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Assessment of Soil Contamination of a Cattle Market around River Ogun Basin, Isheri, Nigeria

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Additional information is available at the end of the chapter

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1. Introduction

Continuous increase in environmental pollution caused by the expansion and amplification of domestic, industrial, and agricultural waste generation has resulted in steadily growing number of contaminants release into the environment [1]. The uncontrolled discharge of pollutants into natural sinks such as aquatic ecosystems in developing countries like Nigeria has prompted a need for periodic assessment of the level of pollutants released into the environment. Contamination of water resources and soil with toxic metals and priority organic pollutants represents a major environmental challenge being a source of human exposure to these toxicants with potential deleterious human health effects. Soils in several parts of Nigeria have accumulated considerable amount of toxic elements arising largely from unsustainable consumption and production activities such as illegal mining of solid minerals, uncontrolled land filling of post-consumer hazardous wastes including electronic waste or e-waste [2, 3], uncontrolled industrial emissions, and vehicular emissions; as well as environmentally unsound petroleum exploration, production and exploitation activities, and accidental crude and petroleum products oil spills etc., [3].

Soil is the foundation of terrestrial ecosystems and a non-renewable fundamental agricultural resource, inextricably linked to productivity, land development and environmental quality [4]. Soils may contain many organic and inorganic compounds of natural and anthropogenic origin. The concentrations and toxicity of these compounds present in environmental media range very widely and depend on possible interactions (synergies) among chemicals. The continuous introduction of these contaminants into the environment has resulted in their accumulation. Soil pollution with heavy metals occurs not only near mines and smelters, but also on agricultural land because of the application of sewage sludge as fertiliser and metal-based pesticides [5]. Extensive soil contamination with hazardous pollutants including

inorganic (i.e. Cd, Pb, Cu, Hg, As etc) and organic (i.e. pesticides, dioxins, polyaromatic hydrocarbons etc) pollutants has increasingly been of global concern over the last decades, especially in Asian [6] and other developing countries, where urbanization and industrialization have occurred rapidly and haphazardly.

Heavy metals continue to receive increasing attention due to a better understanding of their fate as well as toxicological relevance in ecosystems and human health [7]. Pollution of soils by heavy metals represents one of the most important ecological problems today [8]. Anthropogenic emission of heavy metals in the environment during the last century has led to increasing accumulation of metals in soils and natural waters in both urban and rural areas. Heavy metals are ecologically harmful because they tend to bio-accumulate over time in soils and plants with ability to have a negative influence on the physiological activities of plants (e.g. photosynthesis, gaseous exchange and nutrient absorption), influencing reductions in plant growth, dry matter accumulation and yield [9]. Heavy metal pollution exerts toxic effects on soil microbial biomass [10] and microbial processes such as soil respiration, nitrogen mineralization, and enzyme activities [11]. Soil contamination by heavy metals has also been shown to inhibit soil microbial activities [12], in turn reducing soil fertility and inhibiting the germination of certain seed plants [13]. Heavy metals contamination may also produce nutrient imbalance in plants with adverse effects on the synthesis and functioning of many biologically active compounds [14]. Subsequent accumulation of metals in the food chain [15] is detrimental to human health.

Heavy metals transport in soil profile is a major environmental concern because even slow transport through the soil may eventually lead to deterioration of groundwater quality. Preferential flow can accelerate the movement of water and solutes through soil profile [16]. Soil pollution can lead to water pollution if toxic chemicals leach into groundwater, or if contaminated runoff reaches streams, lakes, or oceans. The decomposition of organic materials in soil can release sulphur dioxide and other sulphur compounds, causing acid rain which can leach heavy metals from soil. Thus, there is need to reduce the introduction of heavy metals into the environment from anthropogenic sources since metals are persistent, toxic and non-biodegradable [3]. In addition, chemicals that are not water-soluble contaminate plants that grow on polluted soils, and they also tend to accumulate increasingly toward the top of the food chain. Both organic and inorganic contaminants are important in soil management. The most prominent chemical groups of organic contaminants are petroleum hydrocarbons, Polycyclic Aromatic Hydrocarbons (PAHs), Polychlorinated Biphenyls (PCBs), chlorinated aromatic compounds, detergents, and pesticides. Inorganic species include nitrates, phosphates, and heavy metals such as cadmium, chromium and lead.

Organochlorine pesticides not only accumulate in animal tissues; many are extremely stable and persist in soil and plants, and if soluble enough can reach groundwater or surface waters. They can therefore enter the food chain not only via their target and non-target organisms, but also imbibed water and via plants eaten by herbivores, including cattle [17]. Their persistence in soils depends both on the nature of the soil and their own physico-chemical properties. Light soils facilitate the water-borne transport of soluble pesticides [18]. Soils with high clay and organic matter contents tend to retain both the more soluble pesticides (because of their high

water storage capacity) and the more hydrophobic pesticides (because of their high specific surface area and other sorption-favouring properties) [19,20]. Because of the dangers they pose to non-target organisms, DDT and a number of other organochlorine pesticides were banned in most countries in the 1970s and 1980s, at least for agricultural use. However, because of their resistance to degradation processes and immobility, many are still found in high concentrations in soils to which they were formerly applied, where they constitute a reservoir and secondary source of ongoing contamination of waters, wildlife, and crops [21,22,23].

1.1. Health and environmental effects of heavy metals

Metals are particularly toxic to the sensitive, rapidly developing systems of fetuses, infants, and young children, otherwise known as "vulnerable group". Some metals, such as lead and mercury, easily cross the placenta of mothers and damage the brain of fetuses. Childhood exposure to some metals such as lead and mercury can result in learning difficulties, memory impairment, damage to the nervous system, and behavioural problems such as aggressiveness and hyperactivity. At higher doses, heavy metals can cause irreversible brain damage. Children may receive higher doses of metals from food than adults, since they consume more food for their body weight than adults [24].

Exposure to manganese (Mn) is usually via inhalation, which results in the main cause of its toxicity. Mn toxicity has been reported through occupational (e.g. welder, miner) and dietary overexposure and is evidenced primarily in the central nervous system, although lung, cardiac, liver, reproductive and fetal toxicity have been noted [24]. Mn neurotoxicity results from an accumulation of the metal in brain tissue [25]. Brain permeability to manganese is higher than that to iron and zinc. Manganese is easily concentrated in the brain, especially in the basal ganglia, and can cause an irreversible neurological syndrome similar to Parkinson's disease [24].

Following long-term exposure to cadmium, the main health concerns are its toxicity to the kidney and bones, arising via ingestion and inhalation, and its lung carcinogenicity seen in exposed workers following inhalation [26]. Over a period of time, cadmium accumulates in the kidney and, if the organ concentration exceeds a critical threshold, the tubule cells become damaged and renal function impaired. This cadmium build-up also affects vitamin D metabolism, disturbing the calcium balance within the body, which may lead to a decrease in the mineral content within the bones, resulting in osteoporosis and osteomalacia [26,27]. Its toxicity is linked with reproduction problem because it affects sperm and reduces birth weight. It is a potential carcinogen and seems to be a causal factor in cardiovascular diseases and hypertension. Large concentrations of Cd in the soil are associated with parent material (black slates) and most are manmade (burning of fossil fuels, application of fertilizers, sewage sludge, and plastic waste) [28,29]. In humans, long-term exposure is associated with renal dysfunction. The average daily intake for humans is estimated as 0.15 µg from air and 1 µg from water. Smoking a packet of cigarettes can lead to the inhalation of around 2-4 µg of cadmium, but levels may vary widely [27].

Mercury is a toxic substance which has no known function in human biochemistry or physiology and does not occur naturally in living organisms [27]. Mercury is a toxic heavy metal

and a persistent environmental pollutant. Known sources of Hg in soil e.g. mercury-in-bulb thermometers used in hospitals; alkyl mercury compounds especially methyl mercury used as fungicide in agriculture, present in coal and hydrocarbon gas etc. Exposure to mercury is associated with serious adverse health and developmental effects, especially in pregnant women, developing fetuses, and young children [24]. This heavy metal is toxic even at low concentration to a wide range of organisms including humans. The organic form of mercury can be particularly toxic, and the methyl- and ethyl-forms have been the cause of several major epidemics of poisoning in humans resulting from the ingestion of contaminated food, e.g. fish. Two major epidemics in Japan were caused by the release of methyl and other mercury compounds from an industrial site followed by accumulation of the chemicals in edible fish. The poisoning became well-known as Minamata disease [28,29]. Inorganic mercury poisoning is associated with tremors, gingivitis and/or minor psychological changes, together with spontaneous abortion and congenital malformation. Monomethylmercury causes damage to the brain and the central nervous system, while foetal and postnatal exposure have given rise to abortion, congenital malformation and developmental changes in young children [27]. The negotiations under UNEP of a new Minamata Mercury Convention is under way to underscore international concerns about the environmental and health impact of mercury and the need for coordinated global action to address the issue effectively. Average concentrations of mercury in soil are 6.6 mg/kg, 6.6 mg/kg, 24 mg/kg and 50 mg/kg in agricultural, residential/parkland, commercial and industrial soils, respectively [30].

Lead has been known to be toxic since the 2nd century BC in Greece. It is a widespread contaminant in soils. Lead poisoning is one of the most prevalent public health problems in many parts of the world. It was the first metal to be linked with failure in reproduction. It can cross the placenta easily. It also affects the brain, causing hyperactivity and deficiency in the fine motor functions, thus, it results in damage to the brain. The nervous systems of children are especially sensitive to Pb leading to retardation. It is also cardiotoxic and contributes to cardiomyopathy (disease of the heart muscle leading to the enlargement of the heart) [28,29]. Lead affects almost every organ system in the human body. The central nervous system is particularly vulnerable in infants and children under age six. The effects are the same whether it is breathed or swallowed. Large amounts of lead exposure may lead to blood anaemia, severe stomach ache, muscle weakness, and brain damage. Lower levels of exposure, may affect a child's mental and physical growth leading to learning disabilities and seizures [24]. Major sources of human exposure to lead include old lead water pipes, tetraethyl lead from gasoline, lead in paint and improper disposal of used lead acid battery (ULAB) in dump sites. In humans, exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Various effects occur over a broad range of doses, with the developing foetus and infant being more sensitive than the adult. High levels of exposure may result in toxic biochemical effects in humans, which in turn cause problems in the synthesis of haemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system. Lead poisoning, which is so severe as to cause evident illness, is now less common. This could be due to international efforts at phasing out lead in gasoline and paints in many parts of the world including developing countries [31] indeed. At intermediate concentrations, however, there is persuasive evidence that lead can

have small, subtle, subclinical effects, particularly on neuropsychological developments in children. Some studies suggest that there may be a loss of up to 2 IQ points for a rise in blood lead levels from 10 to 20 $\mu\text{g}/\text{dl}$ in young children [26]. Uncontaminated soil contains lead concentrations less than 50 ppm but soil lead levels in many urban areas exceed 200 ppm [32]. The EPA's standard for lead in bare soil in play areas is 400 ppm by weight and 1200 ppm for non-play areas [33].

Arsenic is well-known as a poison and a carcinogen. It has an average concentration in the soil of 5 to 6 mg/kg [28]. Its amount in the soil is related to rock type and industrial activity [34]. It is used in combination with other materials in pigments, poison gases and insecticides (such as Paris green, calcium arsenate and lead arsenate) and is well known from former use as a rat poison. Arsenic has a long history of medical applications; before penicillin was developed an arsenic compound was used to treat syphilis and yaws. It is used in ammunition manufacturing, semi-conductor manufacturing, as a preservative in tanning and taxidermy, as well as on the exterior of wood such as deck and playground materials as well as by-product of copper smelting [34]. Acute (short-term) arsenic poisoning may cause nausea, vomiting, diarrhea, and weakness, loss of appetite, shaking, cough and headache while chronic (long-term) exposure may lead to a variety of symptoms including skin pigmentation, numbness, cardiovascular disease, diabetes, and vascular disease. Arsenic is also known to cause a variety of cancers including skin cancer (non-melanoma type), kidney, bladder, and lung, prostate and liver cancer.

Chromium is required for carbohydrate and lipid metabolism and the utilization of amino acids. Its biological function is also closely associated with that of insulin and most Cr-stimulated reactions depends on insulin. However, excessive amount of the metal can cause toxicity. Toxic levels are common in soils applied with sewage sludge [28,29]. Chromium is used in metal alloys and pigments for paints, cement, paper, rubber, and other materials. Low-level exposure can irritate the skin and cause ulceration. Long-term exposure can cause kidney and liver damage, and damage to circulatory and nerve tissue. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium [27].

Nickel occurs in the environment only at very low levels. Humans use nickel for many applications like the use of nickel as an ingredient of steel and other metal products [27], in the metallurgical, chemical and food processing industries, especially as catalysts and pigments [35]. Foodstuffs have low natural content of nickel but high amounts can occur in food crops growing in polluted soils. Humans may also be exposed to nickel by inhalation, drinking water, smoking, and eating contaminated food [27]. Uptake of high quantities of nickel can cause death, systemic effects, respiratory effects, cardiovascular effects, gastrointestinal, haematological musculoskeletal, hepatic, renal, endocrine, metabolic, immunological and lymphoreticular, neurological, reproductive, developmental effects and cancer [36]. Nickel occurs naturally in the Earth's crust with an average concentration of 0.0086% (86 ppm). The nickel content of soil may vary depending on local geology [37].

Copper is an essential substance to human life, but in high doses it can cause anaemia, liver and kidney damage, and stomach and intestinal irritation. People with Wilson's disease are at

greater risk for health effects from overexposure to copper. Copper normally occurs in drinking water from copper pipes, as well as from additives designed to control algal growth [28]. The major sources of environmental copper releases include the mining, smelting and refining of copper, industries producing products from copper such as wire, pipes and sheet metal, and fossil fuel combustion [38].

1.2. Health and environmental effects of some common Persistent Organic Pollutants (POPs)

Persistent organic Pollutants (POPs) are associated with serious human health problems, including cancer, neurological damage, birth defects, sterility, and immune system defects. US Environmental Protection Agency (USEPA) and the Stockholm Convention have classified certain POPs as probable human carcinogens, including aldrin, dieldrin, chlordane, Dichlorodiphenyltrichloroethane (DDT), heptachlor, Hexachlorobenzene (HBC), toxaphene, and Polychlorinatedbiphenyls (PCBs) [39,40,41]. Laboratory studies have shown that low doses of POPs may affect organ systems. Chronic exposure to low doses of certain POPs may affect the immune and reproductive systems. Exposure to high levels of certain POPs can cause serious health effects or death. The primary potential human health effects associated with POPs are cancer; immune system suppression; nervous system disorder; reproductive damage; altered sex ratio; reduced fertility; birth defects; liver, thyroid, kidney, blood, and immune system damage; endocrine disruption; developmental disorders; shortened lactation in nursing women; and chloracne and other skin disorders.

Studies have linked POPs exposure to declines, diseases, or abnormalities in a number of wildlife species, including certain kinds of fish, birds, and mammals [39,42]. Wildlife also can act as sentinels for human health: abnormalities or declines detected in wildlife populations can sound an early warning bell for people. For example, the behavioural abnormalities and birth defects in fish, birds, and mammals in and around the Great Lakes. People are mainly exposed to POPs through contaminated foods. Less common exposure routes include drinking contaminated water and direct contact with the chemicals. In people and other mammals alike, POPs can be transferred through the placenta and breast milk to developing offspring. In addition, sensitive populations, such as children, the elderly, and those with suppressed immune systems, are typically more susceptible to many kinds of pollutants, including POPs. Because POPs have been linked to reproductive impairments due to their endocrine disrupting properties, men and women of child-bearing age may also be at risk [43-47].

Organochlorine pesticides are a large class of multipurpose chlorinated hydrocarbon chemicals, some of which are POPs. They break down slowly in the environment and accumulate in the fatty tissues of animals. Thus, they stay in the environment and food web long after being applied [48]. Many organochlorine pesticides are endocrine disrupting chemicals, meaning they have subtle toxic effects on the body's hormonal systems [27]. Endocrine disrupting chemicals often mimic the body's natural hormones, disrupting normal functions and contributing to adverse health effects. Organochlorine pesticide is ubiquitous environmental contaminants because they break down very slowly. The effects that some of the most common organochlorine pesticides have on humans as well as animal's health are as follows:

Acute exposure to chlordane can possibly cause neurological effects while long-term exposure can damage the liver, kidney, and other internal organs. Significant immune system changes have also been reported in exposed workers. There is some evidence of carcinogenicity [49]. Research has also indicated that chlordane is an endocrine disruptor. The half-life of chlordane in soil has been reported to be from one to three years. Chlordane binds to aquatic sediments and bioconcentrates in the fat of organisms.

DDT is a possible human carcinogen; some of its metabolites Dichlorodiphenyldichloroethylene (DDE) and Dichlorodiphenyldichloroethane (DDD) are probable human carcinogens [49]. DDT and its breakdown products are thought to be endocrine disruptors. DDT is lipophilic and will both bio-concentrate and bio-magnify. It is present almost everywhere in the environment, and residue has been detected in the arctic. DDT breaks down into the related compounds; DDE and DDD. In the environment, DDT and its metabolites have a half life of 10 to 15 years in soil. DDT is highly toxic to birds and fish, DDE and DDD are also toxic and persistent [50]. Some DDT may evaporate from soil and enter the air, and some may be broken down by the sun or microorganisms.

Heptachlor is metabolised in animals to heptachlor epoxide, whose toxicity is similar to that of heptachlor [49]. Both binds to animal fat. Heptachlor and heptachlor epoxide are possible human carcinogens and are thought to be endocrine disruptors. At high levels or from chronic exposure, they can cause central nervous system and liver damage. The half life of heptachlor in temperate soil is up to two years. Heptachlor has been found in treated wastewater from industrial processes including coal mining, foundries, and nonferrous metals manufacturing. It has been detected in the blood of cattle in the U.S. and heptachlor has been strongly implicated in the decline of several wild bird populations [50].

Mirex is probably a carcinogen and is also thought to be an endocrine disruptor. It may cause damage to skin, liver, nervous, and reproductive systems at high levels [49]. Crustaceans may be the most sensitive organisms to mirex. It can bio-accumulate and bio-magnify and is very persistent, with a half life of up to 10 years in soil. It has been detected in arctic freshwater.

Lindane, which belongs to the class of new POPs under the Stockholm Convention may be a carcinogen and is thought to be an endocrine disruptor. It can cause nervous system effects and pulmonary oedema from short, and acute exposures. Long-term exposure can cause liver and kidney damage, as well as various blood disorders [49]. Lindane bio-concentrates slightly in fish and crustaceans, and can remain in the air for up to 17 weeks and travel long distances. It is broken down quickly in water [50]. Lindane exposure has been associated with recurrent miscarriage. Lindane also disrupts natural levels of estrogens, androgens and thyroid hormones in rodents [51]. Lindane produces behavioural and neurochemical changes in developing rats at doses that do not produce symptoms in adults. This is significant because it suggests that lindane may have the greatest effect during development [52]. Both acute and sub-chronic exposures to lindane were found to reduce dopamine concentrations in the brains of rats by about 46%. Dopamine is an important neurotransmitter with effects on mood and behaviour [53]. Lindane exposure during postnatal development in rats was associated with alterations in levels of detoxification enzymes in the brain that lasted until adulthood. It is not

known how this alteration might affect the outcome of future exposures [54]. Exposure to lindane decreased both thyroid hormones and progesterone in developing lambs [55S].

Dieldrin can cause poisoning in humans and mammals following exposure via the skin, oral intake or inhalation. It acts as a stimulant to the central nervous system and accumulates in fatty tissue causing severe damage to the liver and kidneys. Animal experiments have revealed a carcinogenic effect, but as yet no teratogenic action. Residue levels of aldrin (mostly present as dieldrin) do not accumulate indefinitely, as the result of yearly applications at a constant dosage rate, but will reach a maximum level which is, in practice, of the order of that resulting from a single annual dose [56,57]. There is virtually no leaching of aldrin into deeper soil layers and thus no contamination of groundwater, which is eventually used as drinking or irrigation water [58,59].

Endosulfan is highly toxic to the nervous system and can cause circulatory problems, headache, vomiting and diarrhea. Thus, it is one of the new POPs under the Stockholm Convention. It is also a suspected hormone disruptor [49]. Endosulfan has shown no potential to accumulate over time in animals. It is more water soluble than other organochlorine pesticides, such as DDT, and is less persistent in the body because it metabolises quickly [60].

1.3. Health and environmental effects of Polycyclic Aromatic Hydrocarbons (PAHs)

Because of combustion of fossil fuels and organic waste, PAHs are ubiquitous in the environment. Studies show that certain PAHs metabolites interact with DNA and are genotoxic, causing malignancies and heritable genetic damage in humans. Many of these compounds have carcinogenic and mutagenic activities and present a hazard for human health [61]. In humans, heavy occupational exposure to mixtures of PAHs entails a substantial risk of lung, skin, or bladder cancer. PAHs generally have a low degree of acute toxicity to humans. The most significant endpoint of PAHs toxicity is cancer. Increased incidences of lung, skin, and bladder cancers are associated with occupational exposure to PAHs. It is difficult to ascribe observed health effects in epidemiological studies to specific PAHs because most exposures are to PAHs mixtures. Animal studies show that certain PAHs affect the hematopoietic, immune, reproductive, and neurologic systems and cause developmental effects [62].

1.4. Soil contamination by cattle wastes

Cattle manure is a major waste product of agricultural practice involving the breeding and rearing of cattle. Inappropriate disposal of manure can create environmental problems such as odours and leaching of nitrate ion and other pollutants into groundwater. Repeated annual application of manure with high salt content caused a build up of soluble salts in soils, sufficient to lower their productivity [63]. During the last three decades, dairy farm facilities have received attention from the public and regulations due to increased environmental concern. These facilities concentrate in certain regions of the USA (e.g. California, New York, Minnesota, and Pennsylvania) and generate considerable amount of manure, which can harm soil and water quality. Manure varies in mineral composition depending on the type of animal and the ration fed. It was reported that cattle (*Bos Taurus*) manure contains 2.7 to 9.5% N, 0.5 to 0.8%

O, 1.7 to 2.9% K, 1.4 to 20% Ca, and 0.61 to 0.76% Mg (% dry waste basis) [64]. In addition, varying amounts of Al, Fe, Mn, S, Cl, Cu, Zn, and B and trace concentrations of Co, Cd, Cr, Ni, As and Se are present. Large fractions of these elements are present in a water-soluble form. With high precipitation, almost all regions where dairy farm facilities concentrate, great quantities of these elements are lost through surface runoff and leaching into groundwater. Manure contains a large amount of soluble and insoluble organic substances. Organic matter content ranges between 80% and 90% (dry weight basis) [64]. Pyrolysis field ionization mass spectroscopy (Py-FIMS) was also used to analyse cow manure samples [65]. The organic components that were identified include lignins, dimeric lignins, pesticides, lipids, monoesters, fatty acid, sterols, and heterocyclic nitrogen compounds.

The aim of this study was to determine the distribution, concentration and profiles of some ubiquitous environmental pollutants such as heavy metals, polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides in soil of a cattle market around River Ogun Basin, Isheri, Nigeria so as to ascertain the level of contamination of the soil resulting from the anthropogenic activities taking place in the area.

2. Experimental

2.1. General description of ogun river basin

The River Ogun basin is situated in south western part of Nigeria covering a total area of 22.44 cubic kilometres. It arises in Oyo state, on the southern side of Yoruba plateau, and runs south into Ogun state, passing through Abeokuta before entering Lagos state and finally discharging into the Lagos Lagoon. The elevation of the northern, eastern, southern, and western boundaries are 457 m, 366 m, 426 m, and 230 m, respectively above the sea level [66]. Various organizations are active in the development of socio-economic conditions of the Ogun river basin. The Ogun-Osun River Basin Development Authority (OORBDA) is responsible for the management of the water resources. The Ogun river basin is among others contributing a diversion at Mokoloki for irrigated farming of the upland. Another is the Ogun State Agricultural Development Project, which has incorporated a fishery component to increase fish production and availability. Ogun River is used as a source of water supply for domestic, industrial, agricultural, and recreational purposes along the states it traverses. This site has become a place of interest considering its constant and continuous pollution owing to the fact that it serves as a focal point of some commercial activities in the ever growing cattle market around the basin [67]. Figure 1 shows the map of the study area.

2.2. Sampling design

The soil samples were collected from the cattle market situated around the Ogun River, Isheri along Lagos-Ibadan Express Road. The soil samples were collected at two different depths of 0-15 cm and 15-30 cm with non-metallic sampler. The sampling site was divided into three zones as follows:

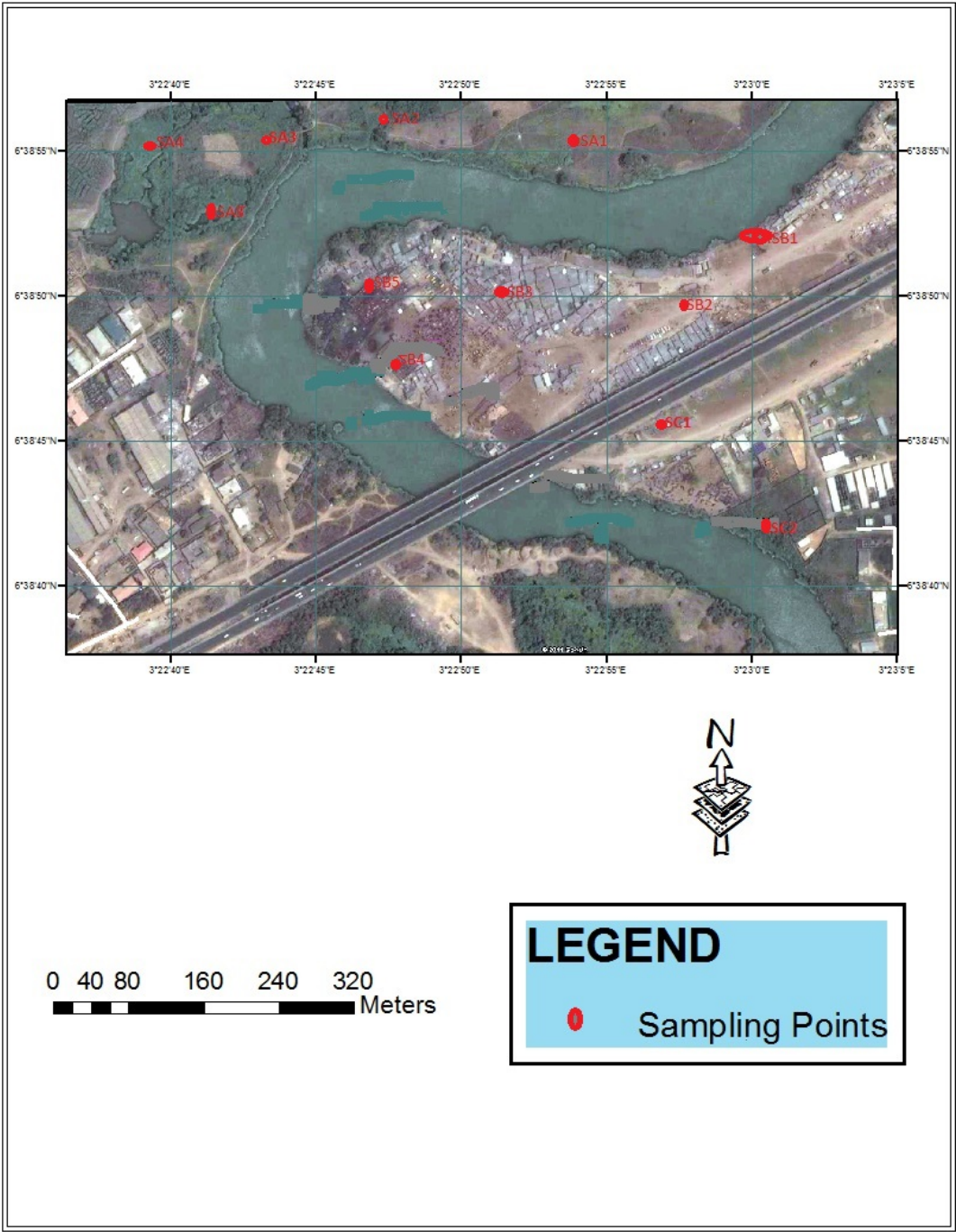


Figure 1. Map of river Ogun showing the Sampling Points

1. Samples were collected at five different spots (SA1-SA5) upstream the market across the river at a distance of about 100 m to the market. The major human activities on this side of the river were sand mining and fishing. The fishing activity was simple and involved the use of paddled canoe and boat with fishing net and hooks. The natural physical feature of these areas was shrub growth. The samples from this area were pooled together to form a representative sample, A1S1 (representing composite sample of the random samples

collected from 0-15 cm depth), and A2S2 (representing composite sample of the random samples collected from 15-30 cm depth).

2. Random samples were also collected at five different locations including the market centre and the areas surrounding it. The activities and the features observed at the different points were;
 - i. SB1: Old car scraps, marshy area located about 50 m to the market centre
 - ii. SB2: Auto-mechanic workshop and residential tents built with planks and polypropylene materials
 - iii. SB3: Cattle rearing and selling with other petty trading
 - iv. SB4: Slaughter houses, wastewater discharge point, animal hair and horn burning with tyres, animal blood cooking and processing, and solid waste dumpsite
 - v. SB5: Children playground at the river bank

The samples from this area were pooled together and a representative sample, B1S1 (representing composite sample of the random samples collected from 0-15 cm depth), and B2S2 (representing composite sample of the random samples collected from 15-30 cm depth) were obtained for the analysis.

3. Two samples were collected downstream the market from two points to form a composite samples C1S1 and C2S2 for the 0-15 cm and 15-30 cm depths, respectively. The activities around this point are
 - i. SC1: Petty commercial activities around a police post in a slum with most houses built with plank, rust iron sheet and polypropylene material;
 - ii. SC2: A dumpsite that was almost swept off by erosion into the river situated at the river bank.

2.3. Sample collection, treatment and preservation

Two samples were collected from each area of sampling around the cattle market to form a composite. Control sample was also collected in a rural community, Lalupon in Ibadan. The sample portion that is to be analysed for PAHs and organochlorine pesticides were collected in a glass bottle wrapped with aluminium foil to prevent exposure to sunlight, as organochlorine pesticides are known to be sensitive to sunlight, while the sample to be analysed for heavy metals and physico-chemical parameters were collected in a polythene bag. The samples were preserved in an ice chest for onward transportation to the laboratory, where they were kept in a refrigerator. The samples collected for heavy metals and physico-chemical parameters were air-dried at room temperature until they were properly dried and large objects (sticks, stones, wood, and e.t.c) were manually removed. The samples were then gently ground with a porcelain mortar and pestle, and sieved through a 2 mm sieve and stored in polythene bags until sample digestion. The samples

collected for PAHs and organochlorine pesticides analyses were not air-dried to minimise loss of those components which can vaporise easily [68].

2.4. Analytical procedure

2.4.1. Determination of soil pH

Approximately 20.0 g each of the air-dried and sieved soil samples (< 2 mm) were weighed, 50 ml distilled water was added and then mixed and allowed to stand for 30 minutes. Suspension was stirred every 10 minutes during this period. The suspension was allowed to settle for another 30 minutes and a pH meter electrode (Jenway 3510) was placed in the suspension and the reading was taken after some seconds. The electrode was removed from the suspension and rinsed thoroughly with distilled water and excess water was carefully dried.

2.4.2. Determination of soil organic matter

About 0.70 g each of the air-dried and sieved soil samples were weighed and 10.0 ml of 1.0 N K_2CrO_7 solution and 20.0 ml concentrated H_2SO_4 were added immediately [69]. The solution was mixed for 1 minute by swirling until the soil and reagents were thoroughly mixed. The mixture was allowed to stand for 30 minutes after which 100 ml distilled water was added and then allowed to cool under running water. 3-4 drops of Ferroin indicator was added and then titrated with 0.5 N Ferrous Ammonium Sulphate. Near the end-point, the solution took a greenish colour and later changed to dark green. At this point, the 0.5 N Ferrous Ammonium Sulphate was added drop by drop until the colour changed from green to reddish-brown at the end point. The Ferrous Ammonium Sulphate solution was standardized using 1 N potassium dichromate before use. Blank titration was carried out in the same manner, but without the soil sample.

The % organic Carbon was determined as follows:

$$\% \text{ Organic Carbon} = \frac{(\text{meq. FAS for blank} - \text{meq FAS for sample}) (0.003 \times 100f)}{\text{Weight in g of air-dried soil}}$$

Where, $f = 1.334$

$$\% \text{ Organic matter} = 1.729 \times \% \text{ Total Organic Carbon}$$

meq- Milligram equivalent = normality of solution x ml of solution used.

2.4.3. Determination of soil particle size by the Bouyoucos hydrometer method

This is a measure of the size distribution of individual particles in a soil sample. Particle size distribution analysis is often used in soil science to evaluate soil texture. The soil texture is based on different combination of sand, silt, and clay separately, that makes up the particle size distribution. The size range of sand is 2.0 mm-0.05 mm, silt is 0.05 mm-0.002 mm and clay is less than 0.002 mm (< 0.002 mm). Particle size distribution analysis result can be used to predict the water retention capacity and unsaturated hydraulic conductivity of soils [70]. About 50.0 g of air-dried soil sample sieved to < 2 mm was weighed into 250 ml beaker. 20 ml

of 5.0 % Sodium Hexametaphosphate was added along with 350 ml distilled water. The mixture was stirred mechanically on an end-to-end shaker at 100 revolutions per minutes for 5 minutes. The water-soil slurry was transferred to a sedimentation cylinder and sufficient water was added to bring the level to the 1000 ml mark. The top of the cylinder was covered and inverted several times until all the soil particles are in suspension. The cylinder was placed on the flat surface and the time was recorded. The soil hydrometer was placed on the suspension carefully and slid slowly into the suspension until the hydrometer was floating. The first reading was taken on the hydrometer at 60 s after the cylinder was set down. The hydrometer was removed and the temperature of the suspension was measured. After the first hydrometer reading, the suspension was left standing for 3 hours and the second reading was taken. The temperature of the suspension was also measured at this point. The first reading measured the percentage of silt and clay in suspension while the second reading indicated the percentage of clay in the suspension. When taking the hydrometer reading, the hydrometer was carefully lowered into the cylinder about 25 s before the reading was taken to ensure that it came to rest before the appointed reading time. The readings were taken at the top of the meniscus formed by the suspension around the stem of the hydrometer. As soon as the reading was taken, the hydrometer was carefully removed and rinsed with distilled water. The results were corrected to a temperature of 20 °C and 2.0 were subtracted to compensate for the added dispersing agent.

Correction factor for Temperature = $0.3 [\text{Observed Temperature (T } ^\circ\text{C)} - 20 ^\circ\text{C}]$

% Clay + % Silt = $[H_1 + 0.3 (T_1 - 20) - 2.0] \times 2$

% Clay = $[H_2 + 0.3 (T_2 - 20) - 2.0] \times 2$

Sand = $100 - [H_1 + 0.3 (T_1 - 20) - 2.0] \times 2$

Silt = $100.0 - (\% \text{ Sand} + \% \text{ Clay})$

Where,

H_1 = Hydrometer reading at 60 s

T_1 = observed Temperature at 60 s (= 28 °C)

H_2 = Hydrometer reading at 3 hours

T_2 = observed Temperature at 3 hours (= 28 °C)

2.4.4. Metal analysis

Acid digestion procedure was employed for the determination of the concentrations of the environmentally available metals in the soil samples. Prior to the determination of the metal concentration in soil, sample digestion is a necessary pre-treatment step. The most common method for determining the concentrations of metal contained in a soil sample is the total elemental analysis. The review on total metal concentration determination in soil samples revealed that heavy metals bound to non-silicates and silicate structures were determined with concentrated acids such as HCl, HClO_4 , and HF [71]. However, in recent times, strong acid

extractant such as concentrated nitric acid, aqua regia (a mixture of concentrated HCl and concentrated HNO_3 in ratio 3:1) and dilute form of the acids are used to determine total metals in contaminated soils [72]. The acids dissolve almost all elements that could become environmentally available especially metal oxides and carbonates [73].

However, heavy metals bound to silicate structures are not normally dissolved since they are not usually mobile in the environment [74] but the extractant normally give a reliable measure of metals added to soils as non-silicates from industrial sources that has potential for natural leaching and biological processes. The use of perchloric acid and hydrofluoric acid is generally fading away since complete dissolution of the soil is no longer required for total metal analysis in environmental work [75].

Most current environmental analysis work that involved total metal analysis has employed the use of 2 M HNO_3 [3,76,77]. The levels of heavy metals extracted with 2 M HNO_3 have been reported to represent maximum contents of potentially available metals for plants [77]. In this study, approximately 1.0 g each of the composite soil samples were digested with 20 ml of 2 M HNO_3 by heating the vessel in a water bath between 90-100°C for 2 hours with shaking every 20 minutes. The vessel was allowed to cool to room temperature. The digestate was filtered and made up to mark with distilled water. Two replicate samples were digested in the same way together with a reagent blank and all the samples were analyzed using Buck 200A Atomic Absorption Spectrophotometer using air-acetylene flame.

2.5. Organochlorine pesticides and PAHs analysis

2.5.1. Soil sample extraction

A solvent mix of pesticide residue (PR) grade acetone and methylene chloride (50:50) was prepared and 50 ml of the solvent mix was added to about 10 g of the sample, spiked with 1 ml of surrogate standard [78,79]. The sample was placed in the ultrasonic bath (Grant Instruments) and sonicated for about 10-15 minutes at 70°C. Then 10 g of anhydrous sodium sulphate (Na_2SO_4) was added to the sample to remove the water present initially in the sample and shaken gently until a clear extract was developed. The procedure was repeated once more with an additional 50 ml of solvent mix. The solvent was then concentrated on a rotary evaporator (Buchi equipment) and exchanged with 5 ml of n-hexane then re-concentrated to 1 ml. The concentration of the sample extract was necessary to remove the acetone and methylene chloride used in the extraction. In the course of the concentration of the solvent on the evaporator, the acetone and methylene chloride was removed leaving n-hexane with the extract. This is necessary to prepare the extract for clean-up and fractionation in a column containing n-hexane-mixed silica slurry. The extracted sample was then fractionated into the aliphatic and aromatic fractions (PAHs) using silica gel column [80]. The same procedure was repeated for the extraction of organochlorine pesticide in the sample using acetone and dichloromethane (DCM) solvent mixture (50:50).

2.5.2. Column packing for fractionation and clean-up of extract

Glass column was packed with 10 g of 100-200 mesh silica gel preconditioned (baked) at 105°C overnight. The silica was mixed with n-hexane to form slurry. The column was then eluted

with about 15 ml of PR grade n-hexane and the solvent was collected to waste. Caution was taken not to allow the column to dry up. Using 1 ml pipette, 1 ml of the extract in n-hexane was added onto the column and then eluted with 60 ml of n-hexane. The aliphatic fraction was collected and the column was then eluted with 40 ml of PR grade dichloromethane (DCM) and another fraction was collected, which is the Polycyclic Aromatic Hydrocarbons (PAHs) fraction. Each of these fractions was concentrated to 1 ml using a rotary evaporator. After concentrating the PAH fraction to 1 ml, 5 ml of PR grade n-hexane was added and was further concentrated to remove the DCM using the rotary evaporator. The concentrates were later transferred into 2 ml sample vials using the graduated 2 ml pipettes. The final volumes of the extracts were noted and the sample extracts were subjected to GC-MS analysis. The same clean-up procedure was carried out on the organochlorine pesticide extract by eluting the column with PR grade n-hexane.

2.5.3. Instrumental analysis

The extracts were analysed for PAHs and organochlorine pesticides using a GC equipped with MS detector. Separation was achieved by injecting about 1 µL of each extract into the GC system (in a splitless mode) through a capillary column (3.0 m length, 0.25 mm internal diameter, 0.25 µm film thickness). Helium gas was used as the carrier gas. Table 1 summarize the GC/MS condition. The quantification limit of the PAHs in the standard and the samples was 0.001 ppm, while that of the organochlorine pesticide residue was 0.002 ppm. The average response factor for the weight ranges were calculated and used for sample quantification.

GC/MS condition	PAHs	Organochlorine pesticide
Instrument	Shimadzu GC-MS QP2010	Shimadzu GC-MS QP2010
Column	HP-1MS (Cross linked PH ME siloxane) 19091S-933 Film thickness: 0.25 µm, Length: 3.0 m, Column ID: 0.25 mm	HP-1MS (Cross linked PH ME siloxane) 19091S-933 Film thickness: 0.25 µm, Length: 3.0 m, Column ID: 0.25 mm
Injection method	Splitless mode	Splitless mode
Injection volume	1.0 µL	1.0 µL
Carrier gas	Helium (1.2 ml/min)	Helium (1.18 ml/min)
Injection temperature	250 °C	250 °C
Oven temperature programme	GC oven temperature was kept 60 °C for 1 min First ramp at 5 °C/ min to 180 °C Second ramp at 10 °C/min to 280 °C Final temperature at 10 °C/min to 300 °C	GC oven temperature was kept 80 °C for 1 min First ramp at 5 °C/ min to 200 °C Final temperature at 10 °C/min to 270 °C
MS mode	Total ion current (TIC) mode	Selected Ion Monitoring Mode (SIM)
Ion source temperature	200 °C	200 °C
Interface temperature	250 °C	250 °C

Table 1. Operational conditions of GC/MS for PAHs and organochlorine pesticide

The concentration of each analyte was determined by calculating the amount of analyte or hydrocarbon range injected from the peak response in area ratio. The contribution from the solvent front and the surrogate compound were excluded from the total area of the sample.

$$C_f = \frac{A(p) \times R_f \times V_f \times D_f \times 1000}{W_i}$$

Where,

C_f = Final Sample concentration ($\mu\text{g/L}$)

$A(p)$ = Measured area of peak (peaks)

W_i = Initial weight extracted (g dry weight)

V_f = Final extract volume (ml).

D_f = Dilution factor of sample or extract if diluted.

R_f = Response factor from the calibration standard calculation

$$R_f = \frac{\text{Concentration (P)}}{\text{Area (P)}}$$

Concentration (p) = Total concentration of range

3. Results and discussion

3.1. Soil pH

Soil pH is one of the most important physico-chemical properties which control many other soil physical, chemical, and biological properties. The pH of a soil is affected by the concentration of CO_2 in the soil air, salt concentration (salt effect), and the presence of colloidal particles (suspension effect). The higher the CO_2 concentration in the soil solution, the lower the pH, and the pH of a neutral or calcareous soil is very sensitive to small changes in CO_2 concentration. pH greatly affects the solubility of minerals in soils. Most minerals are more soluble in acid soils than in neutral or slightly basic solutions [81]. The pH of a soil is related to the bioavailability of metals in the soil to plants. At low pH, metals are easily bioavailable because there is increase in the solubility of metals. However, at high pH i.e. slightly alkaline to highly alkaline conditions, metals are not easily mobilized, because they are not easily soluble at high pH, hence not easily bio available [82]. The pH of the composite soils collected at the five different points (SA1-SA5) opposite the market at a distance of about 100 m to the market was slightly acidic with the pH of the topsoil (0-15cm) slightly lower than that of the subsoil (15-30cm) except at the downstream of the river (sampling area C) (Table 2).

3.2. Soil Organic Matter

Soil organic matter is any material produced originally by living organisms (plant or animal) that is returned to the soil and goes through the decomposition process. At any given time, it

Physical Parameter	Sampling Area A		Sampling Area B		Sampling Area C	
	A ₁ S ₁	A ₂ S ₂	B ₁ S ₁	B ₂ S ₂	C ₁ S ₁	C ₂ S ₂
	(0-15cm)	(15-30cm)	(0-15cm)	(15-30cm)	(0-15cm)	(15-30cm)
pH	5.43	5.58	6.69	7.19	6.82	6.11
% Organic matter content	0.83	1.05	0.97	1.80	0.88	1.31
% Clay	24.8	20.8	22.8	26.8	24.8	28.8
% Silt	20	24	18	28	24	22
% Sand	55.2	55.2	59.2	45.2	51.2	49.2

Table 2. Summary of Soil physicochemical parameters

consists of a range of materials from the intact original tissues of plants and animals to the substantially decomposed mixture of materials known as humus. Most soil organic matter originates from plant tissue. Plant residues contain 60-90 percent moisture. The remaining dry matter consists of carbon (C), oxygen, hydrogen (H) and small amounts of sulphur (S), nitrogen (N), phosphorus (P), potassium (K), calcium (Ca) and magnesium (Mg). Although present in small amounts, these nutrients are very important from the viewpoint of soil fertility management [83]. Soil organic matter (SOM) serves as a soil conditioner, nutrient reservoir, substrate for microbial activity, preserver of the environment, and major determinant for sustaining and increasing agricultural productivity. The OM content of soils ranges from less than 1% in desert soils to close to 100% in organic soils. A typical agricultural soil may contain between 1 and 5% OM in the top 15 cm [84]. The percentage organic matter of the soil samples collected around the site is shown in Table 2. Generally, the subsoil has more organic matter content than their respective topsoil. The top soil contains less than 1% OM while the subsoil contains higher values. Soil organic matter performs very important functions in the soil such as: acts as a binding agent for mineral particles, this is responsible for producing friable (easily crumbled) surface soils; increases the amount of water that a soil may hold; and provides food for organisms that inhabit the soil. Humus is an integral component of organic matter because it is fairly stable and resistant to further decomposition. Humus is brown or black and gives soils its dark colour. Like clay particles, humus is an important source of plant nutrients.

3.3. Particle size distribution (soil texture)

Particle size is a fundamental property of any sediment, soil or dust deposit that can provide important clues to nature and provenance and influences a variety of other properties [85]. Soil particle size distribution is of great importance to soil water movement, soil erosion and soil solute migration [86]. It is the determination of the proportion of each soil fraction in the samples and includes the % clay, % silt and % sand. Generally, in all the soil samples collected, sand has the highest percentage. The topsoil of the site has the highest percentage of sand in all the sampling areas. Figure 2 shows the variation in the physico-chemical parameters in the soil.

3.4. Concentration of heavy metals in soil

The results of heavy metals analyzed in the soil samples are shown in Table 3 while Figure 3 shows the distribution around the study site. There is variation in the distribution of the metals around the market with some of the metals such as lead (23.8 mg/kg) and copper (10.4 mg/kg) having the highest concentrations in the subsoil (15-30 cm). The concentrations of all the metals around the market is the highest when compared to the downstream and upstream of the river. This may be attributed to the anthropogenic activities in this area. In most cases, the subsoil has higher concentration of the metals than their respective topsoil, except Zn, Cd, and Ni. However, Cadmium compounds being of very low solubility in water will have little downward movement and accumulate in the topsoil [87]. This may be due to strong adsorption of Cd by the surface soils, which have a higher organic matter content and higher pH; factors which are known to increase Cd adsorption in soils [88]. Also, it was reported that Cd accumulated in the soil surface layers and had low vertical movement when mobility of heavy metals contained in the sludge and the wastewater used for the irrigation was studied in the soil samples collected from the soil profiles from the surface to 100 cm depth of farmland [89]. The mean concentrations and standard deviation of Pb, Zn, Cu, Cr, Cd and Ni in the topsoil (0 – 15cm) and subsoil (15 – 30cm) around the river basin at Isheri are 14.6 ± 4.5 mg/kg and 18.1 ± 8.1 mg/kg; 38.0 ± 27 mg/kg and 44.6 ± 28 mg/kg; 6.41 ± 3.3 mg/kg and 7.77 ± 3.7 mg/kg; 7.35 ± 0.1 mg/kg and 10.5 ± 0.4 mg/kg; 0.74 ± 0.3 mg/kg and 0.63 ± 0.03 mg/kg ; and 3.81 ± 0.5 mg/kg and 5.70 ± 0.3 mg/kg, respectively.

Comparing the results of heavy metal concentrations obtained in this study with the control sample collected at a rural community, Lalupon in Ibadan and some typical values in rural and urban soil around the world (Table 4). The average metal concentrations in both the top and subsoil were higher than the values obtained from the control sample. There are no background and baseline data on toxic metals concentrations in Nigeria. Metal concentrations in the study site when compared to the control sample suggested that anthropogenic inputs have occurred over the years. The concentrations of all the metals were below the values reported [90] except Cd which appeared higher in both the top and the subsoil of the study area.

Metals	Sampling Area A		Sampling Area B		Sampling Area C		Mean Conc.	
	A ₁ S ₁	A ₂ S ₂	B ₁ S ₁	B ₂ S ₂	C ₁ S ₁	C ₂ S ₂	Topsoil	Subsoil
	(0-15cm)	(15-30cm)	(0-15cm)	(15-30cm)	(0-15cm)	(15-30cm)	(mg/kg)	(mg/kg)
Pb	12.9	13.9	17.7	23.8	11.4	12.4	14.6±4.5	18.1±8.1
Zn	20.8	20.7	57.0	64.7	19.0	24.5	38.0±4.5	44.6±28
Cu	6.12	6.19	8.73	10.4	4.09	5.14	6.41±3.3	7.77±3.7
Cr	10.4	10.4	7.3	10.7	7.4	10.2	7.35±0.1	10.5±0.4
Cd	0.73	0.55	0.93	0.61	0.55	0.65	0.74±0.3	0.63±0.03
Ni	5.27	4.72	4.19	5.91	3.43	5.48	3.81±0.5	5.70±0.3

Table 3. Heavy metal concentrations (mg/kg) in the soil around the cattle market in Isheri, Nigeria

There is positive and significant correlation between Zn, Pb and Cu and Ni with Cr. Atmospheric fallout of the metals such as lead from the motor vehicle exhaust from the nearby busy Lagos-Ibadan express road as well as movement of goods around the market may have contributed to the high concentrations of heavy metals in the soil. Also, there is positive and significant correlation between organic matter and Ni, Pb, and Cu.

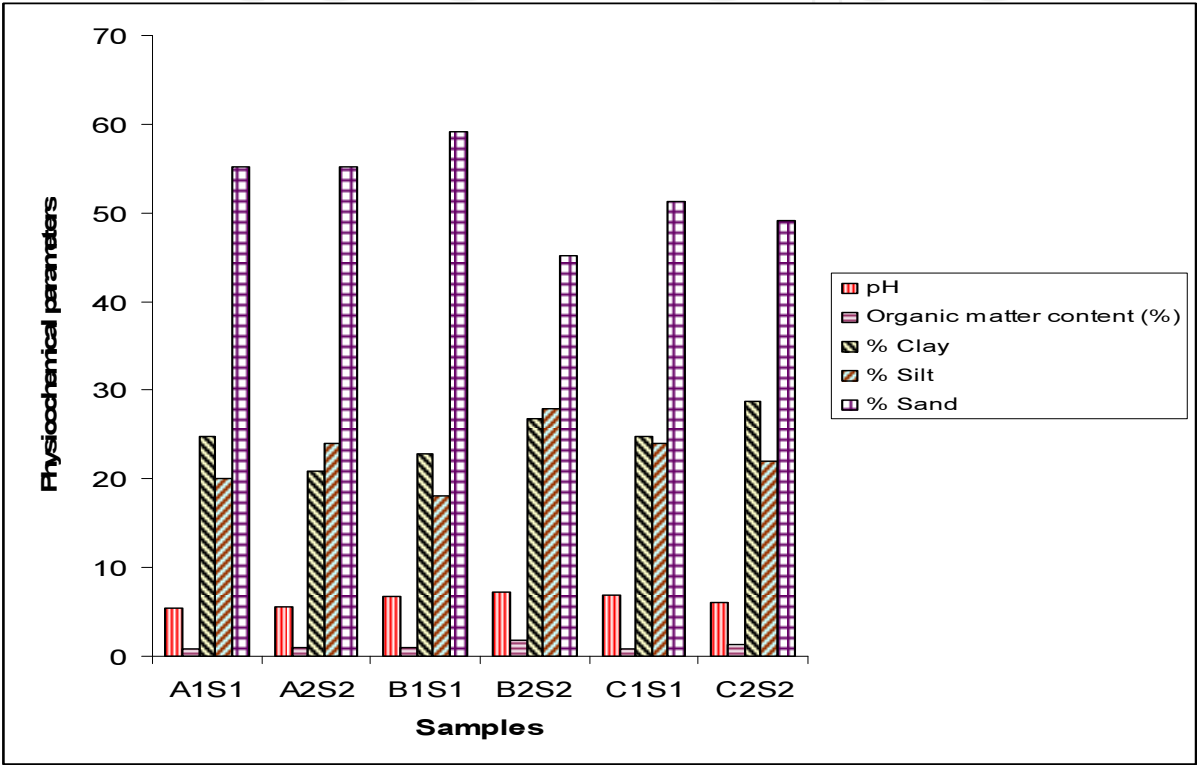


Figure 2. Variation in the physicochemical parameters in the soil around the cattle market in Isheri, Nigeria

	Pb	Zn	Cd	Cu	Cr	Ni
Topsoil (this study)	14.6	38	0.74	6.41	7.35	3.81
Subsoil (this study)	18.1	44.6	0.63	7.77	10.5	5.70
Control site (0-15cm)	9.12	ND	ND	4.57	4.83	0.57
Rural–urban	35	90	0.35	30	70	-
Soils average (Bowen, 1979)						

Table 4. Comparison of mean concentrations (mg/kg) of metals in this study with the control sample and typical soil values around the world

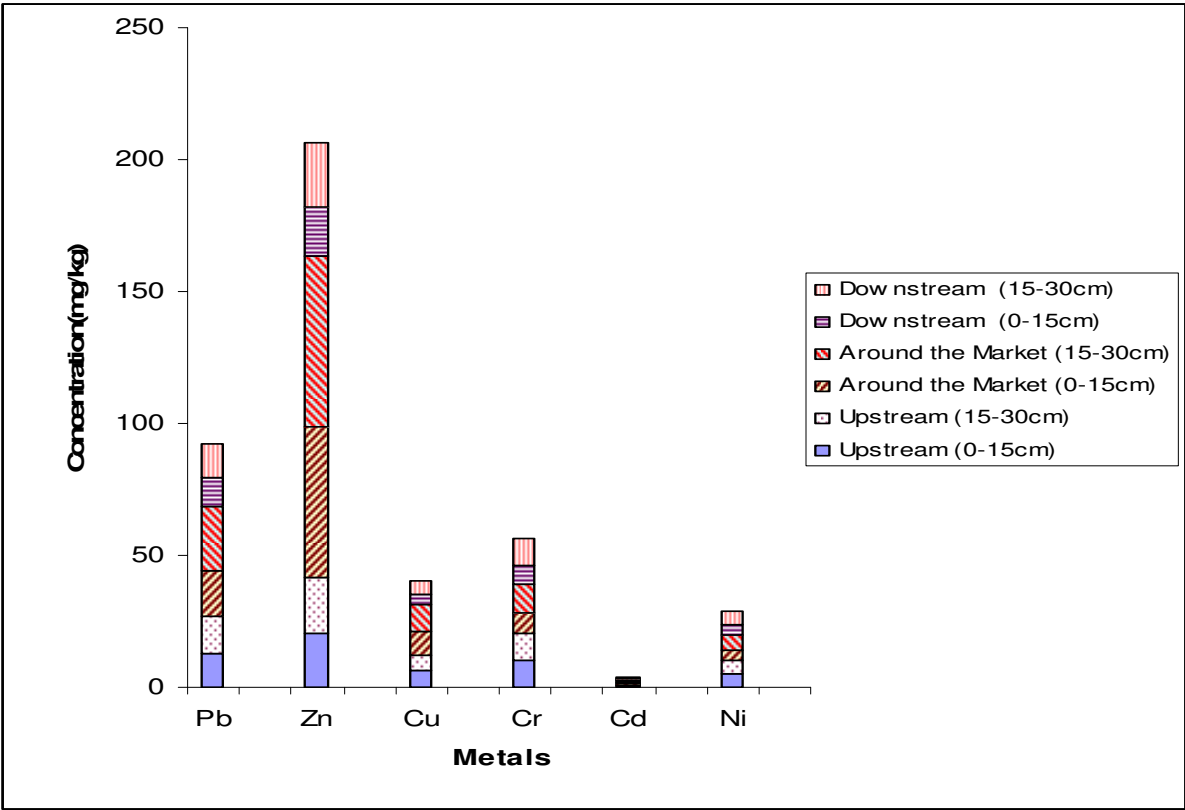


Figure 3. Heavy metal distribution in the soil around the cattle market in Isheri, Nigeria

3.5. Concentration of Polynuclear Aromatic Hydrocarbons (PAHs)

The results of the PAHs in the soil samples collected along the River Ogun basin at Isheri, along Lagos-Ibadan Express road are shown in the Table 5. Regular burning of all kinds of waste, tyres etc. was observed in this area and this might be responsible for the presence of PAHs around the study site. Some of the PAHs such as naphthalene, phenanthrene, fluoranthene, chrysene benzo(a)anthracene and perylene, were found at significantly higher concentrations around the area. Out of the seven species regarded as potential carcinogenic compounds, namely: chrysene, benzo(a)anthracene, benzo(k)flouranthene, benzo(g,h,i)perylene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene, and benzo(a)pyrene, chrysene has the highest concentration in the samples collected at all the sampling points. Its concentration was relatively higher in the subsoil (15-30cm) than the topsoil (0-15cm) except at sampling point C (downstream), where there is little variation in the concentrations in both layers. Figure 4 shows the variation in the concentration of PAHs with depth.

PAHs Component	Sampling area A		Sampling area B		Sampling area C	
	A ₁ S ₁	A ₂ S ₂	B ₁ S ₁	B ₂ S ₂	C ₁ S ₁	C ₂ S ₂
	(0-15 cm)	(15-30 cm)	(0-15 cm)	(15-30 cm)	(0- 15 cm)	(15-30 cm)
Naphthalene	419	244	159	663	668	609
2-methyl Naphthalene	158	103	64.3	234	245	227
Acenaphthylene	8.1	4.0	8.4	24.2	20.2	25.8
Acenaphthene	3.7	19.7	3.8	9.3	9.1	69.2
Flourene	17.9	9.3	18.3	18.1	29.6	18.4
Phenanthrene	60.4	47.5	91.7	76.4	129	85.7
Anthracene	14.8	11.9	17.2	8.3	22.9	6.4
Flouranthene	41.2	121	69.1	31.8	69.8	38.9
Pyrene	14.8	69.1	57.5	18.7	43.7	19.6
Chrysene	93.4	273	81.4	239	193	192
Benzo(a)anthracene	105	115	ND	53.2	50.3	ND
Benzo(k)flouranthene	19.8	59.3	25.2	7.1	12.0	9.3
Benzo(b)flouranthene	5.8	18.0	4.1	18.5	51.1	49.5
Perylene	10.6	30.3	181	ND	641	399
Benzo(g,h,i)perylene	ND	12.5	8.5	ND	ND	ND
Dibenzo(a,h)anthracene	ND	12.6	ND	ND	ND	ND
Indeno(1,2,3-cd)pyrene	3.6	ND	ND	ND	32.0	ND
Total PAHs Concentration (µg/kg)	976	1150	790	1400	2220	1750

Table 5. PAHs concentration (µg/kg) in the soil around the cattle market in Isheri, Nigeria

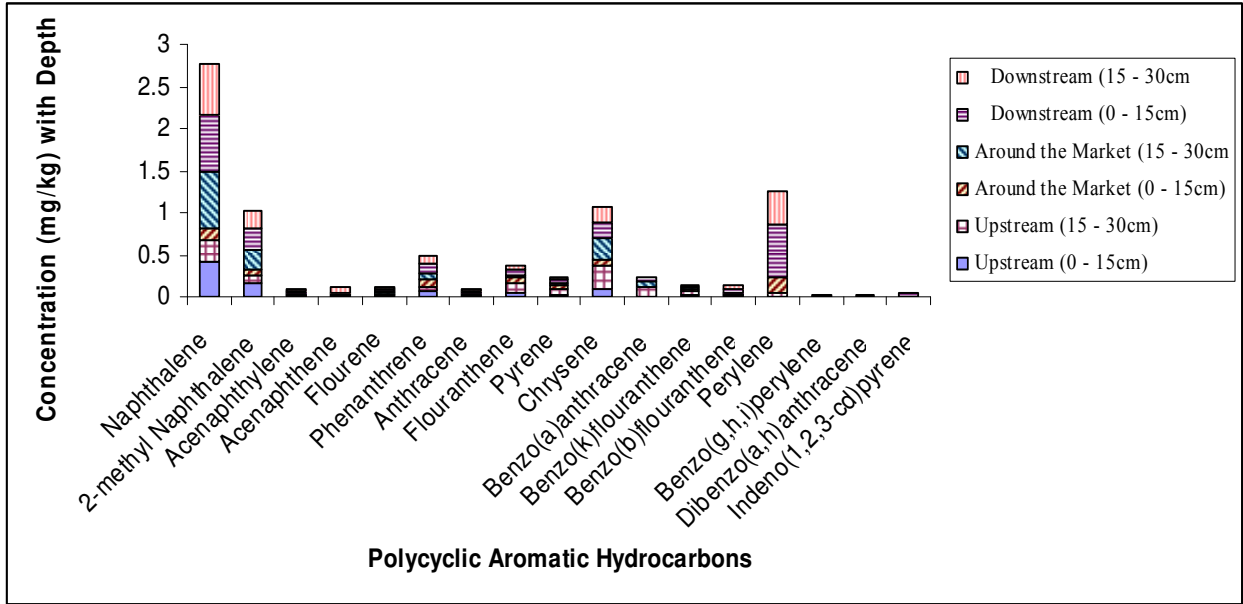


Figure 4. Variation in the concentration of PAHs with respect to depth in the soil around the cattle market in Isheri, Nigeria

Comparing the values obtained in this study with background soil concentrations of PAHs (Table 5) [91], the concentrations obtained in this study was higher than the concentrations in rural and agricultural soils in most cases except benzo(g,h,i) perylene and indeno(1,2,3-cd)pyrene. There is a significant and positive correlation between phenanthrene versus flourene and perylene; flouranthene versus pyrene, benzo(k)flouranthene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene; and benzo(k) flouranthene versus benzo(g,h,i)perylene and dibenzo(a,h)anthracene.

Compounds	Concentrations (x 10 ⁻³ mg/kg)		
	Rural Soil	Agricultural Soil	Urban Soil
Acenaphthene	1.7	6	NE
Acenaphthylene	NE	5	NE
Anthracene	NE	11-13	NE
Benzo(a)anthracene	5-20	56-110	169-59,000
Benzo(a)pyrene	2-1,300	4.6-900	165-220
Benzo(b)fluoranthene	20-30	58-220	15,000-62,000
Benzo(c)perylene	NE	53-130	60-14,000
Benzo(g,h,i)perylene	10-70	66	900-47,000
Benzo(k)fluoranthene	10-110	58-250	300-26,000
Chrysene	38.3	78-120	251-640
Fluoranthene	0.3-40	120-210	200-166,000
Fluorine	NE	9.7	NE
Indeno(1,2,3-cd)pyrene	10-15	63-100	8,000-61,000
Phenanthrene	30.0	48-140	NE
Pyrene	1-19.7	99-150	145-147,000

Note: NE-Not established

Table 6. Background soil concentrations of PAHs

3.6. Organochlorine pesticides

There is variation in the concentrations of the organochlorine pesticides (OCP) in the soil samples collected around the cattle market (Table 6). The major OCP residue identified in the area with their percentage concentrations were p,p'-DDT, 344 µg/kg (24.5%), δ-BHC, 290 µg/kg (20.7%), Endosulfan sulphate, 186 µg/kg (13.2%), lindane (γ-BHC), 129 µg/kg (9.1%), Endrin, 110 µg/kg (7.8%), Aldrin, 93.9µg/kg (6.7%), Dieldrin, 93.8 µg/kg (6.7%), o,p-DDE, 45.0 µg/kg (3.2%), β-BHC, 42.1 µg/kg (3.0%), Endosulfan II, 34.5 µg/kg (2.5%), and Heptachlor, 22.8 µg/kg (1.6%). The variation in the concentrations of the organochlorine pesticides with respect to depth around the cattle market is presented in Figure 4. Dieldrin, a metabolite of aldrin is present at higher concentration in most of the sampling points when compared to the parent aldrin. The presence of o,p' DDE revealed that there is historical use as well as recent us of the parent DDT in the vicinity of the cattle market. Though, DDT has been banned for over 20

years, it's presence around the cattle market indicate that it is illegally imported into the country as it is not produced in Nigeria. Also, lindane, one of the nine new POPs was found at high concentration around the market. The presence of some of the banned chemical residue around the cattle market revealed that there is weak regulation and low enforcement on banned chemicals in the country.

In most cases, the concentrations of organochlorine pesticides is highest at the sampling point C which could be attributed to the use of pesticides to control household pests and insects in the area; as the area is a slum with most houses built of planks, rust iron sheets and polypropylene material and a dumpsite at the bank of the river. There is very strong and significant correlation at the 0.01 levels (2-tailed) between DDT versus δ -BHC, heptachlor, aldrin and dieldrin; dieldrin versus δ -BHC, heptachlor and aldrin; aldrin versus heptachlor as well as endrin versus δ -BHC.

	Sampling area A		Sampling area B		Sampling area C	
	A ₁ S ₁	A ₂ S ₂	B ₁ S ₁	B ₂ S ₂	C ₁ S ₁	C ₂ S ₂
Organochlorine Pesticide	(0-15cm)	(15-30cm)	(0-15cm)	(15-30cm)	(0-15cm)	(15-30cm)
α -BHC	13.2	ND	ND	ND	ND	ND
β -BHC	34.5	7.6	ND	ND	ND	ND
Lindane	108.5	12.0	7.5	ND	ND	ND
δ -BHC	47.4	ND	53.7	60.8	64.4	63.5
Heptachlor	3.3	ND	3.7	5.3	6.0	4.5
Aldrin	13.6	ND	14.2	16.4	34	14.7
Heptachlor-epoxide	ND	ND	ND	ND	ND	ND
cis-Chlordane	ND	ND	ND	ND	ND	ND
Endosulfan I	ND	ND	ND	ND	ND	ND
trans-Chlordane	ND	ND	ND	ND	ND	ND
DDE	ND	ND	14.0	14.3	16.7	ND
Dieldrin	15.2	ND	15.1	16.4	22.2	24.9
Endrin	23.4	ND	28.0	23.7	13.5	20.9
Endosulfan II	ND	ND	ND	ND	15.8	18.7
Endosulfan sulphate	ND	ND	ND	ND	186	ND
p,p' DDT	45.6	ND	59.4	66.0	97.8	75.2
Methoxychlor	ND	ND	ND	ND	ND	ND
Total organochlorine pesticides concentration ($\mu\text{g/kg}$)	305	19.6	196	203	456	222

Table 7. Organochlorine pesticides concentrations ($\mu\text{g/kg}$) in the soil around the cattle market in Isheri, Nigeria

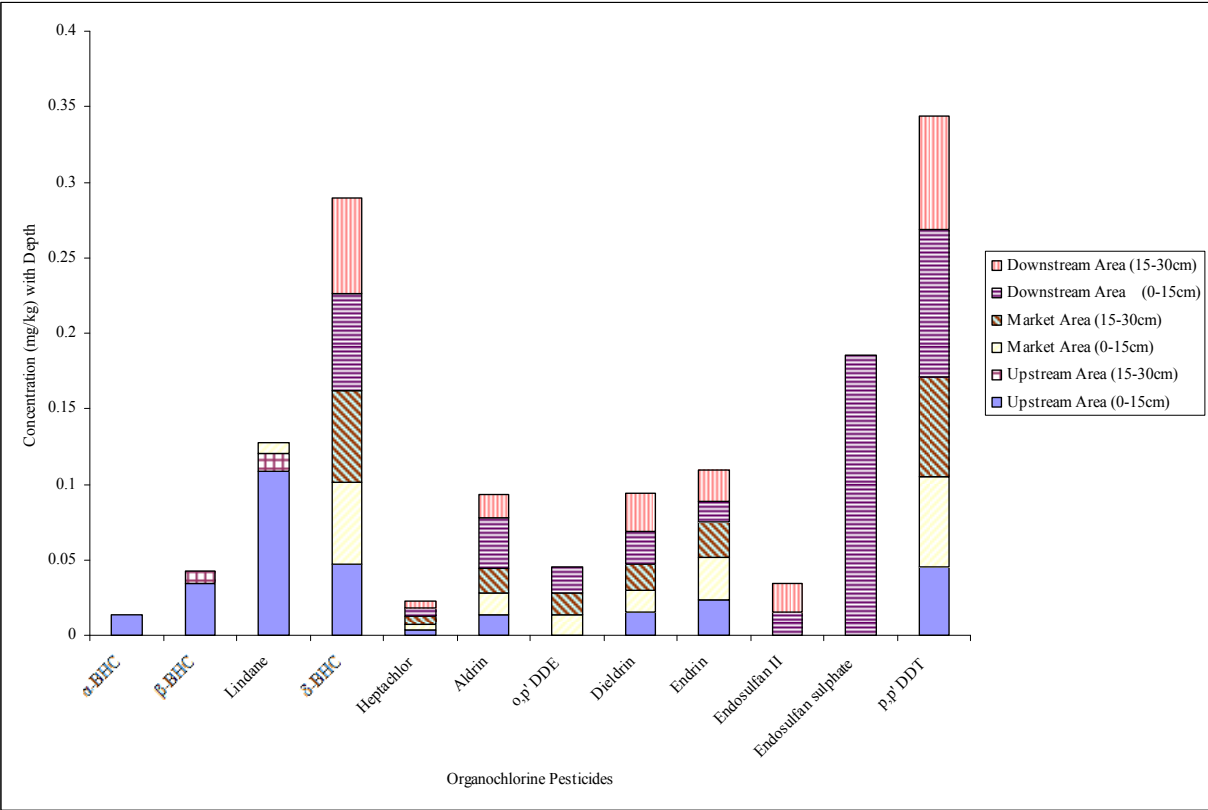


Figure 5. Variation in organochlorine pesticides residue concentrations with respect to depth in the soil around the cattle market in Isheri, Nigeria

4. Conclusion

In this study, the distribution, concentration and profiles of some ubiquitous environmental pollutants such as heavy metals (Pb, Ni, Cu, Cr, Zn and Cd), polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides in soil of a cattle market around River Ogun Basin, Isheri, Nigeria were assessed as well as some soil physico-chemical characteristics. The pH of the top soil was observed to be lower than the corresponding subsoil in most of the areas sampled except the areas downstream of the river. The pH of the topsoil being lower than the subsoil may be responsible for the high metal concentrations in the subsoil. Low pH of top soil means more heavy metals will be dissolved in top soil and the texture of the soil being sandy and loose also might favour the migration/leaching of heavy metals to lower fractions. The solubilising heavy metals in the top soil may be migrating into the subsoil, except in cadmium, which was concentrated in the top soil. The soil of the entire sample area was sandy loamy soil with low concentration of organic matter. The cattle wastes released in the area might have relatively increased the organic matter content of the soil. Though, the topography of the area and the location of the cattle market, being sloppy and close to the river basin favoured the washing away of the top soil by run-off into the river and this might be responsible for the high organic matter in the subsoil. The pH of the soil of the area was slightly acidic to neutral.

The soil sample with high organic matter content has high metal concentrations in most cases except Cd, Pb, Cu and Cr. Generally, there is positive and significant correlation between the organic matter content versus Pb, Zn, Cu, Ni and Cr. There is variation in the concentrations of PAHs and organochlorine pesticides residues with depth around the river basin. The detection of banned organochlorine pesticides in the soil of the area could be attributed to both the historical use as well as recent use of these chemicals in the area. Thus, there is need for stricter regulations on banned chemicals to safe our environment from ubiquitous and persistent environmental pollutants.

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