0.00	0.02
	MAX	643	63.4	63.4	15.2	19.2	72.1	60.2	87.0	105	12.9
	MEAN	72.5	5.71	5.16	2.89	2.98	3.91	7.17	12.41	4.34	2.67

4.23   Geoaccumulation index a year after the major flooding

The geoaccumulation index of these soil profiles a year after the major flooding are shown in Table 4.37. The *Igeo* values of all metals except Cd fitted into *Igeo* class 1 which indicated that these soils were not polluted. However, *Igeo* values for Cd indicate that 26%, 23 % and 26% of all sites and depth fall into unpolluted to moderately polluted (class 2), moderately polluted (class 3) and moderately polluted to strongly polluted (class 4) respectively. Only the topsoil of site OK2 was in the strongly polluted to very polluted range (class 6).

Table 4.37: Geoaccumulation index of metals a year after major flooding

Sites	Depth (cm)	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Ba	Al	Fe
AS1	0 - 15	-1.17	-4.40	-6.45	-6.01	-7.52	-3.56	-4.47	-2.86	-4.24	-5.98	-10.3
	15 - 30	1.59	-3.57	-2.15	-2.69	-5.29	-3.00	-1.66	-2.46	-3.91	-3.61	-9.22
	30 - 45	-1.59	-4.25	-6.88	-6.31	-5.97	-5.79	-4.32	-3.79	-3.52	-10.2	-9.76
AS2	0 - 15	1.59	-2.19	-2.05	-3.31	-2.27	-3.56	-2.50	-1.16	-3.91	-4.61	-2.66
	15 - 30	2.42	-1.33	-1.50	-2.52	-1.14	-3.00	-1.04	-1.19	-2.96	-3.68	-1.79
	30 - 45	1.15	-2.63	-2.61	-4.10	-3.07	-7.29	-2.93	-0.76	-4.56	-4.78	-1.09
AS3	0 - 15	0.29	-4.11	-3.53	-4.29	-5.33	-5.11	-2.87	-1.12	-5.96	-5.00	-4.12
	15 - 30	0.74	-4.11	-3.02	-3.78	-6.05	-5.04	-2.35	-1.34	-5.95	-4.58	-3.55
	30 - 45	-1.17	-5.83	-4.52	-3.99	-10.3	-7.29	-4.98	-11.5	-11.8	-4.94	-4.34
AS4	0 - 15	1.92	-1.19	-1.89	-1.99	-2.09	-3.35	-0.58	-0.64	-2.79	-3.40	-2.30
	15 - 30	0.29	-2.32	-3.78	-2.51	-3.84	-4.02	-1.40	-1.30	-2.86	-3.85	-4.10
	30 - 45	2.56	-1.42	-1.36	-2.34	-1.86	-3.01	-1.06	-1.06	-3.09	-3.29	-1.63
AS5	0 - 15	0.74	-3.37	-3.11	-3.38	-4.13	-4.73	-1.85	-1.30	-4.55	-5.29	-3.71
	15 - 30	1.00	-3.20	-2.73	-2.13	-3.91	-4.21	-0.32	-0.67	-4.10	-4.90	-3.21
	30 - 45	0.29	-3.76	-3.61	-4.01	-4.97	-4.97	-2.17	-2.07	-5.16	-5.91	-4.29
OK1	0 - 15	1.78	-2.03	-1.87	-2.83	-3.22	-3.45	-1.40	-1.02	-3.46	-3.96	-2.46
	15 - 30	1.92	-1.87	-2.04	-3.57	-3.07	-4.91	-1.61	-1.47	-3.69	-4.22	-2.32
	30 - 45	1.22	-1.59	-2.77	-3.02	-2.45	-3.99	-1.66	-1.42	-2.89	-4.04	-3.09
OK2	0 - 15	4.24	-2.76	-2.88	-4.29	-3.25	-4.12	-2.09	-1.27	-4.65	-5.09	-3.37
	15 - 30	-0.85	-3.32	-5.01	-4.44	-4.25	-4.89	-4.28	-1.47	-5.13	-6.09	-6.97
	30 - 45	0.53	-3.32	-3.59	-4.04	-4.22	-4.85	-3.08	-2.23	-4.13	-6.07	-4.01
OK3	0 - 15	0.29	-3.63	-3.23	-3.54	-5.17	-3.80	-2.85	-0.94	-4.72	-4.56	-4.09
	15 - 30	0.00	-4.03	-3.59	-4.23	-5.89	-3.74	-3.67	-1.40	-5.50	-5.53	-4.79
	30 - 45	-0.36	-4.45	-4.16	-4.97	-6.18	-5.44	-3.77	-2.15	-6.09	-6.80	-5.21
AB1	0 - 15	-1.17	-4.45	-6.76	-6.01	-7.94	-5.50	-3.84	-2.77	-4.18	-5.92	-10.5
	15 - 30	-1.59	-2.26	-6.94	-4.94	-3.57	-4.47	-2.56	-1.88	-2.96	-6.27	-9.34
	30 - 45	2.12	-1.53	-1.64	-2.81	-1.53	-2.67	-1.63	-1.93	-3.30	-3.54	-1.94
AB2	0 - 15	2.56	-1.40	-1.18	-1.88	-1.92	-2.69	-0.69	3.00	-2.53	-2.74	-1.55
	15 - 30	-1.17	-5.83	-2.82	-2.34	-10.2	-7.41	-5.42	-10.5	-11.8	-2.78	-1.54
	30 - 45	2.66	-1.31	-0.96	-1.72	-1.63	-2.33	-0.96	-1.05	-2.44	-2.52	-1.54
AB3	0 - 15	2.45	-1.29	-1.23	-2.09	-1.69	-2.75	-1.41	-1.23	-2.74	-3.02	-1.70
	15 - 30	2.74	-0.88	-0.77	-1.66	-1.05	-2.28	-0.70	-1.37	-2.30	-2.17	-1.24
	30 - 45	2.81	-0.71	-0.70	-1.66	-0.92	-2.14	-0.79	-1.43	-2.64	-2.14	-1.13
AB4	0 - 15	0.83	-2.57	-2.58	-3.33	-3.08	-3.95	-2.53	-1.63	-4.43	-4.58	-3.14
	15 - 30	0.15	-2.80	-0.31	-2.87	-4.00	-0.12	-3.30	-2.77	-5.39	-6.30	-3.91
	30 - 45	1.42	-2.08	-2.12	-2.84	-2.22	-3.64	-1.70	-1.81	-3.79	-4.55	-2.59
AB5	0 - 15	2.19	-1.36	-1.50	-2.32	-1.11	-2.79	-1.46	-1.53	-2.87	-3.79	-1.87
	15 - 30	2.22	-1.33	-1.34	-2.31	-1.45	-2.94	-1.23	-1.72	-2.82	-3.48	-1.76
	30 - 45	1.47	-2.24	-2.07	-2.86	-2.54	-3.65	-1.89	-2.30	-3.74	-4.32	-2.43
	MIN	-1.59	-5.83	-6.94	-6.31	-10.3	-7.41	-5.42	-11.5	-11.8	-10.2	-10.5
	MAX	4.24	-0.71	-0.31	-1.66	-0.92	-0.12	-0.32	3.00	-2.30	-2.14	-1.09
	MEAN	1.00	-2.74	-2.85	-3.33	-3.85	-4.01	-2.28	-1.99	-4.29	-4.58	-3.81

4.24   Pollution Load index a year after the major flooding

The pollution load index a year after the major flooding are shown in Table 4.38. The pollution load index in these soil profiles a year after the major flooding ranged from 0.02 to 0.75. The highest and lowest PLI values were found at sites AB2 (0-15 cm depth) and AS3 (30-45 cm depth). The PLI of all sites and depths were also less than 1 denoting perfection as in three months after the major flooding.

Table 4.38: Pollution load index of metals a year after major flooding

Sites	Depth (cm)	CFCd	CFCo	CFCr	CFCu	CFMn	CFNi	CFPb	CFZn	CFBa	CFAl	CFFe	PLI
AS1	0 - 15	0.67	0.07	0.02	0.02	0.01	0.13	0.07	0.21	0.08	0.02	0.00	0.04
	15 - 30	4.50	0.13	0.34	0.23	0.04	0.19	0.48	0.27	0.10	0.12	0.00	0.16
	30 - 45	0.50	0.08	0.01	0.02	0.02	0.03	0.08	0.11	0.13	0.00	0.00	0.03
AS2	0 - 15	4.50	0.33	0.36	0.15	0.31	0.13	0.27	0.67	0.10	0.06	0.24	0.28
	15 - 30	8.00	0.60	0.53	0.26	0.68	0.19	0.73	0.66	0.19	0.12	0.44	0.49
	30 - 45	3.33	0.24	0.25	0.09	0.18	0.01	0.20	0.89	0.06	0.05	0.70	0.19
AS3	0 - 15	1.83	0.09	0.13	0.08	0.04	0.04	0.21	0.69	0.02	0.05	0.09	0.11
	15 - 30	2.50	0.09	0.19	0.11	0.02	0.05	0.30	0.59	0.02	0.06	0.13	0.13
	30 - 45	0.67	0.03	0.07	0.09	0.00	0.01	0.05	0.00	0.00	0.05	0.07	0.02
AS4	0 - 15	5.67	0.66	0.40	0.38	0.35	0.15	1.01	0.96	0.22	0.14	0.30	0.47
	15 - 30	1.83	0.30	0.11	0.26	0.10	0.09	0.57	0.61	0.21	0.10	0.09	0.23
	30 - 45	8.83	0.56	0.59	0.30	0.41	0.19	0.72	0.72	0.18	0.15	0.48	0.50
AS5	0 - 15	2.50	0.14	0.17	0.14	0.09	0.06	0.42	0.61	0.06	0.04	0.11	0.17
	15 - 30	3.00	0.16	0.23	0.34	0.10	0.08	1.21	0.95	0.09	0.05	0.16	0.25
	30 - 45	1.83	0.11	0.12	0.09	0.05	0.05	0.33	0.36	0.04	0.03	0.08	0.12
OK1	0 - 15	5.17	0.37	0.41	0.21	0.16	0.14	0.57	0.74	0.14	0.10	0.27	0.33
	15 - 30	5.67	0.41	0.37	0.13	0.18	0.05	0.49	0.54	0.12	0.08	0.30	0.28
	30 - 45	3.50	0.50	0.22	0.18	0.27	0.09	0.48	0.56	0.20	0.09	0.18	0.30
OK2	0 - 15	28.3	0.22	0.20	0.08	0.16	0.09	0.35	0.62	0.06	0.04	0.15	0.23
	15 - 30	0.83	0.15	0.05	0.07	0.08	0.05	0.08	0.54	0.04	0.02	0.01	0.08
	30 - 45	2.17	0.15	0.12	0.09	0.08	0.05	0.18	0.32	0.09	0.02	0.09	0.13
OK3	0 - 15	1.83	0.12	0.16	0.13	0.04	0.11	0.21	0.78	0.06	0.06	0.09	0.15
	15 - 30	1.50	0.09	0.13	0.08	0.03	0.11	0.12	0.57	0.03	0.03	0.05	0.10
	30 - 45	1.17	0.07	0.08	0.05	0.02	0.03	0.11	0.34	0.02	0.01	0.04	0.07
AB1	0 - 15	0.67	0.07	0.01	0.02	0.01	0.03	0.11	0.22	0.08	0.02	0.00	0.04
	15 - 30	0.50	0.31	0.01	0.05	0.13	0.07	0.26	0.41	0.19	0.02	0.00	0.08
	30 - 45	6.50	0.52	0.48	0.21	0.52	0.24	0.49	0.39	0.15	0.13	0.39	0.41
AB2	0 - 15	8.83	0.57	0.66	0.41	0.40	0.23	0.93	12.0	0.26	0.23	0.51	0.75
	15 - 30	0.67	0.03	0.21	0.30	0.00	0.01	0.04	0.00	0.00	0.22	0.52	0.03
	30 - 45	9.50	0.61	0.77	0.46	0.49	0.30	0.77	0.73	0.28	0.26	0.51	0.63
AB3	0 - 15	8.17	0.61	0.64	0.35	0.46	0.22	0.57	0.64	0.22	0.18	0.46	0.52
	15 - 30	10.0	0.81	0.88	0.47	0.73	0.31	0.92	0.58	0.31	0.33	0.64	0.72
	30 - 45	10.5	0.92	0.92	0.47	0.79	0.34	0.87	0.56	0.24	0.34	0.68	0.73
AB4	0 - 15	2.67	0.25	0.25	0.15	0.18	0.10	0.26	0.48	0.07	0.06	0.17	0.21
	15 - 30	1.67	0.22	1.21	0.21	0.09	1.38	0.15	0.22	0.04	0.02	0.10	0.20
	30 - 45	4.00	0.36	0.35	0.21	0.32	0.12	0.46	0.43	0.11	0.06	0.25	0.29
AB5	0 - 15	6.83	0.58	0.53	0.30	0.69	0.22	0.55	0.52	0.20	0.11	0.41	0.47
	15 - 30	7.00	0.59	0.59	0.30	0.55	0.20	0.64	0.46	0.21	0.13	0.44	0.48
	30 - 45	4.17	0.32	0.36	0.21	0.26	0.12	0.41	0.30	0.11	0.08	0.28	0.28
	MIN	0.50	0.03	0.01	0.02	0.00	0.01	0.04	0.00	0.00	0.00	0.00	0.02
	MAX	28.3	0.92	1.21	0.47	0.79	1.38	1.21	12.0	0.31	0.34	0.70	0.75
	MEAN	4.67	0.32	0.34	0.20	0.23	0.15	0.43	0.80	0.12	0.09	0.24	0.27

4.25   Ecological risk assessment of metals a year after major flooding

The computed ecological risk of metals in the study sites a year after the major flooding are shown in Table 4.39. The potential ecological risk (Er) of Cr, Cu, Co, Mn, Ni, Pb and Zn were in the low potential ecological risk category which indicated that these aforementioned metals have limited environmental impact in this study area. The ER values of Cd in 22 samples out of the 39 samples were greater than 80 indicating potential ecological risk of Cd. There was higher potential ecological risk with soils of the downstream section of the floodplain than the upstream and mid-stream sections of the floodplain. Similarly, the RI values a year after the major flooding were greater than 80 in the majority of the sites which indicates potential ecological risk with significant impact from Cd pollution. The potential ecological risks of the metals followed the order Cd > Pb > Zn > Cu > Ni > Cr > Mn > Co respectively.

Table 4.39: Ecological risk assessment of metals a year after major flooding

Sites	Depth (cm)	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	RI
AS1	0 - 15	20.0	0.14	0.03	0.12	0.01	0.64	0.34	0.21	21.5
	15 - 30	135	0.25	0.67	1.16	0.04	0.94	2.38	0.27	141
	30 - 45	15.0	0.16	0.03	0.09	0.02	0.14	0.38	0.11	15.9
AS2	0 - 15	135	0.66	0.72	0.76	0.31	0.64	1.33	0.67	140
	15 - 30	240	1.19	1.06	1.31	0.68	0.94	3.65	0.66	250
	30 - 45	100	0.48	0.49	0.44	0.18	0.05	0.99	0.89	104
AS3	0 - 15	55.0	0.17	0.26	0.38	0.04	0.22	1.03	0.69	57.8
	15 - 30	75.0	0.17	0.37	0.54	0.02	0.23	1.48	0.59	78.4
	30 - 45	20.0	0.05	0.13	0.47	0.00	0.05	0.24	0.00	20.9
AS4	0 - 15	170	1.31	0.81	1.89	0.35	0.74	5.03	0.96	181
	15 - 30	55.0	0.60	0.22	1.32	0.10	0.46	2.85	0.61	61.2
	30 - 45	265	1.12	1.17	1.48	0.41	0.93	3.59	0.72	274
AS5	0 - 15	75.0	0.29	0.35	0.72	0.09	0.28	2.09	0.61	79.4
	15 - 30	90.0	0.33	0.45	1.72	0.10	0.40	6.03	0.95	100
	30 - 45	55.0	0.22	0.25	0.47	0.05	0.24	1.66	0.36	58.2
OK1	0 - 15	155	0.74	0.82	1.06	0.16	0.69	2.85	0.74	162
	15 - 30	170	0.82	0.73	0.63	0.18	0.25	2.45	0.54	176
	30 - 45	105	1.00	0.44	0.92	0.27	0.47	2.38	0.56	111
OK2	0 - 15	850	0.44	0.41	0.38	0.16	0.43	1.76	0.62	854
	15 - 30	25.0	0.30	0.09	0.34	0.08	0.25	0.39	0.54	27
	30 - 45	65.0	0.30	0.25	0.46	0.08	0.26	0.89	0.32	67.6
OK3	0 - 15	55.0	0.24	0.32	0.64	0.04	0.54	1.04	0.78	58.6
	15 - 30	45.0	0.18	0.25	0.40	0.03	0.56	0.59	0.57	47.6
	30 - 45	35.0	0.14	0.17	0.24	0.02	0.17	0.55	0.34	36.6
AB1	0 - 15	20.0	0.14	0.03	0.12	0.01	0.17	0.53	0.22	21.2
	15 - 30	15.0	0.63	0.02	0.24	0.13	0.34	1.28	0.41	18.0
	30 - 45	195	1.04	0.96	1.07	0.52	1.18	2.43	0.39	203
AB2	0 - 15	265	1.14	1.33	2.04	0.40	1.17	4.66	12.01	288
	15 - 30	20.0	0.05	0.43	1.48	0.00	0.04	0.18	0.00	22.2
	30 - 45	285	1.21	1.54	2.28	0.49	1.50	3.86	0.73	297
AB3	0 - 15	245	1.23	1.28	1.77	0.46	1.12	2.83	0.64	254
	15 - 30	300	1.63	1.76	2.37	0.73	1.54	4.61	0.58	313
	30 - 45	315	1.83	1.85	2.37	0.79	1.70	4.34	0.56	328
AB4	0 - 15	80.0	0.51	0.50	0.74	0.18	0.49	1.30	0.48	84.2
	15 - 30	50.0	0.43	2.42	1.03	0.09	6.88	0.76	0.22	61.8
	30 - 45	120	0.71	0.69	1.05	0.32	0.60	2.31	0.43	126
AB5	0 - 15	205	1.17	1.06	1.51	0.69	1.08	2.73	0.52	214
	15 - 30	210	1.19	1.19	1.52	0.55	0.98	3.19	0.46	219
	30 - 45	125	0.64	0.72	1.03	0.26	0.60	2.03	0.30	131
	MIN	15.0	0.05	0.02	0.09	0.00	0.04	0.18	0.00	15.9
	MAX	850	1.83	2.42	2.37	0.79	6.88	6.03	12.01	854
	MEAN	140	0.64	0.67	0.99	0.23	0.77	2.13	0.80	146

4.26 Human exposure and health risk assessment of metals a year after the major flooding

4.26.1 Non-carcinogenic hazard

The non-carcinogenic hazard calculated based on total metal concentration for children and adults are shown in Table 4.40. The non-carcinogenic hazard of metals a year after the major flooding were similar to those obtained three months after the major flooding. In Table 4.40, the mean values of the different exposure pathways showed that HQ is in the order of HQing > HQdermal >> HQinh for children and adults. The non-carcinogenic hazards for the children case via dermal contact were higher than those for adults. The computed hazard index (HI) for all sites and depths a year after the major flooding ranged from 0.08 to 2.07 with a mean of 0.72 for children and 0.01 to 0.27 with a mean of 0.09 for adult scenario. The non-carcinogenic hazards were greater in children than adults. The HI values for the majority of the sites and depth were < 1 for the adults and children scenarios. However, some sites and depths had HI values greater than 1 for the children exposure suggesting that there is a probability of health effects arising from metal contamination in these sites.

Table 4.40: Non-carcinogenic health risk of exposures to metal in soils a year after major flooding

		CHILD				ADULT			
		HQing	HQinh	HQderm	HI	HQing	HQinh	HQderm	HI
AS1	0 - 15	0.10	0.0001	0.002	0.10	0.01	0.0001	0.0003	0.01
	15 - 30	0.38	0.0004	0.028	0.41	0.05	0.0004	0.0043	0.05
	30 - 45	0.08	0.0002	0.001	0.08	0.01	0.0002	0.0002	0.01
AS2	0 - 15	0.67	0.0021	0.030	0.70	0.08	0.0021	0.0047	0.09
	15 - 30	1.19	0.0041	0.045	1.24	0.15	0.0041	0.0071	0.16
	30 - 45	0.89	0.0026	0.022	0.91	0.11	0.0026	0.0034	0.12
AS3	0 - 15	0.24	0.0005	0.011	0.26	0.03	0.0005	0.0017	0.03
	15 - 30	0.32	0.0005	0.015	0.33	0.04	0.0005	0.0024	0.04
	30 - 45	0.15	0.0002	0.005	0.16	0.02	0.0002	0.0008	0.02
AS4	0 - 15	1.11	0.0027	0.035	1.14	0.14	0.0027	0.0054	0.15
	15 - 30	0.48	0.0009	0.010	0.49	0.06	0.0009	0.0016	0.06
	30 - 45	1.24	0.0033	0.050	1.29	0.16	0.0033	0.0077	0.17
AS5	0 - 15	0.34	0.0008	0.015	0.35	0.04	0.0008	0.0023	0.05
	15 - 30	0.48	0.0010	0.019	0.50	0.06	0.0010	0.0030	0.06
	30 - 45	0.24	0.0005	0.010	0.25	0.03	0.0005	0.0016	0.03
OK1	0 - 15	0.78	0.0017	0.034	0.82	0.10	0.0017	0.0054	0.11
	15 - 30	0.80	0.0018	0.031	0.83	0.10	0.0018	0.0048	0.11
	30 - 45	0.73	0.0019	0.019	0.75	0.09	0.0019	0.0030	0.10
OK2	0 - 15	0.52	0.0013	0.027	0.55	0.07	0.0013	0.0042	0.07
	15 - 30	0.17	0.0004	0.004	0.18	0.02	0.0004	0.0007	0.02
	30 - 45	0.27	0.0007	0.011	0.29	0.03	0.0007	0.0017	0.04
OK3	0 - 15	0.30	0.0005	0.013	0.31	0.04	0.0005	0.0021	0.04
	15 - 30	0.20	0.0003	0.010	0.21	0.03	0.0003	0.0016	0.03
	30 - 45	0.14	0.0003	0.007	0.15	0.02	0.0003	0.0011	0.02
AB1	0 - 15	0.09	0.0001	0.002	0.09	0.01	0.0001	0.0002	0.01
	15 - 30	0.29	0.0007	0.002	0.29	0.04	0.0007	0.0003	0.04
	30 - 45	1.07	0.0034	0.041	1.11	0.13	0.0034	0.0064	0.14
AB2	0 - 15	1.42	0.0034	0.056	1.48	0.18	0.0034	0.0087	0.19
	15 - 30	0.70	0.0013	0.017	0.71	0.09	0.0013	0.0027	0.09
	30 - 45	1.48	0.0037	0.064	1.55	0.19	0.0037	0.0100	0.20
AB3	0 - 15	1.30	0.0035	0.053	1.36	0.16	0.0035	0.0083	0.18
	15 - 30	1.86	0.0051	0.073	1.93	0.23	0.0051	0.0114	0.25
	30 - 45	1.99	0.0055	0.077	2.07	0.25	0.0055	0.0120	0.27
AB4	0 - 15	0.50	0.0013	0.021	0.53	0.06	0.0013	0.0032	0.07
	15 - 30	0.74	0.0012	0.094	0.84	0.09	0.0012	0.0148	0.11
	30 - 45	0.70	0.0021	0.029	0.73	0.09	0.0021	0.0045	0.09
AB5	0 - 15	1.14	0.0041	0.045	1.19	0.14	0.0041	0.0070	0.15
	15 - 30	1.22	0.0037	0.049	1.27	0.15	0.0037	0.0077	0.16
	30 - 45	0.70	0.0020	0.030	0.74	0.09	0.0020	0.0046	0.10
	MIN	0.08	0.0001	0.001	0.080	0.01	0.0001	0.0002	0.01
	MAX	1.99	0.0055	0.094	2.071	0.25	0.0055	0.0148	0.27
	MEAN	0.69	0.0018	0.028	0.723	0.09	0.0018	0.0044	0.09

4.26.2 Carcinogenic health Risk

The carcinogenic risk calculated based on total metal concentration for children and adults a year after the major flooding are shown in Table 4.41. In Table 4.41, the mean values of the different exposure pathways showed that risk is in the order of dermal >ingestion > inhalation for children and ingestion > dermal > inhalation for adults. The cancer risk via ingestion, inhalation and dermal contact a year after the major flooding ranged from 1.52×10^{-8} to 4.56×10^{-7}, 2.07×10^{-10} to 1.86×10^{-8} and 3.13×10^{-8} to 2.81×10^{-6} respectively for children and 2.27×10^{-8} to 6.91×10^{-7}, 1.10×10^{-9} to 9.86×10^{-8} and 1.40×10^{-9} to 1.26×10^{-7} respectively for adults. The observed inhalation cancer risk was low compared to those of ingestion and dermal contact. The cancer risk via ingestion and inhalation obtained a year after the major flooding for adults were also higher than the children scenario while cancer risks for the children case via dermal contact were higher than for adults. The total cancer risks for all the sites and depths ranged from 4.72×10^{-8} to 2.62×10^{-6} with a mean value of 9.73×10^{-7} and 2.52×10^{-8} to 9.15×10^{-7} with a mean value of 3.34×10^{-7} for children and adults respectively. The total cancer risk values obtained in this study a year after the major flooding indicates low potential cancer risk as the cancer risk were lower than the potentially acceptable carcinogenic target risk values of 10^{-6} set by USEPA (2011).

Table 4.41: Carcinogenic health risk of exposures to metal in soils a year after major flooding

		CHILD				ADULT			
		$RISK_{ING}$	$RISK_{INH}$	$RISK_{DERM}$	TOTAL CANCER RISK	$RISK_{ING}$	$RISK_{INH}$	$RISK_{DERM}$	TOTAL CANCER RISK
AS1	0 - 15	1.61E-08	3.06E-10	4.20E-08	5.84E-08	2.41E-08	1.62E-09	1.88E-09	2.76E-08
	15 - 30	1.88E-07	5.19E-09	7.89E-07	9.82E-07	2.82E-07	2.74E-08	3.53E-08	3.44E-07
	30 - 45	1.52E-08	2.14E-10	3.18E-08	4.72E-08	2.27E-08	1.13E-09	1.42E-09	2.52E-08
AS2	0 - 15	1.68E-07	5.53E-09	8.41E-07	1.01E-06	2.51E-07	2.92E-08	3.76E-08	3.18E-07
	15 - 30	2.94E-07	8.14E-09	1.24E-06	1.54E-06	4.39E-07	4.30E-08	5.55E-08	5.38E-07
	30 - 45	1.17E-07	3.76E-09	5.74E-07	6.95E-07	1.75E-07	1.99E-08	2.57E-08	2.21E-07
AS3	0 - 15	7.55E-08	1.99E-09	3.04E-07	3.81E-07	1.13E-07	1.05E-08	1.36E-08	1.37E-07
	15 - 30	1.08E-07	2.84E-09	4.34E-07	5.45E-07	1.62E-07	1.50E-08	1.94E-08	1.96E-07
	30 - 45	3.07E-08	9.99E-10	1.53E-07	1.84E-07	4.60E-08	5.28E-09	6.83E-09	5.81E-08
AS4	0 - 15	2.85E-07	6.20E-09	9.49E-07	1.24E-06	4.27E-07	3.28E-08	4.25E-08	5.02E-07
	15 - 30	1.18E-07	1.70E-09	2.62E-07	3.82E-07	1.77E-07	9.00E-09	1.17E-08	1.98E-07
	30 - 45	3.12E-07	8.97E-09	1.37E-06	1.69E-06	4.67E-07	4.74E-08	6.12E-08	5.76E-07
AS5	0 - 15	1.21E-07	2.66E-09	4.07E-07	5.30E-07	1.81E-07	1.40E-08	1.82E-08	2.13E-07
	15 - 30	2.48E-07	3.47E-09	5.39E-07	7.91E-07	3.71E-07	1.84E-08	2.42E-08	4.14E-07
	30 - 45	9.10E-08	1.89E-09	2.90E-07	3.83E-07	1.36E-07	1.00E-08	1.30E-08	1.59E-07
OK1	0 - 15	2.28E-07	6.31E-09	9.63E-07	1.20E-06	3.42E-07	3.33E-08	4.31E-08	4.18E-07
	15 - 30	2.00E-07	5.58E-09	8.53E-07	1.06E-06	3.00E-07	2.95E-08	3.82E-08	3.68E-07
	30 - 45	1.46E-07	3.40E-09	5.18E-07	6.67E-07	2.18E-07	1.79E-08	2.32E-08	2.59E-07
OK2	0 - 15	1.23E-07	3.33E-09	4.78E-07	6.05E-07	1.84E-07	1.76E-08	2.14E-08	2.23E-07
	15 - 30	2.80E-08	7.26E-10	1.09E-07	1.38E-07	4.19E-08	3.84E-09	4.89E-09	5.06E-08
	30 - 45	7.01E-08	1.91E-09	2.91E-07	3.63E-07	1.05E-07	1.01E-08	1.30E-08	1.28E-07
OK3	0 - 15	8.71E-08	2.46E-09	3.73E-07	4.63E-07	1.30E-07	1.30E-08	1.67E-08	1.60E-07
	15 - 30	6.22E-08	1.94E-09	2.93E-07	3.57E-07	9.30E-08	1.03E-08	1.31E-08	1.16E-07
	30 - 45	4.59E-08	1.30E-09	1.97E-07	2.44E-07	6.86E-08	6.85E-09	8.83E-09	8.43E-08
AB1	0 - 15	1.97E-08	2.32E-10	3.47E-08	5.46E-08	2.95E-08	1.23E-09	1.55E-09	3.22E-08
	15 - 30	3.95E-08	2.07E-10	3.13E-08	7.10E-08	5.91E-08	1.10E-09	1.40E-09	6.16E-08
	30 - 45	2.42E-07	7.40E-09	1.12E-06	1.37E-06	3.62E-07	3.91E-08	5.03E-08	4.52E-07
AB2	0 - 15	3.70E-07	1.02E-08	1.55E-06	1.93E-06	5.54E-07	5.37E-08	6.94E-08	6.77E-07
	15 - 30	8.21E-08	3.22E-09	4.93E-07	5.78E-07	1.23E-07	1.70E-08	2.21E-08	1.62E-07
	30 - 45	3.87E-07	1.18E-08	1.80E-06	2.20E-06	5.79E-07	6.24E-08	8.05E-08	7.22E-07
AB3	0 - 15	3.11E-07	9.80E-09	1.49E-06	1.81E-06	4.65E-07	5.18E-08	6.67E-08	5.83E-07
	15 - 30	4.48E-07	1.35E-08	2.05E-06	2.52E-06	6.70E-07	7.12E-08	9.20E-08	8.33E-07
	30 - 45	4.56E-07	1.41E-08	2.15E-06	2.62E-06	6.82E-07	7.48E-08	9.64E-08	8.54E-07
AB4	0 - 15	1.27E-07	3.84E-09	5.85E-07	7.16E-07	1.90E-07	2.03E-08	2.62E-08	2.37E-07
	15 - 30	4.62E-07	1.86E-08	2.81E-06	3.29E-06	6.91E-07	9.86E-08	1.26E-07	9.15E-07
	30 - 45	1.90E-07	5.30E-09	8.09E-07	1.00E-06	2.84E-07	2.80E-08	3.62E-08	3.49E-07
AB5	0 - 15	2.68E-07	8.14E-09	1.24E-06	1.51E-06	4.01E-07	4.30E-08	5.54E-08	5.00E-07
	15 - 30	3.04E-07	9.09E-09	1.39E-06	1.70E-06	4.55E-07	4.81E-08	6.21E-08	5.65E-07
	30 - 45	1.86E-07	5.47E-09	8.34E-07	1.03E-06	2.78E-07	2.89E-08	3.74E-08	3.44E-07
	MIN	1.52E-08	2.07E-10	3.13E-08	4.72E-08	2.27E-08	1.10E-09	1.40E-09	2.52E-08
	MAX	4.56E-07	1.86E-08	2.81E-06	2.62E-06	6.91E-07	9.86E-08	1.26E-07	9.15E-07
	MEAN	1.81E-07	5.17E-09	7.87E-07	9.73E-07	2.71E-07	2.73E-08	3.52E-08	3.34E-07

4.27   Correlation analysis a year after the major flooding

The results of the correlation analysis of metals a year after the major flooding are shown in Table 4.42. The correlation patterns of metals in these soil profiles a year after the major flooding were similar to those observed three months after the major flooding event.

Table 4.42: Correlation among the metals in the floodplain soil a year after the major flooding

	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Ba	Al	Fe
Cd	1.00	0.23	0.25	0.12	0.24	0.17	0.25	0.13	0.12	0.16	0.26
Co		1.00	0.92**	0.95**	0.89**	0.85**	0.87**	0.37	0.93**	0.87**	0.93**
Cr			1.00	0.93**	0.87**	0.89**	0.79**	0.52*	0.88**	0.92**	1.00**
Cu				1.00	0.81**	0.83**	0.92**	0.53*	0.93**	0.94**	0.94**
Mn					1.00	0.83**	0.64*	0.27	0.81**	0.70**	0.88**
Ni						1.00	0.65*	0.50*	0.89**	0.85**	0.89**
Pb							1.00	0.56*	0.84**	0.85**	0.81**
Zn								1.00	0.55*	0.69*	0.55*
Ba									1.00	0.92**	0.90**
Al										1.00	0.93**
Fe											1.00
15-30 cm											
Cd	1.00	0.87**	0.51*	0.62*	0.89**	-0.01	0.65*	0.29	0.70**	0.63*	0.69*
Co		1.00	0.50*	0.52*	0.95**	0.07	0.56*	0.27	0.89**	0.54*	0.65*
Cr			1.00	0.50*	0.50*	0.83**	0.21	-0.20	0.24	0.33	0.44
Cu				1.00	0.58*	0.12	0.69*	0.09	0.50*	0.79**	0.72**
Mn					1.00	0.05	0.56*	0.26	0.79**	0.58*	0.73**
Ni						1.00	-0.13	-0.31	-0.09	-0.13	-0.06
Pb							1.00	0.69*	0.61*	0.34	0.37
Zn								1.00	0.30	-0.19	-0.08
Ba									1.00	0.50*	0.43
Al										1.00	0.83**
Fe											1.00
30-45 cm											
Cd	1.00	0.94**	0.98**	0.95**	0.94**	0.95**	0.96**	0.63*	0.83**	0.93**	0.79**
Co		1.00	0.94**	0.92**	0.98**	0.92**	0.95**	0.59*	0.87**	0.92**	0.75**
Cr			1.00	0.97**	0.95**	0.96**	0.94**	0.58*	0.81**	0.96**	0.80**
Cu				1.00	0.91**	0.95**	0.95**	0.51*	0.84**	0.97**	0.70**
Mn					1.00	0.95**	0.92**	0.53*	0.81**	0.92**	0.77**
Ni						1.00	0.92**	0.42	0.84**	0.94**	0.64*
Pb							1.00	0.60*	0.85**	0.90**	0.68*
Zn								1.00	0.51*	0.49	0.81**
Ba									1.00	0.81**	0.55*
Al										1.00	0.74**
Fe											1.00

*Pearson Correlation is significant at the 0.05 level (1 tailed)
** Pearson Correlation is significant at the 0.01 level (1 tailed)

4.28   Principal Component Analysis (PCA) a year after the major flooding

Results of PCA application to all sites and depths a year after the major flooding are presented in Table 4.44. At the 0-15 cm depth a year after the major flooding, only one component factor was extracted and accounts for 75.70 % of the variability in the data and the solution could not be rotated. At the 15-30 cm depth a year after the major flooding event, three factors were identified accounting for 83.46% of the variability in the data (Table 4.43 and Figure 17). Factor 1 explains 49.27 % of the total variance and was characterised by positive loading of Cd, Co, Mn, Al and Fe. This indicates that these metals are associated with Fe, Mn and Al oxides/ hydroxide phase in this soil horizon. Factor 2 accounts for 19.48 % of the total variance. It was dominated by Pb, Zn, Ba and Cu. Factor 3 accounts for 14.71 % of the total variance and was characterised by high loadings of Cr and Ni. However, at the 30-45 cm depth a year after the major flooding, only one component factor was extracted and accounts for 79.66 % of the variability in the data and the solution could not be rotated.

Table 4.43: PCA Factor loadings after Varimax with Kaiser normalization rotation for metals in soils at 15-30 cm depth a year after the major flooding.

Heavy Metals	Component		
	Factor 1	Factor 2	Factor 3
Cd	.839		
Co	.777	.413	
Cr			.918
Cu	.588	.569	.413
Mn	.824		
Ni			.963
Pb	.479	.758	
Zn		.869	
Ba		.634	
Al	.919		
Fe	.930		
Variance %	**49.27**	**19.48**	**14.71**
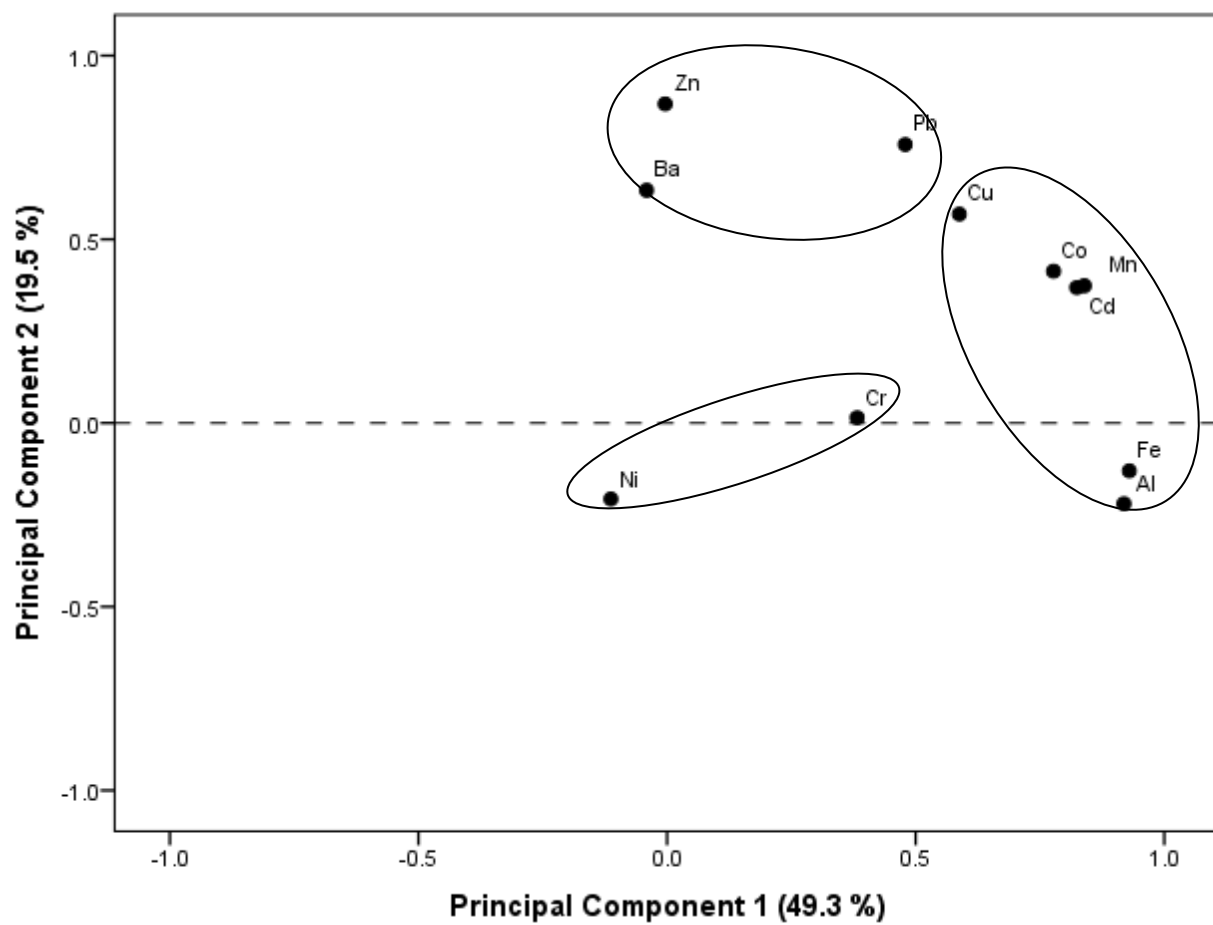
Figure 17: The loading plot of PCA of metals in the floodplain soils (15-30 cm depth) a year after the major flooding.

4.29   Chemical Fractionation of metals a year after the major flooding

The results for the concentrations of metals in different extraction phases a year after the major flooding are shown in Tables 4.45 to 4.53, while the fractionation patterns of the studied metals are shown in Figures 18 to 26.

Cadmium

A year after the major flooding event, the majority of Cd exists in the residual and reducible phases in these soil profiles. The percentage of total Cd in the residual phase ranged from 3.7 to 93.8 % (Table 4.44 and Figure 18 a-c). The reducible phase constituted 3.0 to 85.2 % of the total Cd in these soil profiles a year after the flooding in the form of Cd-oxides in these sites. About 1.9 to 85.7 % of the total Cd were found in the oxidizable phase. Cadmium was not found in the oxidizable phase in majority of the samples a year after the major flooding. The highest fraction of Cd in the oxidizable phase was observed at 30-45 cm depth of site OK3. The exchangeable/acid soluble phase constituted 0.5 to 29 % of the total Cd in these soil profiles and the 15-30 cm depth of site AB2 had the highest fraction.

Table 4.44: Concentrations and percentages of Cadmium in different extraction phases of the floodplain soils of the lower reaches of River Niger a year after the major flooding

| Sites	Depth (cm)	CONCENTRATION (µg g^{-1})						PERCENTAGE (%)				
		F1	F2	F3	F4	SUM	TM	F1	F2	F3	F4	RECOVERY
AS1	0 - 15	0.02	0.08	0.04	0.09	0.23	0.20	8.2	36.7	15.3	39.8	115.0
	15 - 30	0.04	0.08	ND	1.23	1.35	1.35	3.0	5.9	-	91.1	100.0
	30 - 45	ND	0.08	ND	0.07	0.15	0.15	-	53.3	-	46.7	100.0
AS2	0 - 15	ND	0.32	ND	1.03	1.35	1.35	-	23.7	-	76.3	100.0
	15 - 30	0.04	0.36	ND	2.00	2.40	2.40	1.7	15.0	-	83.3	100.0
	30 - 45	0.12	0.92	ND	0.04	1.08	1.00	11.1	85.2	-	3.7	108.0
AS3	0 - 15	0.04	0.08	ND	0.43	0.55	0.55	7.3	14.5	-	78.2	100.0
	15 - 30	0.04	0.04	ND	0.67	0.75	0.75	5.3	5.3	-	89.3	100.0
	30 - 45	ND	0.04	ND	0.16	0.20	0.20	-	20.0	-	80.0	100.0
AS4	0 - 15	0.12	0.36	0.40	0.82	1.70	1.70	7.1	21.2	23.5	48.2	100.0
	15 - 30	0.12	0.20	ND	0.23	0.55	0.55	21.8	36.4	-	41.8	100.0
	30 - 45	0.12	0.08	0.05	2.40	2.65	2.65	4.5	3.0	1.9	90.6	100.0
AS5	0 - 15	0.16	0.40	ND	0.19	0.75	0.75	21.3	53.3	-	25.3	100.0
	15 - 30	0.08	0.24	ND	0.58	0.90	0.90	8.9	26.7	-	64.4	100.0
	30 - 45	0.12	0.04	ND	0.39	0.55	0.55	21.8	7.3	-	70.9	100.0
OK1	0 - 15	0.16	1.12	ND	0.27	1.55	1.55	10.3	72.3	-	17.4	100.0
	15 - 30	ND	0.24	ND	1.46	1.70	1.70	-	14.1	-	85.9	100.0
	30 - 45	0.12	0.48	0.05	0.40	1.05	1.05	11.4	45.7	4.8	38.1	100.0
OK2	0 - 15	0.04	0.92	ND	7.54	8.50	8.50	0.5	10.8	-	88.7	100.0
	15 - 30	ND	0.04	ND	0.21	0.25	0.25	-	16.0	-	84.0	100.0
	30 - 45	0.04	0.04	ND	0.57	0.65	0.65	6.2	6.2	-	87.7	100.0
OK3	0 - 15	0.08	0.04	ND	0.43	0.55	0.55	14.5	7.3	-	78.2	100.0
	15 - 30	ND	0.04	ND	0.41	0.45	0.45	-	8.9	-	91.1	100.0
	30 - 45	ND	ND	0.30	0.05	0.35	0.35	-		85.7	14.3	100.0
AB1	0 - 15	0.06	0.09	ND	0.09	0.24	0.20	23.8	38.1	-	38.1	120.0
	15 - 30	0.02	0.10	ND	0.05	0.17	0.15	9.8	58.5	-	31.7	113.3
	30 - 45	ND	0.12	ND	1.83	1.95	1.95	-	6.2	-	93.8	100.0
AB2	0 - 15	0.12	0.72	ND	1.81	2.65	2.65	4.5	27.2	-	68.3	100.0
	15 - 30	0.07	0.07	ND	0.10	0.23	0.20	29.0	29.0	-	41.9	115.0
	30 - 45	0.08	0.32	ND	2.45	2.85	2.85	2.8	11.2	-	86.0	100.0
AB3	0 - 15	0.12	0.40	ND	1.93	2.45	2.45	4.9	16.3	-	78.8	100.0
	15 - 30	0.08	0.36	0.15	2.41	3.00	3.00	2.7	12.0	5.0	80.3	100.0
	30 - 45	0.16	0.20	ND	2.79	3.15	3.15	5.1	6.3	-	88.6	100.0
AB4	0 - 15	0.04	0.12	ND	0.64	0.80	0.80	5.0	15.0	-	80.0	100.0
	15 - 30	ND	0.08	ND	0.42	0.50	0.50	-	16.0	-	84.0	100.0
	30 - 45	ND	0.24	ND	0.96	1.20	1.20	-	20.0	-	80.0	100.0
AB5	0 - 15	0.08	0.52	0.05	1.40	2.05	2.05	3.9	25.4	2.4	68.3	100.0
	15 - 30	0.08	0.48	0.15	1.39	2.10	2.10	3.8	22.9	7.1	66.2	100.0
	30 - 45	0.08	0.24	ND	0.93	1.25	1.25	6.4	19.2	-	74.4	100.0

F1 = Exchangeable fraction; F2 = Reducible fraction; F3 = Oxidizable fraction; F4 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil
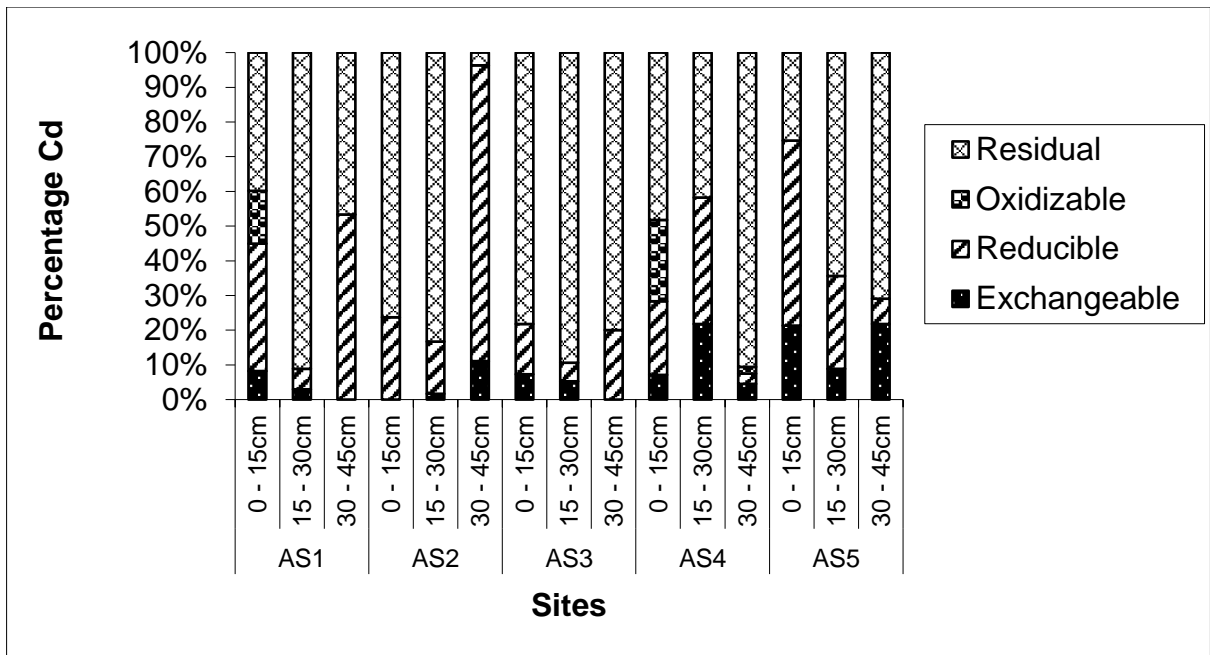
(18a)
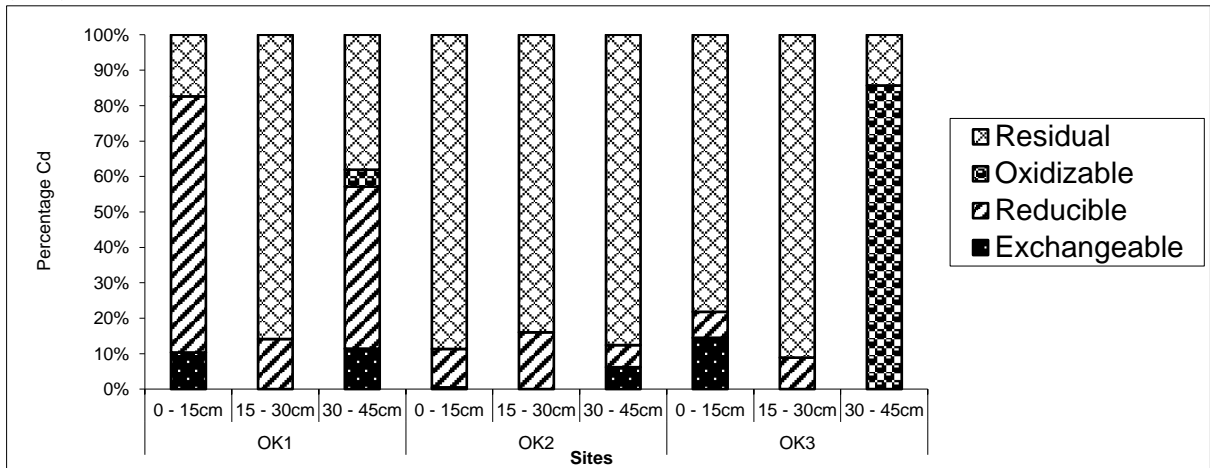
(18b)
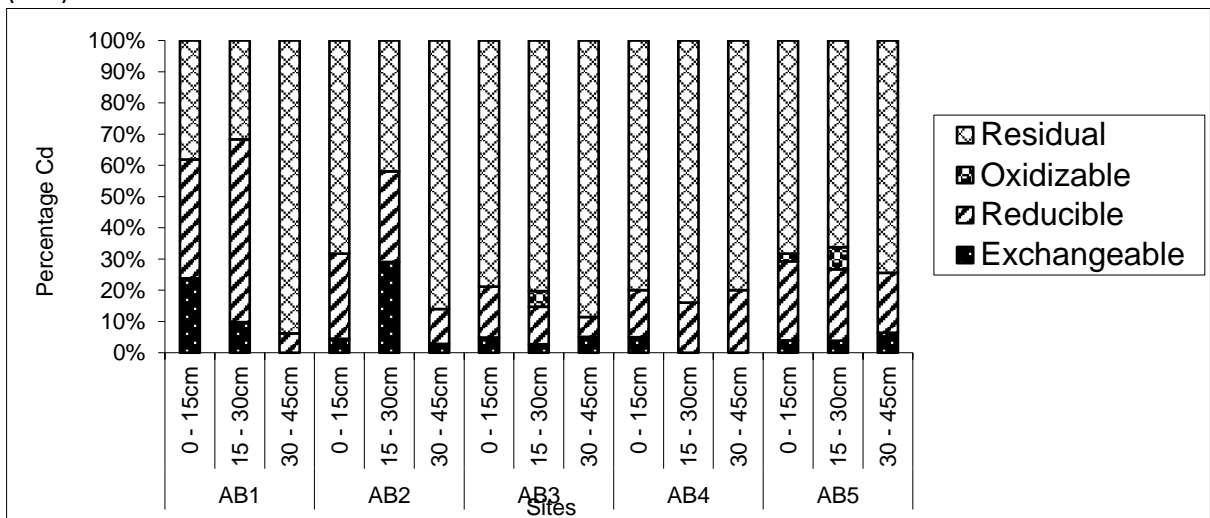
(18c)

Figure 18: Percentage of Cadmium in the various extraction phases as a function of total Cadmium content in these soils a year after the major flooding

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Cobalt

The partition scheme of Co indicates its association with all the extraction phases except for Fe-Mn oxide phase in some depths from sites AS1, AS3 and OK3. The proportion of Co ranged from 1.5 to 40 %, 4.8 to 82.9 %, 2.9 to 54.7 % and 2.4 to 92.1 % for exchangeable for exchangeable/acid soluble phase, reducible, oxidizable and residual phases respectively (Table 4.45 and Figure 19 a-c).

Table 4.45: Concentrations and percentages of Cobalt in different extraction phases of the floodplain soils of the lower reaches of River Niger a year after the major flooding

| Sites	Depth (cm)	CONCENTRATION (μg g⁻¹) F1	F2	F3	F4	SUM	TM	PERCENTAGE (%) F1	F2	F3	F4	RECOVERY
AS1	0 - 15	0.44	0.20	0.15	0.56	1.35	1.35	32.6	14.8	11.1	41.5	100.0
	15 - 30	0.32	ND	ND	2.08	2.40	2.40	13.3	-	-	86.7	100.0
	30 - 45	0.28	ND	ND	1.22	1.50	1.50	18.7	-	-	81.3	100.0
AS2	0 - 15	0.60	3.20	0.50	1.95	6.25	6.25	9.6	51.2	8.0	31.2	100.0
	15 - 30	0.52	5.32	0.75	4.76	11.35	11.35	4.6	46.9	6.6	41.9	100.0
	30 - 45	0.24	1.32	0.30	2.74	4.60	4.60	5.2	28.7	6.5	59.6	100.0
AS3	0 - 15	0.32	0.08	ND	1.25	1.65	1.65	19.4	4.8	-	75.8	100.0
	15 - 30	0.08	ND	0.05	1.52	1.65	1.65	4.8	-	3.0	92.1	100.0
	30 - 45	0.20	ND	0.05	0.25	0.50	0.50	40.0	-	10.0	50.0	100.0
AS4	0 - 15	1.24	2.96	1.45	6.80	12.45	12.45	10.0	23.8	11.6	54.6	100.0
	15 - 30	0.52	3.24	0.88	1.41	6.05	5.70	8.6	53.6	14.5	23.3	106.1
	30 - 45	0.16	1.24	0.40	8.85	10.65	10.65	1.5	11.6	3.8	83.1	100.0
AS5	0 - 15	0.96	0.32	0.30	1.17	2.75	2.75	34.9	11.6	10.9	42.5	100.0
	15 - 30	0.92	0.32	0.40	1.46	3.10	3.10	29.7	10.3	12.9	47.1	100.0
	30 - 45	0.48	0.16	0.15	1.31	2.10	2.10	22.9	7.6	7.1	62.4	100.0
OK1	0 - 15	2.28	0.48	0.95	3.29	7.00	7.00	32.6	6.9	13.6	47.0	100.0
	15 - 30	1.80	1.84	0.55	3.61	7.80	7.80	23.1	23.6	7.1	46.3	100.0
	30 - 45	0.44	7.88	1.15	0.03	9.50	9.50	4.6	82.9	12.1	0.3	100.0
OK2	0 - 15	0.56	0.80	0.35	2.49	4.20	4.20	13.3	19.0	8.3	59.3	100.0
	15 - 30	0.28	0.72	0.35	1.50	2.85	2.85	9.8	25.3	12.3	52.6	100.0
	30 - 45	0.28	ND	0.25	2.32	2.85	2.85	9.8	-	8.8	81.4	100.0
OK3	0 - 15	0.36	ND	0.15	1.79	2.30	2.30	15.7	-	6.5	77.8	100.0
	15 - 30	0.20	ND	0.05	1.50	1.75	1.75	11.4	-	2.9	85.7	100.0
	30 - 45	0.20	ND	ND	1.10	1.30	1.30	15.4	-	-	84.6	100.0
AB1	0 - 15	0.12	0.55	0.10	0.61	1.37	1.30	8.6	39.8	7.0	44.7	105.4
	15 - 30	0.37	4.38	0.52	1.84	7.10	5.95	5.2	61.6	7.3	25.9	119.3
	30 - 45	0.40	4.20	ND	5.30	9.90	9.90	4.0	42.4	-	53.5	100.0
AB2	0 - 15	2.36	3.72	1.20	3.52	10.80	10.80	21.9	34.4	11.1	32.6	100.0
	15 - 30	0.03	0.13	0.16	0.22	0.54	0.50	5.9	23.7	29.6	40.7	108.0
	30 - 45	0.36	2.16	0.25	8.73	11.50	11.50	3.1	18.8	2.2	75.9	100.0
AB3	0 - 15	0.52	3.88	0.95	6.30	11.65	11.65	4.5	33.3	8.2	54.1	100.0
	15 - 30	0.48	6.32	1.10	7.55	15.45	15.45	3.1	40.9	7.1	48.9	100.0
	30 - 45	0.44	7.40	10.00	0.44	18.28	17.40	2.4	40.5	54.7	2.4	105.1
AB4	0 - 15	1.08	0.72	0.60	2.40	4.80	4.80	22.5	15.0	12.5	50.0	100.0
	15 - 30	0.48	0.52	0.30	2.80	4.10	4.10	11.7	12.7	7.3	68.3	100.0
	30 - 45	0.44	2.60	0.45	3.26	6.75	6.75	6.5	38.5	6.7	48.3	100.0
AB5	0 - 15	1.64	4.80	1.10	3.56	11.10	11.10	14.8	43.2	9.9	32.1	100.0
	15 - 30	3.08	3.12	1.30	3.80	11.30	11.30	27.3	27.6	11.5	33.6	100.0
	30 - 45	2.36	0.96	0.80	1.93	6.05	6.05	39.0	15.9	13.2	31.9	100.0

F1 = Exchangeable fraction; F2 = Reducible fraction; F3 = Oxidizable fraction; F4 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil sample
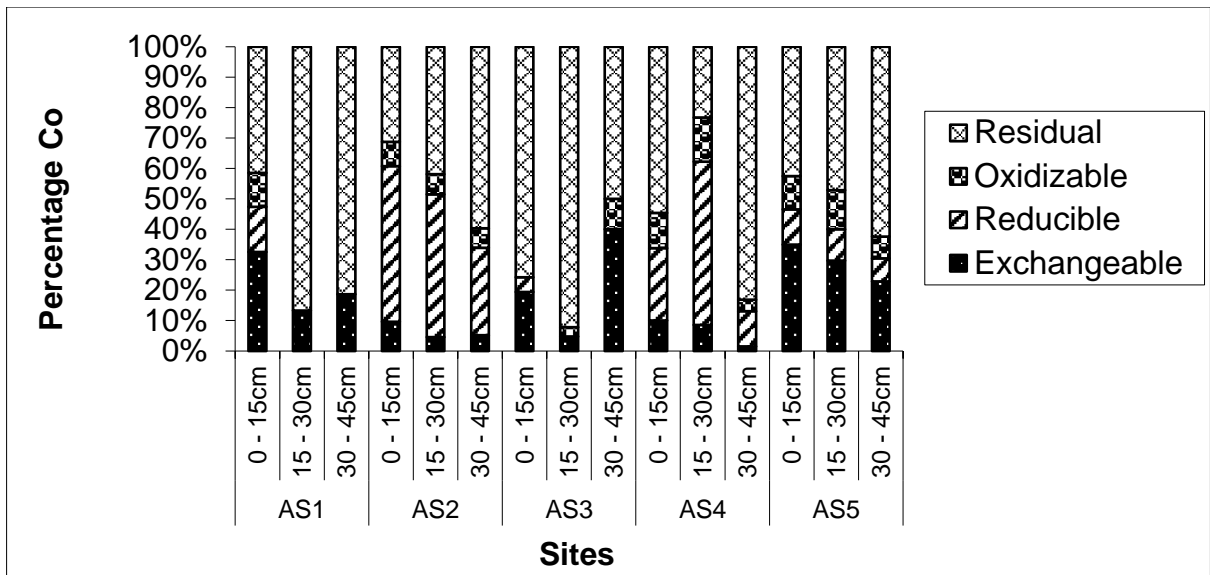
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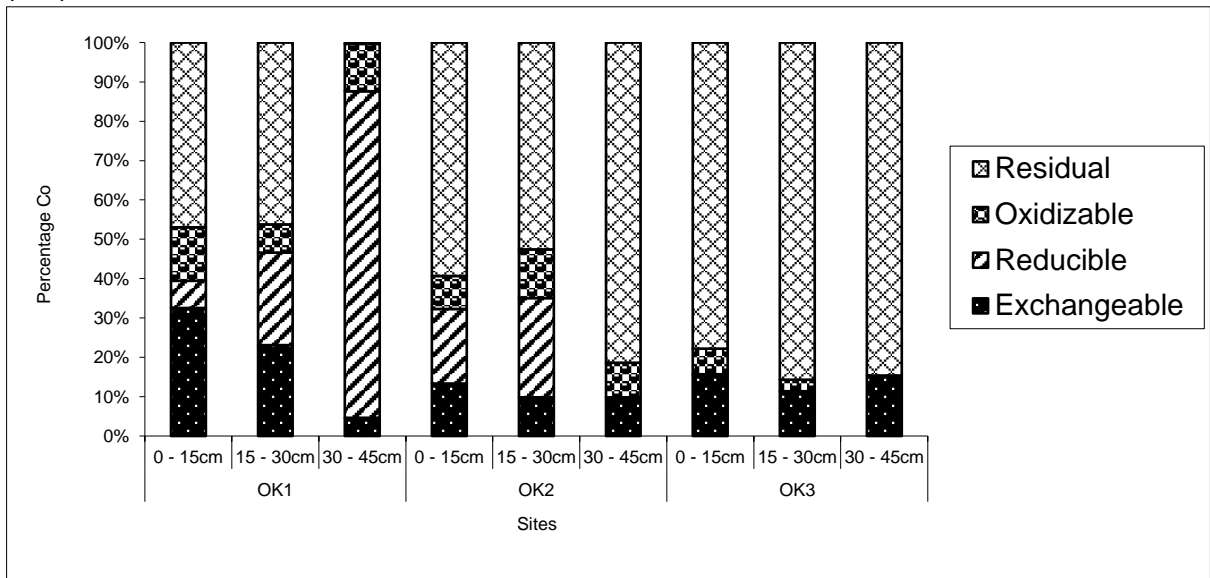
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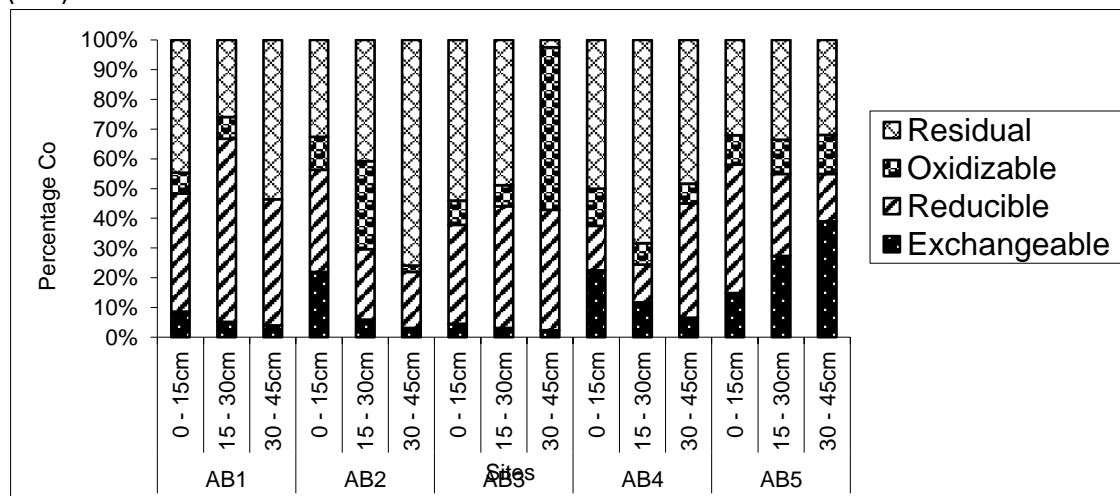
(19c)

Figure 19: Percentage of Cobalt in the various extraction phases as a function of total Cobalt content in soils a year after the major flooding

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Chromium

A year after the major flooding, the partition scheme of Cr indicates that it is associated with all the extraction phases (Table 4.47 and Figure 20). This variation may be as a result of anthropogenic inputs and mobility of Cr in these soil profiles. The residual fraction consist of 17.5 to 94.8 % of the total Cr in these sites a year after the major flooding. The reducible phase constituted 1.4 to 37.9 % of Cr in these soil profiles. The fraction of Cr in the oxidizable fraction a year after the major flooding ranged from 1.8 to 67.4 % of the total Cr. 15-30 cm and 30-45 cm depth in site AB2 had the highest and lowest oxidizable fractions of Cr. Chromium was found in exchangeable/acid soluble fractions in all sites and depth and constituted 0.1 to 4.8 % of the total Cr. Since Cr was found in exchangeable and acid soluble phase at very low fractions a year after the major flooding is an indication that Cr is not mobile in these soil profiles.

Table 4.46: Concentrations and percentages of Chromium in different extraction phases of the floodplain soils of the lower reaches of River Niger a year after the major flooding

| Sites | Depth (cm) | CONCENTRATION (µg g^{-1}) | | | | | | PERCENTAGE (%) | | | | |
		F1	F2	F3	F4	SUM	TM	F1	F2	F3	F4	RECOVERY
AS1	0 - 15	0.02	0.15	0.67	0.75	1.59	1.55	1.2	9.7	42.0	47.1	102.6
	15 - 30	0.40	1.88	1.50	26.57	30.35	30.35	1.3	6.2	4.9	87.5	100.0
	30 - 45	0.03	0.10	0.51	0.57	1.21	1.15	2.2	8.1	42.3	47.4	105.2
AS2	0 - 15	0.24	4.64	6.60	21.02	32.50	32.50	0.7	14.3	20.3	64.7	100.0
	15 - 30	0.12	5.40	8.15	34.08	47.75	47.75	0.3	11.3	17.1	71.4	100.0
	30 - 45	0.12	2.20	4.10	15.73	22.15	22.15	0.5	9.9	18.5	71.0	100.0
AS3	0 - 15	0.32	1.60	3.30	6.48	11.70	11.70	2.7	13.7	28.2	55.4	100.0
	15 - 30	0.32	1.32	4.20	10.86	16.70	16.70	1.9	7.9	25.1	65.0	100.0
	30 - 45	0.28	2.00	3.60	ND	5.88	5.88	4.8	34.0	61.2	-	100.0
AS4	0 - 15	0.20	5.68	13.60	16.92	36.40	36.40	0.5	15.6	37.4	46.5	100.0
	15 - 30	0.11	1.49	5.34	3.08	10.02	9.85	1.1	14.9	53.3	30.7	101.7
	30 - 45	0.12	1.60	6.90	44.03	52.65	52.65	0.2	3.0	13.1	83.6	100.0
AS5	0 - 15	0.20	2.96	0.53	11.92	15.60	15.60	1.3	19.0	3.4	76.4	100.0
	15 - 30	0.24	3.52	0.84	15.80	20.40	20.40	1.2	17.3	4.1	77.5	100.0
	30 - 45	0.20	1.76	3.90	5.19	11.05	11.05	1.8	15.9	35.3	47.0	100.0
OK1	0 - 15	0.32	5.68	11.65	19.40	37.05	37.05	0.9	15.3	31.4	52.4	100.0
	15 - 30	0.12	3.84	6.25	22.69	32.90	32.90	0.4	11.7	19.0	69.0	100.0
	30 - 45	0.24	7.52	9.00	3.09	19.85	19.85	1.2	37.9	45.3	15.6	100.0
OK2	0 - 15	0.12	4.36	4.25	9.62	18.35	18.35	0.7	23.8	23.2	52.4	100.0
	15 - 30	0.08	1.17	2.29	0.75	4.28	4.20	1.9	27.2	53.4	17.5	101.9
	30 - 45	0.28	1.64	3.10	6.18	11.20	11.20	2.5	14.6	27.7	55.2	100.0
OK3	0 - 15	0.24	1.76	5.10	7.30	14.40	14.40	1.7	12.2	35.4	50.7	100.0
	15 - 30	0.16	1.00	3.10	6.99	11.25	11.25	1.4	8.9	27.6	62.1	100.0
	30 - 45	0.24	0.72	1.50	5.09	7.55	7.55	3.2	9.5	19.9	67.4	100.0
AB1	0 - 15	0.01	0.19	0.48	0.63	1.30	1.25	0.5	14.3	36.8	48.3	104.0
	15 - 30	0.01	0.18	0.41	0.56	1.15	1.10	0.7	15.5	35.5	48.3	104.5
	30 - 45	0.24	2.96	10.10	30.05	43.35	43.35	0.6	6.8	23.3	69.3	100.0
AB2	0 - 15	0.20	11.20	16.50	31.80	59.70	59.70	0.3	18.8	27.6	53.3	100.0
	15 - 30	0.20	6.04	12.90	ND	19.14	19.14	1.0	31.6	67.4	-	100.0
	30 - 45	0.20	5.32	1.25	62.58	69.35	69.35	0.3	7.7	1.8	90.2	100.0
AB3	0 - 15	0.20	6.60	14.40	36.35	57.55	57.55	0.3	11.5	25.0	63.2	100.0
	15 - 30	0.28	4.76	15.75	58.51	79.30	79.30	0.4	6.0	19.9	73.8	100.0
	30 - 45	0.20	4.76	13.95	64.29	83.20	83.20	0.2	5.7	16.8	77.3	100.0
AB4	0 - 15	0.16	2.52	5.30	14.57	22.55	22.55	0.7	11.2	23.5	64.6	100.0
	15 - 30	0.16	1.56	3.90	103.28	108.90	108.90	0.1	1.4	3.6	94.8	100.0
	30 - 45	0.16	3.36	6.60	21.03	31.15	31.15	0.5	10.8	21.2	67.5	100.0
AB5	0 - 15	0.24	7.64	10.90	29.02	47.80	47.80	0.5	16.0	22.8	60.7	100.0
	15 - 30	0.24	7.12	12.35	33.74	53.45	53.45	0.4	13.3	23.1	63.1	100.0
	30 - 45	0.28	4.72	6.70	20.50	32.20	32.20	0.9	14.7	20.8	63.7	100.0

F1 = Exchangeable fraction; F2 = Reducible fraction; F3 = Oxidizable fraction; F4 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil sample
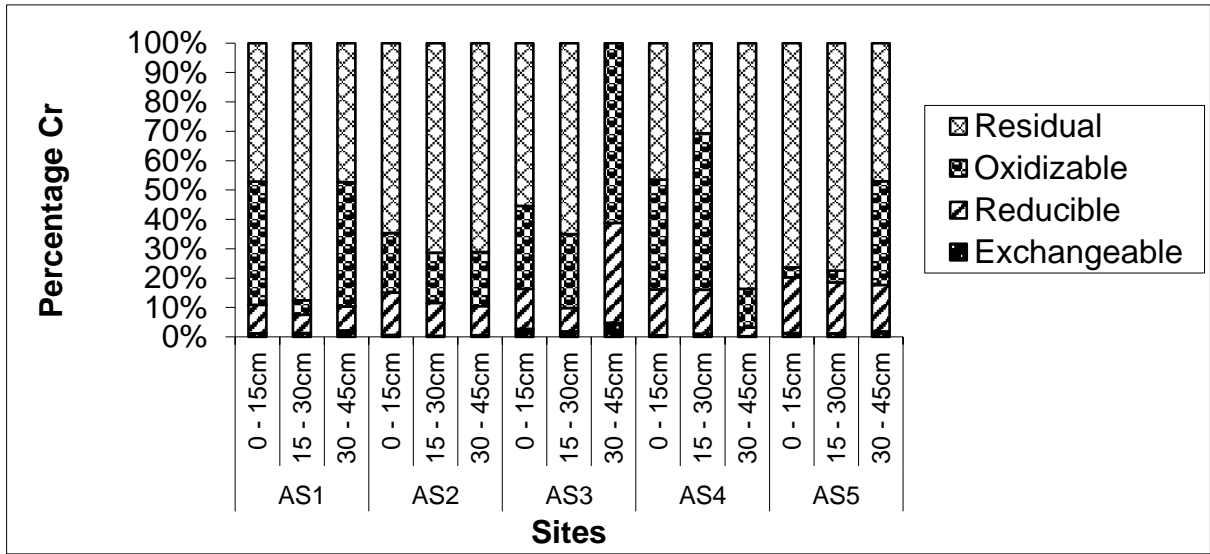
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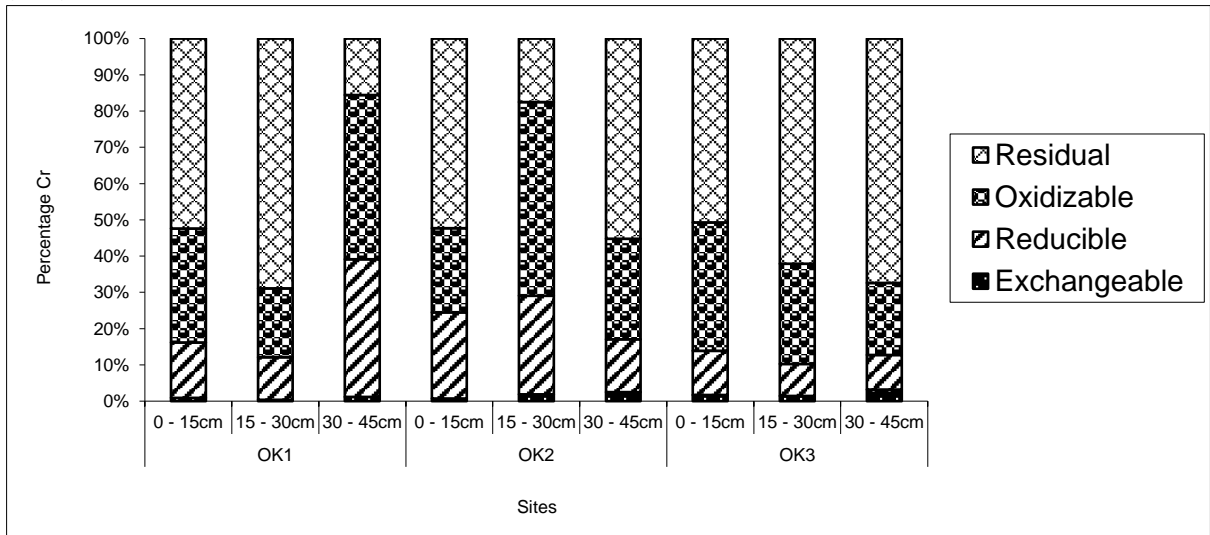
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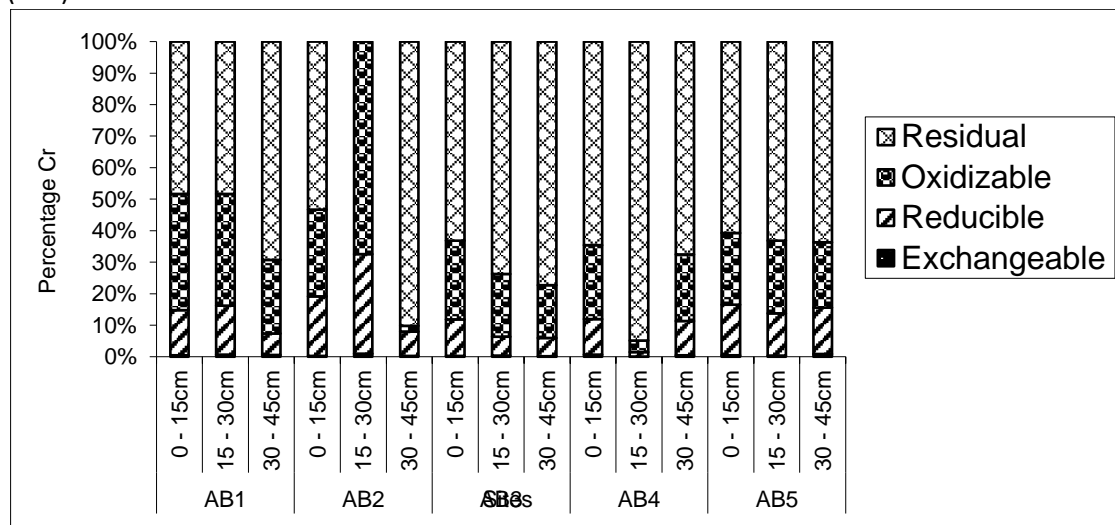
(20c)

Figure 20: Percentage of Chromium in the various extraction phases as a function of total Chromium content in soils a year after the major flooding

Copper

Like Cr, the partition scheme of Cu indicates that it is associated with all the extraction phases a year after the major flooding. The proportion of Cu in the various extraction phases in these soil profiles a year after the major flooding ranged from 0.3 to 27.8 %, 3.3 to 52.4%, 2.5 to 49.3 % and 3.5 to 56.8 % for exchangeable/acid soluble, reducibles, oxidizable and residual phases respectively (Table 4.47 and Figure 21 a-c). Copper was not found in the residual fraction at 30-45 cm depth in sites AS3 and AB2. During this sampling period, majority of Cu exist in the oxidizable fraction. This is as a result of the formation of stable Cu-organic matter complex (Huaug et al., 2002; Iwegbue, 2007; Iwegbue, 2009; Ashrat, 2012). Significant amount of Cu in the reducible fraction suggest anthropogenic source.

Table 4.47: Concentrations and percentages of Copper in different extraction phases of the floodplain soils of the lower reaches of River Niger a year after the major flooding

| Sites	Depth (cm)	CONCENTRATION (µg g^{-1})						PERCENTAGE (%)				
		F1	F2	F3	F4	SUM	TM	F1	F2	F3	F4	RECOVERY
AS1	0 - 15	0.03	0.25	0.32	0.53	1.12	1.05	2.5	22.1	28.4	47.0	106.7
	15 - 30	0.72	3.32	0.90	5.51	10.45	10.45	6.9	31.8	8.6	52.7	100.0
	30 - 45	0.00	0.03	0.48	0.50	1.02	0.85	0.3	3.3	46.9	49.5	120.0
AS2	0 - 15	0.64	2.72	2.90	0.54	6.80	6.80	9.4	40.0	42.6	7.9	100.0
	15 - 30	0.56	4.04	3.40	3.75	11.75	11.75	4.8	34.4	28.9	31.9	100.0
	30 - 45	0.08	2.06	1.17	0.74	4.05	3.95	1.9	50.9	29.0	18.2	102.5
AS3	0 - 15	0.27	1.32	1.41	0.68	3.67	3.45	7.3	35.8	38.4	18.5	106.4
	15 - 30	0.44	2.28	1.75	0.43	4.90	4.90	9.0	46.5	35.7	8.8	100.0
	30 - 45	0.20	1.96	2.10	ND	4.26	4.26	4.7	46.0	49.3	-	100.0
AS4	0 - 15	0.80	6.00	8.30	1.90	17.00	17.00	4.7	35.3	48.8	11.2	100.0
	15 - 30	1.56	4.88	3.95	1.46	11.85	11.85	13.2	41.2	33.3	12.3	100.0
	30 - 45	0.56	2.48	2.70	7.56	13.30	13.30	4.2	18.6	20.3	56.8	100.0
AS5	0 - 15	0.80	2.25	2.60	1.14	6.80	6.50	11.8	33.1	38.3	16.8	104.6
	15 - 30	0.92	2.60	4.70	7.23	15.45	15.45	6.0	16.8	30.4	46.8	100.0
	30 - 45	0.78	1.17	1.30	1.20	4.45	4.20	17.6	26.4	29.1	26.9	106.0
OK1	0 - 15	1.30	4.52	2.39	1.90	10.11	9.50	12.9	44.7	23.7	18.8	106.4
	15 - 30	0.64	2.56	2.30	0.20	5.70	5.70	11.2	44.9	40.4	3.5	100.0
	30 - 45	1.20	3.88	4.05	0.83	9.96	8.30	12.0	39.0	40.7	8.3	120.0
OK2	0 - 15	0.18	1.42	1.00	1.17	3.78	3.45	4.9	37.7	26.6	30.9	109.6
	15 - 30	0.19	0.84	1.54	0.76	3.32	3.10	5.6	25.2	46.3	22.9	107.1
	30 - 45	0.72	1.44	1.50	0.44	4.10	4.10	17.6	35.1	36.6	10.7	100.0
OK3	0 - 15	1.20	1.68	2.45	0.47	5.80	5.80	20.7	29.0	42.2	8.1	100.0
	15 - 30	0.52	1.39	1.51	0.64	4.06	3.60	12.9	34.2	37.1	15.8	112.8
	30 - 45	0.63	0.52	0.71	0.39	2.25	2.15	27.8	23.0	31.7	17.5	104.7
AB1	0 - 15	0.05	0.25	0.35	0.58	1.24	1.05	4.4	20.5	28.2	46.9	118.1
	15 - 30	0.14	0.61	0.60	1.04	2.39	2.20	6.0	25.4	25.2	43.4	108.6
	30 - 45	0.84	3.72	4.15	0.94	9.65	9.65	8.7	38.5	43.0	9.7	100.0
AB2	0 - 15	1.60	5.68	5.30	5.77	18.35	18.35	8.7	31.0	28.9	31.4	100.0
	15 - 30	1.60	7.00	4.75	ND	13.35	13.35	12.0	52.4	35.6	-	100.0
	30 - 45	1.60	5.20	4.40	9.35	20.55	20.55	7.8	25.3	21.4	45.5	100.0
AB3	0 - 15	1.40	5.88	6.05	2.57	15.90	15.90	8.8	37.0	38.1	16.2	100.0
	15 - 30	1.24	5.80	6.30	7.96	21.30	21.30	5.8	27.2	29.6	37.4	100.0
	30 - 45	1.12	6.60	5.20	8.43	21.35	21.35	5.2	30.9	24.4	39.5	100.0
AB4	0 - 15	0.05	3.68	0.18	3.30	7.21	6.70	0.7	51.0	2.5	45.8	107.6
	15 - 30	0.44	1.68	2.10	5.03	9.25	9.25	4.8	18.2	22.7	54.4	100.0
	30 - 45	0.76	2.24	2.60	3.85	9.45	9.45	8.0	23.7	27.5	40.7	100.0
AB5	0 - 15	0.68	3.36	3.35	6.16	13.55	13.55	5.0	24.8	24.7	45.5	100.0
	15 - 30	1.32	4.04	4.10	4.19	13.65	13.65	9.7	29.6	30.0	30.7	100.0
	30 - 45	1.92	2.92	1.90	2.56	9.30	9.30	20.6	31.4	20.4	27.5	100.0

F1 = Exchangeable fraction; F2 = Reducible fraction; F3 = Oxidizable fraction; F4 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil sample
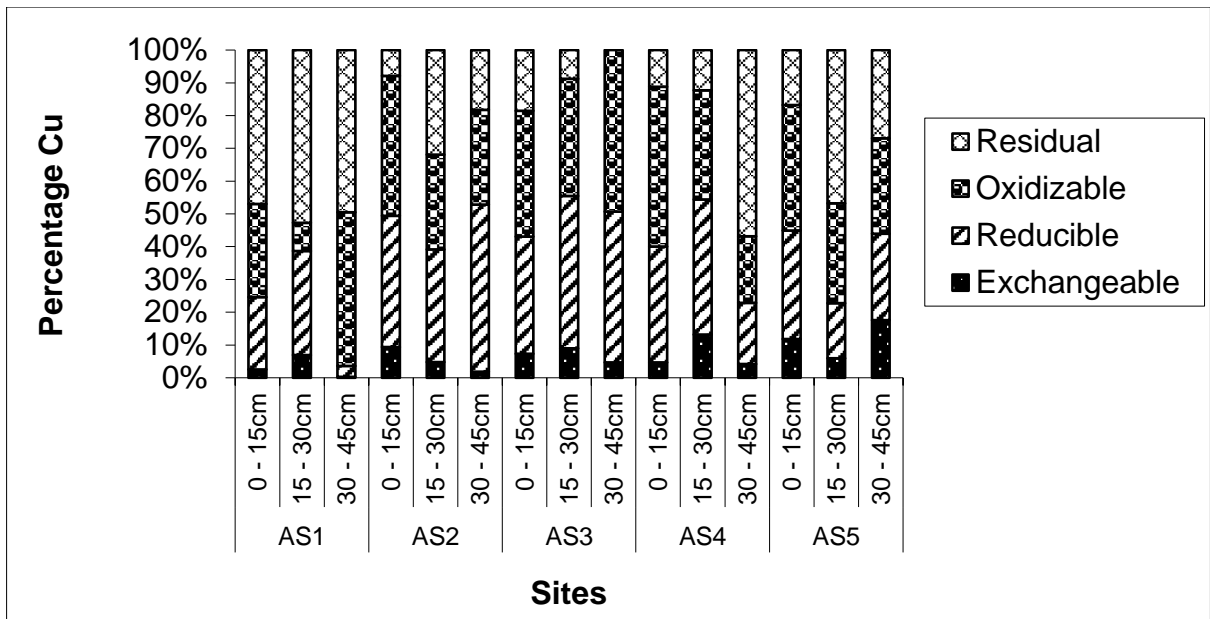
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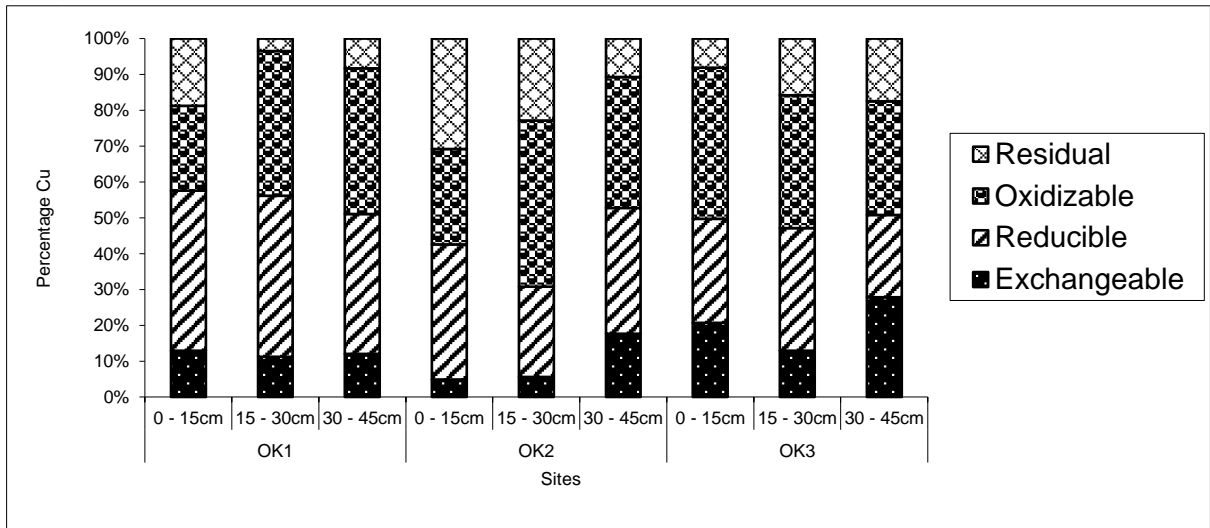
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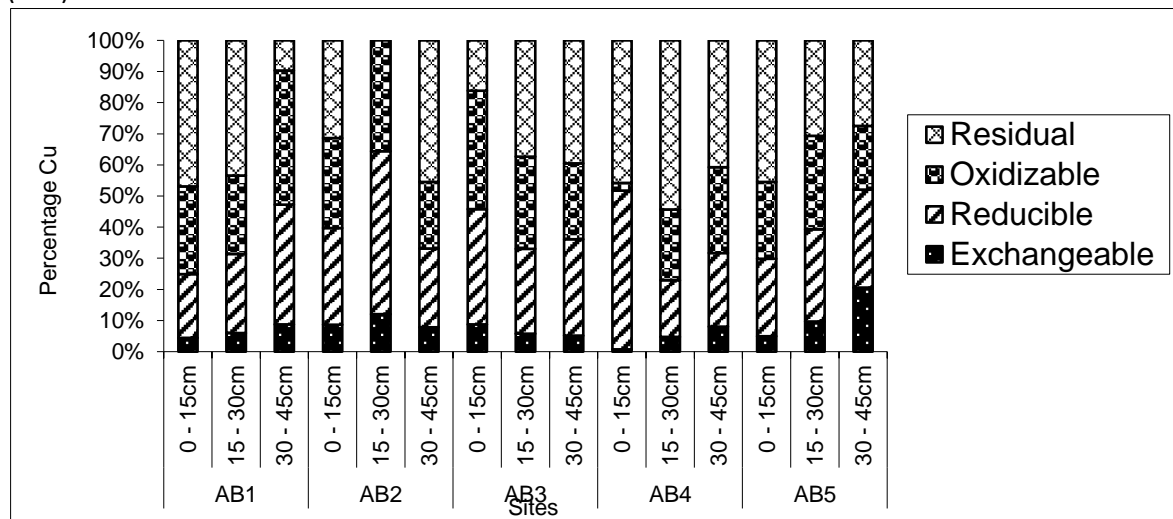
(21c)

Figure 21: Percentage of Copper in the various extraction phases as a function of total Copper content in soils a year after the major flooding
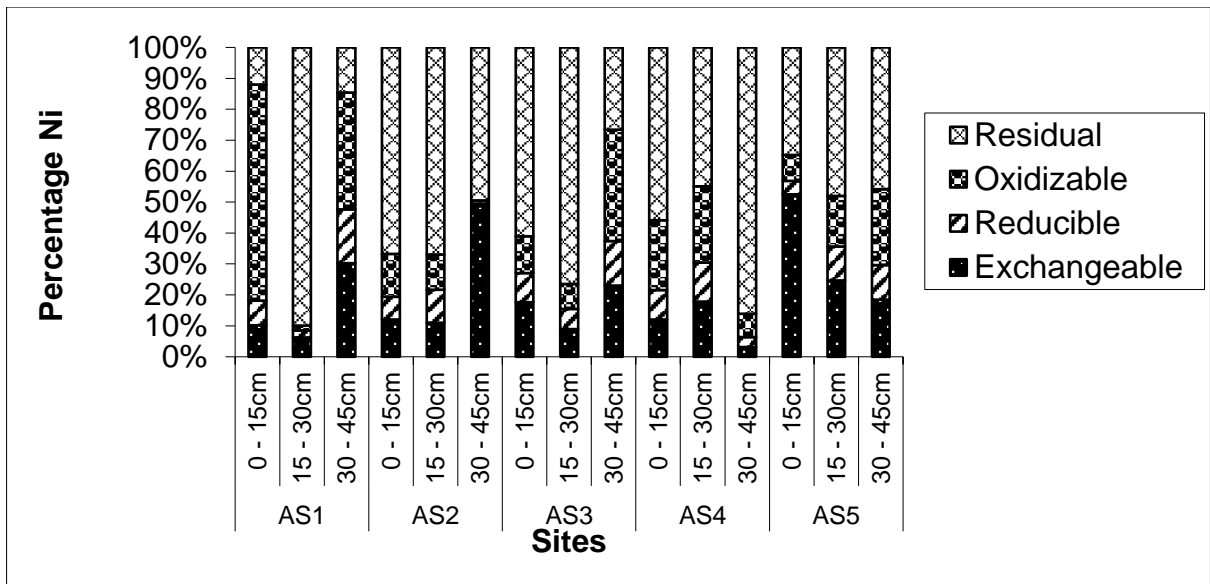
Manganese

A year after the major flooding, Mn was associated with all the extraction phases. The association of Mn in the different extraction phases followed the order; Reducibles > Residuals > Exchangeable/acid soluble > oxidizable phase. The proportion of Mn in the various extraction phases ranged from 0.2 to 70.8 %, 5.0 to 73.7 %, 0.4 to 36.8 % and 0.5 to 82.8 % for exchangeable/acid soluble, reducibles, oxidizable and residual phases respectively (Table 4.48 and Figure 22 a-c). Manganese in these soil profiles a year after the major flooding is more mobile than in the soil profiles three months after the major flooding. The high proportion of Mn in the reducible phase is consistent with the reduction of Mn oxides by hydroxylamine chloride and the specificity of this dissolution with respect to ferric oxide (Herondez-Moreno et al., 2007; Teixera et al., 2010; Iwegbue, 2011). Also, the significant proportions of Mn in the oxidizable and reducible phases imply that changes in soil conditions such as pH and redox potential may result in significant remobilization of Mn.

Table 4.48: Concentrations and percentages of Manganese in different extraction phases of the floodplain soils of the lower reaches of River Niger a year after the major flooding

| Sites	Depth (cm)	CONCENTRATION ($\mu g\ g^{-1}$)						PERCENTAGE (%)				
		F1	F2	F3	F4	SUM	TM	F1	F2	F3	F4	RECOVERY
AS1	0 - 15	1.06	1.44	2.68	2.10	7.28	6.95	14.6	19.7	36.8	28.8	104.7
	15 - 30	2.40	1.64	1.55	26.96	32.55	32.55	7.4	5.0	4.8	82.8	100.0
	30 - 45	1.68	1.64	4.45	12.53	20.30	20.30	8.3	8.1	21.9	61.7	100.0
AS2	0 - 15	54.04	196.44	14.85	1.33	266.66	264.00	20.3	73.7	5.6	0.5	101.0
	15 - 30	69.32	376.28	24.85	106.55	577.00	577.00	12.0	65.2	4.3	18.5	100.0
	30 - 45	0.24	82.16	8.45	61.45	152.30	152.30	0.2	53.9	5.5	40.3	100.0
AS3	0 - 15	14.36	8.08	2.90	6.26	31.60	31.60	45.4	25.6	9.2	19.8	100.0
	15 - 30	1.48	1.36	1.90	14.56	19.30	19.30	7.7	7.0	9.8	75.4	100.0
	30 - 45	0.36	0.16	0.09	0.57	1.18	1.05	30.3	13.6	7.4	48.7	112.4
AS4	0 - 15	88.32	140.72	32.30	37.71	299.05	299.05	29.5	47.1	10.8	12.6	100.0
	15 - 30	11.42	36.00	5.44	38.19	91.05	89.00	12.5	39.5	6.0	41.9	102.3
	30 - 45	18.20	80.56	11.20	240.99	350.95	350.95	5.2	23.0	3.2	68.7	100.0
AS5	0 - 15	43.84	11.76	5.35	11.90	72.85	72.85	60.2	16.1	7.3	16.3	100.0
	15 - 30	43.92	13.04	6.00	21.89	84.85	84.85	51.8	15.4	7.1	25.8	100.0
	30 - 45	24.72	7.76	4.15	4.12	40.75	40.75	60.7	19.0	10.2	10.1	100.0
OK1	0 - 15	66.00	17.24	1.14	52.57	136.95	136.95	48.2	12.6	0.8	38.4	100.0
	15 - 30	60.36	46.92	10.60	33.82	151.70	151.70	39.8	30.9	7.0	22.3	100.0
	30 - 45	19.67	137.64	1.30	75.70	234.31	232.70	8.4	58.7	0.6	32.3	100.7
OK2	0 - 15	51.76	52.44	8.90	21.00	134.10	134.10	38.6	39.1	6.6	15.7	100.0
	15 - 30	18.92	33.60	9.20	5.18	66.90	66.90	28.3	50.2	13.8	7.7	100.0
	30 - 45	23.20	26.84	9.20	9.01	68.25	68.25	34.0	39.3	13.5	13.2	100.0
OK3	0 - 15	13.68	3.76	4.60	13.51	35.55	35.55	38.5	10.6	12.9	38.0	100.0
	15 - 30	6.00	1.24	2.80	11.41	21.45	21.45	28.0	5.8	13.1	53.2	100.0
	30 - 45	7.68	2.20	1.90	5.77	17.55	17.55	43.8	12.5	10.8	32.9	100.0
AB1	0 - 15	0.51	1.94	0.28	2.69	5.42	5.20	9.4	35.9	5.1	49.6	104.2
	15 - 30	5.37	49.24	6.67	47.90	109.19	107.55	4.9	45.1	6.1	43.9	101.5
	30 - 45	26.04	221.40	4.15	191.41	443.00	443.00	5.9	50.0	0.9	43.2	100.0
AB2	0 - 15	146.92	174.36	27.80	11.73	360.81	337.35	40.7	48.3	7.7	3.3	107.0
	15 - 30	0.06	0.49	0.06	0.60	1.21	1.10	4.6	40.2	5.3	49.9	110.0
	30 - 45	59.40	138.04	27.20	187.96	412.60	412.60	14.4	33.5	6.6	45.6	100.0
AB3	0 - 15	45.48	197.28	30.55	120.89	394.20	394.20	11.5	50.0	7.7	30.7	100.0
	15 - 30	44.16	281.44	2.60	288.30	616.50	616.50	7.2	45.7	0.4	46.8	100.0
	30 - 45	28.60	304.48	43.80	297.12	674.00	674.00	4.2	45.2	6.5	44.1	100.0
AB4	0 - 15	74.68	0.64	12.55	63.43	151.30	151.30	49.4	0.4	8.3	41.9	100.0
	15 - 30	21.00	20.52	6.65	31.38	79.55	79.55	26.4	25.8	8.4	39.4	100.0
	30 - 45	42.12	146.36	14.65	69.72	272.85	272.85	15.4	53.6	5.4	25.6	100.0
AB5	0 - 15	194.76	335.32	30.30	30.12	590.50	590.50	33.0	56.8	5.1	5.1	100.0
	15 - 30	220.92	164.16	29.90	51.12	466.10	466.10	47.4	35.2	6.4	11.0	100.0
	30 - 45	154.80	3.12	13.60	47.03	218.55	218.55	70.8	1.4	6.2	21.5	100.0

F1 = Exchangeable fraction; F2 = Reducible fraction; F3 = Oxidizable fraction; F4 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil sample
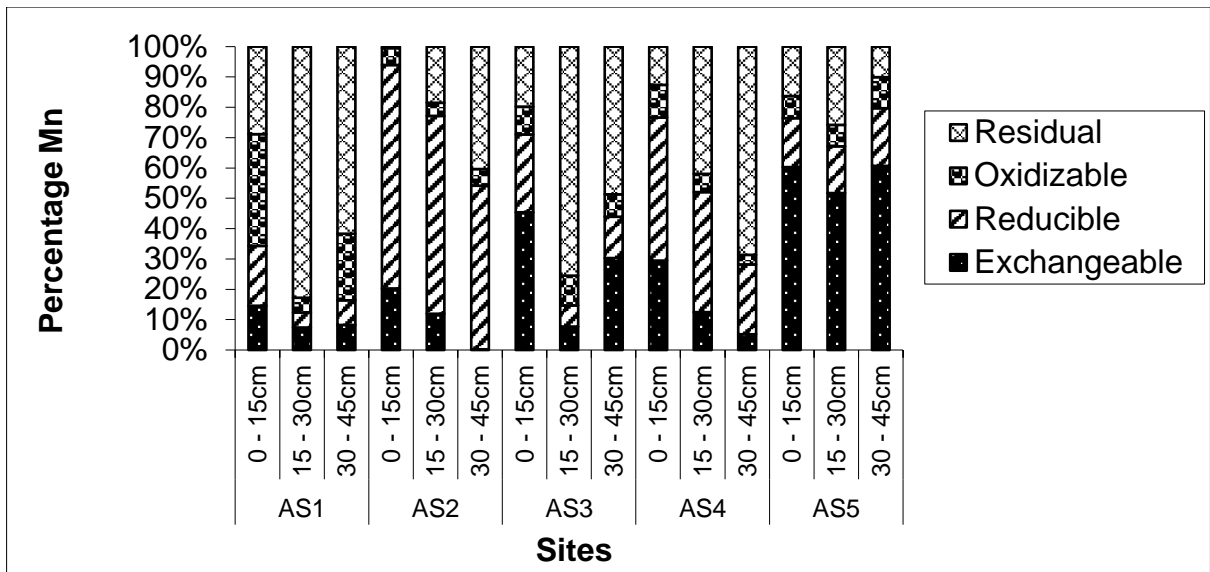
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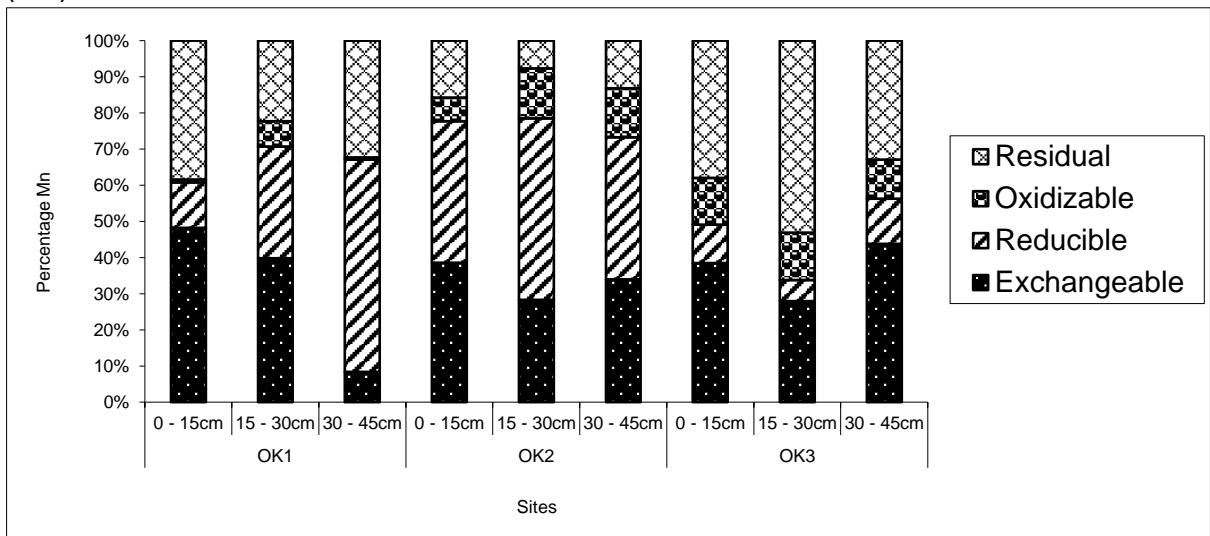
(22b)
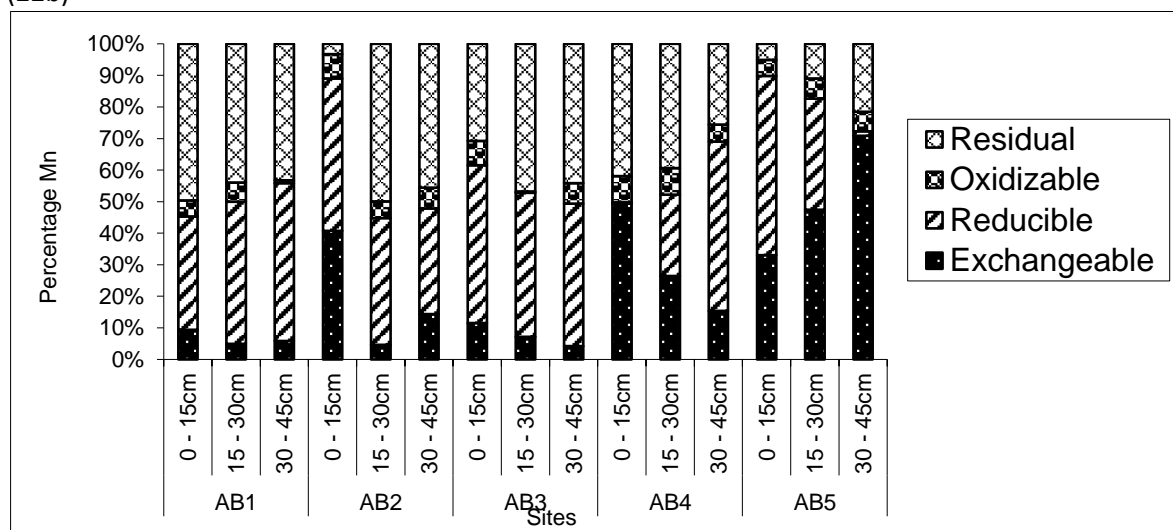
(22c)

Figure 22: Percentage of Manganese in the various extraction phases as a function of total Manganese content in soils a year after the major flooding

Nickel

The speciation pattern of Ni are presented in Table 4.49 and Figure 23 a-c. The residual fraction consists of 12.0 to 98.9 % of the total Ni in these soil profiles while oxidizable fraction consist of 0.8 to 69.9 % of Ni. The oxidizable fraction of Ni were higher in the soil profiles a year after the flooding than three months after the major flooding. This might be due to the formation of Ni-organic complex a year after the major flooding. The reducible fraction consist of 0.2 to 62.2 % of the total Ni a year after the major flooding. The exchangeable/acid soluble fraction constituted 3.2 to 52.5 % of the total Ni. The proportion of Ni in the exchangeable/acid soluble fraction in these soil profiles a year after the major flooding were higher than those of three months after the major flooding.

Table 4.49: Concentrations and percentages of Nickel in different extraction phases of the floodplain soils of the lower reaches of River Niger a year after the major flooding

| Sites	Depth (cm)	CONCENTRATION (µg g⁻¹)						PERCENTAGE (%)				
		F1	F2	F3	F4	SUM	TM	F1	F2	F3	F4	RECOVERY
AS1	0 - 15	0.88	0.68	6.05	1.04	8.65	8.65	10.2	7.9	69.9	12.0	100.0
	15 - 30	0.80	0.28	0.20	11.47	12.75	12.75	6.3	2.2	1.6	90.0	100.0
	30 - 45	0.56	0.32	0.70	0.27	1.85	1.85	30.3	17.3	37.8	14.6	100.0
AS2	0 - 15	1.04	0.64	1.20	5.77	8.65	8.65	12.0	7.4	13.9	66.7	100.0
	15 - 30	1.40	1.36	1.45	8.54	12.75	12.75	11.0	10.7	11.4	67.0	100.0
	30 - 45	0.37	0.01	0.01	0.38	0.76	0.65	48.7	0.8	1.0	49.5	116.9
AS3	0 - 15	0.52	0.28	0.35	1.80	2.95	2.95	17.6	9.5	11.9	61.0	100.0
	15 - 30	0.28	0.20	0.25	2.37	3.10	3.10	9.0	6.5	8.1	76.5	100.0
	30 - 45	0.18	0.11	0.28	0.21	0.78	0.65	23.0	14.4	36.0	26.6	120.0
AS4	0 - 15	1.20	0.96	2.25	5.59	10.00	10.00	12.0	9.6	22.5	55.9	100.0
	15 - 30	1.12	0.80	1.55	2.83	6.30	6.30	17.8	12.7	24.6	44.9	100.0
	30 - 45	0.40	0.40	0.95	10.90	12.65	12.65	3.2	3.2	7.5	86.2	100.0
AS5	0 - 15	2.13	0.18	0.34	1.41	4.05	3.85	52.5	4.4	8.3	34.8	105.2
	15 - 30	1.36	0.60	0.90	2.64	5.50	5.50	24.7	10.9	16.4	48.0	100.0
	30 - 45	0.60	0.36	0.80	1.49	3.25	3.25	18.5	11.1	24.6	45.8	100.0
OK1	0 - 15	1.72	0.60	1.70	5.33	9.35	9.35	18.4	6.4	18.2	57.0	100.0
	15 - 30	1.20	0.64	0.85	0.71	3.40	3.40	35.3	18.8	25.0	20.9	100.0
	30 - 45	1.44	0.96	1.45	2.55	6.40	6.40	22.5	15.0	22.7	39.8	100.0
OK2	0 - 15	0.56	0.48	0.85	3.96	5.85	5.85	9.6	8.2	14.5	67.7	100.0
	15 - 30	0.36	0.32	1.45	1.32	3.45	3.45	10.4	9.3	42.0	38.3	100.0
	30 - 45	0.44	0.32	0.65	2.14	3.55	3.55	12.4	9.0	18.3	60.3	100.0
OK3	0 - 15	0.64	0.20	0.70	5.76	7.30	7.30	8.8	2.7	9.6	78.9	100.0
	15 - 30	0.48	0.28	0.50	6.39	7.65	7.65	6.3	3.7	6.5	83.5	100.0
	30 - 45	0.44	0.12	0.35	1.44	2.35	2.35	18.7	5.1	14.9	61.3	100.0
AB1	0 - 15	0.68	0.38	0.59	0.80	2.45	2.25	27.9	15.5	24.0	32.6	108.9
	15 - 30	1.72	1.00	1.20	0.68	4.60	4.60	37.4	21.7	26.1	14.8	100.0
	30 - 45	1.24	0.92	3.97	9.87	16.00	16.00	7.8	5.8	24.8	61.7	100.0
AB2	0 - 15	3.56	2.08	2.20	8.01	15.85	15.85	22.5	13.1	13.9	50.5	100.0
	15 - 30	0.15	0.12	0.09	0.32	0.68	0.60	21.8	17.2	13.9	47.1	113.3
	30 - 45	2.44	1.16	1.15	15.60	20.35	20.35	12.0	5.7	5.7	76.7	100.0
AB3	0 - 15	1.24	1.28	1.75	10.93	15.20	15.20	8.2	8.4	11.5	71.9	100.0
	15 - 30	2.76	2.12	2.90	13.22	21.00	21.00	13.1	10.1	13.8	63.0	100.0
	30 - 45	1.80	1.64	1.35	18.31	23.10	23.10	7.8	7.1	5.8	79.3	100.0
AB4	0 - 15	0.92	2.60	1.25	1.83	6.60	6.60	13.9	39.4	18.9	27.7	100.0
	15 - 30	0.04	0.20	0.75	92.61	93.60	93.60	0.0	0.2	0.8	98.9	100.0
	30 - 45	1.24	0.44	0.90	5.62	8.20	8.20	15.1	5.4	11.0	68.5	100.0
AB5	0 - 15	2.12	1.16	1.70	9.72	14.70	14.70	14.4	7.9	11.6	66.1	100.0
	15 - 30	1.48	8.51	1.41	2.27	13.67	13.30	10.8	62.2	10.3	16.6	102.8
	30 - 45	1.44	0.56	1.15	4.95	8.10	8.10	17.8	6.9	14.2	61.1	100.0

F1 = Exchangeable fraction; F2 = Reducible fraction; F3 = Oxidizable fraction; F4 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil sample

(23a)
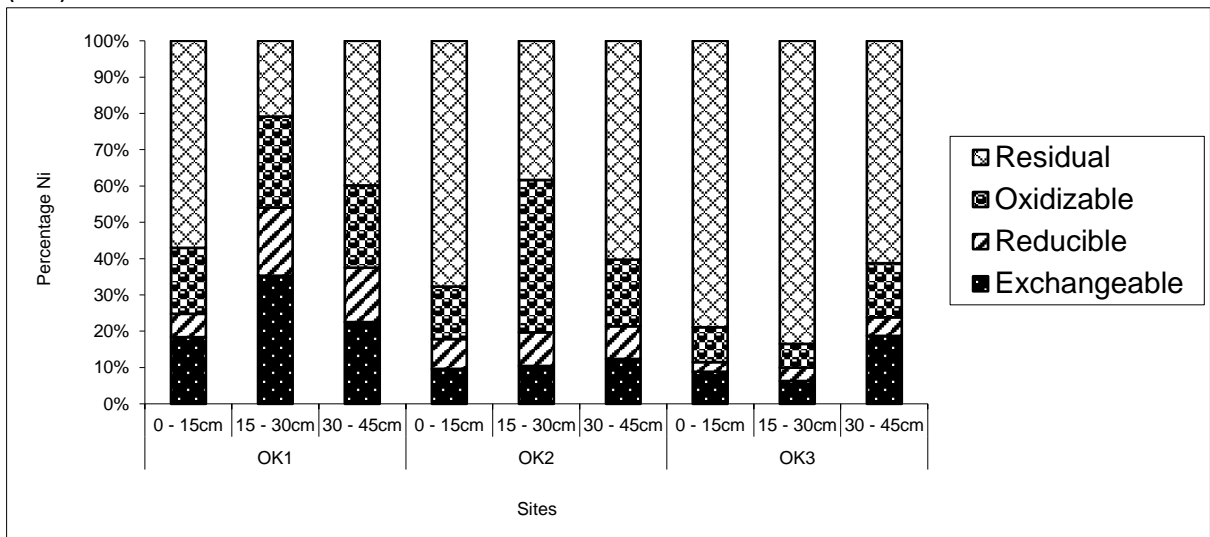
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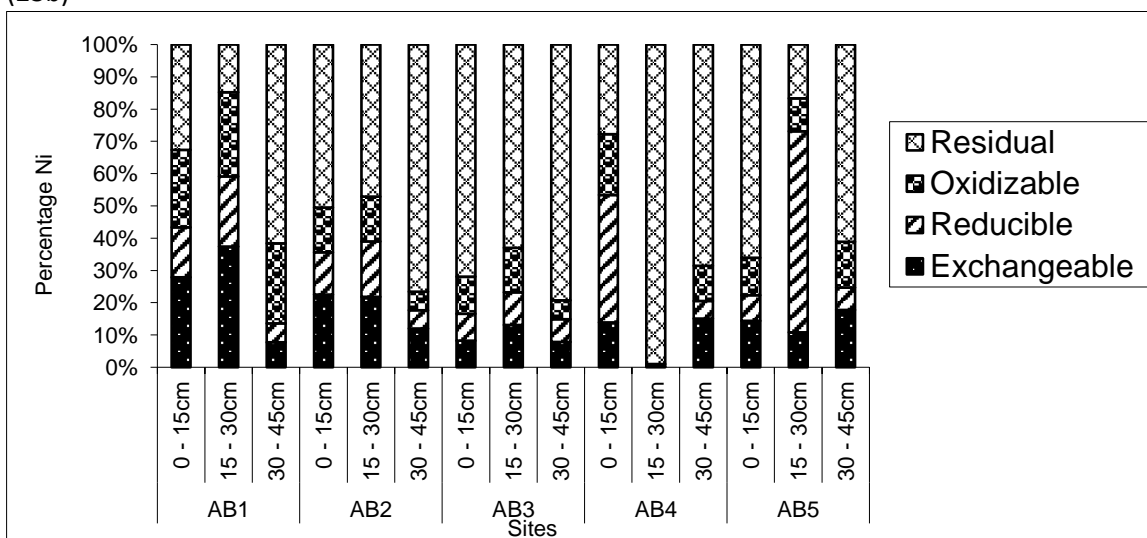
(23c)

Figure 23: Percentage of Nickel in the various extraction phases as a function of total Nickel content in soils a year after the major flooding

Lead

A year after the major flooding, the association of Pb in these soil profiles followed the order reducible> residual> exchangeable/acid soluble > oxidizable. Pb was associated with all the fractions a year after the major flooding (Table 4.50 and Figure 24 a-c). The residual fraction constituted 0.1 to 59.8 % of the total Pb. The reducible fraction constituted 5.3 to 62.3 % of the total Pb in these soil profiles. The exchangeable/acid soluble phase consist of 1.0 to 54.5 % of total Pb while the oxidizable phase Pb constituted 2.9 to 47.9 % of the total Pb a year after the major flooding.

Table 4.50: Concentrations and percentages of Lead in different extraction phases of the floodplain soils of the lower reaches of River Niger a year after the major flooding

| Sites	Depth (cm)	F1	F2	F3	F4	SUM	TM	F1	F2	F3	F4	RECOVERY
		CONCENTRATION (µg g⁻¹)						PERCENTAGE (%)				
AS1	0 - 15	0.02	0.57	0.26	0.71	1.55	1.35	1.0	36.5	16.8	45.6	114.8
	15 - 30	0.52	4.56	3.40	1.02	9.50	9.50	5.5	48.0	35.8	10.7	100.0
	30 - 45	0.12	0.51	0.25	0.74	1.62	1.50	7.6	31.4	15.6	45.4	108.0
AS2	0 - 15	1.24	1.42	0.95	1.84	5.46	5.30	22.8	26.0	17.5	33.8	103.0
	15 - 30	ND	7.72	3.80	3.08	14.60	14.60	-	52.9	26.0	21.1	100.0
	30 - 45	0.77	1.86	0.43	1.16	4.22	3.95	18.2	44.0	10.2	27.6	106.8
AS3	0 - 15	1.05	0.59	2.20	0.83	4.67	4.10	22.6	12.5	47.0	17.9	113.9
	15 - 30	0.12	3.56	2.75	0.53	6.96	5.90	1.7	51.1	39.5	7.6	118.0
	30 - 45	0.08	0.25	0.24	0.49	1.05	0.95	7.8	23.3	22.6	46.3	110.5
AS4	0 - 15	2.20	12.52	5.35	0.03	20.10	20.10	10.9	62.3	26.6	0.1	100.0
	15 - 30	1.28	7.32	0.94	2.65	12.18	11.40	10.5	60.1	7.7	21.8	106.8
	30 - 45	4.04	1.52	2.85	5.94	14.35	14.35	28.2	10.6	19.9	41.4	100.0
AS5	0 - 15	2.84	1.68	0.75	3.38	8.65	8.35	32.8	19.5	8.6	39.1	103.6
	15 - 30	0.68	12.16	1.40	9.86	24.10	24.10	2.8	50.5	5.8	40.9	100.0
	30 - 45	0.71	1.96	2.03	2.03	6.73	6.65	10.5	29.2	30.2	30.1	101.2
OK1	0 - 15	0.20	3.08	1.30	6.82	11.40	11.40	1.8	27.0	11.4	59.8	100.0
	15 - 30	0.88	4.84	3.95	0.13	9.80	9.80	9.0	49.4	40.3	1.3	100.0
	30 - 45	1.62	5.05	2.45	0.95	10.07	9.50	16.0	50.2	24.3	9.5	106.0
OK2	0 - 15	1.92	1.52	1.00	2.61	7.05	7.05	27.2	21.6	14.2	37.0	100.0
	15 - 30	0.26	0.42	0.25	0.82	1.75	1.55	14.9	23.8	14.4	47.0	112.9
	30 - 45	0.28	0.00	1.70	1.57	3.55	3.55	7.9	0.0	47.9	44.2	100.0
OK3	0 - 15	1.54	0.69	0.53	1.51	4.27	4.15	36.1	16.2	12.4	35.3	102.9
	15 - 30	1.36	0.52	0.17	0.45	2.49	2.35	54.5	20.7	6.8	18.0	106.0
	30 - 45	0.81	0.14	0.32	1.04	2.30	2.20	35.1	6.0	13.8	45.2	104.5
AB1	0 - 15	ND	0.70	0.62	0.93	2.25	2.10	-	30.9	27.6	41.5	107.1
	15 - 30	ND	2.79	0.92	1.53	5.23	5.10	-	53.3	17.6	29.2	102.5
	30 - 45	1.29	4.01	3.40	1.44	10.14	9.70	12.7	39.5	33.6	14.2	104.5
AB2	0 - 15	2.68	10.76	0.55	4.66	18.65	18.65	14.4	57.7	2.9	25.0	100.0
	15 - 30	0.01	0.25	0.13	0.37	0.77	0.70	1.2	32.6	17.5	48.7	110.0
	30 - 45	1.72	6.88	1.35	5.50	15.45	15.45	11.1	44.5	8.7	35.6	100.0
AB3	0 - 15	0.12	6.02	4.06	1.86	12.06	11.30	1.0	49.9	33.7	15.4	106.7
	15 - 30	2.16	8.96	3.70	3.63	18.45	18.45	11.7	48.6	20.1	19.7	100.0
	30 - 45	0.48	5.84	6.45	4.58	17.35	17.35	2.8	33.7	37.2	26.4	100.0
AB4	0 - 15	1.11	0.93	1.66	1.84	5.54	5.20	20.1	16.7	29.9	33.3	106.5
	15 - 30	0.71	0.89	0.60	1.05	3.25	3.05	21.8	27.3	18.5	32.3	106.6
	30 - 45	3.36	3.60	ND	2.29	9.25	9.25	36.3	38.9	-	24.8	100.0
AB5	0 - 15	5.24	0.58	ND	5.08	10.90	10.90	48.1	5.3	-	46.6	100.0
	15 - 30	2.36	7.28	2.65	0.46	12.75	12.75	18.5	57.1	20.8	3.6	100.0
	30 - 45	0.36	4.64	3.85	0.75	9.60	8.10	3.8	48.3	40.1	7.8	118.5

F1 = Exchangeable fraction; F2 = Reducible fraction; F3 = Oxidizable fraction; F4 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil sample
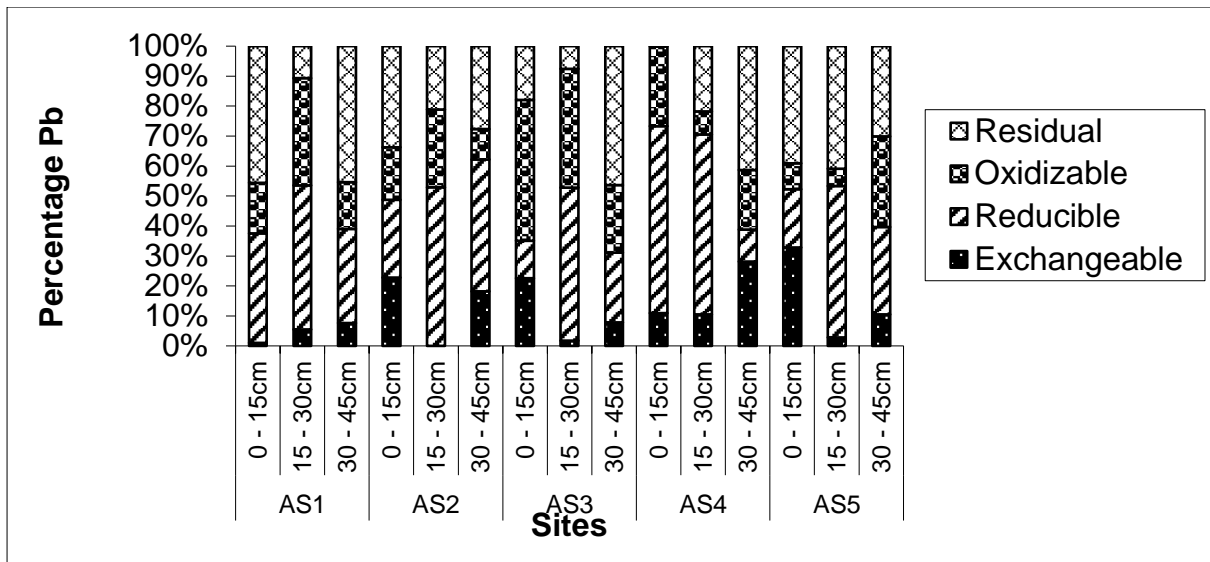
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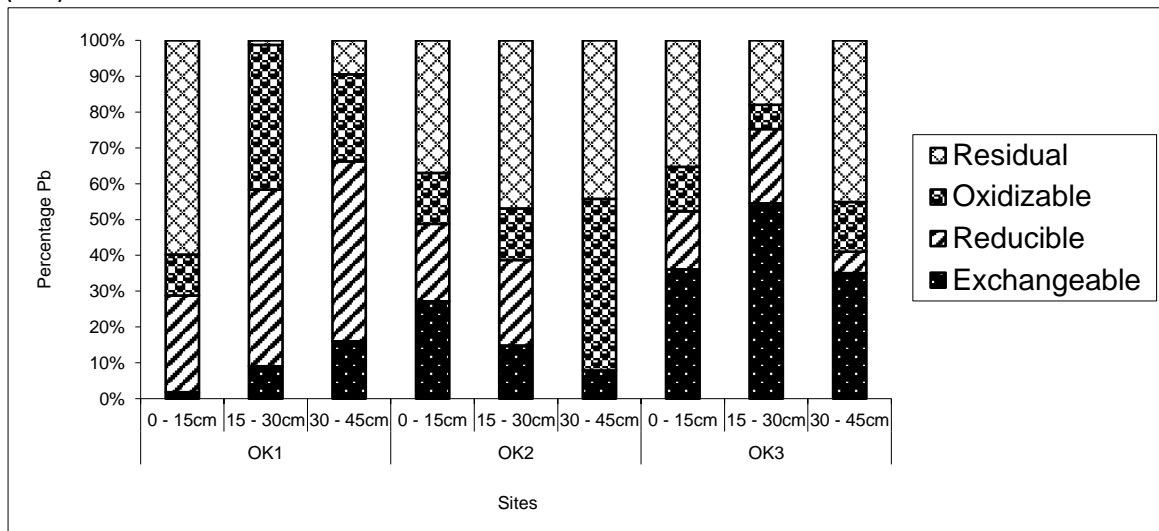
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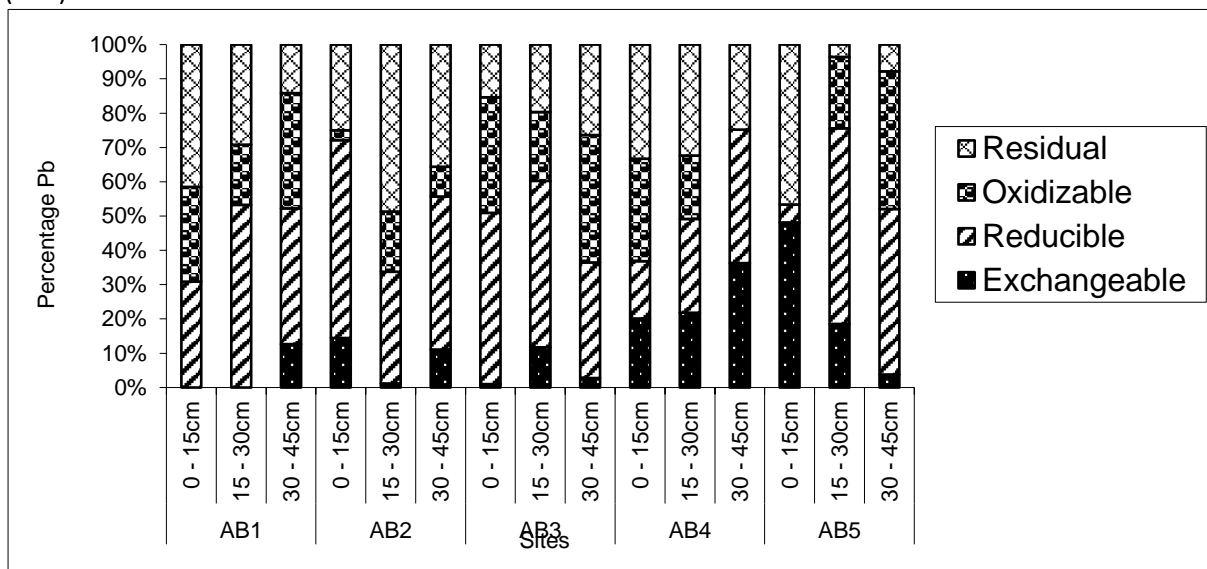
(24c)

Figure 24: Percentage of Lead in the various extraction phases as a function of total Lead content in soils three months after the major flooding

Zinc

A year after the major flooding, Zn was associated with all the extraction phases. The proportion of Zn in the different phases ranged from 2.3 to 79.5 % for exchangeable/acid soluble fraction, 0.9 to 32.0 % for reducible, 1.1 to 44.6 % for oxidizable and 5.1 to 96.3 % for residual fraction (Table 4.51 and Figure 25 a-c).

Table 4.51: Concentrations and percentages of Zinc in different extraction phases of the floodplain soils of the lower reaches of River Niger a year after the major flooding

| Sites	Depth (cm)	CONCENTRATION (µg g⁻¹)						PERCENTAGE (%)				
		F1	F2	F3	F4	SUM	TM	F1	F2	F3	F4	RECOVERY
AS1	0 - 15	0.88	6.28	8.75	3.69	19.60	19.60	4.5	32.0	44.6	18.8	100.0
	15 - 30	1.14	3.60	2.69	18.43	25.85	25.85	4.4	13.9	10.4	71.3	100.0
	30 - 45	5.30	2.39	0.51	2.81	11.01	10.30	48.2	21.7	4.6	25.5	106.9
AS2	0 - 15	39.70	10.47	7.21	7.79	65.16	63.65	60.9	16.1	11.1	12.0	102.4
	15 - 30	17.68	15.16	7.60	22.16	62.60	62.60	28.2	24.2	12.1	35.4	100.0
	30 - 45	ND	8.80	6.45	69.00	84.25	84.25	-	10.4	7.7	81.9	100.0
AS3	0 - 15	12.60	3.76	25.50	23.79	65.65	65.65	19.2	5.7	38.8	36.2	100.0
	15 - 30	20.72	6.52	8.60	20.36	56.20	56.20	36.9	11.6	15.3	36.2	100.0
	30 - 45	0.00	0.01	0.02	0.03	0.06	0.05	5.2	16.3	28.6	49.9	120.0
AS4	0 - 15	14.72	13.72	28.05	34.86	91.35	91.35	16.1	15.0	30.7	38.2	100.0
	15 - 30	1.92	13.80	10.85	31.28	57.85	57.85	3.3	23.9	18.8	54.1	100.0
	30 - 45	6.32	5.92	7.55	48.61	68.40	68.40	9.2	8.7	11.0	71.1	100.0
AS5	0 - 15	29.66	9.66	9.72	10.05	59.10	57.95	50.2	16.3	16.5	17.0	102.0
	15 - 30	42.44	17.00	18.30	12.11	89.85	89.85	47.2	18.9	20.4	13.5	100.0
	30 - 45	16.92	6.01	7.03	4.28	34.24	34.00	49.4	17.6	20.5	12.5	100.7
OK1	0 - 15	41.82	8.55	8.75	11.97	71.08	70.35	58.8	12.0	12.3	16.8	101.0
	15 - 30	21.60	10.00	12.55	7.45	51.60	51.60	41.9	19.4	24.3	14.4	100.0
	30 - 45	8.88	10.80	16.75	16.67	53.10	53.10	16.7	20.3	31.5	31.4	100.0
OK2	0 - 15	41.28	8.60	9.30	0.02	59.20	59.20	69.7	14.5	15.7	0.0	100.0
	15 - 30	31.02	5.92	6.48	8.43	51.85	51.30	59.8	11.4	12.5	16.3	101.1
	30 - 45	19.96	4.48	7.70	1.74	33.88	30.40	58.9	13.2	22.7	5.1	111.4
OK3	0 - 15	49.80	4.71	4.47	15.80	74.78	74.45	66.6	6.3	6.0	21.1	100.4
	15 - 30	43.03	0.48	5.06	5.57	54.13	54.00	79.5	0.9	9.3	10.3	100.2
	30 - 45	18.87	1.45	3.60	8.22	32.14	32.05	58.7	4.5	11.2	25.6	100.3
AB1	0 - 15	10.02	0.47	4.44	6.16	21.09	20.95	47.5	2.2	21.1	29.2	100.7
	15 - 30	13.72	8.88	10.10	5.95	38.65	38.65	35.5	23.0	26.1	15.4	100.0
	30 - 45	0.86	7.88	11.40	17.16	37.30	37.30	2.3	21.1	30.6	46.0	100.0
AB2	0 - 15	17.68	12.08	12.15	1098.59	1140.50	1140.50	1.6	1.1	1.1	96.3	100.0
	15 - 30	0.02	0.02	0.02	0.06	0.12	0.10	16.8	16.5	16.8	49.9	120.0
	30 - 45	12.56	7.72	8.80	39.97	69.05	69.05	18.2	11.2	12.7	57.9	100.0
AB3	0 - 15	26.04	10.68	10.60	13.23	60.55	60.55	43.0	17.6	17.5	21.8	100.0
	15 - 30	22.50	9.33	12.84	10.55	55.21	55.00	40.7	16.9	23.2	19.1	100.4
	30 - 45	16.60	8.60	8.90	18.65	52.75	52.75	31.5	16.3	16.9	35.4	100.0
AB4	0 - 15	24.11	3.61	3.56	14.90	46.18	46.05	52.2	7.8	7.7	32.3	100.3
	15 - 30	10.04	1.01	1.65	8.55	21.25	20.90	47.3	4.7	7.7	40.2	101.7
	30 - 45	22.03	7.34	7.34	4.35	41.07	40.55	53.6	17.9	17.9	10.6	101.3
AB5	0 - 15	20.64	13.76	9.35	5.65	49.40	49.40	41.8	27.9	18.9	11.4	100.0
	15 - 30	20.39	7.67	10.80	4.89	43.75	43.40	46.6	17.5	24.7	11.2	100.8
	30 - 45	13.16	5.50	7.87	2.58	29.11	28.90	45.2	18.9	27.0	8.9	100.7

F1 = Exchangeable fraction; F2 = Reducible fraction; F3 = Oxidizable fraction; F4 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil sample
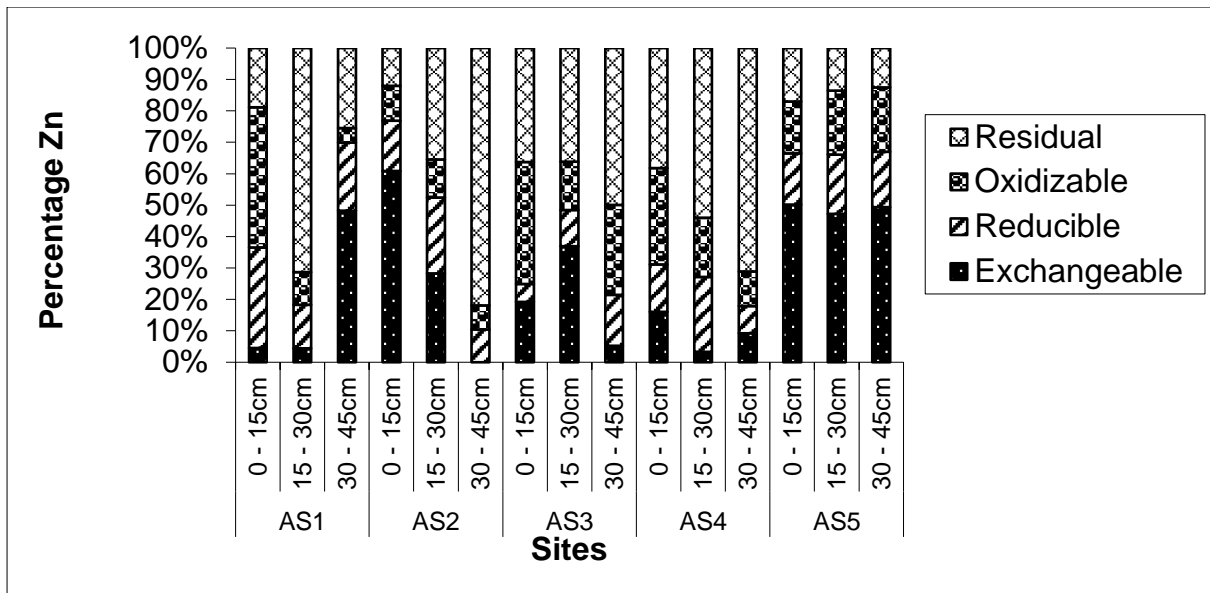
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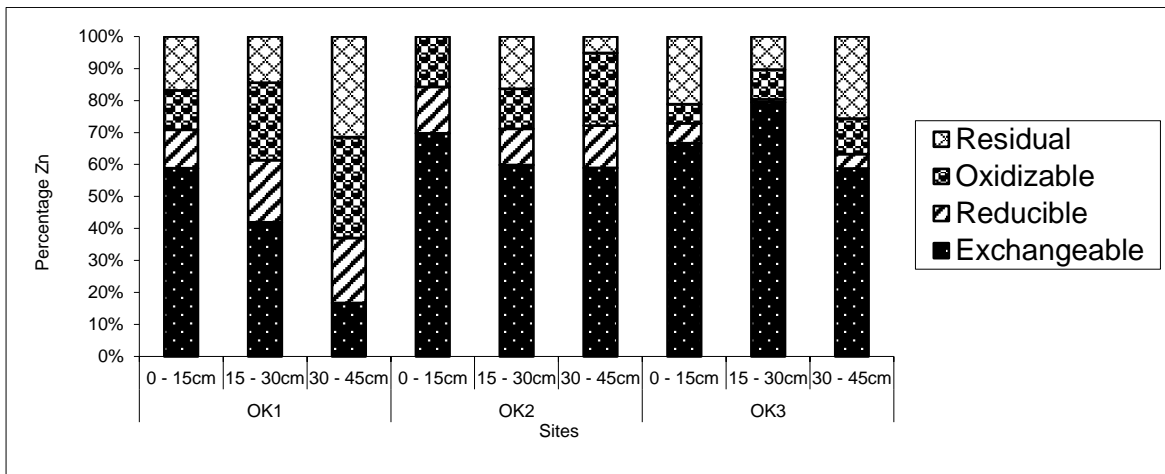
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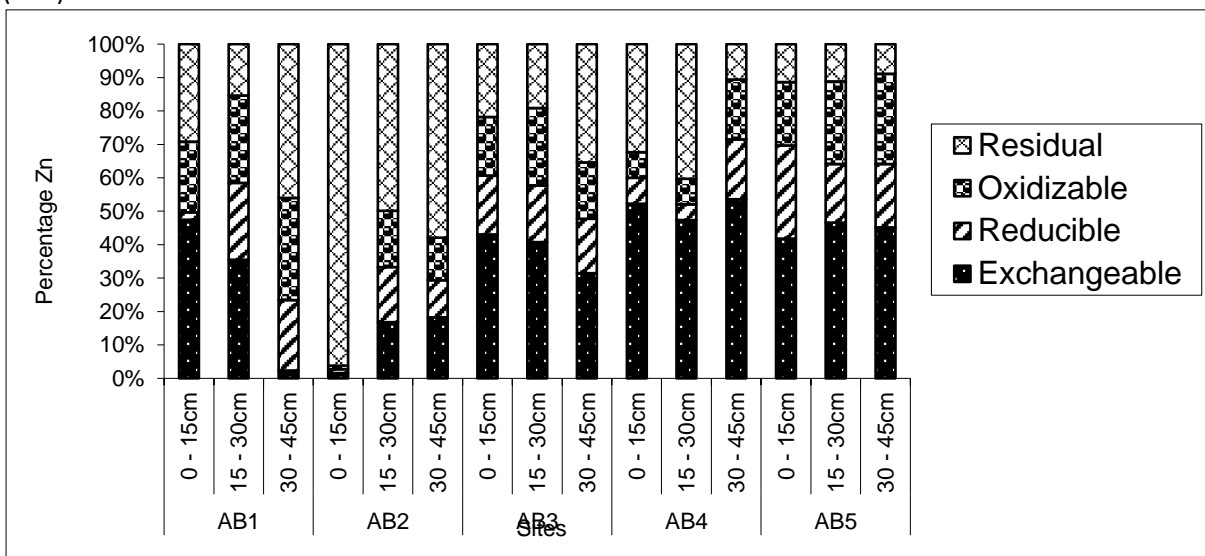
(25c)

Figure 25: Percentage of Zinc in the various extraction phases as a function of total Zinc content in soils a year after the major flooding

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Barium

The exchangeable/acid soluble (6.3 to 78.5 %) and reducible fraction (3.7 to 49.3 %) were the dominant form of Ba in these soil profiles a year after the major flooding (Table 4.52 and Figure 26 a-c). The percentage of total Ba in the oxidizable and residual phases ranged from 3.0 to 37.3 % and 0.4 to 66.6 % respectively. Barium was not detected in the oxidizable fraction in 0-15 cm depth of site AS3. Also, Ba was not detected in the residual phase in 15-30 cm and 30-45 cm depth of site AB3. This result also indicate that Ba was more mobile a year after the major flooding than three months after the major flooding.

Table 4.52: Concentrations and percentages of Barium in different extraction phases of the floodplain soils of the lower reaches of River Niger a year after the major flooding

Sites	Depth (cm)	CONCENTRATION (µg g⁻¹)						PERCENTAGE (%)				
		F1	F2	F3	F4	SUM	TM	F1	F2	F3	F4	RECOVERY
AS1	0 - 15	2.92	18.68	4.45	20.10	46.15	46.15	6.3	40.5	9.6	43.6	100.0
	15 - 30	31.68	15.88	1.75	8.64	57.95	57.95	54.7	27.4	3.0	14.9	100.0
	30 - 45	28.28	14.44	18.25	14.93	75.90	75.90	37.3	19.0	24.0	19.7	100.0
AS2	0 - 15	29.67	15.60	7.24	6.59	59.10	57.70	50.2	26.4	12.3	11.2	102.4
	15 - 30	46.24	44.00	10.50	10.71	111.45	111.45	41.5	39.5	9.4	9.6	100.0
	30 - 45	20.26	8.53	5.91	3.38	38.08	36.85	53.2	22.4	15.5	8.9	103.3
AS3	0 - 15	8.40	3.52	ND	2.03	13.95	13.95	60.2	25.2	-	14.6	100.0
	15 - 30	5.73	2.42	4.37	1.72	14.23	14.10	40.3	17.0	30.7	12.1	100.9
	30 - 45	0.08	0.03	0.04	0.14	0.28	0.25	27.7	10.1	12.6	49.6	112.0
AS4	0 - 15	52.08	45.28	13.35	15.04	125.75	125.75	41.4	36.0	10.6	12.0	100.0
	15 - 30	44.52	46.20	11.35	18.03	120.10	120.10	37.1	38.5	9.5	15.0	100.0
	30 - 45	22.16	13.96	4.70	61.38	102.20	102.20	21.7	13.7	4.6	60.1	100.0
AS5	0 - 15	23.98	7.83	3.22	4.05	39.07	37.05	61.4	20.0	8.2	10.4	105.5
	15 - 30	28.44	14.44	4.00	3.72	50.60	50.60	56.2	28.5	7.9	7.4	100.0
	30 - 45	15.96	3.62	1.94	3.02	24.55	24.30	65.0	14.8	7.9	12.3	101.0
OK1	0 - 15	20.96	16.92	9.70	31.77	79.35	79.35	26.4	21.3	12.2	40.0	100.0
	15 - 30	43.76	20.60	5.05	1.91	71.32	67.50	61.4	28.9	7.1	2.7	105.7
	30 - 45	63.32	44.04	9.15	0.74	117.25	117.25	54.0	37.6	7.8	0.6	100.0
OK2	0 - 15	23.68	7.84	3.35	0.22	35.09	34.65	67.5	22.3	9.5	0.6	101.3
	15 - 30	15.16	4.80	2.42	2.64	25.02	24.85	60.6	19.2	9.7	10.5	100.7
	30 - 45	16.88	4.60	2.60	25.52	49.60	49.60	34.0	9.3	5.2	51.5	100.0
OK3	0 - 15	15.12	3.96	2.60	11.37	33.05	33.05	45.7	12.0	7.9	34.4	100.0
	15 - 30	9.88	2.04	3.15	4.18	19.25	19.25	51.3	10.6	16.4	21.7	100.0
	30 - 45	10.68	1.00	1.50	0.43	13.61	12.75	78.5	7.3	11.0	3.2	106.7
AB1	0 - 15	16.62	10.62	2.63	18.37	48.23	48.05	34.5	22.0	5.5	38.1	100.4
	15 - 30	48.84	49.32	10.45	2.94	111.55	111.55	43.8	44.2	9.4	2.6	100.0
	30 - 45	17.56	3.29	8.70	58.80	88.35	88.35	19.9	3.7	9.8	66.6	100.0
AB2	0 - 15	72.19	53.03	10.31	15.53	151.05	150.80	47.8	35.1	6.8	10.3	100.2
	15 - 30	0.06	0.07	0.01	0.14	0.28	0.25	22.6	24.0	3.5	50.0	112.0
	30 - 45	74.08	47.68	12.50	26.49	160.75	160.75	46.1	29.7	7.8	16.5	100.0
AB3	0 - 15	41.32	51.28	14.95	22.65	130.20	130.20	31.7	39.4	11.5	17.4	100.0
	15 - 30	94.32	67.88	14.75	ND	176.95	176.95	53.3	38.4	8.3	-	100.0
	30 - 45	57.60	68.96	13.40	ND	139.96	139.96	41.2	49.3	9.6	-	100.0
AB4	0 - 15	9.22	2.87	15.12	13.35	40.56	40.35	22.7	7.1	37.3	32.9	100.5
	15 - 30	1.96	3.36	2.80	12.68	20.80	20.80	9.4	16.2	13.5	61.0	100.0
	30 - 45	44.04	11.76	4.30	2.80	62.90	62.90	70.0	18.7	6.8	4.5	100.0
AB5	0 - 15	60.92	40.16	8.60	9.07	118.75	118.75	51.3	33.8	7.2	7.6	100.0
	15 - 30	63.76	37.56	9.60	12.48	123.40	123.40	51.7	30.4	7.8	10.1	100.0
	30 - 45	45.04	13.52	6.15	0.24	64.95	64.95	69.3	20.8	9.5	0.4	100.0

F1 = Exchangeable fraction; F2 = Reducible fraction; F3 = Oxidizable fraction; F4 = Residual fraction; SUM = Sum of all fractions; TM = Total metal concentration in soil sample
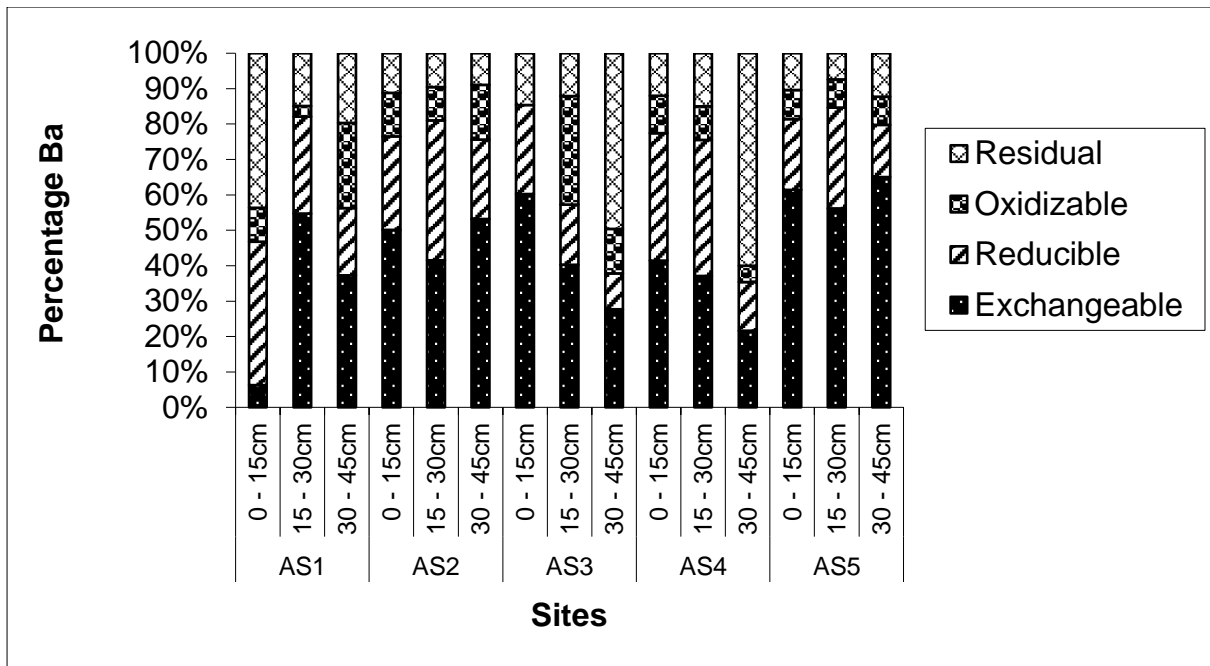
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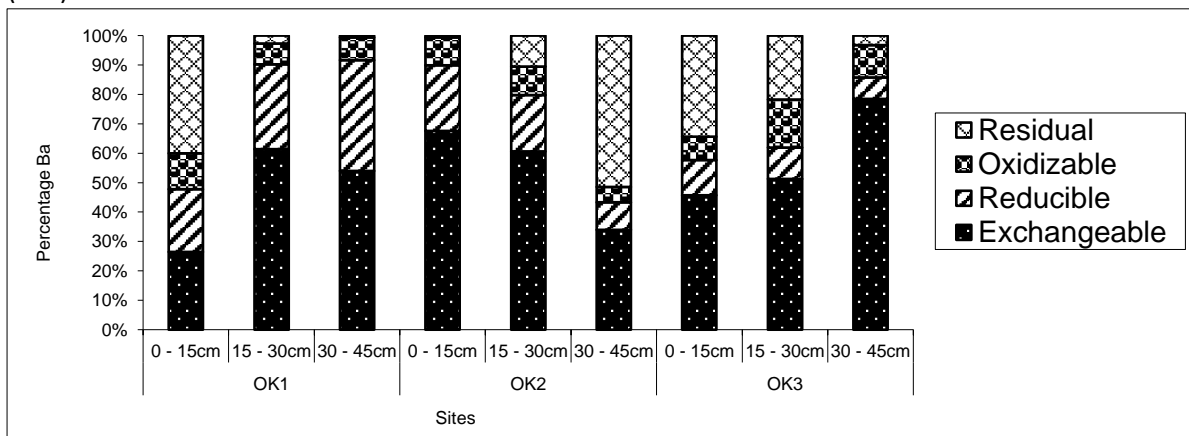
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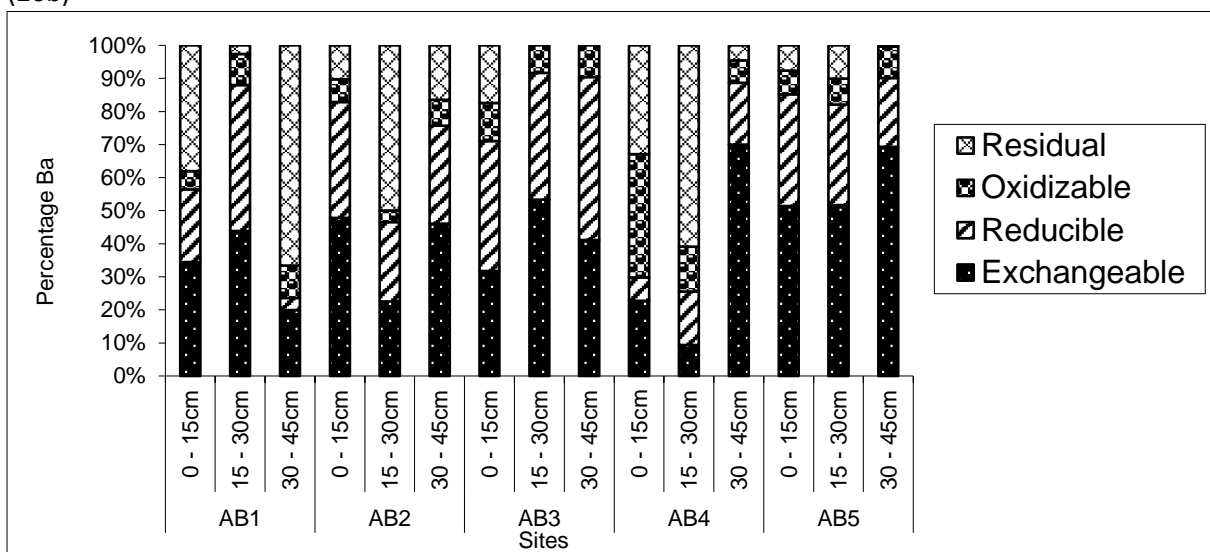
(26c)

Figure 26: Percentage of Barium in the various extraction phases as a function of total Barium content in soils a year after the major flooding

4.30 Mobility of metals in the soil a year after the major flooding

In this study, the potential mobility of the metals a year after the major flooding are shown in Table 4.53. The potential mobility of the metals followed the order Ba > Cu > Pb > Zn > Mn > Co > Ni > Cr > Cd respectively. The proportions of potentially mobile or available metals in the majority of these sites and depth were greater than 20% which indicates that changes in the physicochemical conditions as a result of flooding may lead to significant remobilization of these metals.

Table 4.53: Readily and potential fractions of metals in floodplain soils a year after major flooding

Sites	Depth (cm)	Readily mobile faction									Potential mobile fraction								
		Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Ba	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Ba
AS1	0 - 15	8.2	32.6	1.2	2.5	14.6	10.2	1	4.5	6.3	60.2	58.5	52.9	53	71.1	88	54.3	81.1	56.4
	15 - 30	3	13.3	1.3	6.9	7.4	6.3	5.5	4.4	54.7	8.9	13.3	12.4	47.3	17.2	10.1	89.3	28.7	85.1
	30 - 45	-	18.7	2.2	0.3	8.3	30.3	7.6	48.2	37.3	53.3	18.7	52.6	50.5	38.3	85.4	54.6	74.5	80.3
AS2	0 - 15	-	9.6	0.7	9.4	20.3	12	22.8	60.9	50.2	23.7	68.8	35.3	92	99.6	33.3	66.3	88.1	88.9
	15 - 30	1.7	4.6	0.3	4.8	12	11	-	28.2	41.5	16.7	58.1	28.7	68.1	81.5	33.1	78.9	64.5	90.4
	30 - 45	11.1	5.2	0.5	1.9	0.2	48.7	18.2	-	53.2	96.3	40.4	28.9	81.8	59.6	50.5	72.4	18.1	91.1
AS3	0 - 15	7.3	19.4	2.7	7.3	45.4	17.6	22.6	19.2	60.2	21.8	24.2	44.6	81.5	80.2	39	82.1	63.7	85.4
	15 - 30	5.3	4.8	1.9	9	7.7	9	1.7	36.9	40.3	10.6	7.8	34.9	91.2	24.5	23.6	92.3	63.8	88
	30 - 45	-	40	4.8	4.7	30.3	23	7.8	5.2	27.7	20	50	100	100	51.3	73.4	53.7	50.1	50.4
AS4	0 - 15	7.1	10	0.5	4.7	29.5	12	10.9	16.1	41.4	51.8	45.4	53.5	88.8	87.4	44.1	99.8	61.8	88
	15 - 30	21.8	8.6	1.1	13.2	12.5	17.8	10.5	3.3	37.1	58.2	76.7	69.3	87.7	58	55.1	78.3	46	85.1
	30 - 45	4.5	1.5	0.2	4.2	5.2	3.2	28.2	9.2	21.7	9.4	16.9	16.3	43.1	31.4	13.9	58.7	28.9	40
AS5	0 - 15	21.3	34.9	1.3	11.8	60.2	52.5	32.8	50.2	61.4	74.6	57.4	23.7	83.2	83.6	65.2	60.9	83	89.6
	15 - 30	8.9	29.7	1.2	6	51.8	24.7	2.8	47.2	56.2	35.6	52.9	22.6	53.2	74.3	52	59.1	86.5	92.6
	30 - 45	21.8	22.9	1.8	17.6	60.7	18.5	10.5	49.4	65	29.1	37.6	53	73.1	89.9	54.2	69.9	87.5	87.7
OK1	0 - 15	10.3	32.6	0.9	12.9	48.2	18.4	1.8	58.8	26.4	82.6	53.1	47.6	81.3	61.6	43	40.2	83.1	59.9
	15 - 30	-	23.1	0.4	11.2	39.8	35.3	9	41.9	61.4	14.1	53.8	31.1	96.5	77.7	79.1	98.7	85.6	97.4
	30 - 45	11.4	4.6	1.2	12	8.4	22.5	16	16.7	54	61.9	99.6	84.4	91.7	67.7	60.2	90.5	68.5	99.4
OK2	0 - 15	0.5	13.3	0.7	4.9	38.6	9.6	27.2	69.7	67.5	11.3	40.6	47.7	69.2	84.3	32.3	63	99.9	99.3
	15 - 30	-	9.8	1.9	5.6	28.3	10.4	14.9	59.8	60.6	16	47.4	82.5	77.1	92.3	61.7	53.1	83.7	89.5
	30 - 45	6.2	9.8	2.5	17.6	34	12.4	7.9	58.9	34	12.4	18.6	44.8	89.3	86.8	39.7	55.8	94.8	48.5
OK3	0 - 15	14.5	15.7	1.7	20.7	38.5	8.8	36.1	66.6	45.7	21.8	22.2	49.3	91.9	62	21.1	64.7	78.9	65.6
	15 - 30	-	11.4	1.4	12.9	28	6.3	54.5	79.5	51.3	8.9	14.3	37.9	84.2	46.9	16.5	82	89.7	78.3
	30 - 45	-	15.4	3.2	27.8	43.8	18.7	35.1	58.7	78.5	85.7	15.4	32.6	82.5	67.1	38.7	54.9	74.4	96.8
AB1	0 - 15	23.8	8.6	0.5	4.4	9.4	27.9	-	47.5	34.5	61.9	55.4	51.6	53.1	50.4	67.4	58.5	70.8	62
	15 - 30	9.8	5.2	0.7	6	4.9	37.4	-	35.5	43.8	68.3	74.1	51.7	56.6	56.1	85.2	70.9	84.6	97.4
	30 - 45	-	4	0.6	8.7	5.9	7.8	12.7	2.3	19.9	6.2	46.4	30.7	90.2	56.8	38.4	85.8	54	33.4
AB2	0 - 15	4.5	21.9	0.3	8.7	40.7	22.5	14.4	1.6	47.8	31.7	67.4	46.7	68.6	96.7	49.5	75	3.8	89.7
	15 - 30	29	5.9	1	12	4.6	21.8	1.2	16.8	22.6	58	59.2	100	100	50.1	52.9	51.3	50.1	50.1
	30 - 45	2.8	3.1	0.3	7.8	14.4	12	11.1	18.2	46.1	14	24.1	9.8	54.5	54.5	23.4	64.3	42.1	83.6
AB3	0 - 15	4.9	4.5	0.3	8.8	11.5	8.2	1	43	31.7	21.2	46	36.8	83.9	69.2	28.1	84.6	78.1	82.6
	15 - 30	2.7	3.1	0.4	5.8	7.2	13.1	11.7	40.7	53.3	19.7	51.1	26.3	62.6	53.3	37	80.4	80.8	100
	30 - 45	5.1	2.4	0.2	5.2	4.2	7.8	2.8	31.5	41.2	11.4	97.6	22.7	60.5	55.9	20.7	73.7	64.7	100
AB4	0 - 15	5	22.5	0.7	0.7	49.4	13.9	20.1	52.2	22.7	20	50	35.4	54.2	58.1	72.2	66.7	67.7	67.1
	15 - 30	-	11.7	0.1	4.8	26.4	0	21.8	47.3	9.4	16	31.7	5.1	45.7	60.6	1	67.6	59.7	39.1
	30 - 45	-	6.5	0.5	8	15.4	15.1	36.3	53.6	70	20	51.7	32.5	59.2	74.4	31.5	75.2	89.4	95.5
AB5	0 - 15	3.9	14.8	0.5	5	33	14.4	48.1	41.8	51.3	31.7	67.9	39.3	54.5	94.9	33.9	53.4	88.6	92.3
	15 - 30	3.8	27.3	0.4	9.7	47.4	10.8	18.5	46.6	51.7	33.8	66.4	36.8	69.3	89	83.3	96.4	88.8	89.9
	30 - 45	6.4	39	0.9	20.6	70.8	17.8	3.8	45.2	69.3	25.6	68.1	36.4	72.4	78.4	38.9	92.2	91.1	99.6

4.31   PAHs Concentration in soils a year after the major flooding

The results for the determination of $\sum 16$ PAHs in floodplain soils a year after the major flooding are shown in Table 4.54. The concentration of the $\Sigma 16$ PAHs for the soils ranged from 2.2 to 2634 µg kg^{-1} for all sites and depths. The concentrations of PAHs in these soils varied significantly ($p < 0.05$) with respect to sites and depths. Also, the concentrations of PAHs in the soil a year after the major flooding were significantly lower than the concentrations recorded three months after the major flooding. The concentrations decreased with increasing depth at all sites except sites AS2 and OK3. The soils of the upper sections of the floodplain had higher concentrations of the $\sum 16$ PAHs than the mid and lower sections of the floodplain (Table 4.55). The high concentrations of PAHs in the upper section of the flood plain may be associated with high anthropogenic activities and urbanization. The concentrations of $\sum 16$ PAHs in the floodplain soils a year after the major flooding were comparable to PAHs concentration reported for soils of the Rhine River floodplain (Pies *et al.,* 2007), and with the range reported for agricultural soils (Chen *et al.,* 2005; Morello *et al.,* 2008; Yang *et al.,* 2012). The concentrations of PAHs in these sites in this sampling period were higher than the background value (Edwards, 1983). Also, 18 %, 5 %, 23 % and 48.7 % of the samples falls within the heavily contaminated, contaminated, weakly contaminated and not contaminated categories respectively (Malizewkwa-Kordybach, 1996). Only sites AS1, AS5, OK1 and OK3 were above the PAHs target value of 1000 µg kg^{-1} set by the Dutch Government a year after the major flooding event.

Table 4.54: Concentrations (µg kg^{-1}) of PAHs in floodplain soils after the major flooding

Site	DEPTH (cm)	NaP	Acy	Ace	Flu	Phen	Ant	Flt	Pyr	BaA	Chry	BbF	BkF	BaP	IndP	DahA	BghiP	Total	2R	3R	4R	5R	6R	∑PAH7c
AS1	0-15	ND	ND	4.7	6.7	58.0	ND	ND	604.0	4.7	11.8	ND	502.2	ND	ND	ND	ND	1192.1	ND	69.4	620.5	502.2	ND	518.7
	15-30	ND	ND	ND	28.5	ND	200.8	ND	54.3	ND	ND	194.0	30.0	12.4	ND	ND	48.9	568.9	ND	229.3	54.3	236.4	48.9	236.4
	30-45	ND	ND	ND	ND	ND	ND	3.5	80.0	37.1	9.9	7.2	4.0	ND	ND	ND	ND	141.7	ND	ND	130.5	11.2	ND	58.2
AS2	0-15	ND	33.0	7.0	ND	22.0	8.4	ND	37.6	15.7	ND	ND	ND	ND	ND	ND	ND	123.7	ND	70.4	53.3	ND	ND	15.7
	15-30	ND	ND	7.0	25.4	7.0	ND	ND	3.3	4.1	44.2	ND	66.0	ND	ND	ND	ND	157.0	ND	39.4	51.6	66.0	ND	114.3
	30-45	7.8	ND	74.3	14.6	8.3	ND	28.8	ND	3.9	ND	ND	ND	ND	ND	ND	ND	137.7	7.8	97.2	32.7	ND	ND	3.9
AS3	0-15	ND	ND	82.0	39.0	ND	ND	ND	ND	99.1	ND	0.4	40.0	ND	ND	ND	303.0	563.5	ND	121.0	99.1	40.4	303.0	139.5
	15-30	ND	82.0	ND	ND	ND	ND	405.0	ND	ND	ND	44.0	11.1	ND	ND	ND	15.0	557.1	ND	82.0	405.0	55.1	15.0	55.1
	30-45	ND	ND	ND	ND	ND	ND	26.0	1.0	5.3	0.7	ND	83.1	8.4	ND	ND	ND	124.5	ND	ND	33.0	91.5	ND	97.5
AS4	0-15	ND	ND	ND	ND	ND	ND	ND	642.1	ND	0.3	ND	90.0	33.1	ND	81.0	22.0	868.5	ND	ND	642.4	204.1	22.0	204.1
	15-30	ND	ND	ND	ND	ND	ND	ND	28.2	51.1	ND	44.0	0.9	ND	ND	ND	ND	124.2	ND	ND	79.3	44.9	ND	96.0
	30-45	ND	ND	57.0	4.3	ND	ND	ND	29.9	ND	ND	ND	ND	ND	ND	ND	ND	91.2	ND	61.3	29.9	ND	ND	ND
AS5	0-15	ND	ND	37.2	ND	8.3	ND	480.0	7.4	ND	89.8	ND	2011.3	ND	ND	ND	ND	2634.0	ND	45.5	577.2	2011.3	ND	2101.1
	15-30	4.8	ND	ND	38.8	702.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	620.0	1365.7	4.8	740.9	ND	ND	620.0	ND
	30-45	ND	ND	ND	ND	ND	1083.0	31.0	0.7	359.9	2.1	ND	ND	ND	ND	ND	ND	1476.7	ND	1083.0	393.7	ND	ND	362.0
OK1	0-15	ND	22.0	14.2	0.3	ND	ND	ND	400.2	82.2	ND	ND	ND	ND	ND	ND	ND	518.9	ND	36.5	482.4	ND	ND	82.2
	15-30	ND	8.4	11.0	7.0	ND	ND	520.1	28.1	ND	ND	990.0	ND	ND	ND	ND	ND	1564.6	ND	26.4	548.2	990.0	ND	990.0
	30-45	ND	ND	ND	44.0	ND	ND	ND	2.0	ND	63.3	ND	200.1	ND	ND	ND	ND	309.4	ND	44.0	65.3	200.1	ND	263.4
OK2	0-15	ND	38.2	ND	30.9	ND	ND	40.0	90.7	ND	ND	35.1	ND	ND	ND	ND	ND	234.9	ND	69.1	130.7	35.1	ND	35.1
	15-30	ND	ND	ND	91.0	33.0	ND	11.9	90.0	72.1	81.0	391.1	ND	8.2	ND	ND	ND	778.3	ND	124.0	255.0	399.3	ND	552.4
	30-45	ND	3.8	17.8	ND	ND	ND	ND	27.3	ND	ND	82.0	ND	ND	ND	7.9	ND	138.8	ND	21.6	27.3	89.9	ND	117.2
OK3	0-15	ND	ND	ND	ND	850.0	50.1	29.9	21.5	ND	ND	ND	58.0	ND	ND	ND	0.6	1010.1	ND	900.1	51.4	58.0	0.6	58.0
	15-30	ND	ND	3.0	ND	51.0	ND	ND	ND	ND	ND	ND	93.0	42.0	ND	ND	0.6	189.6	ND	54.0	ND	135.0	0.6	135.0
	30-45	ND	563.0	672.1	21.7	ND	ND	ND	ND	ND	ND	ND	99.2	ND	ND	ND	ND	1356.0	ND	1256.8	ND	99.2	ND	99.2
AB1	0-15	ND	ND	ND	ND	ND	52.2	2.0	53.3	231.7	47.1	5.0	1.4	ND	ND	ND	ND	392.7	ND	52.2	334.1	6.4	ND	285.2
	15-30	ND	ND	ND	ND	ND	ND	ND	28.5	ND	83.1	76.2	ND	ND	ND	ND	7.0	194.8	ND	ND	111.6	76.2	7.0	159.3
	30-45	ND	ND	ND	8.0	ND	ND	ND	2.1	6.7	ND	ND	ND	ND	ND	ND	ND	16.8	ND	8.0	8.8	ND	ND	6.7
AB2	0-15	ND	ND	ND	28.8	ND	ND	96.3	ND	4.3	17.4	ND	59.1	ND	ND	ND	ND	205.9	ND	28.8	118.0	59.1	ND	80.8
	15-30	ND	ND	5.0	0.9	2.0	ND	ND	4.2	6.3	ND	ND	ND	ND	ND	ND	3.3	21.7	ND	7.9	10.5	ND	3.3	6.3
	30-45	ND	ND	3.1	2.8	ND	ND	ND	ND	5.8	ND	ND	6.1	ND	ND	ND	ND	17.8	ND	5.9	5.8	6.1	ND	11.9
AB3	0-15	ND	ND	0.9	603.8	77.8	ND	ND	ND	88.2	ND	1.0	5.3	ND	ND	6.0	ND	783.0	ND	682.5	88.2	12.3	ND	100.5
	15-30	ND	ND	4.2	54.9	37.8	ND	8.1	0.8	ND	ND	ND	ND	ND	ND	ND	72.1	177.9	ND	96.9	8.9	ND	72.1	24.2
	30-45	ND	ND	ND	ND	ND	34.9	8.1	90.0	20.0	4.2	ND	ND	ND	ND	ND	ND	157.2	ND	34.9	122.3	ND	ND	24.2
AB4	0-15	ND	ND	1.3	9.2	26.7	ND	ND	4.2	39.9	29.0	ND	6.2	ND	ND	ND	ND	116.5	ND	37.2	73.1	6.2	ND	75.1
	15-30	ND	ND	8.5	39.0	ND	ND	34.1	7.4	5.3	ND	39.1	ND	ND	ND	ND	ND	133.4	ND	47.5	46.8	39.1	ND	44.4
	30-45	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	3.7	8.1	ND	ND	ND	0.4	12.2	ND	ND	ND	11.8	0.4	11.8
AB5	0-15	ND	ND	20.5	ND	45.8	ND	ND	2.4	ND	62.0	ND	4.0	582.1	ND	ND	ND	716.8	ND	66.3	64.4	586.1	ND	648.1
	15-30	ND	ND	ND	ND	52.9	ND	9.5	65.0	77.3	ND	8.0	ND	37.0	ND	ND	6.6	256.3	ND	52.9	151.8	45.0	6.6	122.3
	30-45	ND	ND	ND	ND	ND	ND	9.7	ND	2.1	ND	0.9	ND	ND	ND	ND	6.4	19.1	ND	ND	11.8	0.9	6.4	3.0

Naphthalene (Nap), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phen), Anthracene (Ant), Fluoranthene (Flt), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chry), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(1,2,3-cd)perylene (IndPr), Dibenzo(a,h)anthracene (DahA) and Benzo(ghi)perylene (BghiP), R= Rings

Table 4.55: Mean concentrations (µg kg^{-1}) of PAHs in soils a year after the major flooding

DEPTH (cm)	Upstream			Midstream			Downstream		
	0-15	15-30	30-45	0-15	15-30	30-45	0-15	15-30	30-45
Nap	ND	4.8±0.0	7.8±0.0	ND	ND	ND	ND	ND	ND
	ND	(ND-4.8)	(ND-7.8)	ND	ND	ND	ND	ND	ND
Acy	33.0±0.0	82±0.0	ND	22.0±0.0	8.4±0.0	283.4±395.4	ND	ND	ND
	(ND-33.0)	(ND-82.0)	ND	(ND-22.0)	(ND-8.4)	(ND-563.0)	ND	ND	ND
Ace	32.7±36.0	7.0±0.0	65.7±12.2	26.2±17.0	11.0±0.0	345.0±462.7	7.6±11.2	5.9±2.3	3.1±0.0
	(ND-82.0)		(ND-74.3)	(ND-38.2)	(ND-11.0)	(ND-672.1)	(ND-20.5)	(ND-8.5)	(ND-3.1)
Flu	22.9±22.8	30.9±7.0	9.5±7.3	0.3±0.0	5.0±2.8	32.9±15.8	213.9±337.8	31.6±27.8	5.4±3.7
	(ND-39.0)	(ND-38.8)	(ND-14.6)	(ND-0.3)	(ND-7.0)	(ND-44.0)	(ND-603.8)	(ND-54.9)	(ND-8.0)
Phen	29.4±25.7	354.6±491.5	8.3±0.0	440.5±579.2	91.0±0.0	ND	50.1±25.8	30.9±26.1	ND
	(ND-58.0)	(ND-702.1)	(ND-8.3)	(ND-850.0)	(ND-91.0)	ND	(ND-77.8)	(ND-52.9)	ND
Ant	8.4±0.0	200.8±0.0	1083.0±0.0	50.1±0.0	42.0±12.7	ND	52.2±0.0	ND	34.9±0.0
	(ND-8.4)	(ND-200.8)	(ND-1083)	(ND-50.1)	(ND-51.0)	ND	(ND-52.2)	ND	(ND-34.9)
Flt	480.0±0.0	405.0±0.0	22.3±12.7	35.0±7.1	266.0±359.4	ND	49.2±66.7	21.8±17.4	8.1±0.0
	(ND-480.0)	(ND-405.0)	(ND-31.0)	(ND-40.0)	(ND-520.1)	ND	(ND-96.3)	(ND-34.1)	(ND-8.1)
Pyr	322.8±347.3	28.6±25.5	27.9±37.3	170.8±201.7	59.1±43.8	2.0±0.0	20.0±28.9	22.6±25.6	33.9±48.7
	(ND-642.1)	(ND-54.3)	(ND-80.0)	(21.5-400.2)	(ND-90.0)	(ND-2.0)	(ND-53.3)	(4.2-65.0)	(ND-90.0)
BaA	39.8±51.6	27.6±33.2	101.6±172.9	82.2±0.0	72.1±0.0	27.3±0.0	91.0±99.9	22.4±36.7	10.8±8.0
	(ND-99.1)	(ND-51.1)	(ND-359.9)	(ND-82.2)	(ND-72.1)	(ND-27.3)	(ND-231.7)	(ND-77.3)	(ND-20.0)
Chry	34.0±48.7	44.2±0.0	4.2±5.0	ND	81.0±0.0	63.3±0.0	38.9±19.7	83.1±0.0	3.2±1.5
	(ND-89.8)	(ND-44.2)	(ND-9.9)	ND	(ND-81.0)	(ND-63.3)	(ND-62.0)	(ND-83.1)	(ND-4.2)
BbF	0.4±0.0	94.0±86.6	7.2±0.0	ND	690.6±423.5	ND	3.0±2.8	41.1±34.1	0.9±0.0
	(ND-0.4)	(ND-194.0)	(ND-7.2)	ND	(ND-990.0)	ND	(ND-5.0)	(ND-76.2)	(ND-0.9)
BkF	660.9±923.8	27.0±28.7	43.6±55.9	35.1±0.0	ND	127.1±63.8	15.2±24.6	ND	4.9±1.7
	(ND-2011.3)	(ND-66.0)	(ND-83.1)	(ND-35.1)	ND	(82.0-200.1)	(ND-59.1)	ND	(ND-6.1)
BaP	33.1±0.0	12.4±0.0	8.4±0.0	58.0±0.0	50.6±60.0	ND	582.1±0.0	37.0±0.0	8.1±0.0
	(ND-33.1)	(ND-12.4)	(ND-8.4)	(ND-58.0)	(ND-93.0)	ND	(ND-582.1)	(ND-37.0)	(ND-8.1)
IndP	ND	ND	ND	ND	ND	ND	ND	ND	ND
DahA	81.0±0.0	ND	ND	ND	42.0±0.0	7.9±0.0	6.0±0.0	ND	ND
	(ND-81.0)	ND	ND	ND	(ND-42.0)	(ND-7.9)	(ND-6.0)	ND	ND
BghiP	162.5±198.7	228.0±339.9	ND	0.6±0.0	0.6±0.0	ND	ND	22.3±33.3	3.4±4.2
	(ND-303.0)	(ND-620.0)	ND	(ND-0.6)	(ND-0.6)	ND	ND	(ND-72.1)	(ND-6.4)
Total	1076.4±955.7	554.6±500.4	394.4±605.4	588.0±392.2	844.2±689.9	601.4±659.0	443.0±298.3	156.8±87.4	44.6±63.0
	(123.7-2634.0)	(124.2-1365.7)	(91.2-1476.7)	(234.9-1010.1)	(189.6-1564.6)	(138.8-1356.0)	(116.5-783.0)	(21.7-256.3)	(12.2-157.2)
2R	ND	4.8±0.0	7.8±0.0	ND	ND	ND	ND	ND	ND
	ND	(ND-4.8)	(ND-7.8)	ND	ND	ND	ND	ND	ND
3R	76.6±31.8	272.9±322.4	413.8±579.8	335.2±489.5	68.1±50.3	440.8±706.8	173.4±285.0	51.3±36.4	16.3±16.2
	(ND-121.0)	(ND-740.9)	(ND-1083)	(36.5-900.1)	(26.4-124.0)	(21.6-1256.8)	(28.8-682.5)	(ND-96.9)	(ND-34.9)
4R	398.5±295.6	147.6±172.1	124.0±156.7	221.5±229.4	401.6±207.3	46.3±26.9	135.6±±112.8	65.9±63.5	37.2±56.8
	(53.3-642.4)	(ND-405.0)	(29.9-393.7)	(51.4-482.4)	(ND-548.2)	(ND-65.3)	(64.4-334.1)	(8.9-151.8)	(ND-122.3)
5R	689.5±901.7	100.6±90.9	51.4±56.8	46.6±16.2	508.1±437.8	129.7±61.1	134.0±253.7	53.4±19.9	6.3±5.5
	(ND-2011.3)	(ND-236.4)	(ND-91.5)	(ND-58.0)	(135.0-990.0)	(89.9-200.1)	(6.20-586.1)	(ND-76.2)	(ND-11.8)
6R	162.5±198.7	228.0±339.9	ND	0.6±0.0	0.6±0.0	ND	ND	22.3±33.3	3.4±4.2
	(ND-303.0)	(ND-620.0)	ND	(ND-0.6)	(ND-0.6)	ND	ND	(ND-72.1)	(ND-6.4)
∑PAH7c	595.9±861.7	125.5±78.0	130.4±159.1	58.4±23.6	559.1±427.5	159.9±90.1	237.9±245.2	66.6±71.0	11.5±8.0
	(15.7-2101.1)	(ND-236.4)	(ND-362.0)	(35.1-82.2)	(135.0-990.0)	(99.2-263.4)	(75.1-648.1)	(0.8-159.3)	(3.0-24.2)

4.32   Occurrence and profiles of PAHs in the soil

The occurrence patterns and profiles of PAHs in these soils are displayed in Figure 27 (a-c). The occurrence patterns and profiles varied with sites and depths. In these soil profiles, the distribution patterns of PAHs a year after the major flooding followed the order $4 > 3 > 5 > 6 > 2$. The four ring PAHs were the dominant PAH compound in the soil profiles. The concentrations of the 3-ringed PAHs was higher than that of 5-ringed PAHs a year after the major flooding. This might be due to decomposition of 5-ringed PAHs into lower molecular weight PAHs. The 2-ring PAH compound (naphthalene) was only detected in two samples a year after the major flooding at a concentration of 4.8 and 7.8 µg kg^{-1} constituting 0.4 and 5.7 % of the Σ16 PAHs.

The concentration of Σ3-ring PAHs (Acy + Ace + Flu + Phe + Ant) ranged from 5.9 to 1256.8 µg kg^{-1} for all sites and depths and constituted 1.69 to 92.68 % of the Σ16 PAHs. The concentrations of the 3-ring PAHs showed a decrease with respect to depth in all sites except for sites AS1, AS2, AS4, AS5, OK1, OK3 and AB4. Fluorene (Flu) was the dominant 3-ring PAH compound in these sites in terms of concentrations and frequency of occurrence in both sampling periods.

The concentrations of Σ4-ringed PAHs (Flt + Pyr+ BaA + Chry) ranged from 5.8 to 642.4 µg kg^{-1} for all sites and depths and constituted 5.0 to 93.0 % of the Σ16 PAHs. Pyrene was the dominant 4-ring PAHs in terms of concentration and frequency of occurrence a year after the major flooding. The 4-ring PAHs decreased with depth in all sites except sites AB3 a year after the major flooding.

The concentration of Σ5-ring PAHs (BbF + BkF + BaP + DahA) in all sites and depth ranged from 0.9 to 2011.3 µg kg^{-1} for these soil samples a year after the major flooding. The 5-ringed PAH constituted 1.6 to 96.7 % of the Σ16 PAHs in the soil profiles. The 5-ring PAHs decreased with depth in all sites except AS1, AS4, AS5, OK1, AB2, AB3 and AB5 a year after the major flooding.
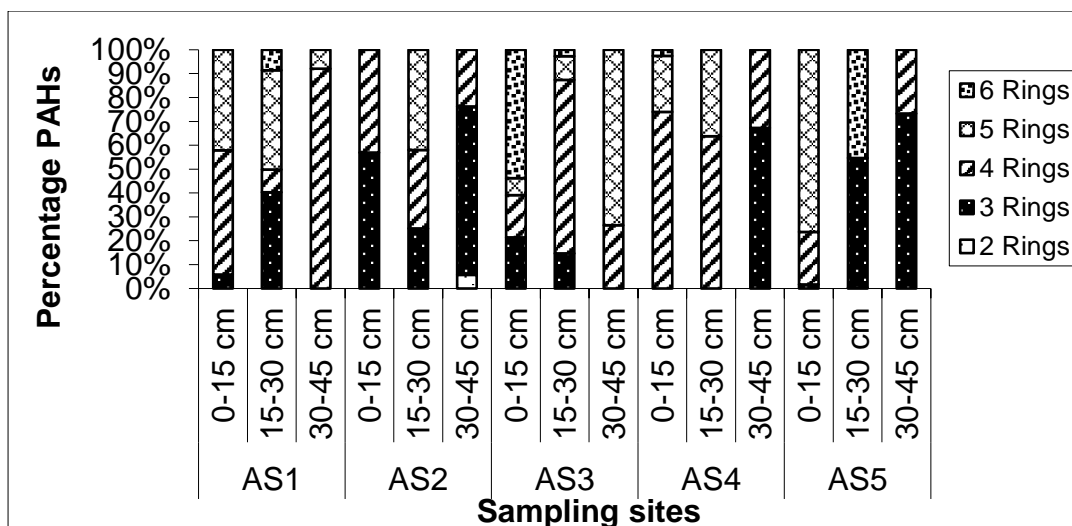
(27a)
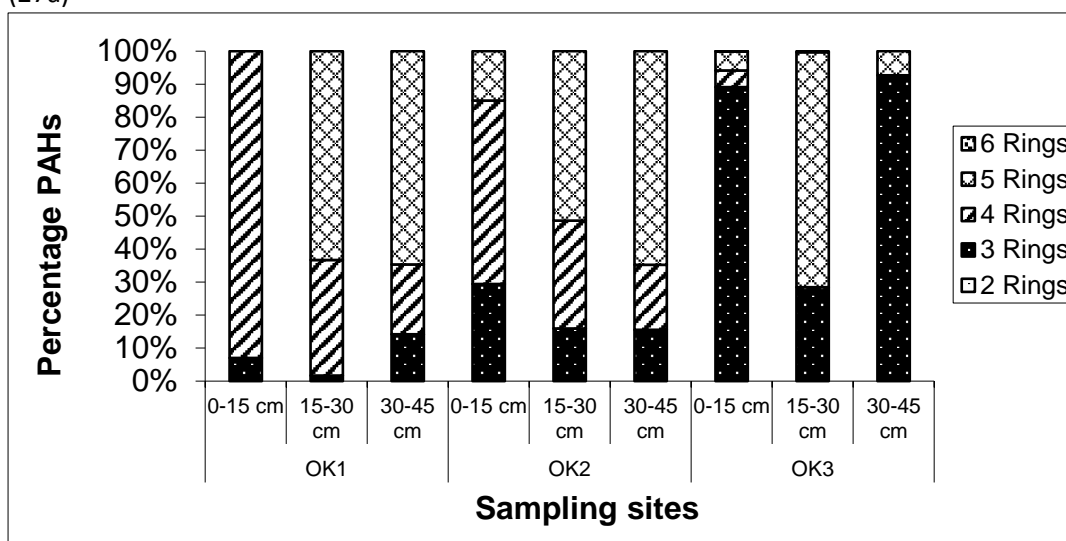
(27b)
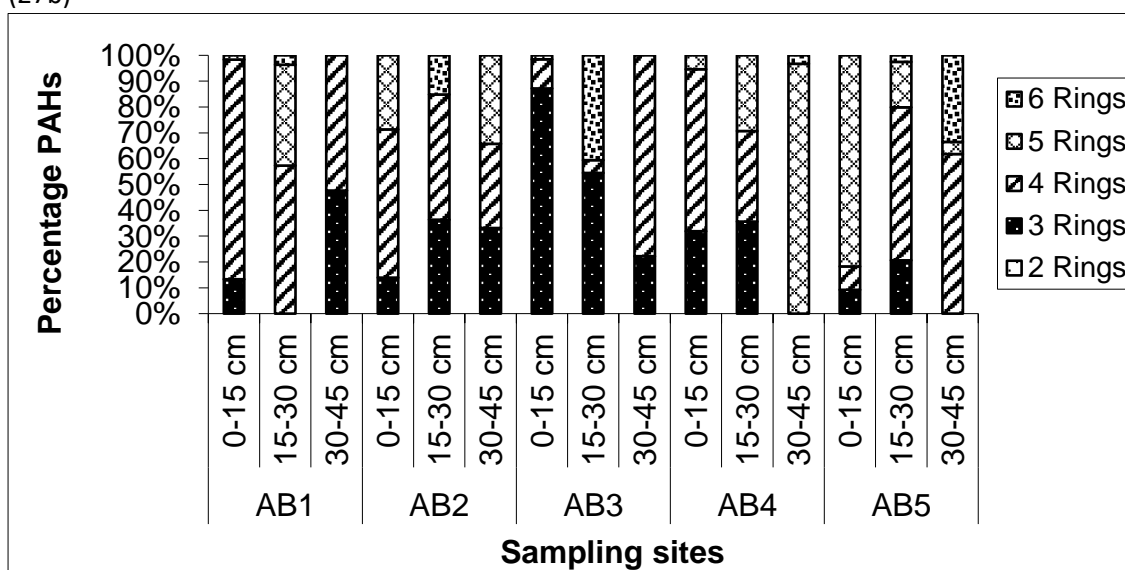
(27c)

Figure 27: PAHs profiles in floodplain soilsa year after the major flooding

Benzo(k)fluoranthene (BkF) was the dominant 5-ring PAHs in terms of concentration and frequency of occurrence a year after the major flooding. Benzo(a)pyrene was detected in 23 % of the soil samples at concentrations in the range of 8.1 to 582.1 µg kg^{-1}.

The concentration of Σ6-ring PAHs (IndP + BghiP) ranged from 0.4 to 620.0 µg kg^{-1} for all sites and depths and constituted 0.1 to 53.7 % of the Σ16 PAHs. Benzo(g,h,i)perylene was the dominant 6-ring PAHs in terms of concentration and frequency of occurrence a year after the major flooding.

4.33   Health Risk Assessment of PAHs a year after the major flooding

In this study, the summation of the 7 carcinogenic PAHs concentrations (∑PAH$_{7c}$) ranged from below detection limit to 2101 µg kg^{-1} in all site and depths a year after the major flooding (Table 4.55). The carcinogenic PAHs constituted 0.5 to 96.7 % of the Σ16 PAHs in the soil profiles a year after the flooding.

The concentrations of BaP$_{TEQ}$ and BaP$_{MEQ}$ ranged from below detection limit to 582 µg kg^{-1} and below detection limit to 584 µg kg^{-1} respectively for all sites (Table 4.57). The BaP$_{TEQ}$ and BaP$_{MEQ}$ obtained after a year were significantly lower than those obtained three months after the major flooding and BaA, BbF and BaP have significant impact on the BaP$_{TEQ}$ and BaP$_{MEQ}$ values obtained. The BaP$_{TEQ}$ and BaP$_{MEQ}$ concentrations obtained a year after were comparable to those reported in the literature (Orecchio, 2010; Yang *et al.,* 2012). In this study, the BaP$_{TEQ}$ in 21 % of the soil samples collected a year after the major flooding were higher than the Dutch target value of 33 µg kg^{-1} (Netherlands Ministry of Housing and Environment, 1994). Only the BaP$_{TEQ}$ obtained at site AB5 (0-15 cm) was above the Method B clean-up level of 137 µg kg^{-1} (Washington State Department of Ecology, 2007).

Table 4.56: BaP$_{TEQ}$ and BaP$_{MEQ}$ concentrations (µg kg^{-1}) for floodplain soils a year after major flooding

	DEPTH (cm)	BaA	Chry	BbF	BkF	BaP	IndP	DahA	BaPTEQ	BaA	Chry	BbF	BkF	BaP	IndP	DahA	BaPMEQ
AS1	0-15	0.47	0.01	ND	5.02	ND	ND	ND	5.50	0.39	0.20	ND	55.24	ND	ND	ND	55.83
	15-30	ND	ND	19.40	0.30	12.40	ND	ND	32.10	ND	ND	48.50	3.30	12.40	ND	ND	64.20
	30-45	3.71	0.01	0.72	0.04	ND	ND	ND	4.48	3.04	0.17	1.80	0.44	ND	ND	ND	5.45
AS2	0-15	1.57	ND	ND	ND	ND	ND	ND	1.57	1.29	ND	ND	ND	ND	ND	ND	1.29
	15-30	0.41	0.04	ND	0.66	ND	ND	ND	1.11	0.34	0.75	ND	7.26	ND	ND	ND	8.35
	30-45	0.39	ND	ND	ND	ND	ND	ND	0.39	0.32	ND	ND	ND	ND	ND	ND	0.32
AS3	0-15	9.91	ND	0.04	0.40	ND	ND	ND	10.35	8.13	ND	0.10	4.40	ND	ND	ND	12.63
	15-30	ND	ND	4.40	0.11	ND	ND	ND	4.51	ND	ND	11.00	1.22	ND	ND	ND	12.22
	30-45	0.53	0.00	ND	0.83	8.40	ND	ND	9.76	0.43	0.01	ND	9.14	8.40	ND	ND	17.99
AS4	0-15	ND	0.00	ND	0.90	33.10	ND	81.00	115.00	ND	0.01	ND	9.90	33.10	ND	23.49	66.50
	15-30	5.11	ND	4.40	0.01	ND	ND	ND	9.52	4.19	ND	11.00	0.10	ND	ND	ND	15.29
	30-45	ND	ND	ND	ND	ND	ND	ND	0.00	ND	ND	ND	ND	ND	ND	ND	0.00
AS5	0-15	ND	0.09	ND	20.11	ND	ND	ND	20.20	ND	1.53	ND	221.24	ND	ND	ND	222.77
	15-30	ND	ND	ND	ND	ND	ND	ND	0.00	ND	ND	ND	ND	ND	ND	ND	0.00
	30-45	35.99	0.00	ND	ND	ND	ND	ND	35.99	29.51	0.04	ND	ND	ND	ND	ND	29.55
OK1	0-15	8.22	ND	ND	ND	ND	ND	ND	8.22	6.74	ND	ND	ND	ND	ND	ND	6.74
	15-30	ND	ND	99.00	ND	ND	ND	ND	99.00	ND	ND	247.50	ND	ND	ND	ND	247.50
	30-45	ND	0.06	ND	2.00	ND	ND	ND	2.06	ND	1.08	ND	22.01	ND	ND	ND	23.09
OK2	0-15	ND	ND	ND	0.35	ND	ND	ND	0.35	ND	ND	ND	3.86	ND	ND	ND	3.86
	15-30	7.21	0.08	39.11	ND	8.20	ND	ND	54.60	5.91	1.38	97.78	ND	8.20	ND	ND	113.26
	30-45	2.73	ND	ND	0.82	ND	ND	7.90	11.45	2.24	ND	ND	9.02	ND	ND	2.29	13.55
OK3	0-15	ND	ND	ND	ND	58.00	ND	ND	58.00	ND	ND	ND	ND	58.00	ND	ND	58.00
	15-30	ND	ND	ND	ND	93.00	ND	42.00	135.00	ND	ND	ND	ND	93.00	ND	12.18	105.18
	30-45	ND	ND	ND	0.99	ND	ND	ND	0.99	ND	ND	ND	10.91	ND	ND	ND	10.91
AB1	0-15	23.17	0.05	0.50	0.01	ND	ND	ND	23.73	19.00	0.80	1.25	0.15	ND	ND	ND	21.20
	15-30	ND	0.08	7.62	ND	ND	ND	ND	7.70	ND	1.41	19.05	ND	ND	ND	ND	20.46
	30-45	0.67	ND	ND	ND	ND	ND	ND	0.67	0.55	ND	ND	ND	ND	ND	ND	0.55
AB2	0-15	0.43	0.02	ND	0.59	ND	ND	ND	1.04	0.35	0.30	ND	6.50	ND	ND	ND	7.15
	15-30	0.63	ND	ND	ND	ND	ND	ND	0.63	0.52	ND	ND	ND	ND	ND	ND	0.52
	30-45	0.58	ND	ND	0.06	ND	ND	ND	0.64	0.48	ND	ND	0.67	ND	ND	ND	1.15
AB3	0-15	8.82	ND	0.10	0.05	ND	ND	6.00	14.97	7.23	ND	0.25	0.58	ND	ND	1.74	9.81
	15-30	0.08	ND	ND	ND	ND	ND	ND	0.08	0.07	ND	ND	ND	ND	ND	ND	0.07
	30-45	2.00	0.00	ND	ND	ND	ND	ND	2.00	1.64	0.07	ND	ND	ND	ND	ND	1.71
AB4	0-15	3.99	0.03	ND	0.06	ND	ND	ND	4.08	3.27	0.49	ND	0.68	ND	ND	ND	4.45
	15-30	0.53	ND	3.91	ND	ND	ND	ND	4.44	0.43	ND	9.78	ND	ND	ND	ND	10.21
	30-45	ND	ND	ND	0.04	8.10	ND	ND	8.14	ND	ND	ND	0.41	8.10	ND	ND	8.51
AB5	0-15	ND	0.06	ND	0.04	582.10	ND	ND	582.20	ND	1.05	ND	0.44	582.10	ND	ND	583.59
	15-30	7.73	ND	0.80	ND	37.00	ND	ND	45.53	6.34	ND	2.00	ND	37.00	ND	ND	45.34
	30-45	ND	0.00	0.09	ND	ND	ND	ND	0.09	ND	0.04	0.23	ND	ND	ND	ND	0.26

4.34   Incremental Lifetime Cancer Risk (ILCR) a year after the major flooding

The computed ILCR values for adults and children a year after the major flooding are displayed in Tables 4.58. The ILCR levels of the soils a year after the major flooding via soil ingestion, inhalation and dermal contacts ranged from 7.71×10^{-7} to 5.61×10^{-3}, 2.13×10^{-15} to 1.55×10^{-11} and 2.80×10^{-7} to 2.04×10^{-3} respectively for children and 4.81×10^{-7} to 3.50×10^{-3}, 1.06×10^{-14} to 7.76×10^{-11} and 2.49×10^{-7} to 1.81×10^{-3} respectively for adults. The observed inhalation cancer risks for PAHs were low when compared to other exposure routes (ingestion and dermal contact).

The total cancer risk ranged from 1.05×10^{-6} to 7.65×10^{-3} with a mean of 4.13×10^{-4} and 7.31×10^{-7} to 7.31×10^{-3} with a mean of 3.08×10^{-4} for children and adults respectively. The ILCR values obtained indicates that there are 443 and 308 chances in a million populations to develop the risk of cancer for children and adults respectively. This indicate a 15-fold decreased in the average total ILCR values when compared with those obtained three months after the major flooding.

As in three months after the major flooding, cancer risk for children cases via ingestion and dermal contact were found to be higher than those for adults while the cancer risk via inhalation for adults was higher than that of children in this study. The potential risks for children and adults cases a year after the major flooding were greater than the standard potentially acceptable risk value of 10^{-6} for soil.

Table 4.57: Incremental Lifetime Cancer Risk (ILCR) a year after the major flooding

	DEPTH (cm)	CHILD				ADULT			
		ILCRIng	ILCRInh	ILCRDerm	Total Cancer Risk	ILCRIng	ILCRInh	ILCRDerm	Total Cancer Risk
AS1	0-15	5.30E-05	1.35E-12	1.93E-05	7.23E-05	3.31E-05	6.76E-12	1.72E-05	5.03E-05
	15-30	3.09E-04	9.26E-13	1.12E-04	4.22E-04	1.93E-04	4.63E-12	1.00E-04	2.93E-04
	30-45	4.32E-05	1.31E-13	1.57E-05	5.89E-05	2.69E-05	6.56E-13	1.40E-05	4.09E-05
AS2	0-15	1.51E-05	4.18E-14	5.50E-06	2.06E-05	9.44E-06	2.09E-13	4.89E-06	1.43E-05
	15-30	1.07E-05	1.98E-13	3.90E-06	1.46E-05	6.70E-06	9.92E-13	3.47E-06	1.02E-05
	30-45	3.76E-06	1.04E-14	1.37E-06	5.12E-06	2.35E-06	5.19E-14	1.22E-06	3.56E-06
AS3	0-15	9.97E-05	3.71E-13	3.63E-05	1.36E-04	6.23E-05	1.86E-12	3.23E-05	9.45E-05
	15-30	4.35E-05	1.47E-13	1.58E-05	5.93E-05	2.71E-05	7.33E-13	1.41E-05	4.12E-05
	30-45	9.41E-05	4.59E-13	3.42E-05	1.28E-04	5.87E-05	2.30E-12	3.04E-05	8.91E-05
AS4	0-15	1.11E-03	3.47E-12	4.03E-04	1.51E-03	6.92E-04	1.74E-11	3.58E-04	1.05E-03
	15-30	9.17E-05	2.56E-13	3.34E-05	1.25E-04	5.73E-05	1.28E-12	2.97E-05	8.69E-05
	30-45	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
AS5	0-15	1.95E-04	5.38E-12	7.08E-05	2.65E-04	1.22E-04	2.69E-11	6.30E-05	1.84E-04
	15-30	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	30-45	3.47E-04	9.59E-13	1.26E-04	4.73E-04	2.16E-04	4.79E-12	1.12E-04	3.29E-04
OK1	0-15	7.92E-05	2.19E-13	2.88E-05	1.08E-04	4.94E-05	1.09E-12	2.56E-05	7.51E-05
	15-30	9.54E-04	2.64E-12	3.47E-04	1.30E-03	5.96E-04	1.32E-11	3.09E-04	9.04E-04
	30-45	1.99E-05	5.50E-13	7.23E-06	2.71E-05	1.24E-05	2.75E-12	6.43E-06	1.89E-05
OK2	0-15	3.38E-06	9.34E-14	1.23E-06	4.61E-06	2.11E-06	4.67E-13	1.09E-06	3.21E-06
	15-30	5.26E-04	1.47E-12	1.91E-04	7.17E-04	3.28E-04	7.36E-12	1.70E-04	4.99E-04
	30-45	1.10E-04	5.20E-13	4.01E-05	1.50E-04	6.89E-05	2.60E-12	3.57E-05	1.05E-04
OK3	0-15	5.59E-04	1.54E-12	2.03E-04	7.62E-04	3.49E-04	7.72E-12	1.81E-04	5.30E-04
	15-30	1.30E-03	3.70E-12	4.73E-04	1.77E-03	8.12E-04	1.85E-11	4.21E-04	1.23E-03
	30-45	9.56E-06	2.64E-13	3.48E-06	1.30E-05	5.97E-06	1.32E-12	3.09E-06	9.06E-06
AB1	0-15	2.29E-04	6.46E-13	8.32E-05	3.12E-04	1.43E-04	3.23E-12	7.40E-05	2.17E-04
	15-30	7.42E-05	2.25E-13	2.70E-05	1.01E-04	4.63E-05	1.12E-12	2.40E-05	7.03E-05
	30-45	6.46E-06	1.78E-14	2.35E-06	8.80E-06	4.03E-06	8.92E-14	2.09E-06	6.12E-06
AB2	0-15	1.00E-05	1.73E-13	3.64E-06	1.36E-05	6.25E-06	8.67E-13	3.24E-06	9.48E-06
	15-30	6.07E-06	1.68E-14	2.21E-06	8.28E-06	3.79E-06	8.39E-14	1.96E-06	5.75E-06
	30-45	6.18E-06	3.17E-14	2.25E-06	8.42E-06	3.86E-06	1.58E-13	2.00E-06	5.85E-06
AB3	0-15	1.44E-04	4.26E-13	5.25E-05	1.97E-04	9.01E-05	2.13E-12	4.67E-05	1.37E-04
	15-30	7.71E-07	2.13E-15	2.80E-07	1.05E-06	4.81E-07	1.06E-14	2.49E-07	7.31E-07
	30-45	1.93E-05	5.44E-14	7.02E-06	2.63E-05	1.21E-05	2.72E-13	6.25E-06	1.83E-05
AB4	0-15	3.93E-05	1.30E-13	1.43E-05	5.36E-05	2.45E-05	6.52E-13	1.27E-05	3.73E-05
	15-30	4.28E-05	1.18E-13	1.56E-05	5.83E-05	2.67E-05	5.91E-13	1.38E-05	4.05E-05
	30-45	7.84E-05	2.25E-13	2.85E-05	1.07E-04	4.89E-05	1.13E-12	2.54E-05	7.43E-05
AB5	0-15	5.61E-03	1.55E-11	2.04E-03	7.65E-03	3.50E-03	7.76E-11	1.81E-03	5.32E-03
	15-30	4.39E-04	1.21E-12	1.60E-04	5.98E-04	2.74E-04	6.06E-12	1.42E-04	4.16E-04
	30-45	8.87E-07	2.95E-15	3.23E-07	1.21E-06	5.54E-07	1.48E-14	2.87E-07	8.41E-07
	HIGHEST	5.61E-03	1.55E-11	2.04E-03	7.65E-03	3.50E-03	7.76E-11	1.81E-03	5.32E-03
	LOWEST	7.71E-07	2.13E-15	2.80E-07	1.05E-06	4.81E-07	1.06E-14	2.49E-07	7.31E-07
	MEAN	3.25E-04	1.12E-12	1.18E-04	4.43E-04	2.03E-04	5.58E-12	1.05E-04	3.08E-04

4.35 PAH Interrelationships a year after the major flooding

The results of PAH interrelationship a year after the major flooding are shown in Table 4.58. A year after major flooding event, significant positive correlations were also observed between individual PAHs at the 0.01 level. Benzo(k)Fluoranthene/Flt (0.94), BghiP/Nap (0.99) and Phen/Nap (1.00) have the highest PAH interrelationships at the 0-15 cm, 15-30 cm and 30-45 cm depth respectively while strong positive correlation was observed between the following pairs; BbF/BaA (0.89), BghiP/Ace (0.81) at 0-15 cm depth; Phen/Nap (0.99), BaA/Pyr (0.76), DahA/IndP (0.92), BghiP/Phen (0.98) at 15-30 cm depth; Ace/Acy (0.99), BaA/Ant (0.99), Chry/Flu (0.81), BkF/Flu (0.78) and BkF/Chry (0.76).

Also, at 0.05 levels, a year after the major flooding, significant positive correlations were also observed between individual PAHs with BkF/Chry, BbF/Flt and BbF/Pyr recording the highest correlation coefficients of 0.68, 0.69 and 0.60 at 0-15 cm, 15-30 cm and 30-45 cm depths respectively. Other pairs that also showed strong positive correlation at the 0-15 cm depth were Chry/Flt (0.69), BbF/Ant (0.65), DahA/Pyr (0.62). At the 15-30 cm depth, Flt/Acy (0.65) was positively correlated while at 30-45 cm depth, Flt/Nap (0.52), Flt/Phen (0.52), Flt/Ant (0.57) and BaA/Flt (0.57) were positively correlated.

Table 4.58: Correlation analysis of PAHs a year after the major flooding

	NaP	Acy	Ace	Flu	Phen	Ant	Flt	Pyr	BaA	Chry	BbF	BkF	BaP	IndP	DahA	BghiP
0-15 cm																
NaP	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acy		1.00	-0.11	-0.14	-0.14	-0.08	-0.16	0.07	-0.01	-0.29	-0.15	-0.16	-0.14	0.00	-0.13	-0.13
Ace			1.00	-0.15	-0.22	-0.31	0.24	-0.25	0.03	0.07	-0.17	0.24	0.03	0.00	-0.21	0.81
Flu				1.00	-0.03	-0.15	-0.12	-0.20	0.21	-0.22	0.10	-0.12	-0.11	0.00	-0.02	-0.03
Phen					1.00	0.63	-0.07	-0.16	-0.21	-0.21	-0.12	-0.12	0.04	0.00	-0.11	-0.12
Ant						1.00	-0.13	-0.21	0.48	0.04	0.65	-0.18	-0.08	0.00	-0.14	-0.14
Flt							1.00	-0.22	-0.25	0.69	-0.14	0.94	-0.13	0.00	-0.12	-0.12
Pyr								1.00	-0.17	-0.31	-0.16	-0.01	-0.16	0.00	0.62	-0.14
BaA									1.00	0.04	0.89	-0.25	-0.22	0.00	-0.18	0.23
Chry										1.00	0.22	0.68	0.40	0.00	-0.22	-0.22
BbF											1.00	-0.14	-0.12	0.00	-0.10	-0.03
BkF												1.00	-0.13	0.00	-0.07	-0.10
BaP													1.00	0.00	-0.04	-0.10
IndP														1.00	0.00	0.00
DahA															1.00	-0.02
BghiP																1.00
15-30 cm																
NaP	1.00	-0.09	-0.21	0.36	0.99	-0.12	-0.13	-0.25	-0.17	-0.15	-0.15	-0.13	-0.13	0.00	-0.08	0.99
Acy		1.00	-0.15	-0.25	-0.12	-0.13	0.65	-0.25	-0.19	-0.17	-0.01	0.03	-0.14	0.00	-0.09	-0.09
Ace			1.00	0.30	-0.25	-0.29	0.40	-0.31	-0.35	-0.17	0.48	0.18	-0.33	0.00	-0.21	-0.22
Flu				1.00	0.35	0.12	-0.24	-0.33	-0.43	-0.28	-0.20	0.20	-0.27	0.00	-0.19	0.44
Phen					1.00	-0.13	-0.16	-0.15	-0.06	-0.09	-0.13	-0.16	-0.12	0.00	-0.11	0.98
Ant						1.00	-0.18	0.35	-0.12	-0.09	0.07	0.28	0.23	0.00	0.16	-0.06
Flt							1.00	-0.12	-0.24	-0.22	0.69	-0.09	-0.20	0.00	-0.13	-0.15
Pyr								1.00	0.76	0.43	0.35	-0.11	0.02	0.00	-0.25	-0.25
BaA									1.00	0.23	0.01	-0.22	0.10	0.00	-0.17	-0.21
Chry										1.00	0.09	0.16	-0.17	0.00	-0.15	-0.18
BbF											1.00	-0.13	-0.17	0.00	-0.15	-0.17
BkF												1.00	-0.14	0.00	-0.13	-0.12
BaP													1.00	0.00	0.92	-0.15
IndP														1.00	0.00	0.00
DahA															1.00	-0.10
BghiP																1.00
30-45 cm																
NaP	1.00	-0.08	0.02	0.17	1.00	-0.09	0.52	-0.16	-0.10	-0.11	-0.09	-0.18	-0.12	0.00	-0.08	-0.09
Acy		1.00	0.99	0.33	-0.08	-0.09	-0.18	-0.16	-0.11	-0.11	-0.09	0.30	-0.12	0.00	-0.08	-0.09
Ace			1.00	0.34	0.02	-0.11	-0.15	-0.17	-0.13	-0.14	-0.12	0.28	-0.15	0.00	-0.07	-0.11
Flu				1.00	0.17	-0.18	-0.15	-0.28	-0.22	0.81	-0.19	0.78	-0.25	0.00	-0.17	-0.18
Phen					1.00	-0.09	0.52	-0.16	-0.10	-0.11	-0.09	-0.18	-0.12	0.00	-0.08	-0.09
Ant						1.00	-0.13	0.99	-0.07	-0.10	-0.18	-0.13	0.00	-0.09	-0.09	
Flt							1.00	-0.12	0.57	-0.18	-0.12	-0.15	0.21	0.00	-0.18	-0.20
Pyr								1.00	-0.07	-0.01	0.60	-0.30	-0.23	0.00	-0.16	-0.08
BaA									1.00	-0.09	-0.01	-0.20	-0.15	0.00	-0.03	-0.12
Chry										1.00	0.05	0.76	-0.15	0.00	-0.11	-0.08
BbF											1.00	-0.18	-0.14	0.00	-0.09	0.04
BkF												1.00	0.05	0.00	0.22	-0.19
BaP													1.00	0.00	-0.12	-0.08
IndP														1.00	0.00	0.00
DahA															1.00	-0.09
BghiP																1.00

*Pearson Correlation is significant at the 0.05 level (1 tailed)

** Pearson Correlation is significant at the 0.01 level (1 tailed)

Naphthalene (Nap), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phen), Anthracene (Ant), Fluoranthene (Flt), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chry), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(1,2,3-cd)perylene (IndP), Dibenzo(a,h)anthracene (DahA) and Benzo(ghi)perylene (BghiP).

4.36   Source estimates from diagnostic ratios of PAHs a year after the major flooding

In this study, the Flt/(Flt + Pyr), Ant/(Ant + Phen), BaA/(Chry + BaA), IndP/(IndP +

BghiP), LMW/HMW ratios a year after the major flooding ranged from 0.04 to 0.98, 0.06 to

0.28, 0.08 to 0.99 and 0.02 to 12.67 (Table 4.59) which indicate that the sources of PAHs in

these floodplains were due to fossil fuel, combustion of wood and traffic emissions

Table 4.59: Diagnostic source ratio of PAHs in the floodplain soils

Depth	Phen/Ant	Fluo/ (Fluo+Pyr)	Ant/ (Ant+Phe)	BaP/BghiP	BaA/ (BaA+Chry)	IP/ (IP+BghiP)	Fluo/Pyr	LMW/ HMW
0-15 cm								
AS1	0.00	0.00	0.00	0.00	0.28	0.00	0.00	0.06
AS2	2.62	0.00	0.28	0.00	0.00	0.00	0.00	1.32
AS3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.27
AS4	0.00	0.00	0.00	1.50	0.00	0.00	0.00	0.00
AS5	0.00	0.98	0.00	0.00	0.00	0.00	64.9	0.02
OK1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08
OK2	0.00	0.31	0.00	0.00	0.00	0.00	0.44	0.42
OK3	0.00	0.58	0.06	96.7	0.00	0.00	1.39	8.18
AB1	0.00	0.04	0.00	0.00	0.83	0.00	0.04	0.15
AB2	0.00	0.00	0.00	0.00	0.20	0.00	0.00	0.16
AB3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6.79
AB4	0.00	0.00	0.00	0.00	0.58	0.00	0.00	0.47
AB5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10
15-30 cm								
AS1	0.00	0.00	0.00	0.25	0.00	0.00	0.00	0.68
AS2	0.00	0.00	0.00	0.00	0.08	0.00	0.00	0.34
AS3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.17
AS4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AS5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.20
OK1	0.00	0.95	0.00	0.00	0.00	0.00	18.5	0.02
OK2	0.00	0.12	0.27	0.00	0.47	0.00	0.13	0.19
OK3	0.00	0.00	0.00	155	0.00	0.00	0.00	0.40
AB1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AB2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.57
AB3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.20
AB4	0.00	0.82	0.00	0.00	0.00	0.00	4.61	0.55
AB5	0.00	0.13	0.00	5.61	0.00	0.00	0.15	0.26
30-45 cm								
AS1	0.00	0.04	0.00	0.00	0.79	0.00	0.04	0.00
AS2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.21
AS3	0.00	0.96	0.00	0.00	0.88	0.00	26.0	0.00
AS4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.05
AS5	0.00	0.98	0.00	0.00	0.99	0.00	44.3	2.75
OK1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.17
OK2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.18
OK3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	12.7
AB1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.91
AB2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.50
AB3	0.00	0.08	0.00	0.00	0.83	0.00	0.09	0.29
AB4	0.00	0.00	0.00	20.3	0.00	0.00	0.00	0.00
AB5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

4.37   Source estimates from principal component analysis (PCA) a year after the major flooding

The results of PCA for PAHs in the soil profiles a year after the major flooding are presented in Tables 4.60 and Figure 28. Also, at the 0-15 cm depth a year after the major flooding, three component factors were also identified which accounts for 55.09 % of the variability in the data set. Factor 1 explains 21.45 % of the total variance and was characterised by high loadings of Flt, Chry and BkF. Flt is a product of coal combustion (Larsen and baker, 2003) and Chry is a product of diesel and natural gas combustion (Khalili et al., 1995). BkF is a tracer for coal and gasoline combustion (Simcik et al., 1999; Li et al., 2003; Wan et al., 2006; Dong and Lee, 2009). Consequently, Factor 1 indicated that coal, diesel and natural gas combustion are the sources of PAHs. Factor 2 explains 18.71 % of the total variance and was characterised by high loading of BaA and BbF and moderate loading of Ant. BaA is a marker for diesel combustion (Khalili et al., 1995), BbF is associated with fossil fuel combustion (Kavouras et al., 2001; Yang et al., 2012) while Ant is a product of wood and coke combustion (Jenkins et al., 1996; Yunker et al., 2002). Thus, Factor 2 indicated that fossil fuels and diesel combustion were the sources of PAHs. Factor 3 which explains 14.93 % of the total variance is characterised by high loadings of Ace and BghiP. Acenapthene is a product of wood combustion (Jenkins et al., 1996) while BghiP is from traffic emissions (Simcik et al., 1999). Thus, from factor 3, the source of PAHs is attributed to wood combustion and traffic emissions.

Table 4.60: PCA Factor loadings after Varimax with Kaiser Normalization Rotation for PAHs in floodplain soils a year after the major flooding

PAHs	0-15 cm depth			15-30 cm depth			30-45 cm depth				
	Component			Component			Component				
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Nap				**.947**					**.989**		
Acy					-.376					**.980**	
Ace			**.907**		-.503	.542				**.987**	
Flu				.562	-.330		**.925**				
Phen			-.487	**.941**					**.989**		
Ant		**.652**	-.571			-.330		**.984**			
Flt	**.910**			-.339	-.452	.553		.656	.574		
Pyr		-.595			**.863**						**.813**
BaA	-.374	**.812**			**.822**			**.978**			
Chry	**.849**	.337			.577		**.944**				
BbF		**.835**		-.341		.557					**.767**
BkF	**.884**						**.861**				
BaP						-**.868**					-.553
IndP						-**.832**					-.316
DahA		-.496									
BghiP			.824	**.964**							
Variance %	**21.45**	**18.71**	**14.93**	**24.25**	**18.63**	**15.27**	**22.07**	**17.59**	**14.29**	**12.70**	**10.92**
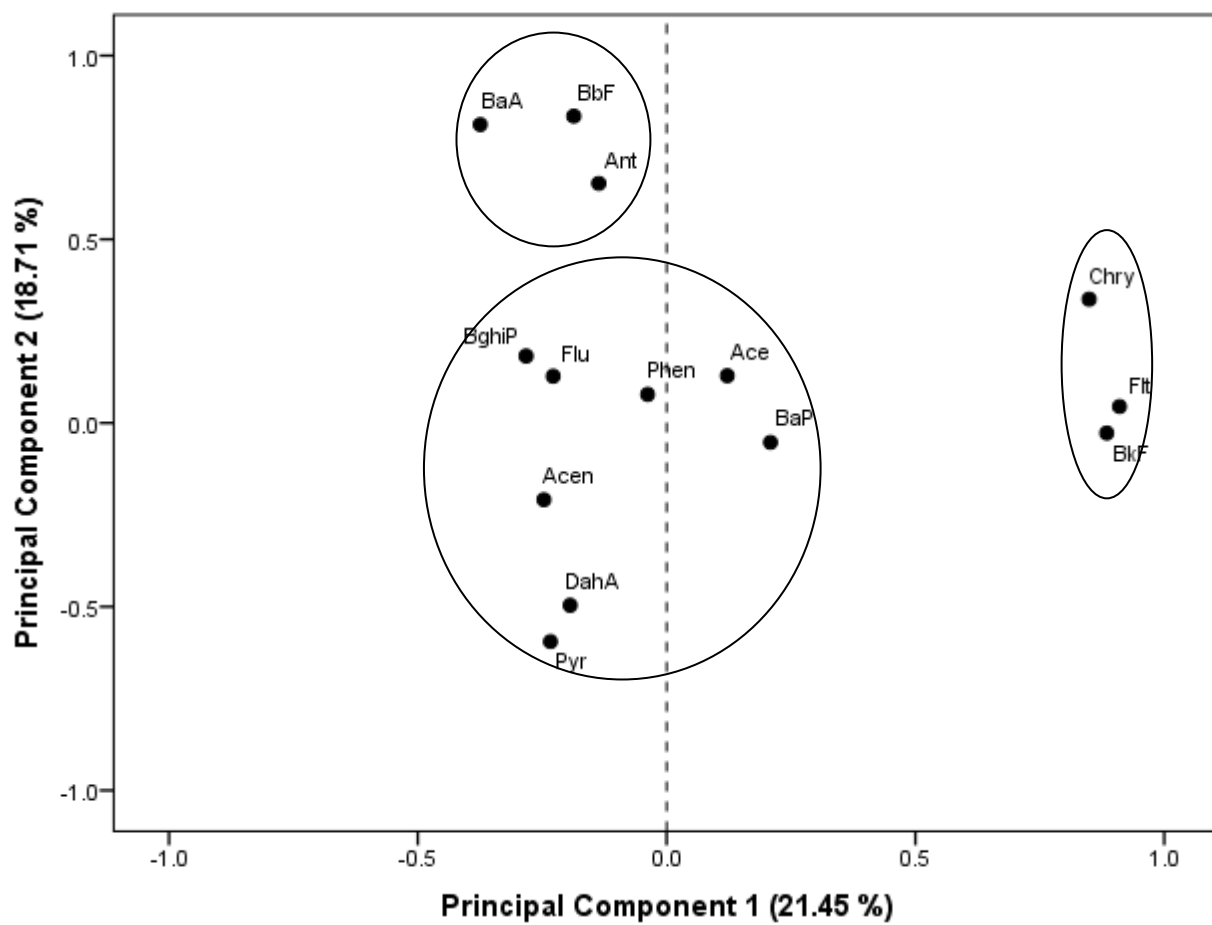
(28a)
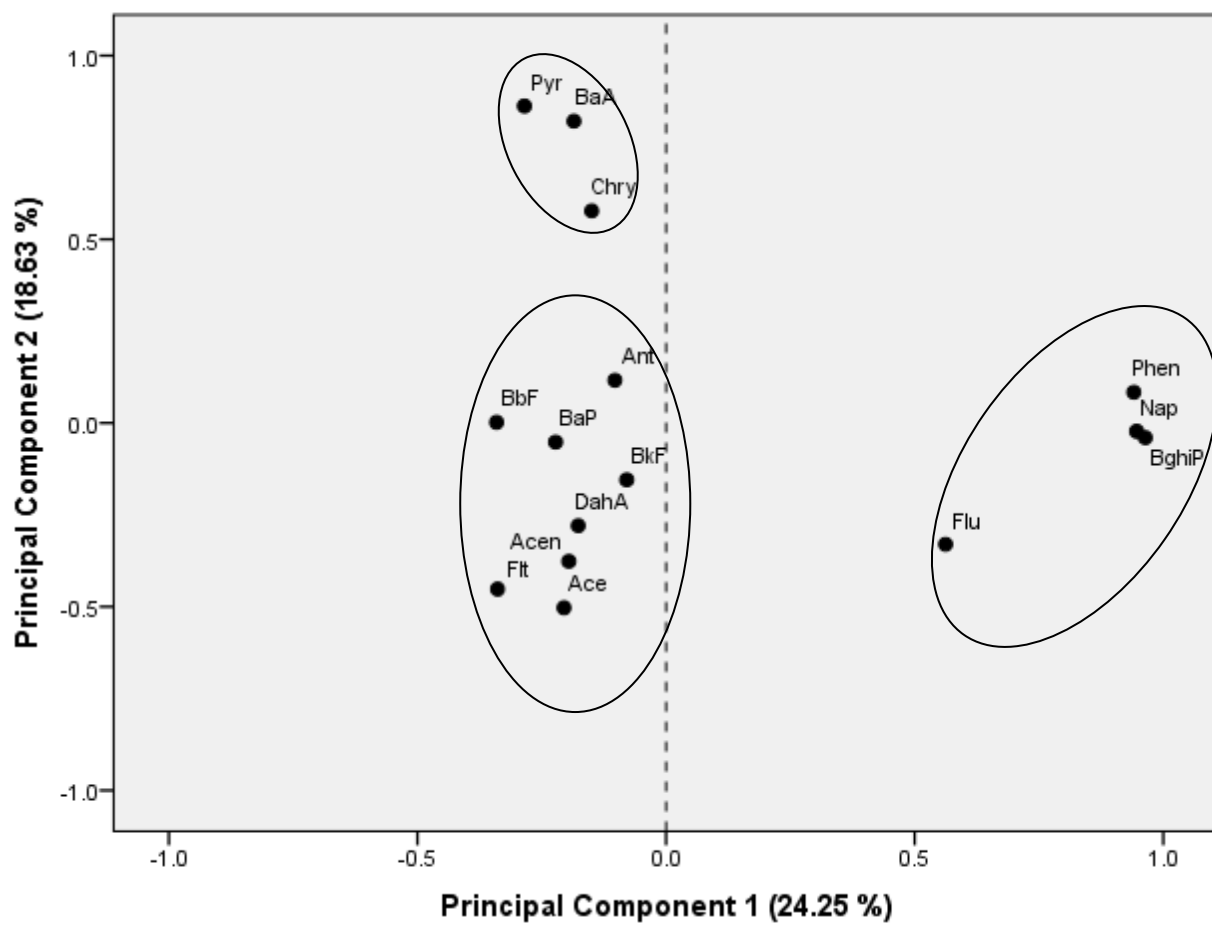
(28b)
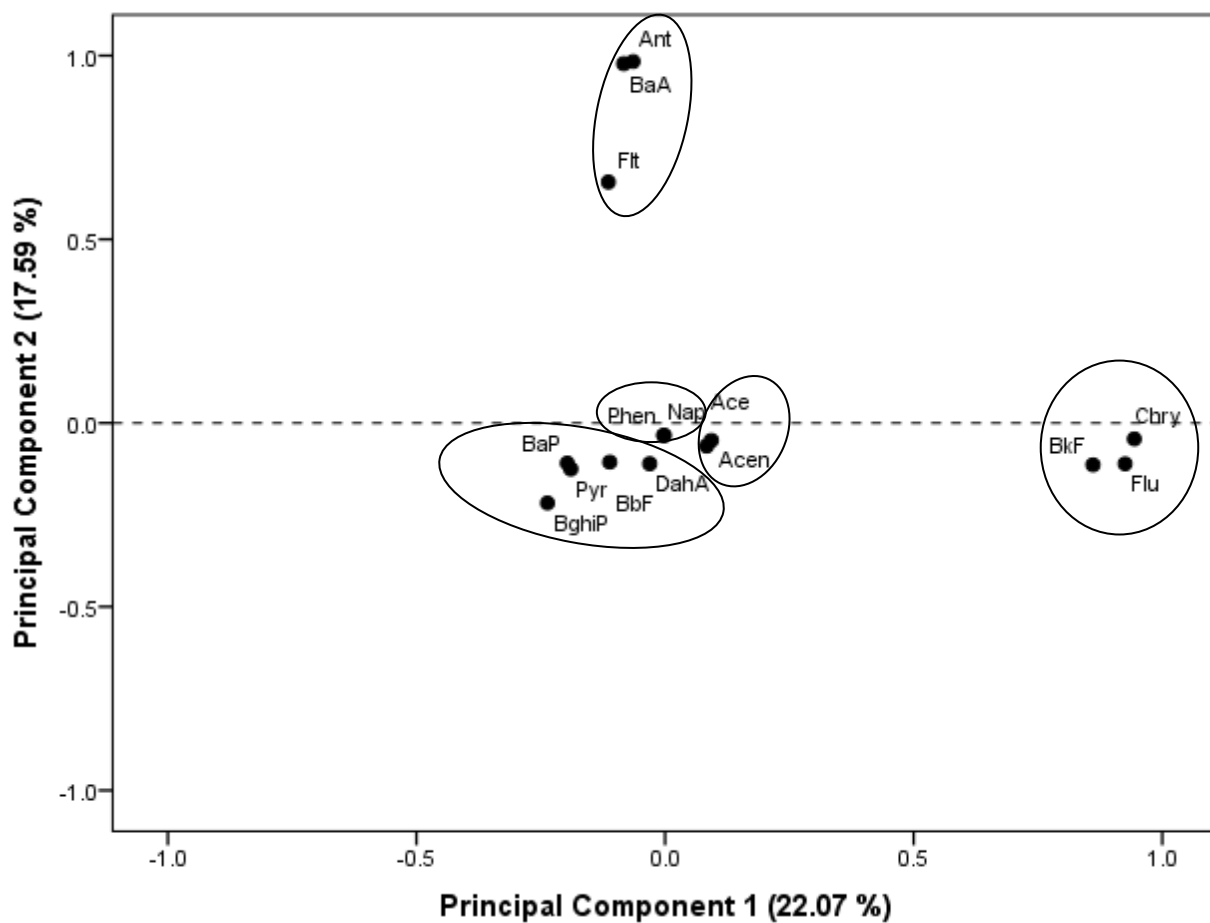
(28c)

Figure 28: The loading plot of PCA of PAHs of the floodplain soils a year after the major flooding. (27a) 0-15 cm depth (27b) 15-30 cm depth and (27c) 30-45 cm depth

Also, at 15-30 cm depth a year after the major flooding, three component factors were also identified accounting for 58.15 % of the variability in the data at this depth. Factor 1 explains 24.25 % of the total variance. This factor was characterised by high loadings of Nap, Phen, BghiP and moderate loading of Flu. Nap suggest incomplete combustion of wood-related sources (Fang et al., 2004; Dong and Lee, 2009). Phen is a product of wood combustion (Jenkins et al., 1996), BghiP is from traffic emiss ions and Flu is a significant product of low temperature pyrogenic processes such as wood combustion (Jenkins et al., 1996; Yang et al., 2012). Thus, Factor 1 indicated that wood combustion and traffic emissions are the sources of PAHs. Factor 2 contributing 18.63 % of the total variance was characterised by high loadings of Pyr and BaA and moderate loading of Ace and Chry. Pyr and BaA are from coal diesel combustion respectively (Larsen and Baker, 2003; Khalili et al., 1995) while Chry is a product of diesel and natural gas combustion (Khalili et al., 1995). Thus, from Factor 2, the source of PAHs is attributed to coal, diesel and natural gas combustion. Factor 3 explains 15.27 % of the total variance and was characterised by moderate loadings of Ace, Flt, and BbF. Ace is associated with wood combustion (Jenkins et al., 1996), Flt is a product of coal combustion (Larsen and Baker, 2003) and BbF is associated with fossil fuels combustion (Kavouras et al., 2001; Yang et al., 2012). Therefore, Factor 3 indicated that fossil fuels combustion was the major source of PAHs.

However, at 30-45 cm depth a year after the major flooding event, five component factors were identified which accounts for 77.57 % of the variability in the data set at this depth. Factor 1 explains 22.07 % of the total variance and was characterised by high loadings of Flu, Chry and BkF. Fluorene is a product of low temperature pyrogenic processes such as wood combustion (Jenkins et al., 1996; Yang et al., 2012). Chrysene is a product of diesel and natural gas combustion (Khalili et al., 1995) and BkF is a tracer for

coal and gasoline combustion (Simcik et al., 1999; Li et al., 2003; Wan et al., 2006; Dong and Lee, 2009). Therefore, wood, diesel and natural gas combustion are the source of PAHs from factor 1. Factor 2 contributing 17.59 % of the total variance was characterised by high loadings of Ant and BaA and moderate loading of Flt. Anthracene is a product of wood and coke combustion (Jenkins et al., 1996; Yunker et al., 2002). Benzo(a)Anthracene is a marker for diesel combustion (Khalili et al., 1995) while Flt is a product of coal combustion (Larsen and Baker, 2003). Thus, Factor 2 indicated that fossil fuels and diesel combustion are the sources of PAHs. Factor 3 explains 14.29 % of the total variance. This factor was characterised by high loadings of Nap and Phen and moderate loading of Flt. Napthalene suggest incomplete combustion of wood-related sources (Fang et al., 2004; Dong and Lee, 2009; Yu et al., 2013) while Phen and Flt are products of wood and coal combustion respectively (Jenkins et al., 1996; Larsen and Baker, 2003). The source of PAHs as indicated by Factor 3 therefore is fossil fuel combustion. Factor 4 which explains 12.7 % of the total variance was characterised by high loadings of Acy and Ace. These are products of wood combustion (Jenkins et al., 1996; Yang et al., 2012). Therefore, factor 4 indicates that the source of PAHs is wood combustion. Factor 5 contributing 10.92 % of the total variance was characterised by high loadings of Pyr and BbF. Pyr is from coal combustion (Larsen and Baker, 2003) and BbF is from fossil fuel combustion (Kavouras et al., 2001; Yang et al., 2012). Therefore, Factor 5 indicates that fossil fuels combustion was the major source of PAHs.

4.38   Reasons for the observed changes between the two sampling periods

Generally, there was a decrease in the concentration of metals between the two sampling periods as well as change in the speciation of the metals. These might be as a result of the secondary transfer of metals deep into the soil profiles and farm management practices and activities, leaching to underground waters, and plant uptake. Metals may

have also undergo bioaccumulation, solubility and mobility. Furthermore, these changes observed in the metal distribution in these soil profiles a year after the major flooding could be due to variations in clay minerals, dry and wet deposition biogeochemical activities and landscape characteristics (Ali et al., 2003). Processes such as inorganic and organic complexation, oxidation-reduction reactions, precipitation/dissolution reactions, and adsorption/ desorption reactions may also have contributed.

The lower concentrations of PAHs obtained a year after the major flooding might be attributed to volatilization of PAHs, absorption, leaching, erosion, biological degradation and landfarming (Pierzynski et al., 2000; Harmsen et al., 2007; Wick et al., 2011). Harmsen et al. (2007) reported that through landfarming, rapid degradation of PAHs in dredged sediments occurred within the first year, followed by slow degradation for the next seven years. After 15 years, PAH concentrations were similar to the background levels in the same area.

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATION

5.1   Summary of major findings

1.   The floodplain soils of the lower reaches of River Niger were contaminated with metals such as Cd, Pb, Ni, Zn, Mn, Cr, Fe, Co, Al, Ba and Cu though the concentrations of these metals in the soil profiles were below their respective regulatory control limits except for Cd and Zn in some sites.

2.   The floodplain soils of the lower reaches of River Niger were heavily contaminated with polycyclic aromatic hydrocarbons and the four rings PAH compounds were the dominant PAH compounds in these soil profiles.

3.   The concentrations of metals in the downstream section of the floodplain were higher than those of midstream and upstream sections while the concentrations of PAHs were higher in the upstream section of the floodplain.

4.   The residual and reducible extraction phases were the predominant phases of metals in these soil profiles with high potential mobility of metals in these soil profiles

5.   There was virtually no correlation between the metal and PAHs concentrations and soil physio-chemical characteristics. This suggests that these contaminants migrate in the soil profiles due to leaching, mechanical turbation through farming activities or bioturbation, continuous input of fresh contamination, the presence of different sources and limited effect of physicochemical parameters on metals in the soil.

6.   The non-carcinogenic and carcinogenic health risk associated with metal exposure in these soil profiles was low.

7.   The incremental life cancer risk (ILCR) associated with PAH exposure in these soil profiles were higher than the potentially acceptable target risk value of 10^{-6} set

by the US EPA signifying a high potential human carcinogenic risk in the study area.

8. There is moderate ecological risk of metals in these soil profiles with significant impact from Cd pollution.

9. Based on the PCA analysis and diagnostic source ratios, the major sources of PAHs in these soils were fossil fuels combustion and traffic emission while the major sources of metals in these soils include industrial emissions, use of agrochemicals, and traffic emissions as well as the drilling and production activities of the oil and gas industries.

10. There was a significant decrease in the concentration of metals and PAHs a year after the major flooding event.

5.2 Contributions to knowledge

The contribution to knowledge of this study include;

i. This study revealed the distribution and concentration of metals and polycyclic aromatic hydrocarbons in the floodplain soils of the lower reaches of River Niger as this study is the first of its kind being carried out on the floodplain.

ii. This study revealed the specific chemical forms of metals in the floodplain soils of the lower reaches of River Niger three months after the major flooding of 2012 and a year after the major flooding.

iii. This study has established that the major sources of PAHs in the soils of the lower reaches of River Niger were fossil fuels combustion and traffic emission while that of metals were industrial emissions, use of agrochemicals, and traffic emissions as well as the drilling and production activities of the oil and gas industries.

iv.   This work established the health risk associated with metals and PAHs exposure in the floodplain soils of the lower reaches of River Niger.

5.3   Conclusion

The results of this study revealed for the first time metal contamination and large scale PAH contamination in floodplain soils of the lower reaches of River Niger. The downstream section of the flood plain contained higher concentrations of the studied metals in its profiles than the upstream and midstream sections of the floodplain while the upstream section contained higher concentrations of PAHs in its profiles than the downstream section of the floodplain. The major sources of metals in these soils include industrial emissions, use of agrochemicals, and traffic emissions as well as the drilling and production activities of the oil and gas industries while the major sources of PAHs in these soils were fossil fuels combustion and traffic emission.

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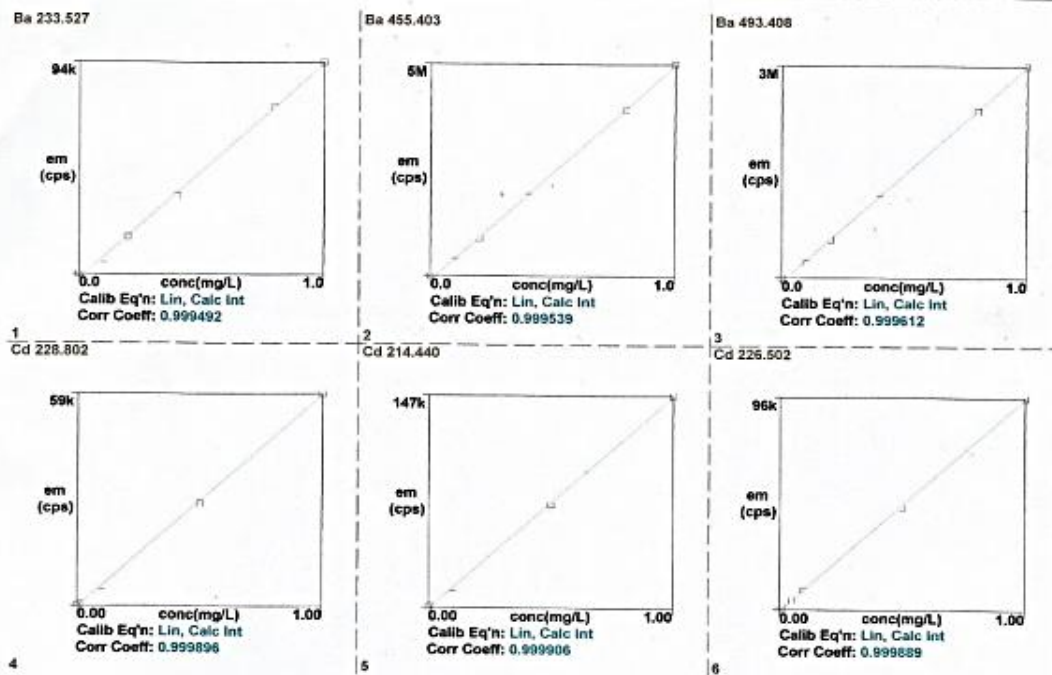
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APPENDIX I
CALIBRATION CURVE OF METALS

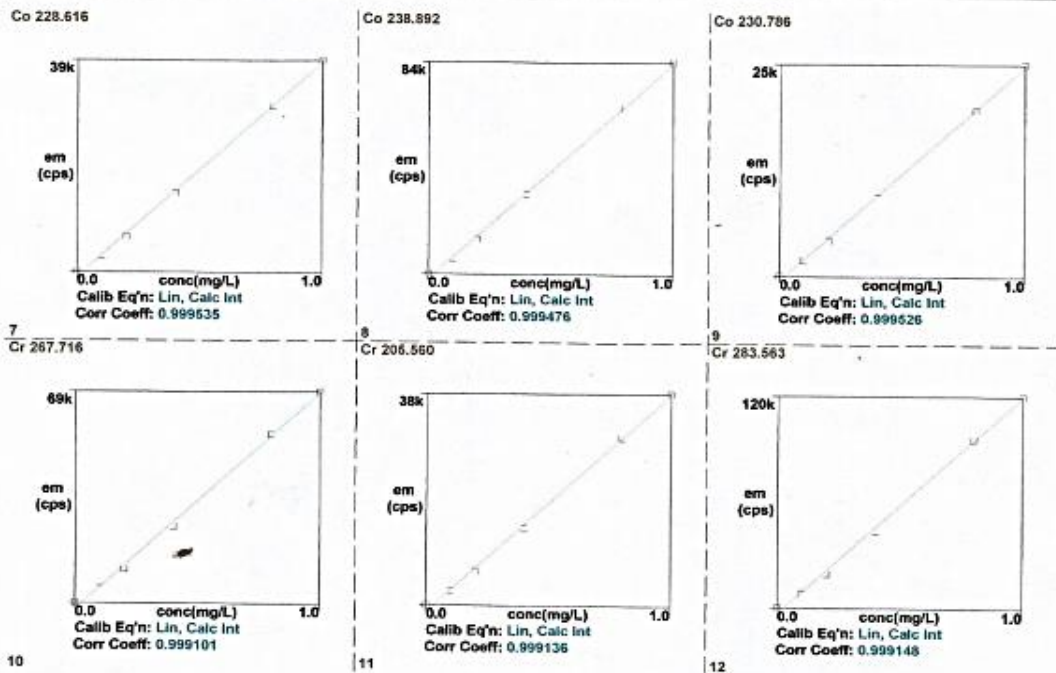Method: MAXWELL BCR2014
Result: Durban soil F3 repeated

Calib

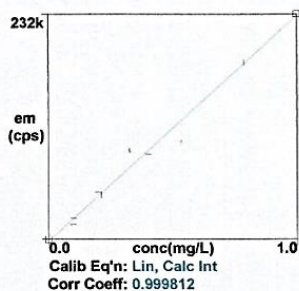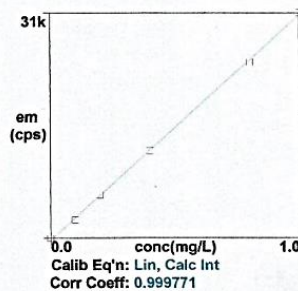Method: MAXWELL BCR2014
Result: Durban soil F3 repeated

Calib

Method: MAXWELL BCR2014
Result: Durban soil F3 repeated

Cu 327.393

113k

em
(cps)

0.0   conc(mg/L)   1.0
Calib Eq'n: Lin, Calc Int
Corr Coeff: 0.999807

13

Cu 324.752

232k

em
(cps)

0.0   conc(mg/L)   1.0
Calib Eq'n: Lin, Calc Int
Corr Coeff: 0.999812

14

Cu 224.700

31k

em
(cps)

0.0   conc(mg/L)   1.0
Calib Eq'n: Lin, Calc Int
Corr Coeff: 0.999771

15

Mn 257.610

97k

em
(cps)

0.0   conc(mg/L)   4.0
Calib Eq'n: Lin, Calc Int
Corr Coeff: 0.999713

16

Mn 259.372

90k

em
(cps)

0.0   conc(mg/L)   4.0
Calib Eq'n: Lin, Calc Int
Corr Coeff: 0.999717

17

Mn 260.568

48k

em
(cps)

0.0   conc(mg/L)   4.0
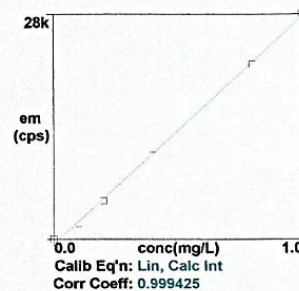**Calib Eq'n:** Lin, Calc Int
Corr Coeff: 0.999708

18

Method: MAXWELL BCR2014
Result: Durban soil F3 repeated

Ni 231.604

41k

em
(cps)

0.0   conc(mg/L)   1.0
Calib Eq'n: Lin, Calc Int
Corr Coeff: 0.999429

19

Ni 221.648

28k

em
(cps)

0.0   conc(mg/L)   1.0
Calib Eq'n: Lin, Calc Int
Corr Coeff: 0.999425

20

Ni 232.003

17k

em
(cps)

0.0   conc(mg/L)   1.0
Calib Eq'n: Lin, Calc Int
Corr Coeff: 0.999251

21

Pb 220.353

33k

em
(cps)

0.0   conc(mg/L)   4.0
Calib Eq'n: Lin, Calc Int
Corr Coeff: 0.999744

22

Pb 217.000

265

em
(cps)

0.0   conc(mg/L)   4.0
Calib Eq'n: Lin, Calc Int
Corr Coeff: 0.999862

23

Pb 261.418

24

CCXC

Method: MAXWELL BCR2014
Result: Durban soil F2 repeated

| Zn 206.200 | Zn 213.857 | Zn 202.548 |

Calib Eq'n: Lin, Calc Int
Corr Coeff: 0.999456

Calib Eq'n: Lin, Calc Int
Corr Coeff: 0.999680

Calib Eq'n: Lin, Calc Int
Corr Coeff: 0.999280
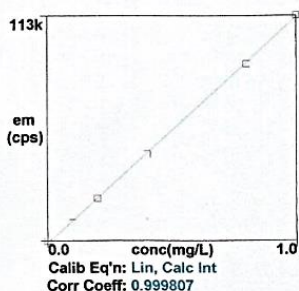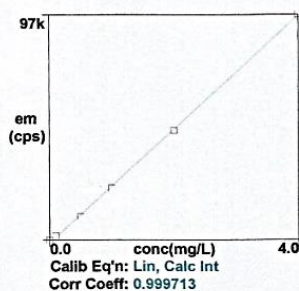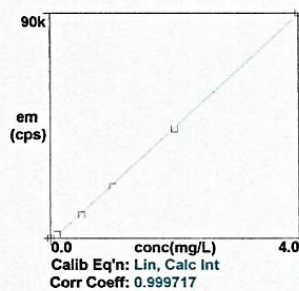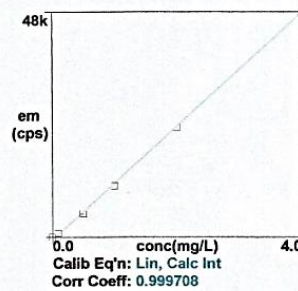
APPENDIX 2
(PAHs CHROMATOGRAMS FEW MONTHS AFTER THE MAJOR FLOODING)

FID1 A, (PAH ON SOIL SAMPLE,AS3 0-15)

FID1 A, (PAH ON SOIL SAMPLE,AS3 15-30)

FID1 A, (PAH ON SOIL SAMPLE,AS3 30-45)

FID1 A, (PAH ON SOIL SAMPLE,AS4 0-15)

FID1 A, (PAH ON SOIL SAMPLE,AS4 15-30)

FID1 A, (PAH ON SOIL SAMPLE,AS4 30-45)

FID1 A, (PAH ON SOIL SAMPLE,AS5 0-15)

FID1 A, (PAH ON SOIL SAMPLE,AS5 15-30)

FID1 A, (PAH ON SOIL SAMPLE,AS5 30-45)

FID1 A, (PAH ON SOIL SAMPLE,CON3 0-15)

FID1 A, (PAH ON SOIL SAMPLE,CON3 15-30)

FID1 A, (PAH ON SOIL SAMPLE,CON3 30-45)

ccxciv

FID1 A, (PAH ON SOIL SAMPLE,AON1 0-15)

FID1 A, (PAH ON SOIL SAMPLE,AON1 15-30)

FID1 A, (PAH ON SOIL SAMPLE,AON1 30-45)

FID1 A, (PAH ON SOIL SAMPLE,BON2 0-15)

FID1 A, (PAH ON SOIL SAMPLE,BON2 15-30)

FID1 A, (PAH ON SOIL SAMPLE,BON2 30-45)

FID1 A, (PAH ON SOIL SAMPLE,AB1 0-15)

FID1 A, (PAH ON SOIL SAMPLE,AB1 15-30)

FID1 A, (PAH ON SOIL SAMPLE,AB1 30-45)

FID1 A, (PAH ON SOIL SAMPLE,AB2 0-15)

FID1 A, (PAH ON SOIL SAMPLE,AB2 15-30)

FID1 A, (PAH ON SOIL SAMPLE,AB2 30-45)

APPENDIX 3
(PAHs CHROMATOGRAMS A YEAR AFTER THE MAJOR FLOODING)

FID1 A, {PAH ON SOIL SAMPLE,AB5 0-15}

FID1 A, {PAH ON SOIL SAMPLE,AB5 15-30}

FID1 A, {PAH ON SOIL SAMPLE,AB5 30-45}

FID1 A, {PAH ON SOIL SAMPLE,AS1 0-15}

FID1 A, {PAH ON SOIL SAMPLE,AS1 15-30}

FID1 A, {PAH ON SOIL SAMPLE,AS1 30-45}

ccci

FID1 A, {PAH ON SOIL SAMPLE,AS2 0-15}

FID1 A, {PAH ON SOIL SAMPLE,AS2 15-30}

FID1 A, {PAH ON SOIL SAMPLE,AS2 30-45}

FID1 A, {PAH ON SOIL SAMPLE,AS3 0-15}

FID1 A, {PAH ON SOIL SAMPLE,AS3 15-30}

FID1 A, {PAH ON SOIL SAMPLE,AS3 30-45}

cccii

FID1 A, {PAH ON SOIL SAMPLE,AS4 0-15}

FID1 A, {PAH ON SOIL SAMPLE,AS4 15-30}

FID1 A, {PAH ON SOIL SAMPLE,AS4 30-45}

FID1 A, {PAH ON SOIL SAMPLE,AS5 0-15}

FID1 A, {PAH ON SOIL SAMPLE,AS5 15-30}

FID1 A, {PAH ON SOIL SAMPLE,AS5 30-45}

ccciii

FID1 A, {PAH ON SOIL SAMPLE,OK1 0-15}

FID1 A, {PAH ON SOIL SAMPLE,OK1 15-30}

FID1 A, {PAH ON SOIL SAMPLE,OK1 30-45}

FID1 A, {PAH ON SOIL SAMPLE,OK2 0-15}

FID1 A, {PAH ON SOIL SAMPLE,OK2 15-30}

FID1 A, {PAH ON SOIL SAMPLE,OK2 30-45}

ccciv

FID1 A, (PAH ON SOIL SAMPLE,OK3 0-15)

FID1 A, (PAH ON SOIL SAMPLE,OK3 15-30)

FID1 A, (PAH ON SOIL SAMPLE,OK3 30-45)

cccv