CHAPTER ONE

INTRODUCTION

1.1 Background Information

The field of ecotoxicology particularly as related to the area of wildlife toxicology continues to be a rapidly developing discipline of wildlife and environmental management (Omonona *et al.,* 2014). Ecotoxicology, being a scientific field, combines the methods of ecology and toxicology in assessing the impacts of toxins and particularly contaminants on the ecosystem (Bhat, 2013). It pays attention to different impacts of environmental pollutants on diverse ecological systems including its components (consisting of plants, fish, wildlife, and so on). Ecotoxicological studies analyze the impacts of xenobiotics or anthropogenic chemicals on ecosystems at varying echelons of biological organization from the molecular and cellular level to the entirety of ecosystems. The existence ofxenobiotics within an ecological system therefore, often epitomizes threat on the entire biota (Bhat, 2013). An example of such xenobiotics within the ecosystem is heavy metal.

Heavy metal is a term that denotes any metallic element that possesses a relatively high density and may be toxic or poisonous even at low concentrations (Lenntech, 2004). They are naturally occurring elements, whose levels in different environments differ as a consequence of diverse anthropogenic actions (Pereira *et al.,* 2006). They have been linked with contamination as well as potential toxicity and eco-toxicity. They are ubiquitous in the environment and most of them have been found in different elemental forms and in a diversity of chemical compounds (Iwegbue *et al.,* 2008). Due to varying anthropogenic utilisation, heavy metals can cause environmental contamination and could be available for bio-magnification along the food chain. The distinguishing characteristic

of heavy metals is their strong attraction to biological tissues and in general their slow removal from biological systems (Nwani *et al.,* 2009). Generally, toxic impacts of heavy metals on the health of fauna species may include immunosuppression, reduction in fitness, interference in reproduction, oxidative stress damage, histopathological and behavioural alterations, and so on (Idowu *et al.,* 2014; Jubril *et al.,* 2016). Heavy metals exist in natural forms and also from anthropogenic origins within the environment with great distinctions in concentrations. Cadmium (Cd), Copper (Cu), Lead (Pb), Chromium (Cr), Zinc (Zn), Nickel (Ni), Mercury (Hg) and Arsenic (As) have been reported to be the most ubiquitous heavy metal contaminants while Pb, Cd, and Hg have been documented to be of utmost concern (Soewu *et al.,* 2014; Stankovic *et al.,* 2014).

The contamination of the environment with heavy metals is a major concern worldwide as it influences not just the functionality of an ecosystem but also its structural integrity (Qadir and Malik, 2009).National parks and other conservation areas cannot be left out, and can be influenced by contamination from outside their boundaries (Lester and van Riper III, 2014). Most of these conservation areas which were once located on the peripheries of cities and towns are now surrounded by human settlements, industries and other anthropogenic activities like vehicular traffic (Gupta, 2013). All these activities lead to environmental pollution and may undesirably affect the health and well-being of the wild animals domiciled in such protected areas. Heavy metals find their ways into organisms through ingestion, dermal contact absorption and direct inhalation, subsequently resulting in potential risk to wildlife (Sardar *et al.,* 2013). The consequences or impacts of heavy metal contamination on wild species are a great concern for wildlife toxicologists and to the field of conservation biology.

Environmental contaminants have been noted to be suspected contributors to global decline in wildlife population species across different taxa (Rai*et al.,* 2008). As such, there is an evident and growing public apprehension concerning environmental contamination. Many terrestrial and aquatic ecosystems, which accommodate wild populations, are frequently contaminated by heavy metal toxicants from sources such as agricultural fertilizers, pesticides and industrial effluents or waste discharges (Schleich *et al.,* 2010). These wastes could have high heavy metal levels and find their way into the ecosystem and subsequently concentrate in animal tissues, which is perilous to animals. Also, anthropogenic activities such as human settlements and agricultural practices within and around the boundary of wildlife habitats are threatening wild species (flora and fauna) with exposure to a variety of environmental contaminants (Gupta and Bakre, 2012a) and the wild animals domiciled within such habitats are at the risk of being exposed to these contaminants.

Xenobiotics or persistent pollutants bioaccumulation in living organisms subject to their position on the food chain is one of the most severe threats to species perpetuation, alongside habitat loss or alteration, pathogen spillover or diseases, climate change or stratospheric ozone depletion, and introduction of invasive or competitive species (Rai *et al.,* 2008).These factors have changed the physical and biological systems and is gradually becoming of increasing concern for the well-being and survival of many species (Hoffmann and Willi, 2008). In some cases, wild animal populations have experienced dire losses or even faced extinction as a result of environmental contamination. For instance, the bald eagle (*Haliaeetus leucocephalus*), peregrine falcon (*Falco peregrinus*), and brown pelican (*Pelecanus occidentalis*) almost went to being declared extinct before

scientists found out that the synthetic insecticide DDT (Dichlorodiphenyltrichloroethane) caused overwhelming reproductive alteration in these bird species (Carson, 1962). Detecting environmental intoxication through the accumulation of contaminants such as heavy metals and their impacts on wildlife is very vital for the assessment of environmental quality as well as to make headway in the comprehension of the tolerance aptitude of animal species to contamination (Sánchez-Chardi *et al.,* 2007).

Various methods have been used to evaluate and bring up a concentration profile of an array of contaminants that might impact wildlife habitats and their inhabitants (Gupta, 2012). Specifically, it is best advised to use a method of contamination assessment which is non-invasive and non-destructive so as not to stress the animals considering the nature of the study area. In other to achieve this, faecal samples were used as biological indicators to study wild animal exposure to heavy metals within Old Oyo National Park, Nigeria. Wild animal health is also dependent on plants (vegetation) and the abiotic components of the environment (water, soil, and air). When any of these is contaminated, there is high possibility of a resultant effect on wild animal health. Therefore, water, soil, plant and wild animals' faecal samples from the study area were investigated for heavy metals (as biomarkers of exposure) while soil and water quality parameters' assessment were also done. To the best of my literature search, very little or no known heavy metal evaluation and water quality assessment studies have been done in Old Oyo National Park.

1.2 Statement of Problem

Globally, wild animals are threatened by habitat destruction and degradation resulting from a multiplicity of factors comprising but not limited to agricultural intensification, urbanization, climate change and environmental contamination. Human disturbance, over-

exploitation of natural resources and invasive species are also significant threats. Environmental contamination is one of the principal ways by which humans have instigated sweeping alterations of wildlife habitat and as such, little thought was given to the ecological consequences of human actions. In light of this, wildlife species could be faced with a bewildering array of contaminants that humans discharge into the environment either by intent or accident or otherwise.

The existence of environmental contaminants such as heavy metals in biological species and in different echelon of the ecosystem, even at low levels, is not desirable as they may have toxic effects on these species. These effects have taken a toll on environmental health (Esteban and Castaño, 2009) especially on the fauna species within the ecosystem. Furthermore, an ample array of physiological and ecological effects of air, soil and water contaminants in animals have been reported and documented (Newman and Mcintosh, 1991). Persistent exposure to environmental contaminants even at very low levels have been averred to induce biochemical, histological and morphological changes in the tissues of animals (Kaoud and El-Dahshan, 2010). As such, the impact of heavy metals on the environment can be a staid risk to the stability of the wildlife ecosystem (Battaglia *et al.,* 2005).

1.3 Justification of the Study

Heavy metals have been reported to form the major contaminants within the environment (Pandey and Madhuri, 2014). In recent years, there has been significant attention given to the consequences of environmental contamination by eclectic variety of contaminants including heavy metals. Scientists have since begun to investigate the various impacts of heavy metals on the ecosystem as well as its inhabitants. The development of industry and

increase in automobile use, in addition to the almost unending over-intensive utilisation of different chemical compounds in agricultural production results to a consistent rise in the concentration of metals within the environment (Adie and Osibanjo, 2009; Yi *et al.,* 2011) with their non-biodegradability making them to easily accumulate to toxic levels.

Different investigations on a variety of wildlife have clearly revealed extensive contamination of soil, vegetation, water, fish, birds and mammalian species by heavy metals. These numerous studies on animals and environmental samples have provided strong evidences of the toxic potential of exposure to heavy metals (Iwegbue *et al.,* 2006a; Inuwa *et al.,* 2007; Bilal *et al.,* 2011; Gupta, 2012; Edward *et al.,* 2013). Also, documented reports of heavy metal levels in wild animals in both in-situ (Gupta and Bakre, 2012a, 2012b; Gupta, 2013) and ex-situ (Gupta and Bakre, 2012c; Gupta, 2013) conservation areas exist. These heavy metals are absorbed by plants and consequently, animals that graze on such contaminated plants and/or animals that drink from contaminated water also bioaccumulate such metals within their body system (Yahaya *et al.,* 2010). Moreover, anthropogenic activities such as fishing, grazing, logging, hunting, fire setting and mining within and around the boundary of wildlife habitats are thought and have been reported to contribute to the pollution load within wildlife habitats (Meduna *et al*., 2009; Akinyemi and Kayode, 2010; Gupta and Bakre, 2012a).

The Old Oyo National Park is being threatened by human activities through the emergence and encroachment by surrounding communities (Oladeji *et al.,* 2012a). Specifically, illegal and indiscriminate small-scale artisanal and mechanical mining activities around Old Oyo National Park (particularly around Sepeteri) is a significant threat and is a probable source of heavy metal contamination. Wild animals on free range

are also exposed to contaminants that are discharged by automobiles plying the roads that traverse the park particularly around Oyo-Ile range. Oladeji *et al*. (2012a) posited that local communities use various chemicals for fishing and hunting wildlife; and these have effects on wildlife population, distribution and their habitat. Also, metropolitan waste waters, run-off of pesticides, and industrial effluents or discharges find their way into tributaries and end up in larger water bodies (Dike *et al.,* 2004) that might be direct or indirect sources of water into Old Oyo National Park. Unprecedented human activities have been identified to generate environmental contaminants including heavy metals and their persistence as well as bioaccumulation within the biota is a concern. Metal distribution within the components of the environment (biotic and abiotic) needs to be critically investigated to accurately assess their influences on ecological systems (Ferreira, 2011). Therefore, assessing heavy metal levels within the biota provides information regarding their route of exposure, accumulation and possible toxicological effects (Torres and Johnson, 2001).

Environmental contamination has been regarded as one of the most severe threat to species perpetuation. As such, the diversity of wildlife species may be threatened due to exposure to environmental contaminants. The significance of the study arose from the intended goal of investigating the occurrence and concentrations of heavy metals within the study areas with a view to assessing the current state of probable contamination of the study areas and exposure to these contaminants. In so doing, the study will raise awareness or public concern regarding environmental contamination and this will enable researchers, experts and authorities of the study area to evaluate, monitor, manage and remediate ecological damage. Information provided by this study will also assist park

management in the better management of resources within the park. Also, the information elicited from this study will also help to enrich the available literature by expanding the knowledge and providing the background for further research and a policy brief on land use within and around the park.

1.4 Research Questions

1. What are the levels of heavy metals in water, soil, plant leaves, and wild animals' faecal samples within the Old Oyo National Park?
2. What are the concentrations of the selected physicochemical parameters in the water and soil samples within Old Oyo National Park?
3. Will seasonal variation have influence on the levels of heavy metals, physicochemical parameters (water and soil) and microbial characteristics (water) to be assessed?
4. What are the microbial characteristics of selected waterholes in Old Oyo National Park?
5. Are there any anthropogenic influence(s) on the concentrations of heavy metals and physicochemical parameters (of water and soil) in Old Oyo National Park?

1.5 Objectives of the Study

The objectives of the study are to:

1. evaluate the levels of heavy metals (Copper, Zinc, Chromium, Lead, Nickel, Cadmium, Iron and Manganese) in water, soil, plant leaves and wild animals' faecal samples in Oyo-Ile, Marguba and Tede ranges of Old Oyo National Park.
2. evaluate the physicochemical parameters of water (such as pH, temperature, total dissolved solids, electrical conductivity, total suspended solids, total solids, dissolved oxygen, nitrate, phosphate, sulphate, chloride, chemical oxygen demand

and biological oxygen demand and soil samples (such as particle size, pH, soil organic matter, soil organic carbon, soil nitrogen, exchangeable bases, exchangeable acidity, available phosphorus and conductivity) in Oyo-Ile, Marguba and Tede ranges of Old Oyo National Park.

3. evaluate the effects of seasonal variations on heavy metal concentrations, physicochemical (water and soil) and microbial (water) characteristics in Oyo-Ile, Marguba and Tede ranges of Old Oyo National Park.
4. investigate the total faecal coliform and fungi count in selected waterholes and faecal samples in Oyo-Ile, Marguba and Tede ranges of Old Oyo National Park.

1.6 Scope of the Study

The study covered only three ranges (out of five) in Old Oyo National Park. These are Oyo-Ile (located in the northern part of the park), Marguba (located in the center or heart of the park) and Tede (located in the southern part of the park). These ranges were purposively selected based on the availability of perennial waterholes and observed anthropogenic activities such as agriculture, charcoal production and mining activities. The study investigated the concentrations of heavy metals in waterholes (rivers), topsoil, plant (leaves) and wild animal faecal samples. Water quality (physico-chemical and microbial characteristics) as well as the level of selected soil physicochemical parameters were also examined. The results from laboratory analysis of the samples were compared with the appropriate standard permissible limits.

1.7 Research Hypothesis

1. There are no significant statistical differences in the levels of heavy metals in water, soil, plant and wild animals' faecal samples across the selected ranges of Old Oyo National Park.

2. There are no significant statistical differences in the physicochemical parameters (water and soil) and microbial characteristics (water) of samples in Old Oyo National Park.
3. There is no significant effect or influence of seasonal variation on heavy metals concentrations and physicochemical parameters (of water and soil) in Old Oyo National Park.
4. There is no significant difference in the most probable number (MPN) of total bacterial and fungal count in the selected waterholes of Old Oyo National Park.

CHAPTER TWO

LITERATURE REVIEW

2.1 Wildlife and Wildlife Management

Wildlife simply refers to any non-cultivated plant or non-domesticated animal and/or other organisms. The term describes all things that are living or existing outside the autonomous direct control of man (Favre, 2010). The Wildlife Society defined wildlife as "free-living animals of major significance to man". They comprise the innumerous varieties of wild plants, animals, fungi and other microorganisms that exist on earth. As such, the importance of wildlife to the environment cannot be over-emphasized. They are major part of nature which goes to a large extent in providing ecosystem stability and means of livelihood for varying categories of people in the world (Toyobo *et al.,* 2014). Indigenous peoples often use wildlife at sustainable levels for food, clothing, and shelter, and the animals play a large role in their culture and spiritual well-being (Decker *et al.,* 2001). Though, certain species of wildlife are being exterminated by natural influences, the ultimate danger to wildlife results from anthropogenic activities. Large scale poaching, illegal pastoral grazing, indiscriminate bush burning, illegal fishing and other anthropogenic activities are capable of degrading existing wildlife habitat (Oladeji *et al*., 2012a). Consequently, there is a clarion call for a proper and most effective management measures to be put in place for the conservation and survival of wildlife in their habitats.

Wildlife Management as specifically defined by Akegbejo-Samsons (1996) is the active manipulation of wild animals as well as their habitat to achieve a goal for the benefit of mankind. Ayodele *et al.* (1999) defined it as human decision and manipulation of wildlife. According to Singh (2005), it is the science and art of manipulation of structure, dynamics

and relations of the wild species, their habitats and the people involved with the purpose of achieving specific human set goals by means of wildlife resources. It also refers to the judicious utilisation of wildlife resources towards the accomplishment of scientific, ecological, economical, ethical, aesthetic and recreational objectives for the interest of man and for the improvement of nature, whereupon all the components of ecosystem depend. Furthermore, it attempts to strike a balance between the needs of wildlife with those of humans using the best available practice (Oyeleke *et al.,* 2015). Simply put again, wildlife management is the art and science of reaching set goals by managing and/or maintaining wildlife habitats and populations. In lieu of this, wildlife management has now become an integrated scientific discipline using other disciplines such as mathematics, chemistry, ecology, biology, climatology and geography to achieve best results. Over the years, anthropogenic activities have been the main reasons for loss of wildlife (Rai*et al.,* 2008). These include habitat degradation and destruction, over-exploitation, poaching, environmental contamination; and these threaten many flora and fauna species. Concerted attempts and efforts made to halt these threats have concentrated on creation of parks or game reserves (Kideghesho, 2006) where they can be properly managed.

Wildlife management is practiced so as to attain the goals of wildlife conservation which is the wise or rational use of wild lands, plants and animals and also includes all human exertions aimed at conserving wild animals and their habitat to save them from any form of threat or extinction. Some management practices have unknown consequences to wildlife and their habitats. For instance, according to Juffe-Bignoli *et al.* (2014), some management interferences can cause habitat degradation and become probable threats to

protected areas which include fire and fire suppression, dams and water management or use, fragmentation and isolation of protected areas in wider landscape. Subsequently therefore, it is expedient that wildlife management should be sustainably beneficial to wildlife.

2.1.1 Utilisation and Values of Wildlife

The utilization of wildlife is as old as man's existence itself. Reported and documented evidences have shown that man has been able to maintain himself successfully and survive for ages by hunting wildlife for food (Ayodele *et al.,* 1999). According to Onyeanusi (2004), there are consumptive and non-consumptive forms of wildlife utilisation. While the former has to do with direct consumption of wild flora and fauna species as a principal source of animal protein (bush meat), the latter deals with non-hunting or non-extractive use of wildlife which involves ecotourism and recreation. Due to the fact that it does not involve killing of the animals, it is designated as non-consumptive utilization. This type of interaction between wildlife and man has potential benefits for conservation especially when considering the long-term effect of changing attitudes towards wild animals and natural habitats (Duffus and Dearden, 1990).

The values, benefits and contributions resulting from the management of wildlife are quite high and the diversity of use arises from their economic, subsistence, recreational, scientific, aesthetic and heritage value, survival value and psychological uses as well as their ecosystem functions. According to Adewoye (2007), wildlife's contributions also include stabilizing hydrological systems; protecting soil; ensuring climate stability; conservation of renewable resources; protecting genetic resources; preserving breeding stocks; population reservoirs and biodiversity; maintaining the natural equilibrium of the environment; supporting tourism and recreation; creating employment opportunities and

providing facilities for research and education. However, regardless of all these numerous benefits, man's viciousness to animals remains strong and unrelenting, such that if not put under control, the survival of man himself is greatly endangered (Toyobo *et al.,* 2014).

2.1.2 Types of Wildlife Management

According to Omonona and Kayode (2011), there are two broad forms of wildlife management:

(a) *Manipulative Management* – this type of wildlife management acts specifically on a population, either changing its numbers via direct means or manipulating numbers by indirect means viz-a-vis altering food supply, habitat, density of predators, or prevalence of disease. This type of management is actually suitable when a population is to be harvested, or when it slides to an unacceptably low density or increases to an unacceptably high level.

(b) *Custodial Management*– this type of wildlife management is preventive or protective in nature. The principal aim is to abate external influences on the population and its habitat. It is appropriate in a protected area where one of its stated goals is to protect ecological processes. It is also appropriate for the conservation of threatened species where the threat is of external origin rather than being intrinsic to the system.

2.2 Wildlife Conservation

Conservation is a prelude to wildlife management and it plays a crucial role in the development of any given society (Ejidike and Ajayi, 2013). It is the management of human use of the biosphere so that it may yield the greatest sustainable benefits to the present generation while maintaining its potentials to meet the needs and aspirations of future generations (IUCN, 1980). It has ethical dimension because it tries to look ahead

and ensure that in meeting immediate human needs, it does not jeopardize those of the future. According to NNPS (2006), conservation refers to the maintenance of wildlife species at the optimum level that commensurate with other types of land use and human activities to ensure continued existence of wildlife for the benefit of the people. As such, the sustainable management of wildlife is fundamental to the conservation of the genetic resources in the ecological system. The scope of conservation is the entire biosphere which includes flora, fauna and the abiotic components of the environment.

Conservation is positive, embracing preservation, maintenance, sustainable utilization and the enhancement of the natural environment. The role that domestication plays in wildlife conservation cannot just be over-emphasized as it tends to divert attentions from the wild as this may be done under the intensive, semi-intensive and extensive systems. The goal of wildlife conservation is to make sure that nature will be available for future generations to enjoy, and to recognize the importance of wildlife and wilderness lands to humans. However, most of the conservation areas in the country have been plagued with recurrent social, ecological and management problems (Meduna *et al.,* 2009), which have diminished their values and utilization. In contemporary times, the "fines and fences approach" or "fortress conservation" (Brockington, 2002) is considered to have failed in its goals of conserving wildlife in the continent (Leader-Williams and Albon, 1988). Instead as an efficient alternative, integrated conservation and development projects (ICDPs) are being promoted and described as a leading example of a comprehensive initiative trying to link conservation and development (Brandon and Wells, 1992). The core values of this approach are shown in their description as "community-based programs, using participatory methods to concurrently empower rural inhabitants and

protect wild animal species (Kiss, 1990). Community-based conservation is regarded as a wildlife conservation effort that carries local communities along as an integral part of a wildlife conservation policy (Hackel, 1999). The main features of this method of conservation are that rural people partake in decision making and management of wildlife, and that they benefit financially from wildlife extractions **(**Metcalfe, 1995) and it is viewed as a better option to the more exclusionary protectionist strategies of the past, which frequently marginalized local communities from wildlife conservation efforts (Western and Wright, 1994).Under this arrangement, local communities are persuaded and won over in form of shared decision-making authority, job, revenue sharing, restricted harvesting of plant and animal species, or provision of facilities for the communities, such as dispensaries, schools, bore holes and roads, in order to get their support for wildlife conservation (Newmark and Hough, 2000). As such, programs that integrate ecological research, conservation, environmental education, income generation and capacity-building, are cost-effective tools that promote community-based biodiversity conservation and poverty reduction (Sekercioglu, 2011). In Nigeria, wildlife species conservation is maintained at the optimum level proportionate with other forms of land use in order to ensure the continued existence of wildlife for the purpose of their sustainable utilization for benefit of the people and this is among the objectives of national park services (NNPS, 2006).

2.2.1 Objectives of Wildlife Conservation

a. To protect the flora, fauna, water resources and archeological heritage if available in the area;

b. To maintain a very stable ecosystem with a high density of animal and plant communities for the sake of aesthetic, genetic conservation and environmental protection;
c. To improve the tourist attraction of the area for local and international demands vis-a-viz the conservation areas;
d. To develop the resources of the conservation areas for education, culture and scientific research;
e. To generate a rural development programme in which the local communities will participate fully and benefit from employment opportunities, increased amenities derivable from such a programme.

2.2.2Proposed Plan for Wildlife Conservation

Any wildlife policy that does not recognize the various needs of the people is most likely not to succeed. Therefore, this calls for a new approach for conservation of endangered species under the Decree No 11 of 1985 of Endangered Species Act. The following are the approaches proposed at that period:

a. Total preservation of endangered species Schedule I for national heritage and to ensure their recovery from possible extinction.
b. Conservation of other species in Schedule II and those that are not in Schedule II for bush meat production especially to enhance their protein intake in the rural areas by encouraging domestication through pilot scheme test of such animals.
c. Promotion of recreation and tourism development.
d. Rational exploitation on a sustainable basis for exportation of wildlife trophies.
e. Conservation for education, research and ecological diversity as well as stability of gene pool for ecological system.

2.3 Protected Area and Its Management

Protected area (PA) is an area of land and/or sea especially dedicated for the protection and maintenance of biological diversity and of natural and associated cultural resources, and managed through legal or other effective means (Dudley and Stolton, 2008). They are clearly defined geographical spaces, recognized, dedicated and managed, through legal or other effective means, to achieve the long-term conservation of nature with associated ecosystem services and cultural services (IUCN, 1980). In fact, they are believed to be refuges of tranquility and peace, where both wild species and human beings interact through biophysical environment and socio-cultural systems that are endowed. The natural serenity of protected areas along with communities of animals in them combine to make each a scenic niche destination (Ejidike, 2008).

The major threats affecting protected areas include poaching of wild animals, habitat encroachment through agricultural production, illegal grazing and urban expansion and development as well as logging and non-timber forest products' collection. Protected area management has achieved considerable success in the following fields: legal establishment, protected area design, resource inventory/assessment, boundary demarcation, and objective-setting (Lacerda, 2004). However, little management success has been recorded in the aspect of relating with local communities, management planning, monitoring and evaluation, law enforcement and budget security. Human-wildlife conflicts and lack of effectiveness in its control, dearth of farming and grazing land, and long-term rights were associated to negative behaviour towards protected area managers (Newmark *et al.,* 1993).

In Africa, the establishment of protected areas is a crucial strategy for wildlife conservation, which stipulates that any member of the adjoining communities who dares to encroach or hunt any animal in the conservation areas becomes immediately labelled a "poacher" and pays a stipulated fine if caught (Spierenburg and Wels, 2006). Protected area management is more successful where effectively planned conservation education and enlightenment programmes are fully connected to the management objectives of the protected area (Lacerda, 2004). The main purposes of management of protected areas include scientific research, wilderness protection, preservation of species and genetic diversity, maintenance of environmental services, protection of specific natural and cultural features, tourism and recreation, education, sustainable use of resources from natural ecosystems and the maintenance of cultural and traditional attributes (IUCN, 1980).

2.3.1 Categories of Protected Areas Management

According to the International Union for Conservation of Nature and Natural Resources (IUCN), there are six categories of protected areas management. They are:

Ia Strict Nature Reserves (SNR) –they are protected from virtually all human use with the intention of preserving all geological and geomorphological features of such regions and their biological diversity, which is usually dense and circumscribed exclusively to scientific monitoring, research or education. Sometimes, SNRs are of spiritual importance to surrounding communities wherein the people are generally permitted to continue the practice of their faith and may be directly involved in the area's conservation and management objectives.

Ib Wilderness Areas – they are often usually bigger than Strict Nature Reserves. The major objective of these areas is to provide an enabling environment wherein biodiversity

and ecosystem processes are permitted to flourish or experience restoration if hitherto disturbed by anthropogenic activities. Human use is restricted, often allowing only those who are willing to travel of their own volition rather than through established touristic activities. Wilderness areas can be categorized as such only if they are devoid of modern infrastructure, although they allow anthropogenic activities to the level of supporting indigenous groups living wilderness-based lifestyles. They are managed mainly for wilderness protection.

II National Parks – they provide protection for functioning ecosystems (similar to the objectives of Wilderness Areas), but tend to be more indulgent with human visitation and the supporting infrastructures. They are managed in such a way that may contribute to local economies via promoting educational and recreational tourism on a scale that will not limit the efficacy of conservation efforts. The support zone areas of a national park may be for consumptive or non-consumptive utilisation, but should nevertheless act as a stumbling block for the defense of the protected area's indigenous species and communities to enable them to remain sustainable in the long term.

III Natural Monuments – they are somewhat smaller areas, particularly allocated to protect a natural monument and its surrounding habitats. They can be natural in the whole sense, or include features that have been influenced or introduced by humans. The latter should hold biodiversity associations or could otherwise be categorized as a historical or spiritual site, although this peculiarity can be quite difficult to ascertain. As such, the classification then falls into two sub-categories; those in which the biodiversity in distinctively related to the conditions of the natural feature, and those in which the existing levels of biodiversity are reliant on the presence of the sacred sites that have formed a fundamentally modified ecosystem.

IV Habitat / Species Management Areas – they pay attention to more precise aspects of conservation in relation to an identifiable species or habitat that requires constant protection and/or management intervention. These protected areas will be satisfactorily controlled to make certain the maintenance, conservation and restoration of specific species and habitats - possibly through traditional means while public education of such areas is widely encouraged as part of the management objectives. Habitat or Species Management Areas may exist as a part of a broader ecosystem or protected area and may require different levels of active intervention including though not restricted to the prevention of poaching, establishment of artificial habitats, stopping natural succession and supplementary feeding practices.

V Protected Landscape / Seascape – they cover whole bodies of land or ocean which involve an array of profit activities within the management plan. The major goal is to safeguard regions that have developed a 'distinct character' in relation to their ecological, biological, cultural or scenic value. Protected Landscapes and Seascapes permit a higher level of sustainable interaction with surrounding communities (including traditional agricultural and forestry systems) and should represent a vital balance between humans and nature. They are managed mainly for the landscape / seascape conservation and recreation.

VI Managed Resource Protected Areas – these are protected areas managed mainly for the sustainable use of natural resources based on a mutually beneficial relationship between nature conservation and the sustainable management of natural resources in correspondence to the livelihoods of surrounding communities. A wide range of socio-economic factors are taken into consideration in creating local, regional and national approaches to the use of natural resources. Though human involvement is a large factor in

the management of these protected areas, developments are not intended to allow for wide scale industrial production. Examples of the categories of protected areas in Nigeria are shown in Table 2.1.

Table 2.1: Examples of Categories of Protected Areas in Nigeria

Categories	Type of Protected Area	Some Examples in Nigeria
Ia	Strict Nature Reserves (SNR)	Omo Biosphere Reserve, Bam Nzelzarma, Milliken Hill
Ib	Wilderness Area	
II	National Parks	Chad basin, Kainji Lake, Kamuku, Gashaka Gumti, Cross River, Okomu, Old Oyo
III	Natural Monuments	Museums of natural history,
IV	Habitat/Species Management Areas	National parks, game reserves, forest reserves
V	Protected landscape / Seascape	NF
VI	Managed Resource Protected Area	NF

Note: NF = Not Found

2.4 National Parks

A national park is a reserve of natural or semi-natural land, declared or owned by a government, set aside for human recreation and environmental recreation and protected from most development. National parks are normally understood to be managed by federal or national governments but in Australia, national parks are administered by state governments and predate the Federation of Australia.National parks are large natural or near natural areas set aside to protect large-scale ecological processes, along with the complement of species and ecosystems characteristic of the area, which also provide a foundation for environmentally and culturally compatible spiritual, scientific, educational, recreational and visitor opportunities (Hayati *et al.,* 2010). They are expected to play a crucial role in the preservation, conservation, protection and management of biodiversity (Mohammed *et al.,* 2013). The Yellowstone National Park is the first national park to be established in the world in 1872 by the United States of America while the largest national park in the world meeting the International Union for the Conservation of Nature (IUCN) definitions and criteria is the Northeast Greenland National Park which was established in the year 1974. In Africa, the Virunga National Park domiciled in the Democratic Republic of Congo is the first national park while the largest is the Mudumu National Park in Namibia with an area of 85,000 km^2. In Nigeria, the first national park to be established is the Kainji Lake National Park in 1979 while Gashaka-Gumti National Park is the largest national park and was established in 1991.

According to Bridgewater *et al.* (1996), the main objective of national parks is to protect natural biodiversity together with its underlying ecological structure and supporting environmental processes, and to promote education and recreation. National parks take

cognizance of the needs and activities of indigenous people and local communities, not excluding subsistence resource use, in as much as these will not negatively affect the primary management objective of the park (NNPS, 2006). Anthropogenic activities such as farming, fishing, grazing, logging, mining, hunting, non-timber forest product collection have been reported to be carried out within and outside the boundaries of national parks in Nigeria (Meduna *et al.,* 2009; Akinyemi and Kayode, 2010). Most often times, these activities are largely carried out in adjoining land to national parks due to the high fertility of the lands and presence of natural resources that support these activities (Nelson *et al*., 2003). The exploitation techniques adopted by local communities around these national parks are destructive and often unsustainable. In fact, Oladeji *et al*. (2012a) reported that local community members sometimes use chemicals for fishing, and poison-coated traps and guns for hunting. Consequently, these anthropogenic activities produce resultant direct or indirect effects that could be bioaccumulative in nature on wildlife health, population, distribution and their habitat.

2.4.1 Objectives and Functions of National Parks in Nigeria

a. The conservation of selective and representative samples of wildlife communities in Nigeria.
b. The establishment of an ecologically and geographically balanced network of protected areas under the jurisdiction and control of the federal government.
c. The protection of endangered species of wild plants and animals and their habitats.
d. The conservation of wildlife throughout Nigeria so that the abundance and diversity of their species are maintained at the optimum level commensurate with other forms of land use, in order to ensure the continued existence of wildlife for the purpose of their sustainable utilization for the benefit of the people.

e. The preservation of outstanding scenic, natural, scientific, recreational and other values in the National parks.
f. The protection and maintenance of crucial wetlands and water catchment areas.

The national parks in Nigeria and their respective locations are shown in Table 2.2.

Table 2.2: National Parks and their locations in Nigeria

Geo-political Zone	State	National Park	Ecological Zone	Area (sq.km)	Year
North East	Bornu	Chad basin	Sahel Savannah	2258	1991
North central	Niger, Kwara	Kainji Lake	Guinea Savannah	5382	1979
North Central	Kaduna	Kamuku	Guinea / Savannah	1121	1999
North Central	Adamawa	Gashaka Gumti	Guinea Savannah / Montane	6731	1991
South South	Cross River	Cross River	Rain Forest	4000	1991
South South	Edo	Okomu	Rain Forest	181	1999
South West	Oyo	Old Oyo	Forest/Guinea Savannah	2512	1991

Source: Adapted from Ejidike and Ajayi (2013); Mohammed *et al.* (2013)

2.4.2 Environmental Significance of National Parks in Nigeria

The environmental importance of national parks in Nigeria basks in the primary focus of the National Park Service of Nigeria, which is essentially to create an ecologically and geographically balanced network of protected areas under the control and prerogative of the Federal Government of Nigeria. The National Park Service is to ensure:

(a) Conservation of wildlife throughout the country so that the abundance and diversity of species are maintained at the optimum levels commensurate with the other forms of land use so as to ensure the continuous existence of wildlife for the purpose of their sustainable use for the benefit of the people;

(b) Preservation of outstanding scenic, natural, scientific, recreational and other values in the National Parks;

(c) Protection and maintenance of wetlands and water catchments areas of crucial significance;

(d) Implementation of relevant international treaties, agreements or other arrangements regarding, relating to, or connected with protected areas and wildlife management to which Nigeria is a party, provided they are conferred on the National Park Service by the Federal Government;

(e) The promotion and provision of wildlife education and nature conservation programmes;

(f) Conservation of biological diversity in Nigeria.

2.4.3 Challenges of National Parks in Nigeria

It is so dismal that the level of wildlife conservation or protection in most Nigeria's conservation areas is rather appalling because the approach is aimed at revenue generation

for the government. Drolet (1990) enumerated conservation challenges facing the National Park in the country, which still remains very active today:

i. A high population growth rate resulting in competition for space between different groups of users, such as the incessant conflict between the Fulani herdsmen and farmers across the country.
ii. Excessive harvest of wildlife by the subsistence and commercial hunters.
iii. Competition for water resources in semi-arid areas of the country, thereby threatening important wetlands used by migratory birds as wintering areas and vital subsistence farming economy.
iv. Inadequate knowledge (catalogue) of fauna and flora populations in the conservation areas as well as outside conservation areas.
v. Inadequate qualified manpower to monitor and manage conservation areas as well as insufficient government attention to conservation which emanates probably from inadequate conservation education or knowledge at all levels of government.
vi. Maladministration and corrupt practices which has led to diversion of funds meant for conservation by top officials.

2.5 Water Source and Pollution

Water covers about three-quarters of earth's surface and is an indispensable resource critical for the existence of all life forms. In addition to domestic uses, water is vital for agriculture, industry, fisheries and tourism, and so on. Almost (about 97%) all the water on earth is available in the seas and oceans with the remaining 3% being fresh water; 75% of which is sealed up in the polar ice caps and in glaciers and quite deep under the earth's surface as underground water. Most water available for use are always in the form of surface and ground water (Thurman *et al*., 1998). Water resources are under major stress

around the globe mainly due to various impacts of anthropogenic activities. In lieu of this, water pollution by anthropogenic activities render water unfit for animal and human consumption and recreational purposes. Water pollution may occur when rain water run-off from urban and industrial area and from agricultural land and mining operations finds its way to receiving waters (river, lake or ocean) and in to the ground (Kulshrestha *et al.,* 2004).

Water is often considered polluted if certain substances or conditions are present to such an extent that the water cannot be used for a specific purpose (Owa, 2013). That is, when the physical (colour, odour, turbidity, taste, temperature and electrical conductivity), chemical (carbonates, sulphates, chlorides, fluorides, nitrates, and metal ions) and biological (algae, fungi, viruses, protozoa and bacteria) parameters have reached beyond a specified concentration or level in water.

2.6 Water Quality

Water as a resource is very crucial for the existence of life and it is absolutely the most precious natural resource in existence (Abowei and George, 2009). It is an excellent universal solvent and is vital for the survival of living species not excluding humans. In fact, humans use water for various purposes such as drinking, agricultural and industrial processes, cooking, waste disposal and recreation (Masood *et al.,* 2015). Specifically, the elementsof river waters also relate to their water quality(Davies-Colleyand Wilcock 2004), which can strongly influence or constraincertain values and uses of river waters. While water plays a vital role in supporting human life and biological diversity, it also has an inordinate potential for transmitting diseases when contaminated (Yakasai *et al.,* 2004).

The significance of water as a resource is not merely applicable to its quantity and availability but to the quality as well, as it supports both terrestrial and aquatic species' existence. Hence, the quality of water is now a great concern for environmentalists as well as the public in all parts of the world (Mehari, 2013). The quality of water within an ecosystem gives salient information about the available resources for supporting life in that ecosystem (Ajibade *et al.,* 2008a). As far as wildlife management is concerned, the main objective of estimation of water quality criteria is to protect wildlife health in the environment. A general insight of water quality is that of a simple understanding that tells if water is contaminated or not. Indeed, water quality is a multifaceted concept in part because water is a complex medium intrinsically tied to the ecology of the earth. It is a measure of the condition of water relativeto the requirements of one or more biotic species and/ or to any human need or purpose (Johnson *et al.,* 1997).

The quality of water can be explained in terms of its physicochemical factors and biological characteristics (Diersing, 2009) and thus to its composition rather than its level, volume or flow which are collectively referred to as water quantity (Davies-Colley, 2013). That is, the physical, chemical and biological characteristics / parameters of water in relation to a set of standards (Garg *et al.,* 2008). Analysis of all these parameters is very necessary because their knowledge is very imperative to aquatic species and human health (Nazir *et al.,* 2015). Water quality in aquatic systems is significant because it maintains the ecological processes that support biological diversity. In fact, the maintenance of healthy aquatic ecosystem is reliant on its physicochemical properties and biological diversity (Venkatesharaju *et al.*, 2010). Changes in water quality can alter the whole ecosystem affecting all dependent flora and fauna species. According to Kolo (1996),

disparity in water qualities could be linked to or explained in terms of dominance of precipitation chemistry, bedrock chemistry or evaporation – crystallization process within the entire water body. In fact, the term water quality is occasionally extended to include biodiversity of waters and biological indicators of river condition or ecological health (Davies-Colley, 2013). It is mostly used by reference to a set of standards against which compliance are usually assessed. The most common standards used to assess water quality relate to drinking water, safety of human contact and for the health of ecosystems (Diersing, 2009). Water quality standards for surface waters vary significantly due to different environmental conditions, ecosystems, and intended human uses (Umunnakwe and Aharanwa, 2014). Furthermore, while some water quality variables relate directly to water composition (e.g. dissolved oxygen, nutrients), others relate only indirectly (e.g. conductivity, visual clarity) and one (temperature) is unaffected by water composition. Declining water quality due to environmental perturbations threatens the stability of the biotic integrity and therefore, hinders the ecosystem services and functions of aquatic ecosystems.

2.6.1. Physicochemical Characteristics of Water

The interactions of both the physical and chemical properties of water play a significant role in composition, abundance, movements and diversity of aquatic organisms (Deepak and Singh, 2014). These properties are responsible for the distribution of organisms in different fresh water habitats according to their adaptations, which allow them to survive in a specific habitat (Jeffries and Mills, 1990). The analysis of the physicochemical parameters of water is necessary to understand ecological and environmental pathways of aquatic resources (Patil *et al.,* 2012). Assessing the physicochemical characteristics of water is also essential because pollutants have been known to be affected by the

physicochemical characteristics of water (Singh *et al.,* 2006) and variations in their concentrations are suggestive of alterations in the condition of the water samples (Gulson *et al.,* 1997).

2.6.1.1 Temperature

Water temperature is one of the most vital physical characteristics of aquatic systems (Deas and Lowny, 2000). Temperature is a purely physical variable essentially unaffected by the composition of water. It is not related to water composition but nevertheless, it is usually considered as part of water quality because it so strongly affects chemical and biochemical equilibrium and reaction rates in water affecting dissolved oxygen solubility in water and rates of dissolved oxygen consumption by respiration (Davies-Colley, 2013). Generally, water temperature affects the capacity of water to hold oxygen, the rate of photosynthesis and the metabolic rates of organisms in water (Garg *et al.,* 2008). As water temperature rises, the rate of photosynthesis increases thereby providing adequate amounts of nutrients (Boulton, 2012).

Also, increase in temperature actually lowers the amount of dissolved oxygen (DO), increase biochemical oxygen demand (BOD), accelerates the nitrification and oxidation of ammonia to nitrates (III) and (V) which eventually lead to oxygen deficit in water (Samuel *et al.,* 2015). Higher temperature also increases the toxicity of several substances (pesticides, heavy metals) and susceptibility of organisms to toxicants (Samuel *et al.,* 2015). Temperature of water is therefore undoubtedly the most significant environmental variable since it impacts metabolic activities, growth, feeding, reproduction, distribution and migratory behaviours of aquatic organisms (Suski *et al*., 2006).

2.6.1.2 pH

The pH is a term used to designate the alkalinity or acidity of a substance as ranked on a scale from 1.0 to 14.0. It is a degree of acid-base equilibrium achieved by water dissolved compounds as well as extent of flocculation and coagulation process of chemicals. The balance of positive hydrogen ions (H^+) and negative hydroxide ions (OH^-) in water determines how acidic or basic the water is. A pH indicates the contamination and acidification in a natural water system (Palaniappan *et al.,* 2010). It is one of the most vital water quality parameters. In fact, extremes of pH can affect the taste of water but the eroding effect on distribution systems is a more urgent problem (IEPA, 2001). It is most paramount in determining the corrosive nature of water. The lower the pH value, the higher is the corrosive nature of water. The pH of water determines the solubility and availability of nutrients and heavy metals. The pH has also been reported to be positively correlated with electrical conductance and total alkalinity (Gupta *et al.,* 2009).

2.6.1.3 Electrical Conductivity (EC)

Electrical conductivity is the normalized degree of the ability of water to pass an electrical current. This capability depends on the presence of ions, their total concentration, mobility, valence, relative concentrations and temperature of measurement (SIT, 2008). It reflects the total ionic content or the total quantity of dissolved ions in the water (Davies-Colley, 2013). Its SI derived unit is the siemens per meter, (mS/cm or μS/cm). It gives a hint about the level of electrolytes in water and is the limiting factor. Electrical conductivity (EC) which is a measure of water's ability to conduct an electric current is related to the amount of dissolved minerals in water, but it does not give an indication of which element is present but higher value of EC is a good indicator of the presence of contaminants such as sodium, potassium, chloride or sulphate (Nazir *et al.,* 2015). Also, if

the conductivity of a river suddenly rises, it means that there is a source of dissolved ions in the locale.

EC is considered to be a rapid and good measure of dissolved solids. EC measurements are used routinely in several industrial and environmental applications as a fast, inexpensive and reliable way of measuring the ionic content in a solution (Gray, 2005). The higher the values of dissolved solids, the more the number of ions in water (Bhatt *et al.,* 1999). EC depends on the occurrence of ions (cations and anions) in water, their total level, mobility and valence, and on water temperature. Field measurements of EC reflect the amount of total dissolved solids (TDS) in natural waters (Ugwu and Wakawa, 2012). Electrical Conductivity has been reported to have a weighty correlation with some parameters including temperature, pH value, alkalinity, total hardness, calcium, total solids, chemical oxygen demand, chloride and iron concentration of water and total dissolved solids (Patil *et al.,* 2012).

2.6.1.4 Total Dissolved Solids (TDS)

Total Dissolved Solids describes the measurement of all solids including inorganic salts, organic matter and other dissolved materials in water (USEPA, 1986). It conveys a typical taste to water and lowers its potability.Total Dissolve Solids (TDS) levels indicate the overall nature of water salinity. It also connotes the inorganic pollution load of an aquatic body (Usha *et al.,* 2008). Generally, it is used to assess the quality of freshwater systems.

2.6.1.5 Total Suspended Solids (TSS)

Total Suspended Solids (TSS) refers to a direct measure of the organic solids with mineral particulate content of river water (Davies-Colley *et al.,* 2011) and it is probably of most concern as regards sedimentation. The relative cost of TSS analysis is high comparable

with cheap optical correlates (visual clarity, turbidity) making it a costly option in routine, indefinite monitoring (McBride *et al.,* 2013). The TSS is also referred to as the substance that cannot pass through a 45 μm diameter filter. The TSS and TDS can be influenced by changes in pH levels. Variations in pH may cause some solutes to precipitate or probably affect the solubility of the suspended mater (Bellingham, 2012).

2.6.1.6 Dissolved Oxygen (DO)

Dissolved Oxygen is one of the most vital water quality parameters which indicates the amount of oxygen present, dissolved or carried in water and critical to all forms of aquatic life including the organisms that break down man-made pollutants (Francis-Floyd, 1993). It is a critical water quality parameter which indicates the health of an aquatic system and determines the distribution of aquatic organisms (Hussain *et al.,* 2013). It gets there by diffusion from the surrounding air, and as a waste product of photosynthesis. Due to the contamination and pollution (like sewage), average concentration of DO decreases. Generally, fast moving water has more dissolved oxygen than slow or stagnant water and colder water contains more dissolved oxygen than warmer water. Also, their concentrations in water tend to decrease as temperature of the water increases (Eze and Ogbaran, 2010).

According to Samuel *et al.* (2015), the maximum quantity of oxygen in clean water is approximately 9 mg/dm^3. Continued exposure to low dissolved oxygen levels (less than 5 to 6 mg/dm^3 oxygen) may not directly kill an aquatic life but will increase its predisposition to other environmental stresses. Exposure to less than 30% saturation (less than 2 mg/dm3 oxygen) for one to four days may kill most of the aquatic organism in a system.The dissolved oxygen is vital in the natural self-purification capacity of water (Zeb

et al., 2011). Quite a number of factors define the DO levels in water including water temperature, which has inverse relationship with DO, photosynthesis by green algae, salinity and pollution ensuing from both natural and human activities (Iqbal *et al.,* 2004).

2.6.1.7 Biological Oxygen Demand (BOD)

Biochemical Oxygen Demand (BOD) is a measure of the amount of oxygen that bacteria will consume while decomposing organic matter under aerobic conditions (Perry and Vanderklien, 1997). It is the amount of dissolved oxygen required for the biochemical decomposition of organic compounds and the oxidation of certain inorganic materials (e.g., iron, sulfites). It is also frequently used as an estimation of pollutants in natural and waste waters and to evaluate the strength of waste, such as sewage and industrial effluent waters (Zeb *et al.,* 2011). BOD is the most ubiquitously used parameter for evaluating the oxygen demand on the receiving water of a municipal or industrial discharge. Its usefulness is also seen in evaluation of the efficiency of treatment processes, and it is an indirect measure of biodegradable organic compounds in water. BOD is also a significant parameter of water reflecting the health scenario of freshwater bodies (Bhatti and Latif, 2011). A high BOD is a clear indication of poor water quality. The lower the BOD, the lesser the organic matter present in water.

A high BOD is sometimes accompanied by a low DO level (Samuel *et al.,* 2015) because the oxygen that is available in the water is being consumed by the bacteria leading to the inability of fish and other aquatic organisms to survive in the river. Uncontaminated natural waters are expected to have a BOD of 5 mg/l or less, and there are no direct health implications for BOD, but an important indicator of overall water quality (Oyhakilome*et al.,* 2012).

2.6.1.8 Chemical Oxygen Demand (COD)

The Chemical Oxygen Demand is another measure of organic material contamination in water specified in mg/l. It is the amount of dissolved oxygen required to cause chemical oxidation of the organic material in water. Both the BOD as well as COD are crucial indicators of the environmental health of a surface water. COD is commonly used in waste water treatment but hardly in general water treatment. Chemical Oxygen Demand indicates the quantity of organic pollutants in water. It estimates the oxygen demand created by toxic organic and inorganic compounds as well as by biodegradable substances (Sawyer *et al*., 1994). The Chemical Oxygen Demand and some other parameters used in the classification of surface water quality are shown in Table 2.3.

Table 2.3: Some parameters used in classification of surface water quality

Parameters	Class I	Class II	Class III	Class IV	Class V
pH	6.5-8.0	6.0 - 8.4	5.0 - 9.0	3.9 - 10.1	<3.9 - >10.1
DO (mg/l)	7.8	6.2	4.6	1.8	<1.8
BOD (mg/l)	1.5	3.0	6.0	12.0	>12.0
COD (mg/l)	10	20	40	80	>80
TSS (mg/l)	20	40	100	278	>278

Class I = excellent quality; Class II = acceptable quality; Class III = slightly polluted;

Class IV = polluted; Class V = heavily polluted.

Source: Adapted from Aiyesanmi *et al*. (2006).

2.6.1.9 Total Nitrate

Nitrate (NO_3^-) exists in water naturally as a result of plant or animal material decomposition, and can also be introduced into water as a result of anthropogenic activities, e.g. in food production where it is used as a preservative; use of agricultural fertilizers and manure; disposal of domestic and industrial sewage (Dimowo, 2013). Nitrate is a key constituent of agricultural fertilizers and is important for crop production. It stimulates the growth of phytoplankton and waterweeds that serve as food for aquatic organisms but simultaneously, they make up for the nutrient load in water, leading to eutrophication which in turn pollutes the water bodies (Ani *et al.,* 2016). The nitrate itself is not a direct toxicant but is a health hazard because of its conversion to nitrite, which reacts with blood haemoglobin to cause methaemoglobinaemia, also known as "blue baby syndrome" (WHO, 2008). Nitrite is very toxic to aquatic living organisms; the toxicity elicits from impairment of oxygen transport and cause acute anorexia, loss of equilibrium and mortality (Palachek and Tomasso, 1984).

Nitrate concentration depends on the activity of nitrifying bacteria which in turn get influenced by the presence of dissolved oxygen. It also indicates the probable occurrence of other more severe residential or agricultural contaminations such as bacteria or pesticide. The nitrate concentration in surface water is normally low, but can reach high levels from agricultural runoff, or from contamination by human or animal wastes (CCME, 2009). Jaji *et al.* (2007) posited that low amount of nitrate is an indication of unpolluted natural waters. Nitrate levels over 10 mg/l in natural waters normally indicate man-made pollution.

2.6.1.10 Total Phosphate

Phosphates (PO_4^{3-}) exists as a free ion in water systems and as a salt in terrestrial environments often used in detergents as water softeners (Turner Designs, 2012). They can be found in organic form (organically-bound phosphates) or inorganic form [including orthophosphates and polyphosphates] (Dimowo, 2013). Man-made sources of phosphate in the environment include domestic and industrial discharges, agricultural runoff where fertilizers are used and changes in land use in areas where phosphorous is naturally abundant in the soil (Ugwu and Wakawa, 2012). In general, natural dissolved phosphates are considered to be largely non-toxic, although certain man-made organophosphates do have toxic effects. It is, however, likely that high concentrations of dissolved phosphate may lead to osmotic stress, as is the case with high nitrate concentrations.

2.6.1.11 Total Sulphate

Sulphates (SO_4^{2-}) are one of the least toxic anions and high amounts would have to be consumed in order for health disorders to occur (especially diarrhoea type symptoms). The availability of sulphate in water can result in obvious unpleasant taste. Also, waters with higher concentration of sulphate may cause intestinal disorders. Nitrate, phosphate and sulfate are important parameters of river water showing the pollution status and anthropogenic load in river water (Khan and Khan, 1997). Sulphates are found in virtually all-natural water bodies with their concentrations varying based on the nature of the terrain through which they navigate. There is a dearth of health-based guideline proposed for sulphate although its presence in drinking-water can cause noticeable taste, and very high levels might cause a laxative effect especially with the presence of magnesium and sodium.

2.6.1.12 Total Chloride

Chloride (Cl^-) is a common aqueous anion found in all-natural waters. Their concentrations often differ and reaching a maximum in sea water (Oyhakilome *et al.,* 2012). In fresh waters, the sources of chloride include soil and rock formations and waste discharges (Aiyesanmi *et al.,* 2006). Natural levels of chloride in most fresh waters are often in the broad range of 15-35 mg/l (Oyhakilome *et al.,* 2012). High concentration of chloride is considered to be the indicator of pollution due to organic wastes of animal origin, regarded harmful to aquatic life and troublesome in irrigation water (Rajkumar *et al.,* 2004).

2.6.1.13 Total hardness

Hardness is often chemically defined as the sum of polyvalent cation concentrations dissolved in water. In fresh waters, the principal hardness-causing ions are Calcium and Magnesium; Strontium, Iron, Barium and Manganese ions also contribute (USEPA, 1976). Total hardness is a parameter of water quality used to describe the effect of dissolved mineral (Ca^{2+} and $Mg^{2+)}$, determining solubility of water for domestic, industrial and drinking purpose attributed to presence of bicarbonates, sulphate, chloride and nitrates of calcium and magnesium (Arya and Gupter, 2013). There is evidence that hard water plays a role in heart diseases. Higher concentration of Mg makes the water unpalatable and act as laxative to human beings (Preeti *et al.,* 2009).

2.6.2 Microbial Characteristics of Water

The presence of microbial pathogens in water poses a considerable health risk to animal and human health. Microbial pathogens that commonly occur in water can be divided into four separate groups. These groups are the viruses, bacteria, pathogenic protozoa and pathogenic helminthes (Igbinosa *et al.,* 2012). The majority of these pathogens are enteric

in origin, that is, they are excreted in faecal matter which contaminates the environment, and then gain access to new hosts through ingestion (Toze, 1999). Different microbial pathogens have different infectious doses. Most enteric viruses and protozoa usually require only ten or less infectious particles or cysts to cause infection. Thus, determination of the numbers of different microbial pathogens in a water or wastewater sample is imperative.

The Total Coliform (TC) and Faecal Coliform (FC) have traditionally been regarded as indicators of microbial contamination of waters (Rompre *et al*., 2002) while *E. coli* have been reported to be the best indicator for the assessment of faecal contamination (Davies-Colley *et al.,* 2008) and the possible presence of enteric pathogens (USEPA, 2002). Faecal coliform is the bacteria which can be found in the intestines of warm-blooded animals (APHA, 1998). They do not cause diseases but are used as an indicator of disease-causing pathogens in the aquatic environment while total coliform refers to the large collection of different bacteria (Bakobie *et al.,* 2015).

The presence of coliform bacteria is an indication of microbial contamination that can lead to water-borne disease burden in the surrounding local communities. The direct public health impact, and possible socio-economic effects that may result from ingesting coliform-infested water, may be far more disastrous on an already vulnerable and predominantly poor population (Cobbina *et al.,* 2009). The most commonly employed method for the detection of total and faecal coliforms in water are multiple tube fermentation (MTF) technique and membrane filtration technique. Microbiological analysis is carried out in-situ so that the microbiological parameters would not change with time.

2.6.3 Anthropogenic activities and their Effects on Water Quality

Humans have engaged in different activities to ensure their continuous survival. Activities such as farming, fishing, grazing, hunting, charcoal production, logging, mining, and so on, have direct and / or indirect effects on water quality with a resultant impact on wildlife health.

2.6.3.1Agriculture

Agricultural pollution can originate from either a point source (e.g. from a slurry store) or diffusely (e.g. run-off from larger areas of farmland).While agriculture is deemed to be a significant factor in many catchments, there is no single management practice that is the main cause of rivers and groundwater containing too many nutrients, pesticides, microbiological pollutants or silt. Agricultural practices may include arable farming, tree crop and cash crop farming, and animal husbandry. These various practices have varying degrees of effects on the environment. Agriculture may affect water quality directly and indirectly. Direct impacts include soil, nutrients and pesticides being transferred from fields to watercourses during rainfall events. An example of an indirect impact might be related to upland drainage designed to improve grassland (Holden *et al.,* 2006).

The effect of land use on rivers' water quality is scale-dependent and differs with time and space. Upstream land use may affect the water quality of large streams, while land use close to small streams may affect water quality in smaller streams (Buck *et al.,* 2004). Dairy milking platforms were estimated to contribute a greater proportion of catchment nitrogen loads than the area other farms types occupy in the catchment (Monaghan *et al*., 2007). Also, near-field agricultural development strongly affects water quality in rivers than far-field agricultural development. The presence of a riparian buffer zone between

streams and agricultural lands is a significant factor in reducing contamination from non-point source loading. Although the preservation of riparian habitat can reduce non-point source pollution, it will not eliminate all water pollutants resulting from agricultural development (Tran *et al.,* 2010). Forest buffer zones have positive impact in reducing the effect of agricultural chemicals and nutrients on surface stream waters (Anbumozhi *et al.,* 2005).

2.6.3.2Grazing

Run-off from pastoral land degrades water quality throughout the world. Under intensive farming practices where inputs, nutrient recycling rates and stocking densities are high, runoff significantly pollutes surface water. Research work has found out that nutrients, sediments and faecal bacteria from soil to water through runoff are major pollutants from pastoral farming (Monaghan *et al.,* 2007; Ajibade *et al.,* 2008b). Faecal contamination can be primarily from agriculture and secondarily from wild animals. Domestic animal species, variations in climatic conditions (rainfall), drainage pattern, stock density and other anthropogenic interferences are directly or indirectly related to faecal contamination. There is a direct link between meteorological conditions and microbial water quality of a river. When there is high rainfall and floods, it is likely to result in a greater incidence of pathogen loads (Nnane *et. al*., 2011). Grazed watershed had extreme case for faecal contamination of surface waters (Fisher *et. al*., 2000). Irrigated water runoff from dairy farming contributed greatly to water quality degradation (high concentrations of E. coli, suspended solids, Nitrogen and Phosphorus) than non-irrigated lands (Monaghan *et al*., 2009). In order to reduce losses of nutrients and faecal indicator organisms to waterways, nitrification should be used in farm managements. This would result in consistent reduction of nutrient losses.

2.6.3.3Logging

Forest removal causes increased stream nutrients and sediment, more variable flow, changed habitat, stream and riparian communities (Nagy *et al.,* 2011). Logging activities affect temperature (Rak *et al.,* 2011), total phosphorus (Glaz *et al.,* 2015) conductivity, Dissolved Oxygen (DO), pH, turbidity and salinity but selective logging management system showed minimum impacts than traditional non selective logging management system (Steedman *et al.,* 2001).

2.6.3.4Mining

The impact of mining activity (surface or underground) on the environment cannot be overemphasized and is of great concern, especially due to acidification of surface water bodies. Mining requires complex planning that takes into account the specificity of techniques and characteristics of the affected environment (Lee, 2003). The main activities of mining (exploration, development, extraction, concentration, processing, refinement and deactivation) and waste disposal practices have a variety of impacts, which may include soil damage, air pollution and water contamination (McAllister and Milioli, 2000).

2.6.4 Water Quality Monitoring

The International Organization for Standardization defined monitoring as the programmed course of sampling, measurement and subsequent recording or signaling, or both, of different water properties, often with the aim of evaluating conformity to set objectives. Bellingham (2012) posited that to mitigate anthropogenic impacts on natural aquatic bodies, it has become highly pertinent to implement a holistic monitoring programme which will measure quality of water, ascertain impairments and enable policy makers to choose land use assessments that will preserve and conserve natural areas, and enhance quality of life. As such, water quality monitoring can provide future management

approach that can be espoused by any authority. In fact, information on river water quality and streams will adequately afford a suitable mechanism for policy makers to formulate management strategies for control of water contamination (Lohdip, 2013). The objectives of water quality monitoring include:

a) To characterize waters and identify changes or trends in water quality over time.
b) To identify specific existing or emerging water quality problems.
c) To gather information to design specific pollution prevention or remediation programmes.
d) To determine whether program goals such as compliance with pollution regulations or implementation of effective pollution control actions are being met.
e) To respond to emergencies, such as spills and floods.

2.7 Toxicology

Toxicology can be seen as the study of harmful effects of chemical substances on biological systems. It is that branch of science that deals with poisons, and a poison can be either by accident or design, to a living organism which by convention includes the study of harmful effects caused by physical phenomena, such as radiation of various kinds and noise (Hodgson, 2004)**.** Toxicology tries to address a variety of questions. For example, in agricultural production, toxicology examines the probable health impacts from exposure to pesticides or herbicides, or the impact of animal feed additives, such as growth factors, on non-target species. Toxicological work is also carried out in laboratories on animal species to establish dose-response relationships. Toxicological and occupational studies concerning pesticides and heavy metals have advanced our knowledge on their dangerous properties and their environmental impacts.

2.8 Ecotoxicology

Ecotoxicology refers to the study of effects of pollutants or contaminants on the structural integrity and functionality of ecological systems (Leblanc, 2017). Being a scientific discipline, it combines the various methods of ecology and toxicology in assessing the impacts of toxic substances and especially pollutants on the environment. It evaluates the effects of contaminants including pesticides, heavy metals, etc. on populations, individuals, natural communities, and ecosystems. It also analyses the impacts of anthropogenic chemicals on natural ecosystems at varying echelons of biological organisation, from the molecular and cellular level to whole ecosystems (Newman and Unger, 2003). Furthermore, one of the key roles of ecotoxicology is to comprehend the mechanisms by which contaminants disturb the natural biological performance and their mode of action, so as to devise apposite measures to prevent adverse impacts of environmental contaminants. According to Bhat (2013), there is a wide range of possible contaminant effects that can compromise the ecological fitness of individual organisms or populations. Ultimately, the impact of a toxic contaminant or contaminant mixture depends on the relative sensitivity of a species, community or ecosystem, and the intensity and timing of exposure. Therefore, ecotoxicology faces the challenge of predicting and assessing the effects of increasing number of chemical stressors on species and ecosystems (Filser *et al.,* 2008).

2.9 Environmental Contaminants and their Effects

The environment plays a key role by forming a habitat for animals and humans. The concept of environment is often used with a broad scope and this includes not just the physical space but also all the non-genetic factors such as diet, lifestyle and infectious agents (Tomatis, 1990). Chemical contamination of the environment is a pervasive,

insidious side effect of human population growth and technological development. The environment has been polluted by natural activities: such as volcanic eruption (on land and in the deep sea), weathering and erosion, and human activities such as tobacco smoking, mining, smelting and refining of metals, fossil fuel combustion, incineration of municipal wastes, manufacture of phosphate fertilizers, vehicle emissions (Herawati *et al*., 2000). These activities have been reported to induce changes in the environment by releasing pollutants such as heavy metals, effluents from industries, agricultural chemicals and vehicle emissions into the environment and these have been noted to cause some health problems. Some of the health problems associated with exposure to these pollutants include immunosuppression, increase incidence of disease, cancers and also physical deformities such as teratogenic abnormalities like extra or missing limbs in frogs, and other birth defects.

2.10 Wildlife Exposure to Environmental Contaminants

Environmental contamination can be referred to as the anthropogenic alteration of chemical or physical characteristics of the environment to an extent that is detrimental to living organisms. Some forms of environmental contamination exert a damaging impact on wildlife by killing or impairing the health of individual species. Environmental contamination has been reported to have elicited from urbanization, industrialization, technology, and other factors such as population explosion and mechanized agriculture that served to provide the necessities of humans (Ezemonye and Kadiri, 2000). It is one of the most disturbing ecological problems facing the developing world currently particularly in developing countries where it is more serious and dire as a result of large amounts of pollution load eliciting from anthropogenic activities (Nighat *et al.,* 2013). The impact of this contamination from industrial effluents and automobile exhausts within the

environment (both aquatic and terrestrial) has probably reached a level of concern that cannot just be overemphasized. As such, the effects of contamination are seen not only at organismal and local levels, but at levels of biotic communities, ecosystems and regions emanating from diffuse sources of contamination.

The use of wildlife (flora or fauna) as monitors of environmental contamination presents important information about the impacts of the contaminants on these species and also on the human species (Maria *et al.,* 1996). As such, their use as sentinels can provide appropriate remarkable information as regards environmental monitoring (Perez-Lopez *et al.,* 2008). Environmental contaminants have been a concern to ecosystem health due to their relatively high concentrations and ability to bioaccumulate and biomagnify within the biota (Azimi *et al.,* 2003). Exposure to certain environmental contaminants, especially neurotoxicants can promote the expression or suppression of behaviors, affect performance and cause instability in the normal biological functioning of animals. The presence of environmental contaminants (like heavy metals) might generate cataclysmic effects on the ecosystems they are released in, including the local extinction of certain species (Ratcliffe, 1967). In lieu of this, environmental contaminants have been indicted to be suspected contributors to global wildlife decline (Beebee and Griffiths, 2005).

2.11 Heavy Metals

2.11.1 Definition and Concept of heavy metals

Heavy metal is the generic term for metallic elements having an atomic weight higher than 40.04 (Ming-Ho, 2005). That is, they are by definition metals having densities higher than 5 $gmL^{-1}$and are of toxicological importance (Jarup, 2003). Heavy metals are ubiquitous and constitute a very heterogeneous group of elements widely varied in their chemical

properties and biological functions. They are classified based on density, atomic weight and chemical toxicity in relation to living organisms. An alternative term to heavy metals is 'toxic metals' of which no consensus of exact definition exists though some literatures have defined it as which is neither essential nor has any beneficial effect. They are non-degradable, persistent environmental contaminants, have bioaccumulative effect and are of special concern (Duruibe *et al.,* 2007; Ipingbemi, 2009). Approximately fifty-three of the ninety naturally occurring elements are called heavy metals. In fact, they are archetypal to maintaining diverse physiological and biochemical functions though they may become toxic when they exceed certain threshold concentrations (Jaishankar *et al.,* 2014). Heavy metals like copper (Cu), iron (Fe) and zinc (Zn) are essential for animal metabolism because they play a crucial role in the normal biological functioning of cells (Flora *et al.,* 2008), while others such as mercury (Hg), cadmium (Cd), arsenic (As) and lead (Pb) have no known role in biological systems (Schmitt *et al.,* 2005; Has-Schon *et al.,* 2007). Heavy metals including both essential and non-essential elements have a precise implication in ecotoxicology since they are highly persistent and all have the potential to be toxic to living organisms (Storelli *et al.,* 2005). The eight most common pollutant heavy metals as listed by the Environment Protection Agency (EPA) are: Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Mercury (Hg), Nickel (Ni), Lead (Pb), and Zinc (Zn) (Athar and Vohora, 2001). Heavy metals are kept under environmental pollutant category due to their toxic effects on plants, animals and humans. They have direct physiologically toxic effects when stored or incorporated in living tissues (Baykov *et al.,* 1996).

Heavy metals are distinguished for their varied environmental dispersion from both natural and anthropogenic activities. Their tendency to accumulate in tissues of the animal

body and their overall potential to be toxic even at relatively minor levels of exposure is one of their characteristic features (Nwani *et al.,* 2009). Within the aquatic system, studies have shown that bioaccumulation / biomagnification of heavy metals in a tissue of aquatic organism is mainly dependent on water concentrations of metals and exposure period although some other environmental factors such as salinity, pH, hardness and temperature play significant roles in metal accumulation (Jeffree *et al.,* 2006; Singh *et al.,* 2006; Has-Schon *et al.,* 2007). Ecological needs, size and age of individuals, their life cycle and life history, feeding habits and the season of capture have also been implicated in tissue accumulation of heavy metals (Kime *et al.,* 1996; Rurangwa *et al.,* 1998).

2.11.2 Sources of Heavy metals

Heavy metals are often very ubiquitous in the environment emanating from various sources (Don-Pedro *et al.,* 2004). Wild animals are generally often exposed to basal levels of heavy metals within their natural habitats. Lester and van Riper III (2014) reported that contaminants, such as heavy metals originate from a variety of point sources. The sources of toxic heavy metals to wildlife in the environment could be traced to both natural and anthropogenic sources (Olomukoro and Ezemonye, 2007). Anthropogenic sources of heavy metal contamination include those associated with fossil fuel and coal combustion (e.g Pb, Hg, Ni, Sn, Cd, As, Sb), manufacturing processes, industrial effluents and products (Cd, Cr, Cu, Ni, As, Pb and Zn), solid waste disposal (e.g. Cd, Cu, Cr, Pb, Hg, Ni, Zn), automobile exhaust (e.g. Pb, Cd), fertilizers (e.g. As, Cr, Pb, Hg, Ni, V), and mining and metal processing (e.g. Pb, Hg,). All these sources produce heavy metals that end-up in plant and animal species within the environment (Golden *et al.,* 2003) accumulating in vital body tissues and organs due to their persistence. For instance, Duruibe *et al.* (2007) reported that long after mining activities might have ceased, emitted

heavy metals continue to persist in the environment in some cases. Heavy metals are undeniably inherent natural constituents of the environment (Edward *et al.,* 2013). Natural sources of contamination include volcanic activities, weathering of mineral deposits, brush burning, windblown dusts and biogeochemical systems (Adriano, 2001). Contamination with heavy metals is a serious threat to wildlife due to their toxicity, bioaccumulation and biomagnification within the food chain (Demirezen and Uruc, 2006).

2.11.3 Categories of Heavy metals

Heavy metals can be classified based on their health importance (Reeves and Baker, 2000; Blaylock and Huang, 2000). Copper, zinc, cobalt, chromium, manganese and iron are essential and also called micronutrients but are toxic when taken in excess of requirements. Barium, lithium and zirconium are non – essential. Heavy metals including both essential and non-essential elements have a particular significance in ecotoxicology since they are highly persistent and all have the potential to be toxic to living organisms (Storelli *et al.,* 2005).Tin and aluminum are less toxic whereas mercury, lead, cadmium and arsenic are highly toxic and are the main toxic metals that accumulate in food chains and have a cumulative effect (Stankovic *et al.,* 2014). Heavy metals such as lead, arsenic, cadmium and mercury are highly persistent, accumulate and non-metabolizable to other intermediate compounds and not easily degradable in the environment (Mukesh *et al.,* 2008) and have also been reported to have no known bio-importance in animal biochemistry and physiology and consumption even at very low concentrations can be toxic.

2.11.4 Heavy metals in the Environment

Our present environment is being subjected to increasing pollution from industrial, urban and agricultural sources and this has elicited a growing urgency to monitor contaminant

levels, and to assess their effect. The increasing awareness and public health concern about contamination and exposure to heavy metals and their attendant adverse effects on wildlife health have led to increase in strategies and methodologies for detecting and monitoring their presence within the environment. Monitoring and systematic gathering of information on heavy metal levels in the environment viz-a-viz exposure and effects are essential components of any contamination-control system.

The nature of metals from both natural and anthropogenic sources within the environment combined with their necessity in biological processes produces a multifaceted system for assessment (Ferreira, 2011). In recent times, humans have released thousands of contaminants such as heavy metals into the environment and altered the distribution of many naturally occurring substances, thereby creating conditions that wildlife species had never experienced in the past. In many instances these new conditions have disrupted the delicate biological machinery evolved by organisms over thousands of years.Heavy metal contamination may have disturbing impacts on the ecological stability of the receiving environment and a diversity of living species (Farombi *et al*., 2007).

2.11.5 Wildlife Exposure to Heavy metals

Heavy metals are one of the groups of contaminants that wildlife have been exposed to in the environment. In fact, studies have suggested that heavy metals still remain major pollutants in current environments despite efforts to reduce their emission and contamination. Heavy metals are conservative pollutants in that they are broken down over such a long-time scale that they effectively become permanent additions to the environment (Mason, 1996).They are accumulated in living organisms when they are taken up from the environment, and stored faster than they are broken down (metabolized) or excreted. They enter wildlife through direct inhalation, ingestion, dermal contact

absorption or transfer via the placenta, resulting in potential risk to wildlife (Sardar *et al.,* 2013) though it has been reported that dietary exposure is the major route for heavy metal bioaccumulation in many marine and terrestrial animals (Kormarnicki, 2000).

In wild animals, the quantity of heavy metal that is actually absorbed from the digestive system can vary widely, depending on the chemical form of the metal and the age and nutritional status of the individual. Once a heavy metal is absorbed, it distributes in tissues and organs within the body. Excretion typically occurs primarily through the kidneys and digestive tract, but metals tend to persist in some storage sites, like the liver, bones, and kidneys, for years or decades. The presence of heavy metals in the environment is a major concern because of their toxicity, effects and threat to plant and animal life, thus disturbing the natural ecological balance (Bhattacharya *et al.,* 2008). The occurrence of these heavy metals within the ecosystems in excess of natural carrying capacity has become a wide spread problem and a matter of concern over the last few decades (Dirilgen, 2001; Vutukuru, 2005). Quantifying the transfer of heavy metals from diet and other sources/routes of transmission to target organs is key to estimating the health risk from their exposure. More so, exposure to heavy metals has been suggested to play a role in the pathophysiology of adverse health effects especially on wildlife.

2.11.6 Heavy metals and their concerns

Metals exist naturally within the earth's crust, and their concentrations in the environment can differ between different regions leading to spatial variations of background levels. Metal distribution in the environment is often dependent on the properties of the metal and impacts of environmental factors (Khlifi and Hamza-Chaffai, 2010). Heavy metals contamination is a great concern at global, regional and local level and influence the

functional and structural integrity of an ecosystem. They are kept under environmental pollutant category due to their toxic effects on plants, humans and food. Heavy metals gain access into the environment via natural and anthropogenic means. These include: natural weathering of the earth's crust, mining, soil erosion, industrial discharge, urban run-off, sewage effluents, pest or disease control agents applied to plants, air pollution fallout, and a number of others (Ming-Ho, 2005).

Heavy metals have continually been natural components of the environment (Okati and Rezaee, 2013) present in very low levels and are released into the environment from natural sources like volcanic activity or weathering of rocks. Likewise, industrial activities and a number of agricultural activities have significantly increased the accumulation of many metals in the environment (Nighat *etal.,* 2013). These metals are substantially detrimental to most living organisms at some level of exposure and absorption (Guven *et al.,* 1999). They have a severe effect on the environment and can threaten the ecosystem's balance (Battaglia *et al.,* 2005). Metals like mercury (Hg), cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), cobalt (Co), and zinc (Zn) are extremely toxic to both flora and fauna components of the ecosystem (Lee *et al.,* 2006).

The main concern with heavy metals is related to their potential toxicity and ability to bioaccumulate in biological systems (Otitoloju and Don-Pedro, 2002a), leading to a number of devastating health effects such as immunosuppression (Carey and Bryant, 1995), induction of stress proteins (Piano *et al.,* 2004), oxidative stress damage (Farombi *et al.,* 2007), histopathological damage (Tarasub *et al.,* 2011), reproductive and endocrine disruption (Kasperczyk *et al.,* 2008) and mortality/acute toxicity (Otitoloju and Don-Pedro, 2002b). Earlier, Cooper and Manalis (1983) associated lead, cadmium and mercury

toxicity with the impairment of pre-synaptic mechanisms such as acetylcholine inhibition in amphibians.

2.11.6.1 Cadmium

Cadmium is a toxic heavy metal widely distributed in the environment as a result of industrial and agricultural practices (Sant Ana *et al.,* 2003; Liu *et al.,* 2009; Salinska *et al.,* 2013). It is a heavy metal recognized as an industrial and environmental pollutant with characteristic long biological decomposition and accumulative toxic effect on living organisms (Karimi *et al.,* 2014). It is a relatively rare metal in natural environments but can be anthropogenically made ubiquitous and available to plants and animals (Church *et al.,* 1997) possessing serious toxicity and potential health threat to animals and wildlife species. It is toxic at extremely low levels and has been described as one of the most dangerous trace elements in food and in the environment, not only for its high toxicity but also for its persistence with no known homeostatic process to regulate its concentration (Battaglia *et al.,* 2005). Exposure to cadmium is known to cause harmful effects on different levels of the trophic chain because of bioaccumulation as toxic effects of it have been reported in kidneys, liver, lungs, testes, foetus, and the immune system of birds (Liu *et al.,* 2009) with these effects being associated with teratogenesis and carcinogenesis (Pius, 2009; Sarkar *et al.,* 2013).

At toxic levels, cadmium affects the kidneys of vertebrate wildlife by interfering with calcium metabolism, disrupting the electrolyte balance, and causing the excretion of calcium, which can lead to brittle bones (Larison, 2001). In fact, cadmium toxicity is more common among natural populations of vertebrates (Soylak *et al.,* 2002). Cadmium induces tissue injury through forming oxidative stress (Karimi *et al.,* 2014). It upsurges lipid

peroxidation, as well as reduces antioxidants, glutathione and protein-bound sulfhydryl groups. Additionally, it upgrades the production of inflammatory cytokines (Liu *et al.,* 2009). The source of cadmium intake is mostly food, and most of the cadmium that is absorbed after oral exposure mainly accumulates in the kidneys and liver (McFarland *et al.,* 2002). Cadmium primarily affects the kidneys, liver and intestine (Sarkar *et al.,* 2013). Larison *et al.* (2000) reported that ingestion of even trace quantities of cadmium can affect not only the physiology and health of individual organisms, but also the demographics and the distribution of species. In birds, Binkowski *et al*. (2013) observed and reported congestion, steatosis of hepatocytes, necrosis of single hepatocytes and leukocyte infiltration in the liver as well as swelling and necrosis epithelium renal tubules and congestion in the kidneys of wild living mallards. Similarly, Karimi *et al.* (2014) also reported reduced body weight and induced histological changes in liver and kidneys of Japanese quail exposed to dietary cadmium. In mammals, cadmium has been reported to induce not only acute renal and liver failures but also pneumonitis and pulmonary oedema in mammals (Annabi *et al.,* 2013).

2.11.6.2 Lead

Lead is a bluish soft metal with atomic number of 82; atomic weight of 207.19, specific gravity of 11.34, melting point of 327^0C and boiling point of about 1740^0C. Unique properties of lead, like softness, high malleability, ductility, low melting point and resistance to corrosion, have resulted in its widespread usage in different industries like automobiles, paint, ceramics, plastics, etc. This in turn has led to a manifold rise in the occurrence of free lead in biological systems and the inert environment (Vegetation *et al.,* 2012). It is the most common industrial metal that has become widespread in air, water, soil and food (Mukesh *et al.,* 2008) and toxic even at low concentrations. Lead is the most

significant toxin of the heavy metals and the inorganic forms are absorbed through ingestion by food and water, and inhalation (Ferner, 2001). It is a pervasive and widely distributed pollutant with no significant and beneficial biological role (Swarup *et al.,* 2007). It occurs naturally in the environment; however, most of the high levels found throughout the environment come from human activities. It is rarely found naturally as a metal, it is usually combined with two or more other elements to form lead compounds (Siddiqui and Gayatri, 2008). Lead has been given special attention throughout the world basically due to its ubiquitous nature and toxic effects even at very concentrations. The toxicity of lead is closely related to age, sex, route of exposure, level of intake, solubility, metal oxidation stage, retention percentage and duration of exposure, frequency of intake, absorption rate and mechanisms and efficiency of excretion (Sanchez-Chardi *et al.,* 2008).

Lead is a metabolic poison and a neurotoxin that binds to essential enzymes and several other cellular components and inactivates them (Cunningham and Saigo, 1997). Toxic effects of lead are seen in haemopoeitic, gastrointestinal, hepatic and renal systems producing serious disorders (Baykov *et al.,* 1996; Kalia and Vegetation, 2005). It has been reported to affect the developing brain and nervous system of birds, including reduced weight gain for nestlings, reduced organ growth, reduced ability to sustain necessary metabolic function and teratogenic effects (Burger, 1995). Tavecchia *et al.* (2001) reported decreased survival of Mallards (*Anasplatyrhynchos*) from lead ingestion in France. Mallards experimentally dosed with lead shot were also reported to have had reduced immunologic cells (Rocke and Samuel, 1991) and depressed antibody production (Trust *et al.,* 1990). In amphibians, Cooper and Manalis (1983) associated the impairment of pre-synaptic mechanisms such as acetylcholine inhibition to heavy metals such as lead.

All these can have serious consequences on the health of wildlife. Generally, impacts of lead on wildlife include decreased survival, poor body condition, behavioral changes, and impaired reproduction (Burger, 1995).

2.11.6.3 Zinc

Zinc is ubiquitous in the environment and occurs in the earth's crust at an average concentration of about 70 mg/kg (Thomas, 1991). The primary anthropogenic sources of zinc in the environment are from metal smelters and mining activities. It is biologically one of the most essential elements and is apparently necessary to all forms of life. It is essential for plant growth as it stimulates germination, maintenance of auxins (growth hormones) and is essential for seed production. Zinc being essential, is required to support biological activities, but when their environmental concentrations rise, they can generate serious toxicological problems (Pérez-Lopez *et al.,* 2008). Zinc is highly concentrated in the liver, kidney, bones and spleen and has definite function on the mammalian blood by forming prosthetic group of enzymes, carbonic anhydrase. It can also form soluble chelation complexes with amino acids and multi-dentate organic acids such as ethylenediaminetetraacetic (EDTA) acid. Zinc salt shows lead poisoning because zinc salt occasionally contains lead. Even though zinc is an important trace element for the function of many enzymes, an excess could as well represent an additional source of stress in birds which are already facing stressful conditions.

Zinc poisoning has been documented in dogs, cats, ferrets, birds, cattle, sheep, and horses, usually as a result of ingesting galvanized metal objects, certain paints and fertilizers, zinc-containing coins, and skin and sunblock preparations containing zinc oxide (Robinette, 1990). Beyer *et al.* (2004) observed high concentration of zinc in the liver and

kidney of waterfowl and subsequently reported pancreatitis in the waterfowl found within the Tri-State Mining District of Oklahoma, Kansas, and Missouri in USA. Ross and Henderson (2006) reported vomiting, epigastric pain, ataxia and breathlessness in possums after ingesting zinc phosphide. Generally, there are no enough recent data on wildlife as regards zinc contamination which necessitates further research in this area but secondary toxicities have been recorded in birds, carnivores and other mammals (Colvin *et al.,* 1991).

2.11.6.4 Copper

Copper is a necessary and essential element for living organisms but it can become toxic to wild species at high concentration (Snively and Flaspohler, 2006). It Is widespread presence in the environment may be due to accumulation of domestic and agricultural wastes (Edward *et al.,* 2013). It is required in trace amounts by animals for the functioning of enzymes and carbohydrate metabolism, formation of haemoglobin and haemocyanin, the oxygen-transporting pigments in the blood of vertebrates and shellfish respectively (Okocha and Adedeji, 2012). Copper toxicity occurs when a specific amount of copper binds to physiologically active biological membranes, generally outcompeting cations injuring the physiological mechanism (Martins and Bianchini, 2008). Also, copper toxicity can be induced by generating reactive oxygen species (Bopp *et al.,* 2008). The threshold level of copper contamination depends on animal species and life stage (MacRae *et al.* 1999). Generally, copper acts by inhibiting enzymes, ATP-driven pumps, and ion channels, resulting in cell toxicity from disruption of cell homeostasis and leading to changes in internal pH balance, membrane potential, and osmosis (Okocha and Adedeji, 2012).

Copper is generally more toxic to aquatic organisms than to birds or mammals though some ungulates are more sensitive to copper toxicity than other mammals (Puls, 1988). The majority of studies on the effect of copper toxicity on aquatic life were performed on freshwater species as copper is generally more toxic to organisms in freshwater than in saltwater (Okocha and Adedeji, 2012). This is because freshwater lacks cations, which compete with Cu^{2+} at the biological action sites, thus reducing copper toxicity (Brooks *et al.,* 2007). In many aquatic animals, copper causes toxicity by impairing osmoregulation and ion regulation in the gill (Blanchard and Grosell, 2005). In mammals, inhibition of growth, muscular dystrophy, anaemia, impaired reproduction and decreased longevity have been reported as effects of copper toxicity (Talmage and Walton, 1991). Copper can also saturate the water and soil, posing risks to wildlife(Brooks *et al.,* 2007).

2.11.6.5 Arsenic

Arsenic (As) is ubiquitous within the environment, present in air, water, soil, and living tissues. It is a colorless, tasteless and naturally present semi-metallic element that is widely distributed in nature (Tan *et al.*, 2014). It exists naturally in the earth's crust with higher levels in some environments and in specific types of rocks and minerals (Duker *et al.,* 2005). There are two forms of arsenic, i.e., inorganic and organic, the former form is of severe health concern (Lima *et al.,* 2010). Organic arsenic compounds are mainly non-toxic while inorganic arsenic compounds are toxic and are of serious concern (Lima *et al.,* 2010; Khan *et al*., 2014). Although most arsenic in soil is derived from the parent rock, the application of arsenic compounds in agriculture and forestry practices may lead to extreme soil contamination and subsequent groundwater contamination, while the burning of coal and smelting of metals may be major sources of airborne arsenic (Gbaruko *et al.,* 2008). Most of the arsenic compounds are used in the manufacture of agricultural

products such as insecticides, herbicides, fungicides, algaecides, wood preservatives, and growth stimulants for plants and animals (Pandey and Madhuri, 2014).Toxicity of arsenic vary from species to species as it exerts both acute and chronic toxicities in different living organisms and has been reported to depend on chemical speciation (Cullen and Reimer, 1989). Despite its toxicity, arsenic has been used as a common treatment against various diseases (Doyle, 2009). Arsenic enters the animal body through ingestion (food and water), inhalation and dermal contact. It accumulates in almost all organs of the animal body but mainly in the liver (Cullen and Thomas, 2000) and its absorption occurs mostly in small intestine (Centeno *et al.,* 2002).

Various forms of arsenic produce a wide range of clinical signs with toxicity signs varying from species to species which could be acute or chronic (Khan *et al.,* 2014). Rana *et al.* (2008) reported clinical signs (loss of weight, weakness, dehydration, anorexia, bloody diarrhoea, ruminal inertia, exhaustion, reddish urine, and anestrus) and lesions (anaemia, congestion and hemorrhage in intestine, liver and kidneys, dermatosis) in buffalo administered 50mg/l water of Arsenic trioxide. Islam *et al.* (2009) also reported clinical signs of depression, decrease body weight, reduced feed intake, dullness and ruffled feathers in ducklings administered 100mg/l water of Arsenic trioxide though no lesions were reported. Arsenic has been reported to induce carcinogenicity with potential impacts that include genotoxicity, alteration of cell proliferation, altered DNA methylation, co-carcinogenesis, and tumor formation (Flora, 2011). Arsenic has also been implicated to disturb signaling pathways and induce oxidative stress in mammals and some marine animals (Poersch *et al*., 2006). It is reported as a carcinogen, and causes foetal death and malformations in many mammal species. Understanding the ecotoxicological effects of

arsenic in the environment is paramount to mitigating its deleterious effects on ecological and human health, particularly on the immune response.

2.11.6.6 Mercury

Mercury (Hg) is a naturally-occurring non-essential element which has several forms known with no biological function and considered as a potential hazard to wildlife (Brasso and Cristol, 2008). It occurs in both inorganic and organic forms, but it is the highly toxic organic methyl mercury (MeHg) that efficiently bioaccumulate in organisms and biomagnifies in food webs (Hall *et al.,* 1998). However, inorganic mercury can be transformed into organic forms through a variety of biological processes. In nature, MeHg is produced by methylation of inorganic Hg, as a consequence of anaerobic microbial activity in environments rich in organic matter. Under most circumstances, wildlife is exposed primarily to MeHg, rather than other chemical forms of mercury. Even though it occurs naturally, its major occurrence and concentration within the environment is as a result of increased anthropogenic activities majorly industrial processes (Fitzgerald *et al.,* 1998). Mercury (Hg) has been described as a pervasive contaminant of significant ecological concern due to its toxicity to wildlife (Scheuhammer *et al.,* 2007) and its tendency to bio-magnify within ecosystems (Hall *et al.,* 1998). Furthermore, mercury uptake in wildlife has been reported to be affected by numerous environmental variables including dietary composition and feeding niche (Eisler, 2006) contributing to their high toxicity even at low concentrations. As such, the toxic effects of mercury have been well documented in varying and multiple taxa. In fish, mercury exposure has been reported to impair growth, behavior, gonad development, and sex hormone production (Crump and Trudeau, 2009).

In amphibians, Burke *et al.* (2010) reported that salamanders are likely more susceptible to mercury exposure and accumulation. Specifically, they reported high concentrations of mercury in two-lined salamanders (*Euryceabis lineata*) which affected their behavior and physiological performance. In birds, associated effects of mercury exposure have been reported to be but not limited to decreased yearly survival, inhibited immunocompetence, altered hormone profiles, embryotoxicity and reduced reproductive success (Hawley *et al.,* 2009). In summary, the main toxic effects of mercury concern the central nervous system (neurotoxicity) especially with the potential to disrupt the brain's ability to effectively control motor functions in animals (Sakamoto *et al.,* 1998). At comparatively low concentrations in wildlife, it affects reproduction, growth and development, behavior, motor coordination, and blood chemistry (Scheuhammer *et al.,* 2007; Brasso and Cristol, 2008). Mercury is also a known mutagen, teratogen, and carcinogen, that is, generally genotoxic and has also been linked to immune suppression, endocrine disruption, physical malformations, and mortality in organisms (Tan *et al.,* 2009; Wada *et al.,* 2009).

2.10.6.7 Chromium

Chromium (Cr) is widespread in the environment, occurring naturally in air, rocks, soil, and water. It is the seventh most abundant element on earth (Mohanty and Kumar Patra, 2013) occurring in several oxidation states in the environment. It is widely used in industry, paints and metal plating as corrosion inhibitor and its contamination of the environment is attributed to increased anthropogenic uses of this metal (Pandey and Madhuri, 2014). Anthropogenically, chromium is released into the environment through sewage and fertilizers, industrial production of stainless steel, electroplating of chrome, use of dyes, leather tanning, and use of wood preservatives (Ghani, 2011). Besides its

important role with its very minute quantities in biological systems, anthropogenic use of chromium has contaminated the environment and has created diverse health effects (Andleeb, 2014).

Chromium is an important microelement essential and required in small amounts for normal carbohydrate, lipid and protein metabolism but becomes toxic at higher concentrations(Anderson, 1981). It exists primarily in the trivalent and hexavalent forms but its hexavalent form is most bioavailable and predominates the trivalent form in the environment and is toxic to both humans and animals due to its higher solubility and mobility. Chromium toxicity is linked mainly with hexavalent chromium, while trivalent chromium is understood to be a highly safe mineral. Hexavalent chromium is more soluble than trivalent chromium and at least five times as toxic (Barceloux, 1999). Adverse effects and toxicity of chromium have been reported to be substantially influenced by a variety of biotic and abiotic factors, including the species, age, and developmental stage of the organism; the temperature, pH, salinity, and alkalinity of the medium; the effects of interactions between chromium and other contaminants; and the duration of exposure and the chemical form of chromium involved (Andleeb, 2014). The hexavalent chromium [Cr (VI)] has been reported to induce oxidative stress, and various levels of genotoxicity, cytotoxicity and clastogenicity (Li *et al.*, 2012; Kumar *et al.*, 2013). In sea turtles and sea lions, Cr (VI) has been reported both as cytotoxic and genotoxic to (Wise *et al.*, 2014).

2.10.6.8 Nickel

Nickel is the 5th most abundant element by weight and 24th most abundant element in the earth crust comprising about 3% of the composition of the earth. It is a nutritionally

important trace metal for many animal species (Cempel and Nikel, 2006) and can naturally occur in a variety of mineral form and widely distributed in the environment. It is found in various oxidation states but the [Ni (II)] is the most common form in biological systems (Denkhaus and Salnikow, 2002). Nickel (Ni) is one of a variety of ubiquitous trace metals emitted into the environment from both natural and anthropogenic sources. Natural sources of atmospheric nickel include dusts from volcanic emissions and the weathering of rocks and soils while natural sources of aqueous nickel are from biological cycles and solubility of nickel compounds from soils (Ilic *et al.,* 2007). Anthropogenic sources of nickel include emissions from fossil fuel consumption, and the industrial production, use, and disposal of nickel compounds and alloys. Nickel is a heavy metal that can be a significant contaminant within the environment. Even though data on nickel toxicity to wildlife are sparse, it has been reported to be haematotoxic, immunotoxic, neurotoxic, genotoxic, reproductive toxic, pulmonary toxic, nephrotoxic and hepatotoxic to other animals (Das *et al.,* 2008; Ololade and Oginni, 2010).

Table 2.4: Detrimental Toxicities Associated with Arsenic, Lead, Mercury and Cadmium

Heavy Metal	Detrimental Effects/Toxicities
Arsenic (As)	Water-soluble inorganic As is readily absorbed from digestive system. Inorganic forms of As are particularly toxic. It causes irritation to lung, stomach and intestine, skin disturbances, and decreased formation of RBCs and WBCs. Very high concentrations of inorganic As can cause infertility, skin disturbances, decreased resistance to infections, heart disruptions, brain damage and death. The acute LD_{50} (oral) of As ranges from 10-300 mg/kg.
Lead (Pb)	It can enter the body through ingestion and inhalation. Its maximum allowable levels may be 5 µg/L (in bottled water) to set elemental impurities limit. It can cause disruption of biosynthesis of Hb, anaemia, high B.P., kidney damage, reproductive/fertility problems and brain or nervous system damage.
Mercury (Hg)	Its prevalence in environment can lead to biomagnification in food chain. The organic Hg, such as methyl Hg, is more toxic than inorganic Hg due to ease of absorption into human system. The toxicity of Hg include: kidney damage, disruption of nervous system, damage to brain, DNA and chromosomal damage, allergic reactions, sperm damage, birth defects and miscarriages. The LD_{50} of Hg is as low as 1 mg/kg in small animals.
Cadmium (Cd)	Cd is more readily absorbed through the lungs than the digestive system. It can damage kidneys, CNS and immune system. It can also cause bone fractures and reproductive problems. It can cause stomachaches, diarrhoea and vomiting. The LD_{50} (oral) of Cd in animals ranges from 63-1125 mg/kg.

Source: Pandey and Madhuri, 2014

Table 2.5: Classification of elements according to toxicity and their uptake

Not critical	Toxic, partially dissolved or easily exposed	Very toxic and easily exposed
Na, C, F, K, S, Sr, H, Cl	Ti, Ga, Hf, Rh, Nb, Ir	Be, As, Au, Cu, Pd, Pb
P, Li, Mg, Al, O, Br, Si	La, Zr, Os, Ta, Ru, Re	Co, Se, Hg, Zn, Ag, Sb
Fe, Rb, Ca, N	W	Ni, Te, Tl, Pt, Sn, Cd, Bi

Source: Wood, 1974; Stankovic *et al.,* 2014

2.11.7 Heavy metals in Wildlife Species

Heavy metal exposure in wildlife is a serious problem that threatens wild animal survival and species perpetuation not excluding the quality of the environment. Studies have indicated that heavy metal played a major role in the contamination and decline of various populations (Battaglia *et al.,* 2005; Rai *et al.,* 2008). This is often and majorly attributed to the negative effects of anthropogenic activities of varying degrees. Continuous exposure to heavy metals overtime can lead to gradual accumulation in various tissues and cause deleterious effects on wildlife.Generally, wild animal species have been noted to be sentinels of environmental contamination. That is, they are good indicators of contaminants' status within the environment because they reveal the occurrence as well as bioavailability of such contaminant. The level of heavy metal absorption in fauna species differ based on species' physiology, metal properties, and bio-availability in the environment (Nighat *et al.,* 2013). After absorption, metals circulate within the body system and are excreted or get deposited in different body tissues, or are sequestered in feathers (for birds).

The increased toxicity of heavy metals in wildlife may lead to thinning of eggshell, reduced reproduction rate, immune system suppression, reduction in growth/weight, and developmental malformations. All these may perhaps lead to decline in animal population (Dauwe *et al.,* 2006). Long-term exposure to heavy metals can also cause disruptive behaviour and reduction in disease resistance and affect other physiological processes (Dauwe *et al.,* 2006). Heavy metals basically interrupt metabolic functions in two ways:

a) Heavy metals accumulate and as a result disrupt vital functions by some organs and glands such as the heart, brain, kidneys, bone, liver, etc.

b) They displace crucial nutritional minerals from their original place, thereby, impeding their biological roles. It is, however, impossible to live in an environment free of heavy metals.

2.11.8 Sources of Heavy metals in Wildlife

Wild animals are generally often exposed to basal levels of heavy metals within their natural habitats. The sources of toxic heavy metals to wildlife in the environment could be traced to both natural and anthropogenic sources (Olomukoro and Ezemonye, 2007). Anthropogenic sources of heavy metal contamination include those associated with fossil fuel and coal combustion (Pb, Hg, Ni, Sn, Cd, As, Sb), manufacturing processes, industrial effluents and products (Cd, Cr, Cu, Ni, As, Pb and Zn), solid waste disposal (Cd, Cu, Cr, Pb, Hg, Ni, Zn), , automobile exhaust (Pb, Cd), fertilizers (As, Cr, Pb, Hg, Ni, V) and mining and metal processing (Pb, Hg). All these sources produce heavy metals that end-up in plant and animal species within the environment (Golden *et al.,* 2003) accumulating in vital body tissues and organs due to their persistence. For instance, Duruibe *et al.* (2007) reported that long after mining activities might have ceased, emitted heavy metals continue to persist in the environment in some cases. Natural routes of contamination include volcanic activities, mineral deposits weathering, brush burning, windblown dusts and biogeochemical systems. Contamination with heavy metals is a serious threat to wildlife due to their toxicity, bioaccumulation and biomagnification within the food chain (Demirezen and Uruc, 2006).

Table 2.6: Anthropogenic activities (or products) and their associated heavy metals

Anthropogenic Activity	Associated heavy metals
Inorganic Agriculture	Pb, Cd, Cr, As, Zn, Cu, Ni, Sb, Co, V
Mining	Au, As, Cd, Pb, Zn, Cu, Hg, Fe, Al, Mg, Se
Coal Combustion	Pb, Hg, Ni, Sn, Cd, As, Sb
Sewage	Cu, Zn, Ag, Pb, Hg, Ni, As, Cr, Cd
Industrial Effluents	Cd, Cr, Cu, Ni, As, Pb, Zn
Automobile Exhaust	Pb, Cd

Source: Adapted from Woods, 1974; Golden *et al*., 2003; Duruibe *et al*., 2007; Stancheva *et al.,* 2014; Stanchovic *et al*., 2014

2.11.9 Heavy Metals Analytical Methods

2.11.9.1 Quantitative Determination

Different approaches have been described in the literatures for detailed quantitative analysis of heavy metals in various environmental and biological samples. Despite the fact that it is a huge challenge to innovate sensitive and specific analytical methods that can quantitatively evaluate even trace concentrations of heavy metals in a variety of samples (Rao, 2005), some optical and electrochemical techniques for quantitative heavy metal determination have been developed. These analytical methods frequently require sample pre-concentration and/or pretreatment for the destruction of the organic matrix such as wet digestion, dry ashing, and microwave oven extraction.

Atomic Absorption Spectrometry (AAS) and Atomic Emission Spectrometry (AES) are the most broadly used techniques for quantitative analysis of heavy metals in environmental and biological samples (Karadjova *et al.,* 2007; Draghici *et al.,* 2010). Quite a lot of AAS can be differentiated based on the mode of sample introduction and atomization. Flame (FAAS), graphite furnace (GFAAS), hydride generation (HGAAS), and cold vapour (CVAAS) systems have been distinguished and described extensively (Ortega, 2002). FAAS and GFAAS are appropriate for quantitative analysis of nearly 70 and 60 elements, respectively. The absorbance wavelengths for determination of some heavy metals using AAS is shown in Table 2.7. Similarly, the AES quantifies the optical emission from excited atoms to assess analyte concentration. Recently, Inductively-Coupled Plasma Atomic Emission Spectrometry (ICP-AES) has clearly outmoded FAAS because it is a truly multi-element technique. Other methods are enumerated in Table 2.8.

Table 2.7: Absorbance Wavelengths for heavy metal determination using Atomic Absorption Spectrophotometer (AAS)

HEAVY METALS	WAVELENGTH (nm)
Cu	324.8
Zn	213.9
Cr	357.9
Pb	283.5
Ni	232.0
Cd	228.9
Fe	248.3
Mn	279.5

Source: WHO, 2005

Table 2.8: The various methods used in determining heavy metals

Technique	Principle	Type of analysis	Applications
Atomic absorption spectrometry (AAS)	absorption of radiant energy produced, by a special radiation source, by atoms in their electronic ground state	-single element; -multi-element analysis (2-6 elements)	widely used
Inductively-coupled plasma with atomic Emission spectrometry (ICP-AES)	measures the optical emission from excited atoms	Simultaneous Multi-element analysis	widely used method for environmental analysis
Inductively-coupled plasma with mass Spectrometry (ICP-MS)	- argon plasma used as ion source; –used for separating ions based on their mass-to charge ratio	Simultaneous Multi-element analysis	-widely used; -isotope determination
Atomic fluorescence Spectrometry (AFS)	measures the light that is reemitted after absorption	single element	-mercury, arsenic, and selenium; -complementary technique to AAS
X-ray fluorescence (XRF)	-X-rays –primary excitation source; -elements emit secondary X-rays of a characteristic Wavelength	Simultaneous determination of most elements	-non-destructive analysis; -less suitable for analysis of minor and trace elements
Neutron activation Analysis (NAA)	-conversion of stable nuclei of atoms into radioactive ones; -measurement of the characteristic nuclear radiation emitted by the radioactive nuclei	Simultaneous Multi-element analysis	-most elements can be determined; - highly sensitive Procedure
Electrochemical Methods	-controlled voltage or current; -polarography; -potentiometry; - stripping voltammetry;	Consecutive analysis of different metal ions	-analysis for transition metals and metalloids (total content or speciation analysis)

Source: Karadjova *et al.,* 2007; Draghici *et al.,* 2010

2.11.9.2 Speciation Analysis

The chemical species of an element are the precise forms of an element referred to as molecular, complex, or nuclear structure, or oxidation state (Ortega, 2002). The major analytical challenges deals with speciation determination of redox and organo-metallic forms of arsenic and antimony, protein-bound cadmium, organic forms of lead (i.e. alkyllead compounds), organomercury compounds, inorganic platinum compounds, inorganic and organometallic compounds of selenium, organo-metallic forms of tin, and redox forms of chromium and vanadium. Lately, speciation analysis has played a distinctive role in the studies of biogeochemical cycles of chemical compounds, determination of toxicity and ecotoxicity of specific elements etc.

Chromatographic methods (such as Liquid Chromatography, Ion Chromatography and Gas Chromatography) and Capillary Electrophoresis (CE) are the most common separation techniques which are chiefly combined with AAS, AES, ICP-AES or ICP-MS (Zhang and Zhang, 2003). Electro-analytical techniques exert their key application in the evaluation of dissolved species in environmental samples. They are species-selective rather than element-selective that can be deployed *in situ* with least sample perturbation. If the main targets of speciation analysis are grouped into redox states, metal(loid) complexes and organometal(loid) compounds, analytes in all three areas can be evaluated by electro-analysis (Town *et al.,* 2003).

2.12 Bio-accumulation

Bioaccumulation is attributed to the process by which living organisms accumulate chemicals directly from the abiotic environment (that is, water, air, soil) as well as from dietary sources (trophic transfer). Chemicals in the environmental are mostly taken up by

organisms by passive diffusion, where the chemical level in an organism achieves a concentration that surpasses that in the water/media as a result of chemical uptake via all routes of exposure (Tao *et al.,* 2012). It noteworthy that bioaccumulation is characteristically much greater from water than from food, and it is not likely that an organism would accumulate a chemical to the same degree from both sources (Bhat, 2013). Bio-accumulation of cadmium is greater than most metals as it is assimilated rapidly and excreted slowly depending on the rate of excretion (Bhat, 2013). It is known that bioaccumulation of heavy metals varies according the sex, size and/or age of the animals (Damek-Poprawa and Sawicka-Kapusta 2004). Control of accumulation of toxic substances in ecosystems is of great value in the context of global atmospheric pollution. Factors that influence bioaccumulation may include but not restricted to environmental persistence, lipophilicity, biotransformation and biomagnification (at higher tropic level).

2.13 Old Oyo National Park in Brief

The Old Oyo National Park (OONP) previously occurred as two contiguous forest reserves; Upper Ogun and Oyo-Ile which were gazetted in 1936 and 1941, respectively (Oyeleke *et al.,* 2015). The park derives its name from ruins of Oyo-lle (Old Oyo), the ancient political capital of Oyo Empire of the Yoruba people. Politically, it domiciled in Oyo State in the Southwest of Nigeria and borders Kwara State in the Northeast. It is surrounded by ten (10) Local Government Areas in Oyo State namely: Atisbo (Tede/Ago-Are) (3.4220E, 8.5420N), Atiba (Oyo) (3.9260E, 7.8400N), Irepo (Kisi) (3.8510E, 9.079N), Oorelope (Igboho) (3.7550 E, 8.8340N), Saki East (Ago-Amodu) (3.6100E, 8.6090N), Iseyin (Iseyin) (3.5760E, 7.9590N), Orire (Ikoyi) (4.1690E, 8.2700N), Itesiwaju (Otu) (3.3970E, 8.2110N), Olorunsogo (Igbeti (4.1350E, 8.7450N), Saki West (Saki) (3.3860E, 8.6620N) and Kaima Local Government Area in Kwara State.

2.13.1 Objectives of Old Oyo National Park

According to Alarape (2002), Old Oyo National Park has the following objectives:

(a) To conserve, preserve and protect the indigenous Nigeria flora and fauna resources in selected ecological enclaves and protection of archaeological/historical sites for the benefits of present and future generations

(b) To enhance development of buffer zones around the park for socio-economic benefits of the local inhabitants

(c) To encourage general education in the knowledge of wild and domestic animals, flora and vegetation by publishing or sponsoring the publication of the research, particularly in relation to Nigeria problems

(d) To cultivate the recreation culture among Nigerians and promote aesthetic and touristic values of our unique natural heritage for sound economic, social and cultural development

(e) To generally fulfill the terms of International Convention on the conservation of natural resources to which Nigeria is signatory

2.13.2 Vegetation and Flora Composition

The vegetation and/or flora composition of the Old Oyo National Park has been classified as Forest / Southern Guinea Savanna (Ejidike and Ajayi, 2013). The forest regions of the park contain areas that have thick and light forest (Figure 2.1). The vegetation of the park was initially classified into four broad groups including Dense woodland and Forest outlier in the Southern portion and the North West corner, Mixed open savanna in the middle and North east portions, Outcrop vegetation in the hilly and rocky areas, and Riparian grassland and fringing woodland and forest vary along major rivers and streams dominated (Geerling, 1973). The management plan of the park described and recognizes

four broad eco-zones to include forest and dense savanna mosaic woodland of the park around Sepeteri axis designated as site A, dense and open savanna woodland mosaic in the central portion of the park, dense savanna woodland, north of Igbeti-Kishi axis zone C and Open savanna woodland, North-east of the park [Oyo-Ile sector] (Afolayan *et al.,* 1997). Oladeji and Agbelusi (2014) also reported the presence of leguminous plants within the central and northern sectors of the park.

The park is richly blessed with abundant tree species such as the mahoganies, *Nauclea diderrichii (*Opepe*), Terminalia ivorensis (*Odigbo*), Terminalia superba (Afara), Triplochiton sceleroxylon (Obeche)* and others known in international market. Other include *Bligia sapida*, *Terminalia glycocens*, *Kigelia africana*, *Pterocarpus macrocarpus*, *Vitellaria paradoxa*, *Khaya grandifolia*, *Afzelia africana, Annogeissus leiocarpus, Ceiba pentandra, Bombax spp., Adansonia digitata, Brachystegia euryloma, Burkea africana, Daniellia oliveri, Detarium microcarpum, Combretum spp., Isoberlinia spp., Annona senegalensis, Lannea schimperi and Grewia mollis.* The dominant perennial grass species as reported by Ayodele (1988) include *Panicum spp., Ctenium elegans, Andropogon spp., Hyparrhenia spp., Cymbogon giganteus and Beckeropsis unisetus.*

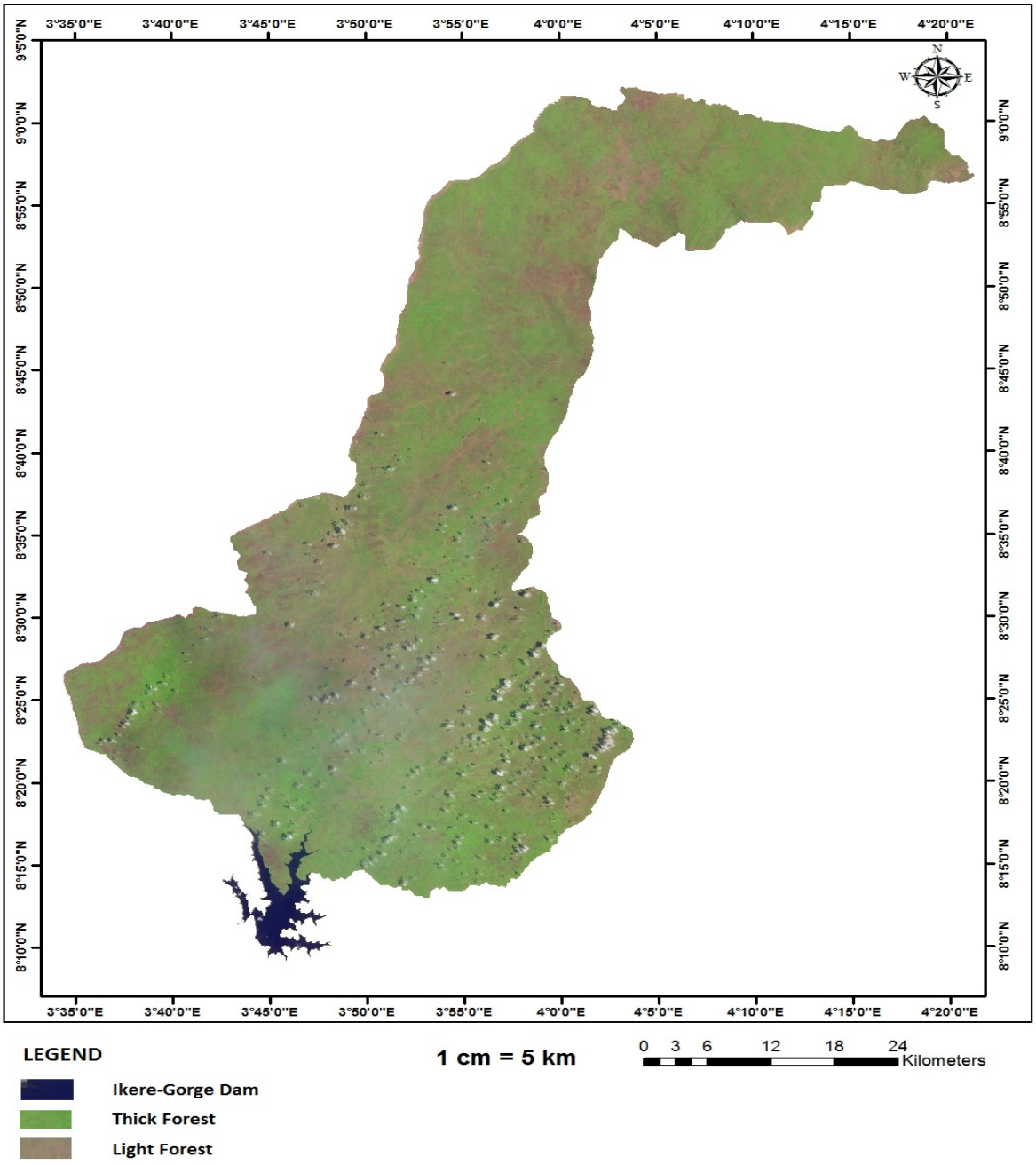

Figure 2.1: Old Oyo National Park Map showing the areas of thick and light forests

Source: Field Survey, 2016

2.13.3 Fauna Composition

The fauna species such as Lion (*Panthera leo*), Leopard (*Panthera pardus*), Greater bustard (*Otis tarda*), Spotted hyena (*Crocuta crocuta*), African Civet cat (*Civettictis civetta*), Aadvark (*Orycteropus afer*), Elephant (*Loxodonta africana*), Buffalo (*Syncerus caffer*), Porcupine (*Hystrix cristata*), Honey-badger (*Mettivora capensis*), Otter (*Aonyx capensis*), Kob (*Kobus kob*), Waterbuck (*Kobus defassa*), Reed buck (*Redunca redunca*), Oribi (*Ourebia ourebi*), Roan antelope (*Hippotragus equinus*), Hare (*Lepus capensis*), Hartebeest (*Alcelaphus buselaphus*), Bush buck (*Tragelaphus scriptus*), Common Warthog (*Phacochoerus aethiopicus*), Grasscutter (*Thryonomys swinderianus*), Crocodile (*Crocodilus niloticus*), Red river hog (*Potamochoerus porcus*), Red flanked duiker (*Cephalophus rufilatus*), Mongoose (*Atilax paludinosus*), Maxwell's duiker (*Philantomba maxwelli*), Patas monkey (*Erythrocebus patas*), Tantalus monkey (*Chlorocebus tantalus*), Olive baboon (*Papio anubis*), Hunting dog (*Lycao pictus*), Waterbuck (*Kobus defassa*), Hedgehog (*Atelerix albiventris*), Genet (*Genetta nigrina*), Grim's duiker (*Sylvicapra grimmia*) and Sooty Mangabey (*Cercocebus atys*) have been reportedly sighted in the park directly or by indirect indices (Petrides, 1962; Ayodele, 1988; Afolayan *et al.,* 1997; Marguba, 2011; Oyeleke *et al.,* 2015). Many of the large mammal species have locally gone into extinction or migrated away since the area was first created as a game reserve (Marguba, 2011). Ibadan malimbe (*Malimbeus ibadanensis*), one of the two endemic bird species in Nigeria has been reportedly sighted in the park (Oyeleke *et al.,* 2015).

2.13.4 Geology and Topography

Alarape (2002) reported that the geology of OONP is such that the largest part of the park has a combination of magmatite, embrechite, gneiss, schist and amphibolites. The extreme Northern part is a plateau while ridges of quartzite stretch from the North-eastern to the

South-eastern part of the park. Some hills and inselbag are also scattered on the eastern boundary of the park with important ones being Yemoso Rock and Gbogun hills. Furthermore, the park lies on crystalline acid rocks with soils derived from them being undifferentiated basement complex material. These soils are generally sandy and are classified as ferruginous tropical soils (Alarape, 2002). The soil colour is darkish-brown on top and becomes lighter down the soil profile. The soil texture is more of loam increasing down the profile with different grades. The topography of most part of the park is typically low-lying land between 330 and 508 metres above sea level.

CHAPTER THREE

METHODOLOGY

3.1 Description of the Study Area

The Old Oyo National Park is located between latitudes 8^0 15` to $9^0$ 05`N and longitudes 3^0 35` to $4^0$ 42`E and centered on North latitude 8° 36′ 00′′ and East longitude 3° 57′ 05′′ (Akinyemi and Kayode, 2010). It is among the seven national parks in Nigeria and was upgraded from game reserve to a national park status in 1991 by decree number 36 (Ejidike and Ajayi, 2013). This decree number was later cancelled and substituted with Act No. 46 of 1999 as a wildlife reserve area. The park has a total land mass area of 2,512 km^2 making it the fourth largest national park in Nigeria (Oladeji *et al.,* 2012b) after Cross River (4,000 km^2), Kainji Lake (5,382 km^2) and Gashaka-Gumti (6,731 km^2) national parks.

The park is divided into five administrative units (hereafter termed "Ranges") as shown in Figure 3.1. They are: Oyo Ile (476 km^2), Marguba (617 km^2), Tede (422 km^2), Sepeteri (607 km^2) and Yemoso (390 km^2). Some of the communities that surround the park include Igboho, Igbeti, Alagutan, Agbago, Sepeteri, Aiyetoro, Okaka, Ikoyi-Ile, Ago-Are, Alafa and so on (Figure 3.2).

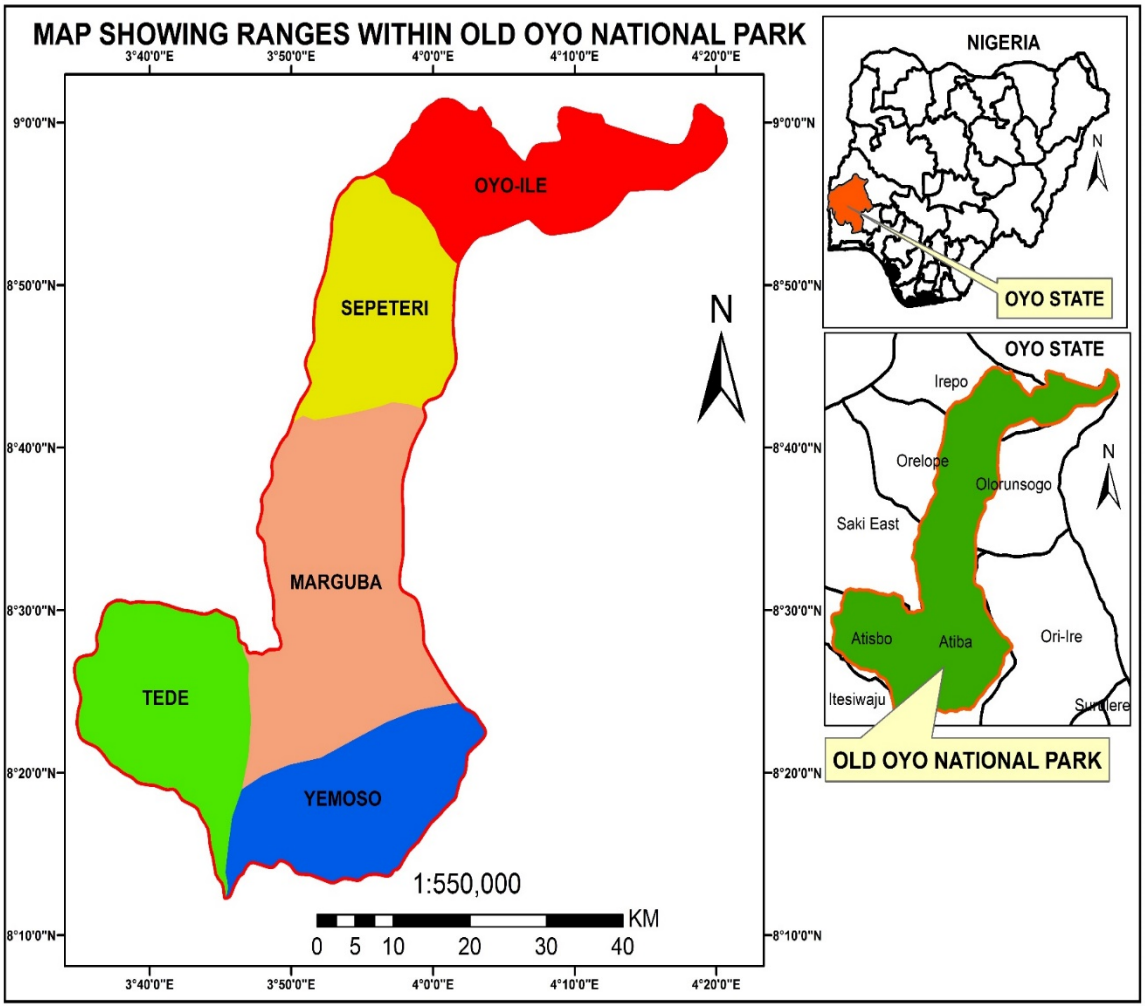

Figure 3.1: Map of Old Oyo National Park showing the ranges

Source: Field Survey, 2016

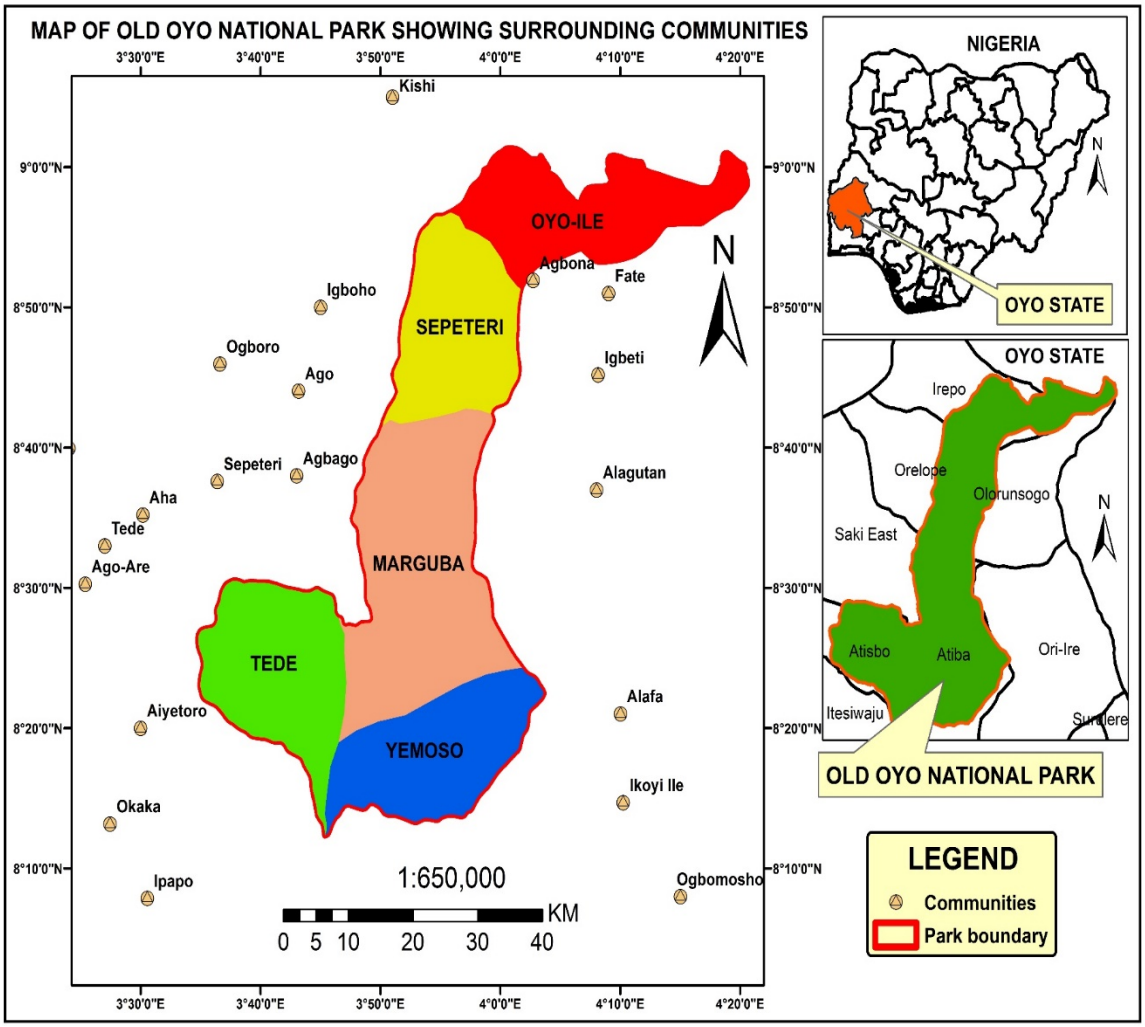

Figure 3.2: Map of Old Oyo National Park showing the surrounding communities

Source: Field Survey, 2016

The Old Oyo National Park is drained mainly by River Ogun, and its network of tributaries that cover the entire Southern part of the park. River Tessi is the main source of water to the wild animals in the Northern part of the park while several tributaries notably Iwa, Oopo, Iwawa, Oowe, Owu, Ayinta, Sooro, Iweke and so on exist in the park (Figure 3.3). The establishment of a dam specifically at Ikere on the Ogun River about 4 km south of the park holds a very large volume of water reaching up to 10 km or more upstream of Rivers Owu, Ogun and Oowe.

Some of the rivers and other surface water in the park are not perennial (Oladeji *et al.,* 2012b). However, most of the rivers break into pools, some quite large, but the Ogun River ensures a very minimal discharge rate during the dry season period. Some of these rivers and their network of tributaries serve as sources of water even for the surrounding communities as shown in Figure 3.4.

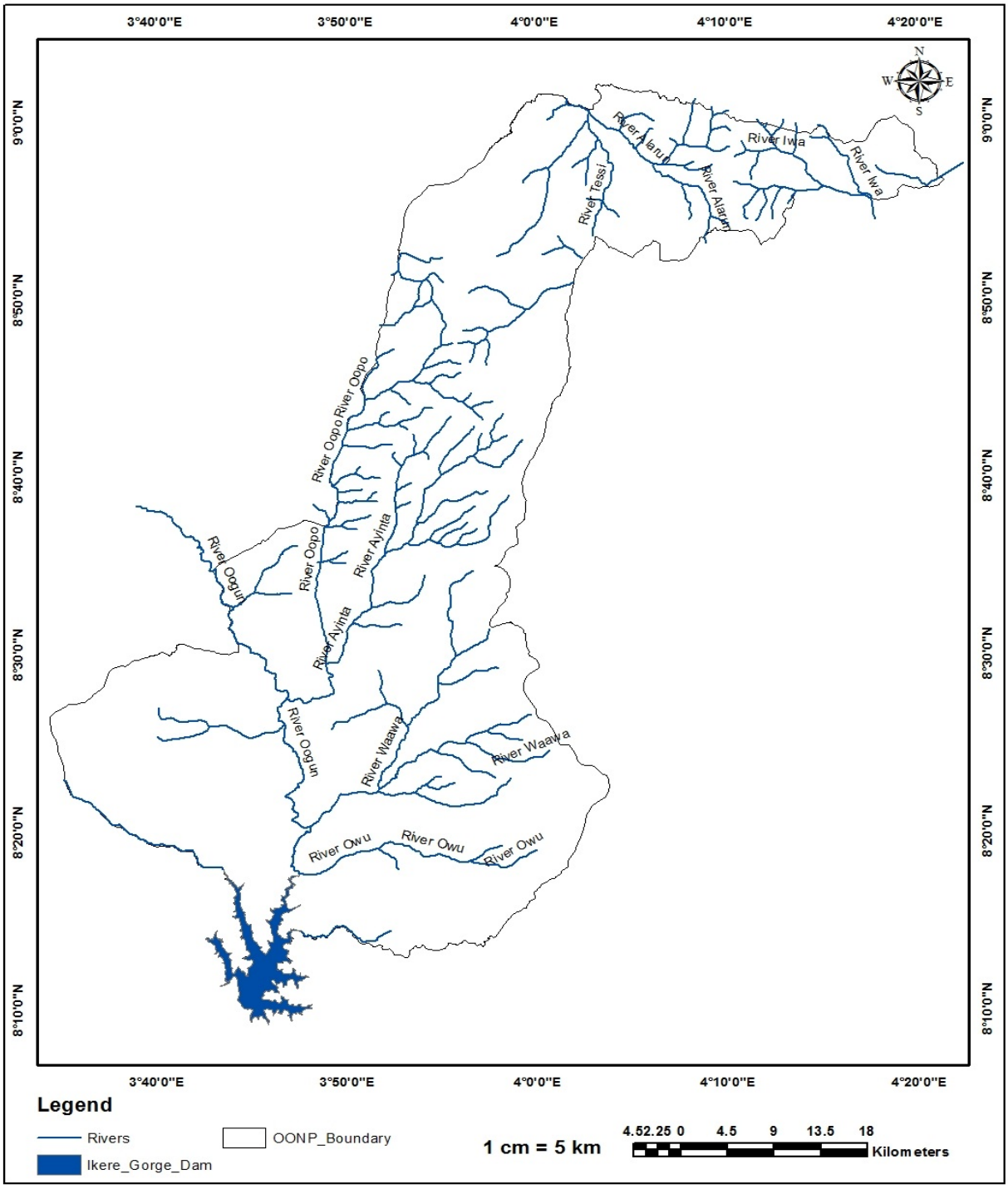

Figure 3.3: Drainage Map of Old Oyo National Park

Source: Field Survey, 2016

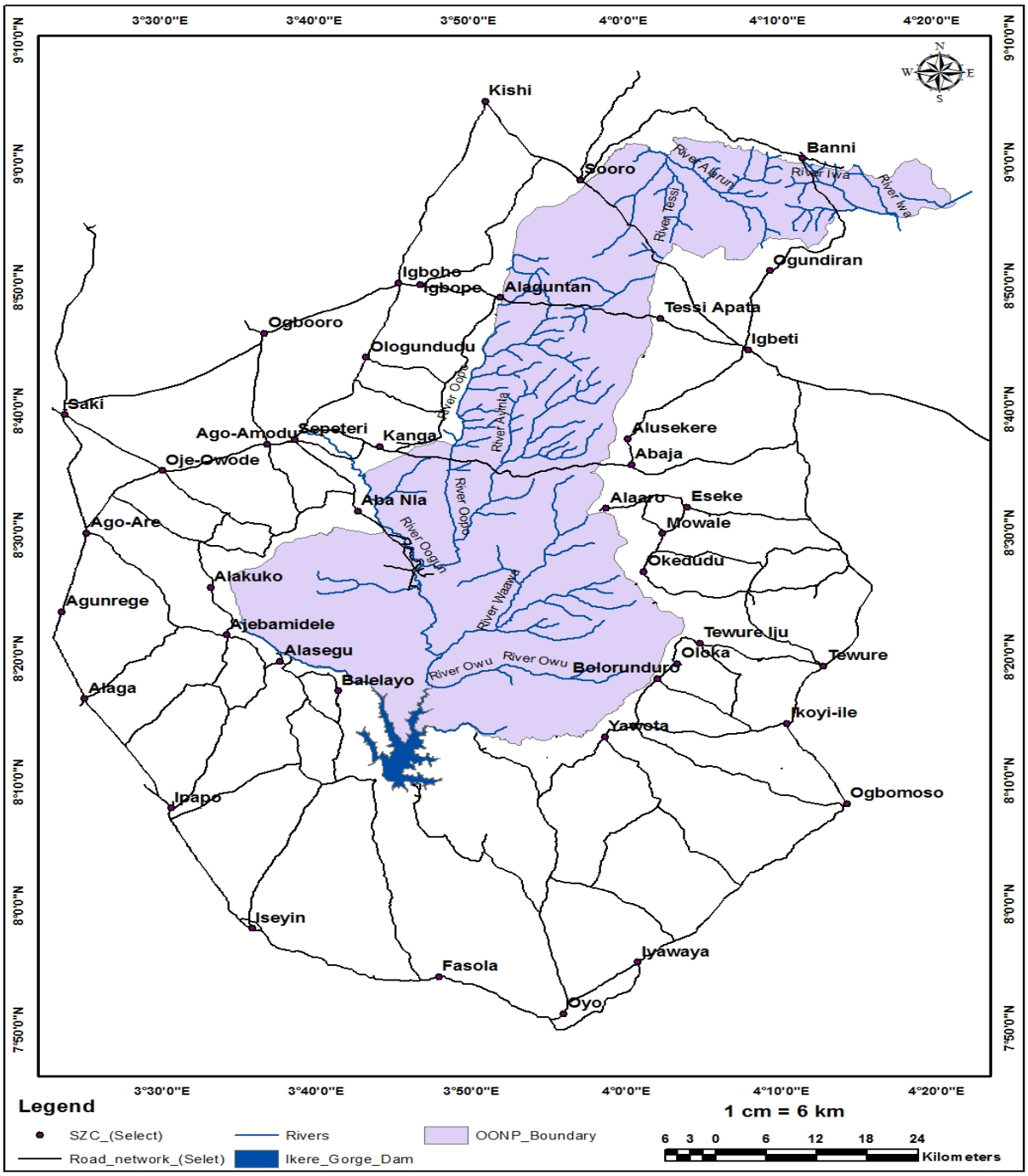

Figure 3.4: Drainage Map of Old Oyo National Park with surrounding communities

Source: Field Survey, 2016

3.2 Sample Site Selection

The study was carried out within three (3) ranges of Old Oyo National Park. The ranges include Oyo-Ile, (located in the northern part of the park), Tede, (located in the southern part of the park) and Marguba (located in the middle or heart of the park). These ranges were purposively selected based on the availability of perennial waterholes, representativeness of the park and observed anthropogenic activities by the surrounding local communities such as agriculture, charcoal production, illegal mining and grazing after a thorough reconnaissance survey was carried out.

3.3 Reconnaissance Survey

Prior to the commencement of this study, repeated visits were made to the head office of Old Oyo National Park, located in Oyo and a reconnaissance survey was carried out in all the five administrative ranges to know the availability of perennial waterholes. Sequel to the reconnaissance survey, three ranges was purposively selected and another reconnaissance survey was done to adequately familiarize with the study/sampling sites and identify suitable and adoptable methods for the study.

3.4 Sample Collection, Preservation and Treatment

3.4.1 Water

Grab sampling was carried out at all the sites for water sample collection from the selected waterholes (rivers). Water samples were collected from River Owu (in Tede range), Rivers Ogun, Oopo and Ayinta (in Marguba range), Rivers Tessi and Sooro (in Oyo-Ile range). Samples were collected into appropriate sample containers at different sampling points (upper, middle and lower courses) along the rivers and subsequently composited for each river. As such, a total of one (Tede range), three (Marguba range) and two (Oyo-Ile range) composited water samples were collected per season of sampling. In all, twenty-

four (24) composited water samples were collected throughout the period of sampling. Sampling was done within four seasons during the rain (April-October) and dry (November-March) seasons for two consecutive years (between 2017 and 2018). The composited samples collected from Marguba range are represented as MW_1 (River Ogun), MW_2 (River Oopo) and MW_3 (River Ayinta) while those of Oyo-Ile range are OW_1 (River Tessi) and OW_2 (River Sooro). The composited water sample collected from Tede range is represented as TW_1 (River Owu). Table 3.1 shows the ranges and geo-referencing (coordinates) of the sampling points.

For water sample preservation and treatment, about 0.5 L of the water samples was taken at each sampling site and acidified with 10% HNO_3 immediately in order to prevent analyte loss as well as release all metals present in the sample (David *et al.,* 2012) and thereafter put in an ice bath and taken to the laboratory. The samples were subsequently filtered via 0.45μm micropore membrane filter and kept at 4^0C prior to analysis (Edward *et al.,* 2013).

Table 3.1: Sampling Ranges, Water Sample Codes and Coordinates

Old Oyo National Park Ranges	Sample Codes	Waterholes	Coordinates (latitude/longitude)
Marguba	MW_1	River Ogun	N $08^0 27^1 16.8$’ E $003^0 46^1 35.2$
	MW_2	River Oopo	N $08^0 27^1 28.3$’ E $003^0 46^1 47$
	MW_3	River Ayinta	N $08^0 58^1 .321$’ E $003^0 86^1 .048$’
Oyo-Ile	OW_1	River Tessi	N $08^0 51^1 .975$’ E $004^0 02.251$
	OW_2	River Sooro	N $08^0 58^1 .339$’ E $003^0 57^1 .485$’
Tede	TW_1	River Owu	N $07^0 22^1 02.6$ E $004^0 06^1 09.7$

3.4.2 Soil

The method of soil sampling by Alarape (2002) was adopted for this study but slightly modified. Topsoil samples (0 – 15 cm) were collected randomly at three different points (upper slope, middle slope and lower slope) along the chosen topographical catena (about 1.2 km in length) using a hand-held auger. Samples were collected into clean polyethene bags and thoroughly mixed to form a composite and were well-labelled appropriately. Three of such topographical catenae (2 – 5 km apart) were selected in Marguba, Oyo-Ile and Tede ranges of Old Oyo National Park. Topsoil samples were collected because previous studies have shown that surface soils are better indicators of metallic burdens (Oyewale and Funtu, 2002; Amusan *et al.,* 2005).

A total of three (Tede range), three (Marguba range) and three (Oyo-Ile range) composited topsoil samples were collected per season of sampling. In all, thirty-six (36) composited topsoil samples were collected throughout the period of sampling. Sampling was done within four seasons during the rain (April-October) and dry (November-March) seasons for two consecutive years (between 2017 and 2018). The composited topsoil samples collected from Marguba range are represented as MS1, MS2 and MS3 while those of Oyo-Ile range are represented as OS1, OS2 and OS3. The composited topsoil samples collected from Tede range are represented as TS1, TS2 and TS3. The coordinates of the sampling points are presented in Table 3.2.

Table 3.2: Sampling Ranges, Soil Sample Codes and Coordinates

Old Oyo National Park Ranges	Sample Codes	Coordinates (latitude/longitude)
Marguba	MS1	N $08^{0}30'04.6$ E $003^{0}44'34.2$
	MS2	N $08^{0}29'49.2"$ E $003^{0}54^{1}18"$
	MS3	N $08^{0}26'52.3"$ E $003^{0}59'13.1"$
Oyo-Ile	OS1	N $08^{0}58.296'$ E $003^{0}57.543$
	OS2	N $08^{0}54.827'$ E $004^{0}00.736'$
	OS3	N $08^{0}57.589'$ E $003^{0}58.280'$
Tede	TS1	N $08^{0}27'39.6"$ E $003^{0}36'46.2"$
	TS2	N $08^{0}29'00.1"$ E $003^{0}33'56.4"$
	TS3	N $08^{0}16'22.8"$ E $003^{0}44'56.4"$

3.4.3 Plant

The Segmented Transect Belt Method (STBM) was adopted for plant sampling (Alarape, 2002). Transect lines of 1.2 km in length were chosen randomly in Marguba, Oyo-Ile and Tede ranges of Old Oyo National Park. On each transect, at about 100 m sampling intervals, four matured plant (leaves) samples were randomly collected. The plant species sampled were the ones that are thought (sequel to reconnaissance survey) to be most preferred by herbivores in each of the chosen ranges. As such, plant species in Marguba (*Blighia sapida*, *Terminalia glaucescens*, *Kigelia africana* and *Pterocarpus erinaceus*), Oyo-Ile (*Vitellaria paradoxa*, *Khaya grandifoliola*, *Afzelia africana* and *Daniella oliverii*) and Tede (*Anogeissus leiocapus*, *Brachystegia euryloma*, *Isoberlinia doka* and *Burkea africana*) ranges were collected, properly labeled and assessed for heavy metals.

The plant species were identified on the field with the help of rangers and later confirmed at the Department of Botany, University of Ibadan. A total of four (Marguba range), four (Oyo-Ile range) and four (Tede range) plant samples were collected per season of sampling. In all, forty-eight (48) plant samples were collected throughout the period of sampling. Sampling was done within four seasons during the rain (April-October) and dry (November-March) seasons for two consecutive years (between 2017 and 2018).

3.4.4 Wild Animal Faeces

Faeces of wild animals were collected randomly within the study area (Marguba, Oyo-Ile and Tede ranges) through opportunistic sighting method (Gupta and Bakre, 2012b) into sample bottles (plastic), properly labeled and evaluated as a biomarker of exposure to heavy metal contamination. A total of 43 faecal samples (belonging to seven species of animals) were collected throughout the period of sampling as shown in Table 3.3.

Table 3.3: Faecal sample codes, Number of samples and Animal Species

Faecal Sample Code	Animal Species	Number of Faecal Samples per range	Total Number of Faecal Samples
F1	Mongoose (*Atilax paludinosus*)	Marguba = 4	4
F2	Olive baboon (*Papio anubis*)	Marguba = 8 Oyo-Ile = 1 Tede = 3	12
F3	African Civet cat (*Civettictis civetta*)	Marguba = 2 Oyo-Ile = 1 Marguba = 6	3
F4	Kob (*Kobus kob*)	Oyo-Ile = 1 Tede = 1	8
F5	Maxwell duiker (*Philantoba maxwelli*)	Marguba = 5 Tede = 1	6
F6	Western hartebeest (*Alcelaphus buselaphus*)	Marguba = 4	4
F7	Patas Monkey (*Erythrocebus patas*)	Marguba = 1 Oyo-Ile = 1 Tede =4	6

The samples were identified on the field using experienced park rangers while further confirmation was done with the use of a field guide. The problem of feasibility affected sample collection during the rainy season and as such, the wild animal faecal samples were only sampled during the dry season (November-March). The map of Old Oyo National Park showing the sampling points for water, soil, plant and wild animal faecal samples is shown in Figure 3.5.

3.5 Parameters Determined

For the heavy metals assayed, Zinc (Zn), Cadmium (Cd), Nickel (Ni), Copper (Cu), Lead (Pb), Chromium (Cr), Iron (Fe) and Manganese (Mn) were analyzed in water, soil, plant and wild animals' faecal samples from the study area. These heavy metals were purposively selected because they constitute part of the eleven heavy metal elements of utmost wildlife protection concern (Beyersmann and Hartwig, 2008) and also based on the observed anthropogenic activities around the study area such as agriculture, charcoal production, illegal mining and vehicular emissions even within the park especially at Oyo-Ile range. Physicochemical characteristics of water samples such as pH, temperature, total dissolved solids (TDS) and electrical conductivity (EC) were determined *in-situ* while total suspended solids (TSS), total solids (TS), Dissolved Oxygen (DO), Nitrate (NO_3^-), Phosphate (PO_4^{3-}), Sulphate (SO_4^{2-}), Chloride (Cl^-), Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) were determined using standard methods. Soil physicochemical parameters such as particle size, pH, soil organic matter (SOM), soil organic carbon (SOC), soil nitrogen, exchangeable bases (Ca, Mg, K, Na), exchangeable acidity, available phosphorus and conductivity. Microbiological characteristics such as total faecal count and fungi count were also determined in the laboratoryusing standard methods.

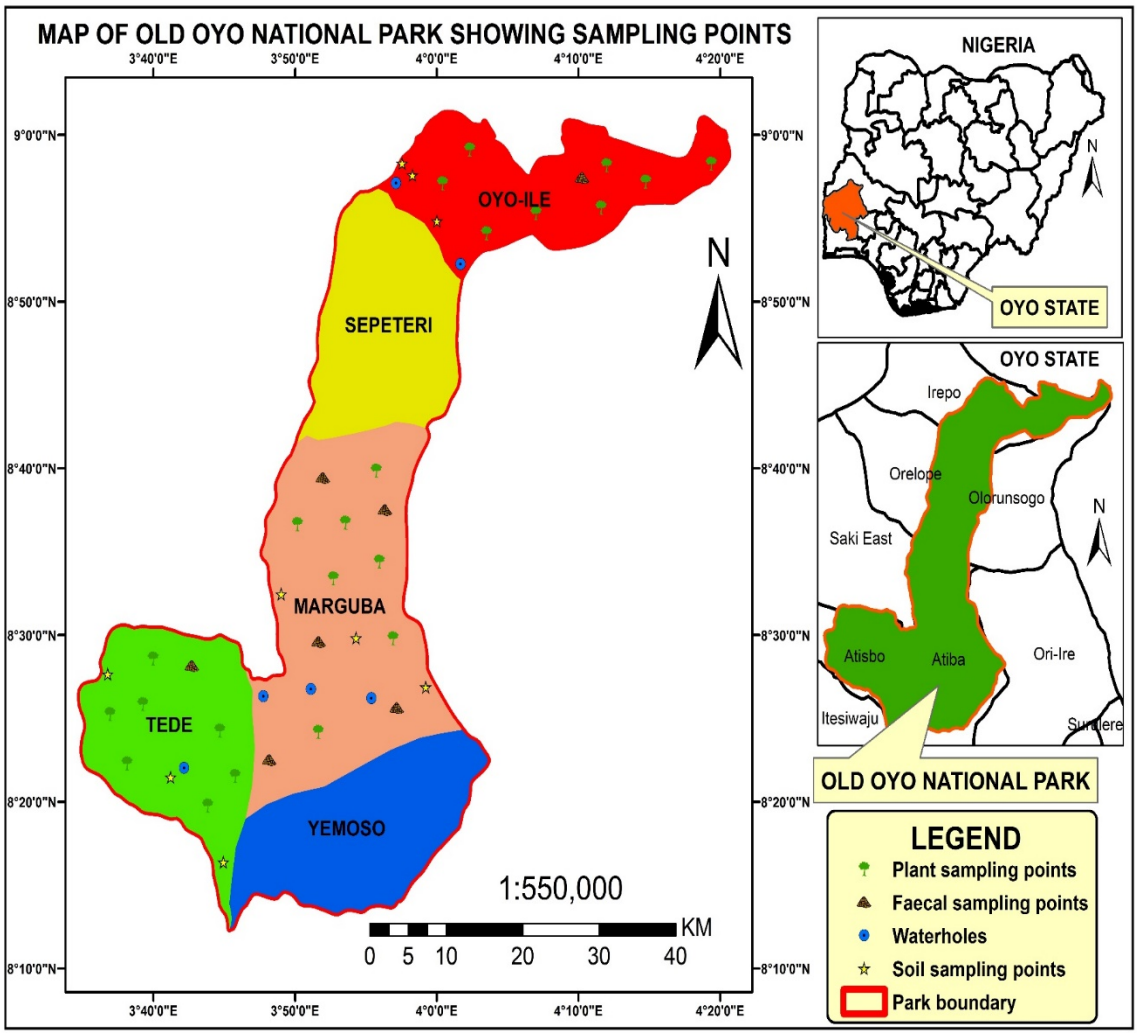

Figure 3.5: Map of Old Oyo National Park showing the sampling points

3.6 Analytical Procedures

3.6.1 Determination of Heavy metals in Water, Soil, Plant and Faecal Samples

About 50 ml of the water sample were transferred into 250 ml beakers and about 5 ml of concentrated nitric acid (HNO_3) was added and boiled slowly on a water bath, then later on a hot plate to the lowest volume possible (about 10 to 20 ml). Another 3 ml of concentrated nitric acid was added and heating continued until digestion was completed as shown by a light-coloured, clear solution (samples were not allowed to evaporate to dryness during digestion). The beaker wall was washed down with distilled water and then filtered. Filtrate was transferred to 100 ml volumetric flask with two 5 ml portion of distilled water, which was added to the volumetric flask. It was cooled, diluted to mark, and mixed thoroughly. The solution thereafter taken for required metal determination using Buck Scientific 210 VGP model Atomic Absorption Spectrophotometer while distilled water for blank determination was also taken through the same procedure.

The metal concentrations in the water samples were determined using the formula;

$$\text{Metal concentration (mg/L)} = \frac{A \times B}{C}$$

Where,A = Concentration of metal (instrument reading) in the digested solution (mg/L)

B = Final volume of digested solution after making up to mark (25 ml)

C = Volume of water sample (mg/l)

For soil samples, approximately 2.0 g each of the sieved soil samples were transferred into 50 ml digestion tubes, 10 ml of 2 M HNO_3 acid was added and the samples were digested on a hot plate (in a fume cupboard) for 2 hours, shaken at 20 min intervals until the

volume was about 3 ml. The residues obtained were further digested with a mixture of concentrated acids containing 5 ml each of HCl, HNO_3 and $HClO_4$ at room temperature for 10 minutes until the solution was brought to a final volume of about 5 ml on a hot plate in fume cupboard.

The digested samples were filtered (using Whatman No.1 filter paper) into 25 ml flask. The filtrates were diluted to mark with deionized water. The digested samples were analysed using Buck scientific VGP Atomic Absorption Spectrophotometer. Blank determination was also carried out without the soil sample. The metal concentrations were determined using the formula:

$$\text{Heavy metal concentration (mg/kg)} = \frac{(M - B) \times V}{W}$$

Where:

M = Concentration (mg/L) of metal in the sample solution from AAS reading.

B = Concentration (mg/L) of metal in the blank solution from AAS reading

W = Weight (g) of soil sample used for digestion

V = Final volume (ml) of the digestate.

For plant sample, sample preparation and analysis were done following the procedures described by Soomro *et al.* (2008). The plant (leaves) samples were oven-dried and pulverized using a pulverizer. Then, about 1.0 g plant samples were appropriately digested using 12 mL concentrated acid mixture (69% HNO_3: 70% $HClO_4$; 3:1 v/v). The mixture was heated over a sand bath in a fume hood until it became clear. After the digested samples were cooled, they were filtered and transferred into a 100 mL volumetric flask and the volume was made to the mark with 5% HNO_3 acid. The concentration of metals in

the samples were subsequently determined using Buck scientific VGP Atomic Absorption Spectrophotometer.

For faecal sample analysis, about 0.5 g of the dry faecal was properly weighed and placed digestion tube. Concentrated nitric acid (HNO_3) and perchloric acid ($HClO_4$) were added to each of the samples in 4:1 ratio (Gaumat and Bakre, 1998). Samples were thereafter kept in water bath for between 5 to 6 hours prior to complete digestion and became clear. Once the samples became clear, about 3 to 4 drops of 30% H_2O_2 was added to neutralize and dissolve the fatty content. Sequel to cooling, each sample was now diluted up to 10 ml with deionized water and transferred to sterilized plastic vial bottles and kept at room temperature prior to analysis (Gupta and Bakre, 2013). The concentration of metals in the samples were subsequently determined using Buck scientific VGP Atomic Absorption Spectrophotometer.

3.6.2 Physicochemical Characteristics in Water

3.6.2.1 Determination of pH

This was measured by using a pH meter (HI98128 pHep®5 Model). The pH meter was calibrated by adjusting the response of the glass electrode of the meter. It was done by immersing it in buffer solution of potassium hydrogen phthalate and necessary adjustment were made to correct the reading to a value of 4.0. the electrode was removed, rinsed thoroughly with distilled water and blotted dry with soft tissue paper. It was then placed in a mixture of potassium hydrogen phosphate and di-sodium hydrogen phosphate (buffer 7) and the needed adjustment were made on the pH meter to a value of 7.4. The electrode was removed, rinsed thoroughly with distilled water and blotted dry with soft tissue paper. It was afterward immersed in the water samples one after the other with successive rinsing

with distilled water and blotting dried after each water sample. The pH measurement was taken right on the field on separate sub-samples which were discarded after measurement.

3.6.2.2 Determination of Electrical Conductivity

This was determined using a conductivity meter (HI9831DiST®5 Model) after calibration at 25^0C. The calibration was done with a standard solution of potassium chloride. Water samples were thereafter placed in a clean beaker, and the probe of conductivity meter was immersed in it for reading, after which it was cleaned with distilled water and blotted dry with tissue paper. It was expressed in micro siemens per centimeter (μscm^{-1})

3.6.2.3 Determination of Temperature

Both ambient and sample temperatures were measured using a mercury-in-bulb thermometer (COM-100 Model) in degree Celsius unit.

3.6.2.4 Determination of Total Dissolved Solids (TDS) by Gravimetry

The filtration apparatus was assembled with a glass fiber filter paper which was washed with distilled water under suction, dried in an oven at 105^0C for one hour, cooled in a desiccator and then weighed. The process was repeated until constant weight was achieved. The glass fiber filter paper was placed in the funnel and moistened with distilled water. About 50 ml of the water samples were measured and passed through the filtration system under suction, to ensure that all the solids in the water were trapped by the filter. The filtrate was evaporated to dryness in a dish (already washed, dried and weighed to a constant weight), on a steam bath, and dried further in an oven for one hour at 105^0C, cooled in a desiccator and weighed. The process was repeated until constant weight was obtained. The increase in the weight of the dish represents the total dissolved solids.

Calculation

$$\text{TDS (mg/L)} = \frac{1000 \times (Mt - Md)}{V}$$

Where

Mt = weight of the dish + dried residue (mg)

Md = weight of the dish (mg) only

V = volume of sample taken (ml)

3.6.2.5 Determination of Total Solids (TS) by Gravimetry

The filtration apparatus was assembled with a glass fiber filter paper which has been washed with distilled water under suction, dried in an oven at 105^0C for one hour, cooled in a desiccator and then weighed. The process was repeated until constant weight was achieved. The glass fiber filter paper was placed in the funnel and moistened with distilled water. About 50 ml of the water samples were measured and passed through the filtration system under suction, to ensure that all the solids in the water were trapped by the filter. The fiber was then removed, dried at 105^0C for one hour in an oven, cooled in a desiccator and weighed. The process of drying, cooling and weighing was repeated until constant weight was obtained. The increase in the weight of the empty dish represents the total solids.

Calculation:

$$\text{TS (mg/L)} = \frac{1000 \times (Mt - Md)}{V}$$

Where

Mt = weight of the dish + dried residue (mg)

Md = weight of the dish (mg) only

V = volume of sample taken (ml)

3.6.2.6 Determination of Total Suspended Solids (TSS)

The TSS was estimated by using the formula below:

$$TSS\ (mg/L) = TS - TDS$$

Where

TSS = Total suspended solid in mg/L

TDS = Total dissolved solid in mg/L

TS = Total solid in mg/L

3.6.2.7 Determination of Total Alkalinity by Titrimetry

About 50 ml of the water samples were measured into 250 ml conical flasks, 2 – 3 drops of phenolphthalein indicator were added and then titrated against standardized 0.02 M sulphuric acid until pink colour was observed, thus determining the phenolphthalein alkalinity. Total alkalinity was determined by continuing the titration above with 3 drops of bromocresol methyl red indicator until pink colour appeared.

Calculation

$$\text{Alkalinity, (mg/L)} = \frac{A \times M \times 50{,}000}{V}$$

Where,

A = volume of standard H_2SO_4 used (ml)

M = molarity of H_2SO_4 used

V = volume of sample taken (ml)

3.6.2.8 Determination of Chloride by Titrimetry

About 25 ml of the water samples were measured and diluted to 50 ml with distilled water. The pH was adjusted to 7.5 with 1 drop of 0.1 M NaOH, followed by 1 ml K_2CrO_4 solution

(Mohr's indicator). This was then titrated with 0.014 M $AgNO_3$ standard solution until the colour changed from yellow to faint red. Reagent blank and distilled water blank was titrated using the same procedure.

Calculation

$$Cl^- \text{ (mg/l)} = \frac{(A - B) \times M \times 35{,}450}{V}$$

Where,

A = volume of $AgNO_3$ used for sample titration (ml)

B = volume of $AgNO_3$ used for blank titration (ml)

M = molarity of standardized $AgNO_3$ solution

V = volume of sample taken (ml)

3.6.2.9 Determination of Phosphate by Colorimetric Method

About 40 ml each of the water samples were measured into a 50 ml standard volumetric flask and 8 ml of reducing agent was added, and thereafter made up to the 50 ml mark with distilled water. The solution was allowed to stand for 10 minutes and its absorbance measured spectrophotometrically at 880 nm. Blank titration was carried out in the same way as that of the water sample. The phosphate concentrations of the samples were estimated by extrapolation from the calibration curve which was obtained from spectrophotometric analysis of phosphate solutions.

Calculation

$$PO_4^{3-}\text{(mg/L)} = \frac{\text{mg } PO_4^{3-} \times 1000}{\text{volume of sample (ml)}}$$

3.6.2.10 Determination of Sulphate by Turbidimetry

About 20 ml buffer solution (prepared from magnesium chloride, sodium acetate, potassium nitrate, and acetic acid) was added to 100 ml of the water samples and mixed with magnetic stirrer. While stirring, a spoonful of $BaCl_2$ crystal was added. It was stirred for 60 ± 2s at constant speed. After stirring, the solution was poured into absorption cell of spectrophotometer which had been standardized and turbidity was measured at 5 ± 0.5minutes. Sample blank in which no $BaCl_2$ was added was carried out in the same way as that of the water samples. The sulphate concentration in the water samples was estimated by comparing turbidity reading with a calibration curve prepared by carrying sulphate ion standard through the entire procedure.

Calculation

$$S0_4^{2-}\ (mg/L) = \frac{Mg\ SO_4^{2-} \times 1000}{\text{volume of sample (ml)}}$$

3.6.2.11 Determination of Nitrate by Phenoldisulphonic acid method

Approximately 50 ml of the water sampled was treated with 50 ml of $AgSO_4$ solution. By filtration This is to prevent interference by chloride. Precipitated chloride was removed filtration and the clarified sample was evaporated to dryness on a hot water bath. The residue obtained was treated with 2 ml phenoldisulphonic acid reagent (prepared by dissolving phenol in concentrated sulphuric acid) until complete dissolution was obtained. This was diluted with 50 ml distilled water and 2 ml phenoldisulphonic acid was added followed by 10 ml concentrated NH_4OH solution until maximum yellow colour developed. Photometric reading was made at 410 nm in a 10 mm quart cell with CAMSPEC M106 spectrophotometer against a blank prepared by taking distilled water through the same procedure. Calibration curve was prepared by taking stock nitrate solution (KNO_3) through

the same procedure and the concentration of nitrate in the samples were obtained from the curve by interpolation.

Calculation:

$$N0_3^- \text{ (mg/L)} = \frac{\text{Mg } N0_3^- \text{ x } 1000}{\text{volume of sample (ml)}}$$

3.6.2.12 Determination of Dissolved Oxygen by Titrimetry (Winkler's method)

The dissolved oxygen (DO) in the water samples was determined by making use of the azide modification of the Winkler Titration method. About 2 ml of manganese sulphate was added into a 300 ml glass-stoppered Biological Oxygen Demand (BOD) bottles that were filled up with water samples collected from the study sites by dipping a calibrated pipette below the surface of the liquid, sequel to which a 2 ml of alkali-iodide-azide reagent was added using the same approach. A brownish-orange cloud of precipitate or floc appeared and was patiently allowed to settle for adequate time so as to react wholly with oxygen. Thereafter, 2 ml of concentrated H_2SO_4 was added by using a pipette held above the surface of the water sample which was cautiously stoppered and inverted more than a few times to dissolve the floc. At this point, the water sample was said to be fixed after which titration with sodium thiosulphate started immediately using starch solution as indicator. The end point of the titration was the first disappearance of the blue colour to colourless. The titration was subsequently repeated for concordant values. The volume of sodium thiosulphate solution added was taken as the DO value in the water samples.

3.6.2.13 Determination of Biological Oxygen Demand (BOD_5) by Titrimetry

Refrigerated water samples were allowed to reach 20^0C before analysis. Leaving the sample at room temperature for 8 hours could reduce the BOD by as much as 40%; thus, the samples were not refrigerated more than 24 hours. The pH of the water samples was measured and adjusted to pH 7 – 8 using HCl or NaOH solution as the case may be. About 400 ml dilution water (prepared daily by adding 1 ml of each of the phosphate buffer, magnesium sulphate, calcium chloride and ferric chloride solutions per litre of water and saturated with air) was placed in 1 L measuring cylinder. The water was poured slowly to the wall of the cylinder to prevent entrainment of air. Then, 200 ml of samples were measured and added to the dilution water, and diluted to 1 L. This was mixed carefully with a mixing rod so as not to entrain air bubbles. Three 250 ml BOD bottles were filled with the diluted sample solution. Dissolved oxygen (DO) in one bottle was determined immediately by Winkler's method. The other two bottles were stoppered, water-sealed, placed in water bath and incubated in the dark for 5 days at 20^0C. After 5 days, the DO was determined by Winkler's method. Three other bottles were filled with the dilution water. Dissolved oxygen was determined in one of the bottles immediately and in the other two bottles after incubating for 5 days. This dilution water blank served as a rough check on the quality of the dilution water and it should not exceed 0.2 mg/L. The average BOD values measured in the two incubated bottles were reported.

Calculation

$$BOD\ (mg/L) = F\ (Di - Df)$$

Where,

Di = initial DO in the sample

Df = DO in the diluted sample after 5 days of incubation

F = dilution factor

$$F = \frac{\text{total volume after dilution (ml)}}{\text{volume of undiluted sample (ml)}}$$

3.6.2.14 Determination of Chemical Oxygen Demand

About 50 ml of water samples were measured into a 500 ml refluxing flask. About 1 g $HgSO_4$ and several glass beads were added to serve as anti-bumping agent. About 5.0 ml sulphuric acid reagent was added slowly to dissolve $HgSO_4$. The flask was allowed to cool while mixing with H_2SO_4 acid reagent to avoid loss of volatile materials. Then, 25 ml of 0.0417 M $K_2Cr_2O_7$ solution was added and mixed together. The flask was then attached to a condenser with water for cooling. The remaining 70 ml of the sulphuric acid reagent was added through the open end of the condenser with swirling and mixing of the solution while adding it. The open end of the condenser was covered and the mixture was refluxed for 2 hours. After cooling, the condenser was washed down with distilled water and its content was diluted to twice its original volume with distilled water.

After cooling to room temperature, excess $K_2Cr_2O_7$ was titrated with standard 0.25 M ferrous ammonium sulphate (FAS) using 0.10 to 0.15 ml (2 to 3 drops) of ferroin indicator. The first sharp colour change from blue-green to reddish-brown was taken as the end point. The same amount of distilled water was taken through the whole procedure for blank determination. Before determining the COD of the sample, COD of potassium hydrogen phthalate solution was carried out as standard check. Potassium hydrogen phthalate (KHP) has a theoretical COD of 1.176 mgO_2/ml and this solution has a theoretical COD of 500 μgO_2/ml

Calculation

$$\text{COD } (MgO_2/l) = \frac{8000 \times M \times (Vb - Vf)}{Vs}$$

Where;

M = molarity of FAS solution = 0.25

Vb = volume of FAS solution used for method blank

Vf = volume of FAS solution used for leachate samples

Vs = volume of sample analysed

3.6.3 Physicochemical Characteristics of Soil

3.6.3.1 Determination of Soil pH

The soil pH was determined with the pH meter using glass electrode in a 1:1 soil to water ratio (Udo *et al.*, 2009). About 20 g of air-dried soil was weighed into sample bottles after sieving with 2 mm sieve. Distilled water of 20 ml was added to the soil sample in a 50 ml beaker and placed on a mechanical shaker to shake for 10 minutes. Thereafter, the solution was left to settle for 10 minutes. The electrode of the soil pH meter (calibrated with buffer solution at pH 4 and pH 7) was inserted into the partially settled solution to measure the pH reading for each of the sample. The result gotten was reported as soil pH measured in water.

3.6.3.2 Determination of Electrical Conductivity

The electrical conductivity of the soil samples was determined in the filtrate of the water extracts by making use of a conductivity meter.

3.6.3.3 Determination of Soil Organic Carbon (SOC)

The organic carbon of the soil was determined using the Walkey-Black wet oxidation method (Udo *et al.*, 2009). The 0.5 g of 0.5 mm sieved soil was weighed into a conical

flask; 10 ml of potassium dichromate ($K_2Cr_2O_7$) solution was measured into each flask and spun gently to disperse the soil. The 20 ml of concentrated sulphuric acid was also added to the soil solution to further disperse the soil. The samples were left to cool for 20 minutes before adding distilled water up to the mixture before titrating the sample with 0.5N ferrous ammonium sulphate solutions. As the end point was approaching, the solution gives a greenish cast and thereafter changes to maroon red. A blank titration was also carried out in the same manner but without soil to standardize the potassium dichromate ($K_2Cr_2O_7$) solution.

Mathematically,

% Organic carbon was calculated as follows:

$$Y = \frac{\text{Volume of } K_2Cr_2O_7 X}{\text{Blank value}} \quad \frac{0.003 \times 100 \times 1.33}{\text{weight of sample}}$$

% Organic carbon = (blank titre value – sample titre value) x Y

3.6.3.4 Determination of Soil Organic Matter

Organic matter of sampled soils was obtained by multiplying % Organic carbon with conventional 'van Bemmelar factor of 1.724.

% SOM = % SOC x 1.724 (Walkley and Black, 1934).

3.6.3.5 Determination of Total Nitrogen

The 0.5 g of 0.5 mm sieved soil samples were weighed into a dry digestion tube and one tablet of selenium tablet was added. The 10 ml of concentrated H_2SO_4 was also added to the samples before heating on a digestion block for 5 hours until the digestion was complete. Chemical decomposition of the samples was indicated when the initially dark coloured medium became colourless. The samples were removed from the digester and allowed to cool. The digest was made up to 50 ml and transferred to sample bottles.

Distillation was then carried out using 5 ml of boric acid which was weighed into the Erlenmeyer flasks and put under the end of the condenser of the distillation apparatus. The 5 ml of the digest solution was then distilled with 5 ml of sodium hydroxide in the distillation flask by opening the funnel stopcock. The condenser was kept cool by permitting enough cold water to flow through and regulate heat to reduce frothing and avoid suck-back. A 50 ml of distillate was collected for each sample that was distilled. The 50 ml of distillate is then titrated with 0.01M HCl. The ammonia reacts with the acid. The colour changed at the end point from green to pink. A blank sample was also made using the same procedure but without the soil sample in it.

Calculation:

$$\% \text{ Nitrogen} = \frac{(T-B) \times 14.01 \times 0.01N \times 100 \times 10}{\text{Weight of soil sample} \times 1000}$$

Where;

T = Volume of acid titrated for the sample (ml)

B = Digested blank titration volume (ml)

3.6.3.6 Determination of Available Phosphorus

Available phosphorus was determined with spectrophotometer using Mehlich III as extractant (Udo *et al*., 2009). This method was carried out by weighing 2 g of 2mm sieved soil into an extracting cup and adding 20 ml of Mehlich III solution to it. The samples were stirred on a mechanical shaker for 10 minutes. The mixture was then filtered using a filter paper to collect 5 ml of the filtrate in a clean sample bottle. About 5 ml of colour reagent was added to the extracted filtrate and this was measured up to 50 ml with distilled water. The phosphorus concentration in the extract was determined by the blue

calorimetric method of Murphy and Riley (1962). The samples were read with the spectrophotometer.

3.6.3.7 Determination of Exchangeable Acidity

KCl extraction method was used to determine the exchangeable acidity present in the soil. Approximately 10 g of 2 mm sieved soil was weighed into an extractant cup; 10 ml of 1.00N KCl was added. The solution was stirred for 10 minutes with mechanical shaker and filtered with filter paper (whatman 9 cm diameter). The 10 ml of filtrate was collected in an extractant cup and 3 drops of phenolphthalein (0.1%) indicator was added to the solution. These samples were titrated against 0.01N NaOH. At the end point of titration, the samples changed colour from colourless to light pink. The volume of base (NaOH) used for titrating each sample was multiplied by 0.5 to get the total exchangeable acidity of the soil samples.

3.6.3.8 Determination of Exchangeable Bases

The 20 ml of Mehlich III solution was measured into 0.5 g of 2 mm sieved soil in an extracting cup buffered at pH 7. The samples were stirred on the mechanical shaker for 10 minutes after which the filtrates were collected with the aid of a filter paper into a sample container. $Ca^{2+,}$ Mg^{2+}, K^{+} and Na^{+} were determined in the extract using Atomic Absorption spectrophotometer (AAS).

3.6.3.9 Determination of Total Exchangeable Bases

These were estimated by adding together, the values for $Ca^{2+,}$ Mg^{2+}, K^{+} and Na^{+}.

3.6.3.10 Determination of Effective Cation Exchange Capacity

The determination of the effective cation exchange capacity (ECEC) was taken or calculated as the summation of exchangeable acidity and that of exchangeable bases:

ECEC = Exchangeable Acidity + Total Exchangeable Bases

3.6.3.11 Determination of Base Saturation

The base saturation (BS) was obtained as a percentage of total exchangeable bases (TEB) by the effective cation exchange capacity (ECEC):

$$BS\ (\%) = \frac{TEB}{ECEC} \times 100\%$$

3.6.3.12 Determination of Particle Size

Particle size analysis was carried out by making use of the Bouyoucos hydrometer method as documented by Udo *et al.* (2009). The 50 g of the sieved soil was dispersed using calgon sodium hexametaphosphate ($Na_3(PO_4)_6$) then 250 ml of water. The soil dispersion cup was permitted to stay for 20 minutes. The suspension was stirred using the mechanical stirrer for 5 minutes. The soil solution was emptied into a sedimentation cylinder via 0.2 mm sieve fixed onto the 1000 ml cylinder. The sand particles were washed to remove the silt and clay particles that adhere to the sand particles.

The sand particles left in the sieve was transferred to a Petridish and oven dried to a constant weight at 105^0C. The solution in the sedimentation cylinder was made to one litre mark. The sedimentation cylinder was shaken 50 times by covering the mouth of the cylinder with polyethene. Hydrometer was gently inserted into the sedimentation cylinder after shaking for 40 seconds to measure the concentration of silt + clay in the suspension. The room temperature was recorded using a thermometer. The hydrometer was removed, washed and used to take the second hydrometer reading (for clay concentration) after two hours. The temperature was also recorded.

Calculation*:*

First hydrometer reading = concentration of silt + clay particles

Second hydrometer reading = concentration of clay particles

Temperature correction at 1 minute and 2 hours = 0.3 (T – 20) °C = X gL^{-1}

$$\% \text{ silt} + \% \text{ clay} = \frac{\text{temperature correction factor + concentration of silt and clay}}{50\ g} \times \frac{100}{1}$$

$$\% \text{ clay} = \frac{\text{temperature correction factor + concentration of clay}}{50\ g} \times \frac{100}{1}$$

$$\% \text{ silt} = (\% \text{ silt} + \% \text{ clay}) - \% \text{ clay}$$

$$\% \text{ coarse sand} = \frac{\text{weight of oven dried sand (g)}}{50\ g} \times \frac{100}{1}$$

% sand + % silt + % clay + % fine sand = 100

% fine sand = 100 - % (coarse sand + silt + clay)

3.6.3.13 Determination of Textural Class

The textural class of the soil was determined by using the United States Department of Agriculture (USDA) textural triangle.

3.6.4 Quantitative Assessment of heavy metal contamination in sampled soils of Old Oyo National Park

To assess, quantify and interpret the level of contamination of heavy metals in the sampled soils of Old Oyo National Park, three (3) quantitative assessment indices such as Contamination Factor (CF), Degree of Contamination (DC) and Geo-accumulation Index (I_{geo}) were employed to evaluate the contamination status of the analysed heavy metals in the sampled soils and identify probable degree of contamination particularly from anthropogenic influences.

3.6.4.1 Contamination Factor (CF)

This is the single index estimated by the equation 1 below as given by Rastmanesh *et al.,* (2010). It is used to evaluate soil contamination by comparing the contaminant level in the surface layer to a background value. Here, a modified contamination factor formula using metals concentrations in the control samples instead of background values, which are currently lacking for Nigeria (Adeyi and Torto, 2014)

$$CF = C_m/B_m \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(Equation 1)}$$

Where CF= contamination factor of the element of interest*;* C_m= mean concentration of each metal in the soil,B_m=background or baseline value (concentration of each metal in the control sample was used). Contamination factor has four categories which include: <1 low contamination; 1-3= moderate contamination; 3-6= considerable contamination; >6= very high contamination factor (Kumar and Edward, 2009).

3.6.4.2 Degree of contamination (Cdeg)

This is the sum of all the contamination factors of all the elements in the soil sample (Rastmanesh *et al.,* 2010). It is indicated as:

$$Cdeg = \Sigma (C_m/B_m) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(Equation 2)}$$

Where C_m=measured concentration in soil; B_m=local background concentration (value) of metal. Four categories have been defined for the degree of contamination which includes: <8=low degree of contamination; 8-16=moderate degree of contamination; 16-32=considerable degree of contamination; >32=very high degree of contamination (Hakanson, 1980).

3.6.4.3 Geo-accumulation Index (Igeo)

The geo-accumulation index is generally used to determine the anthropogenic contamination in soil samples by comparing soil metals concentrations to average shale values (Chai *et al*., 2014; Muller, 1969) and denoted in Equation 3 as:

$$I_{geo} = \text{Log}_2 (C_n) / 1.5(B_n) \quad \text{..... (Equation 3)}$$

Where C_n is the measured concentration of a particular metal in a soil sample and B_n is the background value in average shale of metal n. A factor 1.5 is used as the background matrix correction factor to justify for possible variation in background data due to lithogenic effects (Lu *et al.,* 2010). The classification given for geo-accumulation index (Huu *et al.,* 2010) is : <0 = practically uncontaminated, 0-1 = uncontaminated to low contamination, 1-2 = moderately contaminated, 2-3= moderately to strongly contaminated, 3-4 = strongly contaminated, 4-5 = strongly to extremely contaminated and >5 = extremely contaminated.

3.6.5 Microbial Characteristics of Water and Faecal Samples

For the bacteriological analysis of water samples, Coliform test was performed by the most probable number (MPN) technique (Benson, 1998) and heterotrophic plate count (aerobic) by Pour Plate method (Sugita *et al*., 1993). For identification of total faecal coliform and fungi in water and faecal samples, samples were analyzed for the target presumptive bacterial and fungal pathogens using internationally accepted techniques. The fungi were isolated from the water samples seasonally by using two methods: The direct plate and the dilution plate, two types of growth media were used for isolation of fungi Potato dextrose agar (PDA) and Sabouraud's dextrose agar (SDA) supplemented with chloramphenicol (50 mg/l) and cycloheximide (500 mg/l). Prior to filtration, samples were diluted ten-fold with sterile distilled water. About 50 ml of the appropriate dilution of each

sample was filtered through a 0.45µm pore size membrane filter, aseptically transferred to Petri dishes containing the appropriate selective media.

The isolation of *Escherichia coli* was carried out using Coli-Chromo agar for 24 h at 37°C; while Salmonella and Shigella were isolated on S-S agar for 24 h at 35°C. Total coliforms were determined by mENDO agar for 24 h at 35°C and mFC agar for 24 h at 44.5°C, respectively. The estimation of total heterotrophic bacteria, was done on nutrient agar for 48 h at 37°C. All colonies with different characteristics on their selective media were identified on the basis of their colonial, morphological and biochemical properties following Bergey's Manual of Determinative Bacteriology (Holt *et al*., 1994). Bacterial and fungal populations were expressed as colony forming units per milliliter (cfu/ml).

3.7 Laboratories Used

The Geo-Environmental Research Centre (GRC) Laboratory, Nigeria (Basel Convention Coordinating Centre for Training and Technology Transfer for the African Region, Federal Ministry of Environment - University of Ibadan linkage Centre for Cleaner Production Technology and Hazardous Waste Management, University of Ibadan) and the Department of Agronomy Laboratories (Soil Physics and Soil Chemistry) and the Department of Microbiology Laboratory, University of Ibadan were used.

3.8 Statistical Analysis

Data collected were compared with World Health Organisation (WHO) guidelines / permissible limits and other recognized standards or reference limits and thereafter subjected to descriptive (mean, standard deviation), inferential (Analysis of variance [ANOVA], Pearson's Product Moment Correlation [PPMC], T-test) statistics and Principal Component Analysis (PCA). Post-hoc test (LSD) was used to determine

significant differences in the mean concentrations of heavy metals across the seasons of sampling with statistical significance set at $\alpha_{0.05}$. All the statistical analyseswere performed with SPSS software (version 20.0).

CHAPTER FOUR

RESULTS

4.1. Heavy metals concentration in waterholes (selected rivers) of Old Oyo National Park

The heavy metal concentration in water samples from Old Oyo National Park during the dry seasons of sample collection (2017 & 2018) are shown in Table 4.1. The result showed that in the dry season of 2017, the levels of Cu, Zn (except in Rivers Ayinta, Tessi and Owu), Cr, Pb, Ni and Cd were below detection limit (BDL) while Fe and Mn (except in Rivers Tessi and Sooro) were above the WHO (2011) permissible limit in all the waterholes. In the dry season of 2018, the levels of Cu and Zn were below the comparable WHO (2011) permissible limit while the concentrations of Cr (except in River Owu), Pb, Ni (except in Rivers Oopo and Owu), Cd (except in River Owu), Fe and Mn were above the WHO (2011) permissible limit in all the sampled waterholes. This shows that the dry season of 2018 had a higher heavy metal contamination of the waterholes that the dry season of 2017.

Similarly, the heavy metal concentration in water samples from Old Oyo National Park during the wet seasons of sample collection (2017 & 2018) are shown in Table 4.2. The result showed that in the wet season of 2017, the concentrations of Cu and Zn in all the sampled waterholes were below the WHO (2011) permissible limit while the levels of Cr [except in Rivers Tessi (BDL), Sooro (BDL), Owu], Pb [except in Rivers Tessi (BDL) and Sooro (BDL)] and Ni [except in Rivers Tessi (BDL), Sooro (BDL), Owu] were all above the WHO (2011) guideline in all the sampled waterholes. The concentrations of Cd (in Rivers Oopo and Ayinta), Fe (in all the sampled waterholes) and Mn (in Rivers Ogun,

Oopo, Ayinta and Owu) were also found to be above the WHO (2011) permissible limit. In the wet season of 2018, the levels of Cu and Zn in all the sampled waterholes were below the comparable WHO (2011) permissible limit while the concentrations of Cr, Pb, Ni (except in River Owu), Cd (except in River Owu), Fe and Mn were above the WHO (2011) permissible limit in all the sampled waterholes. This shows that the wet season of 2018 had a higher heavy metal contamination of the waterholes that the wet season of 2017.

Table 4.1: Heavy metals concentration in selected waterholes in Old Oyo National Park [Dry Seasons 2017 and 2018]

Heavy metals	2017 / 2018 River Ogun (MW_1)	2017 / 2018 River Oopo (MW_2)	2017 / 2018 River Ayinta (MW_3)	2017 / 2018 River Tessi (OW_1)	2017 / 2018 River Sooro (OW_2)	2017 / 2018 River Owu (TW_1)	WHO Permissible Limit (2011)
Cu (mg/L)	BDL / 0.11	BDL / 0.13	BDL / 0.06	BDL / 0.12	BDL / 0.14	BDL / 0.07	2.0
Zn (mg/L)	BDL / 0.41	BDL / 0.28	0.12 / 0.04	0.20 / 0.31	BDL / 0.43	0.07 / BDL	5.0
Cr (mg/L)	BDL / 0.98	BDL / 0.12	BDL / 0.06	BDL / 0.16	BDL / 0.11	BDL / BDL	0.05
Pb (mg/L)	BDL / 0.20	BDL / 0.23	BDL / 0.14	BDL / 0.19	BDL / 0.17	BDL / 0.01	0.01
Ni (mg/L)	BDL / 0.08	BDL / 0.06	BDL / 0.09	BDL / 0.10	BDL / 0.08	BDL / BDL	0.07
Cd (mg/L)	BDL / 0.08	BDL / 0.06	BDL / 0.09	BDL / 0.10	BDL / 0.08	BDL / BDL	0.03
Fe (mg/L)	1.97 / 5.84	2.64 / 6.32	3.52 / 6.01	2.11 / 8.80	8.50 / 6.10	3.34 / 4.05	0.3
Mn (mg/L)	0.51 / 1.20	0.63 / 0.88	0.75 / 0.71	0.23 / 0.89	0.22 / 1.14	0.75 / 0.52	0.4

Note: BDL = Below Detection Limit

Table 4.2: Heavy metals concentration in selected waterholes in Old Oyo National Park [Wet Seasons 2017 and 2018]

Heavy metals	2017 / 2018 River Ogun (MW_1)	2017 / 2018 River Oopo (MW_2)	2017 / 2018 River Ayinta (MW_3)	2017 / 2018 River Tessi (OW_1)	2017 / 2018 River Sooro (OW_2)	2017 / 2018 River Owu (TW_1)	WHO Permissible Limit (2011)
Cu (mg/L)	0.05 / 0.82	0.04 / 0.23	0.05 / 0.07	BDL / 0.43	BDL / 0.56	BDL / 0.05	2.0
Zn (mg/L)	0.13 / 0.18	0.12 / 0.21	0.10 / 0.19	0.10 / 0.09	0.31 / 0.16	0.11 / 0.20	5.0
Cr (mg/L)	0.08 / 0.93	0.23 / 0.17	0.07 / 0.09	BDL / 0.19	BDL / 0.23	0.04 / 0.06	0.05
Pb (mg/L)	0.25 / 0.24	0.18 / 0.26	0.19 / 0.12	BDL / 0.18	BDL / 0.19	0.21 / 0.05	0.01
Ni (mg/L)	0.12 / 0.15	0.18 / 0.10	0.09 / 0.10	BDL / 0.12	BDL / 0.17	0.04 / 0.03	0.07
Cd (mg/L)	0.03 / 0.11	0.04 / 0.08	0.04 / 0.06	BDL / 0.12	BDL / 0.10	0.01 / 0.01	0.03
Fe (mg/L)	7.47 / 11.32	8.07 / 10.11	7.98 / 9.05	7.70 / 9.81	17.50 / 14.29	7.17 / 9.21	0.3
Mn (mg/L)	0.67 / 1.73	0.81 / 0.96	0.83 / 0.81	0.17 / 0.75	0.27 / 1.58	0.87 / 0.73	0.4

Note: BDL = Below Detection Limit

The concentration of heavy metals in selected waterholes across the sampled ranges of Old Oyo National Park are shown in Tables 4.3 – 4.5. In Marguba range, the highest concentration of Cu [0.82 (in River Ogun during wet season 2018)], Zn [1.20 (in River Ayinta during dry season 2017)], Cr [0.98 (in River Ogun during dry season 2018)], Pb [0.26 (in River Oopo during wet season 2018)], Ni [0.18 (in River Ayinta during wet season 2017)], Cd [0.11 (in River Ogun during wet season 2018)], Fe [11.32 (in River Ogun during wet season 2018)] and Mn [1.73 (in River Ogun during wet season 2018)] were observed as shown in Table 4.3.

In Tede range, only River Owu was sampled; therefore the highest concentration of Cu [0.07 (in dry season 2018)], Zn [0.20 (in wet season 2018)], Cr [0.06 (in wet season 2018)], Pb [0.21 (in wet season 2017)], Ni [0.04 (in wet season 2017 and dry season 2018)], Cd [0.01 (in wet season 2017 and 2018)], Fe [9.21 (in wet season 2018)] and Mn [0.87 (in wet season 2017)] were observed as shown in Table 4.4.

In Oyo-Ile range, the highest concentration of Cu [0.56 (in River Sooro during wet season 2018)], Zn [0.43 (in River Sooro during dry season 2018)], Cr [0.23 (in River Sooro during wet season 2018)], Pb [0.19 (in River Tessi during dry season 2018 and River Sooro during wet season 2018)], Ni [0.11 (in River Sooro during wet season 2018)], Cd [0.12 (in River Tessi during wet season 2018)], Fe [17.50 (in River Sooro in wet season 2017)] and Mn [1.58 (in River Sooro in wet season 2018)] were observed as shown in Table 4.5.

In summary, Marguba range had the highest mean concentration of Zn (0.24±0.32), Cr (0.23±0.34), Pb (0.15±0.10), Ni (0.08±0.06) and Mn (0.87±0.32) while Oyo-Ile had the highest mean concentration of Cu (0.16±0.22) and Fe (9.35±4.75). The mean

concentrations of Cd were both highest in Marguba (0.05±0.04) and Oyo Ile (0.05±0.05) ranges.

Table 4.3: Concentration of heavy metals in all the selected waterholes in Marguba range of Old Oyo National Park

Sample Code / Season and Year	Cu (mg/L)	Zn (mg/L)	Cr (mg/L)	Pb (mg/L)	Ni (mg/L)	Cd (mg/L)	Fe (mg/L)	Mn (mg/L)
MW_1 (D_{17})	BDL	BDL	BDL	BDL	BDL	BDL	1.97	0.51
MW_2 (D_{17})	BDL	BDL	BDL	BDL	BDL	BDL	2.64	0.63
MW_3 (D_{17})	BDL	1.20	BDL	BDL	BDL	BDL	3.52	0.75
MW_1 (W_{17})	0.05	0.13	0.08	0.25	0.12	0.03	7.47	0.67
MW_2 (W_{17})	0.04	0.12	0.23	0.18	0.18	0.04	8.07	0.81
MW_3 (W_{17})	0.05	0.10	0.07	0.19	0.09	0.04	7.98	0.83
MW_1 (D_{18})	0.11	0.41	0.98	0.20	0.08	0.08	5.84	1.20
MW_2 (D_{18})	0.13	0.28	0.12	0.23	0.06	0.06	6.32	0.88
MW_3 (D_{18})	0.06	0.04	0.06	0.14	0.08	0.09	6.01	0.71
MW_1 (W_{18})	0.82	0.18	0.93	0.24	0.15	0.11	11.32	1.73
MW_2 (W_{18})	0.23	0.21	0.17	0.26	0.10	0.08	10.11	0.96
MW_3 (W_{18})	0.07	0.19	0.09	0.12	0.10	0.06	9.05	0.81
Mean	**0.13**	**0.24**	**0.23**	**0.15**	**0.08**	**0.05**	**6.69**	**0.87**
Std	**0.23**	**0.32**	**0.34**	**0.10**	**0.06**	**0.04**	**2.91**	**0.32**

Note: Std – Standard Deviation; BDL = Below Detection Limit

MW_1 (D_{17}) = River Ogun in Dry season 2017
MW_2 (D_{17}) = River Oopo in Dry season 2017
MW_3 (D_{17}) = River Ayinta in Dry season 2017
MW_1 (W_{17}) = River Ogun in Dry season 2017
MW_2 (W_{17}) = River Oopo in Wet season 2017
MW_3 (W_{17}) = River Ayinta in Wet season 2017
MW_1 (D_{18}) = River Ogun in Dry season 2018
MW_2 (D_{18}) = River Oopo in Dry season 2018
MW_3 (D_{18}) = River Ayinta in Dry season 2018
MW_1 (W_{18}) = River Ogun in Wet season 2018
MW_2 (W_{18}) = River Oopo in Wet season 2018
MW_3 (W_{18}) = River Ayinta in Wet season 2018

Table 4.4: Concentration of heavy metals in the selected waterholes in Tede range of Old Oyo National Park

Sample Code / Season and Year	Cu (mg/L)	Zn (mg/L)	Cr (mg/L)	Pb (mg/L)	Ni (mg/L)	Cd (mg/L)	Fe (mg/L)	Mn (mg/L)
TW_1 (D_{17})	BDL	0.07	BDL	BDL	BDL	BDL	3.34	0.74
TW_1 (W_{17})	0.03	0.11	0.04	0.21	0.04	0.01	7.17	0.87
TW_1 (D_{18})	0.07	BDL	BDL	0.01	0.04	BDL	4.05	0.52
TW_1 (W_{18})	0.05	0.20	0.06	0.05	0.03	0.01	9.21	0.73
Mean	**0.04**	**0.13**	**0.03**	**0.07**	**0.03**	**0.01**	**5.94**	**0.72**
Std	**0.03**	**0.07**	**0.03**	**0.10**	**0.02**	**0.01**	**2.74**	**0.14**

Note:

Std – Standard Deviation; BDL = Below Detection Limit

TW_1 (D_{17}) = River Tede in Dry season 2017

TW_1 (W_{17}) = River Tede in Wet season 2017

TW_1 (D_{18}) = River Tede in Dry season 2018

TW_1 (W_{18}) = River Tede in Wet season 2017

Table 4.5: Concentration of heavy metals in all the selected waterholes in Oyo-Ile range of Old Oyo National Park

Sample Code / Season and Year	Cu (mg/L)	Zn (mg/L)	Cr (mg/L)	Pb (mg/L)	Ni (mg/L)	Cd (mg/L)	Fe (mg/L)	Mn (mg/L)
$OW_1 (D_{17})$	BDL	0.20	BDL	BDL	BDL	BDL	2.11	0.23
$OW_2 (D_{17})$	BDL	BDL	BDL	BDL	BDL	BDL	8.50	0.22
$OW_1 (W_{17})$	BDL	0.096	BDL	BDL	BDL	BDL	7.70	0.17
$OW_2 (W_{17})$	BDL	0.308	BDL	BDL	BDL	BDL	17.50	0.27
$OW_1 (D_{18})$	0.12	0.31	0.16	0.19	0.08	0.10	8.80	0.89
$OW_2 (D_{18})$	0.14	0.43	0.11	0.17	0.07	0.08	6.10	1.14
$OW_1 (W_{18})$	0.43	0.09	0.19	0.18	0.12	0.12	9.81	0.75
$OW_2 (W_{18})$	0.56	0.16	0.23	0.19	0.17	0.10	14.29	1.58
Mean	**0.16**	**0.20**	**0.09**	**0.09**	**0.06**	**0.05**	**9.35**	**0.66**
Std	**0.22**	**0.14**	**0.10**	**0.10**	**0.07**	**0.05**	**4.75**	**0.52**

Note:

Std – Standard Deviation; BDL = Below Detection Limit

$OW_1 (D_{17})$ = River Tessi in Dry season 2017 $OW_1 (D_{18})$ = River Tessi in Dry season 2018

$OW_2 (D_{17})$ = River Sooro in Dry season 2017 $OW_2 (D_{18})$ = River Sooro in Dry season 2018

$OW_1 (W_{17})$ = River Tessi in Wet season 2017 $OW_1 (W_{18})$ = River Tessi in Wet season 2018

$OW_2 (W_{17})$ = River Sooro in Wet season 2017 $OW_2 (W_{18})$ = River Sooro in Wet season 2018

The concentrations of heavy metals in Old Oyo National Park across the seasons of sampling [dry (combined 2017 & 2018) and wet (combined 2017 & 2018)] are shown in Tables 4.6 and 4.7, respectively. The result showed that the wet season had the highest mean concentration of Cu (0.19±0.27), Cr (0.17±0.25), Pb (0.16±0.09), Ni (0.09±0.06), Cd (0.05±0.04), Fe (9.97±3.10) and Mn (0.85±0.45). The mean concentrations of Zn were both highest in the wet (0.16±0.06) and dry (0.16±0.17) seasons. This shows that the sampled rivers were more contaminated with heavy metals during the wet season than the dry season.

The mean values of all the analysed heavy metals in the sampled rivers across the four seasons of sampling (dry season 2017, wet season 2017, dry season 2018 and wet season 2018) revealed that apart from the heavy metals that were below detection limit (BDL), all the heavy metals (except Cu and Zn) were above the comparable WHO (2011) and NSDWQ (2007) guidelines for drinking water (Table 4.8).Also, the mean plot of heavy metals (above the permissible limit) in the sampled waterholes across the selected ranges of Old Oyo National Park is shown in Figure 4.1. Statistically, there were significant differences in the values of all the analysed heavy metals in the sampled rivers across the four seasons of sampling at $P<0.05$ (Appendix: Table I).

Table 4.6: Concentration of heavy metals in all the selected waterholes of Old Oyo National Park in the two Dry Seasons (2017 & 2018)

Sample Code / Season and Year	Cu (mg/L)	Zn (mg/L)	Cr (mg/L)	Pb (mg/L)	Ni (mg/L)	Cd (mg/L)	Fe (mg/L)	Mn (mg/L)
MW_1 (D_{17})	BDL	BDL	BDL	BDL	BDL	BDL	1.97	0.51
MW_2 (D_{17})	BDL	BDL	BDL	BDL	BDL	BDL	2.64	0.63
MW_3 (D_{17})	BDL	0.12	BDL	BDL	BDL	BDL	3.52	0.75
OW_1 (D_{17})	BDL	0.20	BDL	BDL	BDL	BDL	2.11	0.23
OW_2 (D_{17})	BDL	BDL	BDL	BDL	BDL	BDL	8.50	0.22
TW_1 (D_{17})	BDL	0.07	BDL	BDL	BDL	BDL	3.34	0.74
MW_1 (D_{18})	0.11	0.41	0.98	0.20	0.08	0.08	5.84	1.20
MW_2 (D_{18})	0.13	0.28	0.12	0.23	0.06	0.06	6.32	0.88
MW_3 (D_{18})	0.06	0.04	0.06	0.14	0.08	0.09	6.01	0.71
OW_1 (D_{18})	0.12	0.31	0.16	0.19	0.08	0.10	8.8	0.89
OW_2 (D_{18})	0.14	0.43	0.11	0.17	0.07	0.08	6.10	1.14
TW_1 (D_{18})	0.07	BDL	BDL	0.01	0.04	BDL	4.05	0.52
Mean	**0.05**	**0.16**	**0.12**	**0.08**	**0.03**	**0.03**	**4.93**	**0.70**
Std	**0.06**	**0.17**	**0.28**	**0.10**	**0.04**	**0.04**	**2.34**	**0.31**

Note: Std = Standard Deviation; BDL = Below Detection Limit; $MW_1(D_{17})$ = River Ogun in Dry season 2017; $MW_2(D_{17})$ = River Oopo in Dry season 2017; $MW_3(D_{17})$ = River Ayinta in Dry season 2017; $OW_1(D_{17})$ = River Tessi in Dry season 2017; $OW_2(D_{17})$ = River Sooro in Dry season 2017; TW_1 (D_{17}) = River Owu in Dry Season 2017; MW_1 (D_{18}) = River Ogun in Dry Season 2018; MW_2 (D_{18}) = River Oopo in Dry Season 2018; MW_3 (D_{18}) = River Ayinta in Dry Season 2018; OW_1 (D_{18}) = River Tessi in Dry Season 2018; OW_2 = (D_{18}) = River Sooro in Dry Season 2018; TW_1 (D_{18}) = River Owu in Dry Season 2018

Table 4.7: Concentration of heavy metals in all the selected waterholes of Old Oyo National Park in the two Wet Seasons (2017 & 2018)

Sample Code / Season and Year	Cu (mg/L)	Zn (mg/L)	Cr (mg/L)	Pb (mg/L)	Ni (mg/L)	Cd (mg/L)	Fe (mg/L)	Mn (mg/L)
MW_1 (W_{17})	0.05	0.13	0.08	0.25	0.12	0.03	7.47	0.67
MW_2 (W_{17})	0.04	0.12	0.23	0.18	0.18	0.04	8.07	0.81
MW_3 (W_{17})	0.05	0.10	0.07	0.19	0.09	0.04	7.98	0.83
OW_1 (W_{17})	BDL	0.10	BDL	BDL	BDL	BDL	7.70	0.17
OW_2 (W_{17})	BDL	0.31	BDL	BDL	BDL	BDL	17.50	0.27
TW_1 (W_{17})	0.03	0.11	0.04	0.21	0.04	0.01	7.17	0.87
MW_1 (W_{18})	0.82	0.18	0.93	0.24	0.15	0.11	11.32	1.73
MW_2 (W_{18})	0.23	0.21	0.17	0.26	0.10	0.08	10.11	0.96
MW_3 (W_{18})	0.07	0.19	0.09	0.12	0.10	0.06	9.05	0.81
OW_1 (W_{18})	0.43	0.09	0.19	0.18	0.12	0.12	9.81	0.75
OW_2 (W_{18})	0.56	0.16	0.23	0.19	0.17	0.10	14.29	1.58
TW_1 (W_{18})	0.05	0.20	0.06	0.05	0.03	0.01	9.21	0.73
Mean	**0.19**	**0.16**	**0.17**	**0.16**	**0.09**	**0.05**	**9.97**	**0.85**
Std	**0.27**	**0.06**	**0.25**	**0.09**	**0.06**	**0.04**	**3.10**	**0.45**

Note: Std = Standard Deviation; BDL = Below Detection Limit; $MW_1(W_{17})$ = River Ogun in Wet season 2017; $MW_2(W_{17})$ = River Oopo in Wet season 2017; $MW_3(W_{17})$ = River Ayinta in Wet season 2017; $OW_1(W_{17})$ = River Tessi in Wet season 2017; $OW_2(W_{17})$ = River Sooro in Wet season 2017; TW_1 (W_{17}) = River Owu in Wet Season 2017; MW_1 (W_{18}) = River Ogun in Wet Season 2018; MW_2 (W_{18}) = River Oopo in Wet Season 2018; MW_3 (W_{18}) = River Ayinta in Wet Season 2018; OW_1 (W_{18}) = River Tessi in Wet Season 2018; OW_2 = (W_{18}) = River Sooro in Wet Season 2018; TW_1 (W_{18}) = River Owu in Wet Season 2018

Table 4.8: Mean values of heavy metals in the selected waterholes of Old Oyo National Park

Heavy metals	Mean Values ± Standard Deviation				WHO (2011) Guidelines for Drinking water	NSDWQ (2007) Guideline for Drinking water
	Dry Season (2017)	Wet Season (2017)	Dry Season (2018)	Wet Season (2018)		
Cu (mg/l)	BDL	0.04 ± 0.01	0.29 ± 0.16	0.36 ±0.30	2.0	1.0
Zn (mg/l)	0.13 ± 0.07	0.14 ±0.08	0.11 ± 0.03	0.17 ± 0.04	5.0	3.0
Cr (mg/l)	BDL	0.11 ± 0.09	0.29 ± 0.39	0.28 ± 0.33	0.05	0.05
Pb (mg/l)	BDL	0.21 ± 0.03	0.16 ± 0.08	0.17 ± 0.08	0.01	0.01
Ni (mg/l)	BDL	0.11 ± 0.06	0.07 ± 0.02	0.11 ± 0.05	0.07	0.02
Cd (mg/l)	BDL	0.03 ± 0.01	0.08 ± 0.01	0.08 ± 0.04	0.003	0.003
Fe (mg/l)	3.68 ± 2.44	9.32 ± 4.02	6.19 ± 1.52	10.63 ± 1.97	0.3	0.3
Mn (mg/l)	0.51 ± 0.24	0.60 ± 0.31	0.89 ± 0.26	1.09 ± 0.45	0.4	0.2

Note: WHO – World Health Organization; NSDWQ – National Safe Drinking Water Quality; BDL – Below Detection Limit

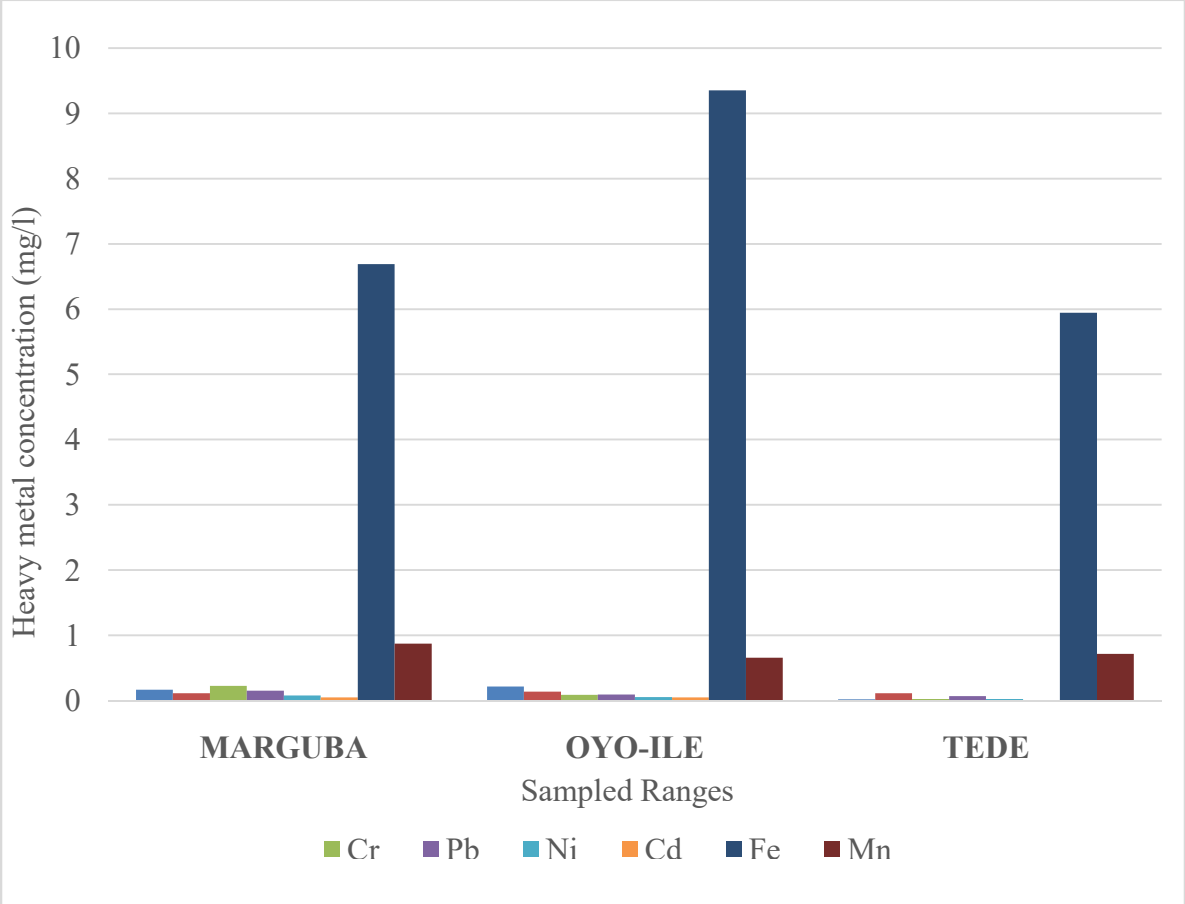

Figure 4.1: Mean plot of heavy metals (above permissible limit) in sampled waterholes across the selected ranges of Old Oyo National Park

4.2 Heavy metals concentration in soil samples of Old Oyo National Park

The heavy metal concentration in soil samples from Old Oyo National Park during the dry seasons of sampling (2017 & 2018) are shown in Table 4.9. The result showed that there are variations in the level of heavy metals in the soil samples. In the dry season of 2017, the concentration of Cu (in MS3), Zn (in MS3 and OS1), Cr (in OS2), Pb (in MS1, MS2, MS3, OS1, OS2 and TS2), Ni (in MS2, MS3, OS1 and OS2) and Cd (all soil samples) were found to be below detection limit (BDL). In the dry season of 2018, only the Cd levels in all the sampled soils were above the maximum allowable limit (shown in Table 4.17) specified by Sweden and Denmark.

Similarly, the heavy metal concentration in soil samples from Old Oyo National Park during the wet seasons of sampling (2017 & 2018) are shown in Table 4.10. In the wet season of 2017, the concentration of Pb (in OS1, OS2 and OS3), Ni (in OS1 and OS2) and Cd (in OS1, OS2 and OS3) were observed to be below detection limit (BDL) while only Cd concentration in soil samples from Marguba (MS1, MS2, MS3) and Tede (TS1, TS2, TS3) ranges were above the maximum allowable limit (shown in Table 4.17) specified by Sweden and Denmark. In the wet season of 2018, Pb (in OS1, OS3 and TS2), Ni (in OS2) and Cd (in OS3 and TS2) were below detection limit (BDL) while only the concentration of Cd in all the sampled soils (except OS3 and TS2) were above the maximum allowable limit (shown in Table 4.17) specified by Sweden and Denmark.

Table 4.9: Heavy metals concentration of sampled soils in Old Oyo National Park [Dry Seasons 2017 and 2018]

Soil Sample code	Sampling Year	Cu (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
MS1	2017	10.40 ± 0.06	27.20 ± 0.21	6.08 ± 0.05	BDL	2.95 ± 0.02	BDL	9.31 ± 0.21	10.44 ± 0.18
	2018	1.58 ± 0.14	1.90 ± 0.15	28.70 ± 0.11	3.90 ± 0.23	1.80 ± 0.17	2.90 ± 0.11	88.80 ± 0.22	97.00 ± 0.008
MS2	2017	3.45 ± 0.04	13.60 ± 0.28	5.33 ± 0.07	BDL	BDL	BDL	8.37 ± 0.74	10.12 ± 0.23
	2018	1.63 ± 0.10	1.80 ± 0.23	26.50 ± 0.08	4.30 ± 0.11	2.90 ± 0.14	2.85 ± 0.02	87.00 ± 0.24	104.00 ± 0.10
MS3	2017	BDL	BDL	2.58 ± 0.02	BDL	BDL	BDL	9.04 ± 0.63	7.55 ± 0.32
	2018	1.74 ± 0.05	1.75 ± 0.12	26.90 ± 0.41	4.10 ± 0.62	1.95 ± 0.02	2.70 ± 0.19	98.80 ± 0.11	105.50 ± 0.16
OS1	2017	0.28 ± 0.02	BDL	3.98 ± 0.03	BDL	BDL	BDL	22.04 ± 0.18	34.82 ± 0.03
	2018	1.30 ± 0.09	3.50 ± 0.01	21.60 ± 0.22	4.30 ± 0.71	1.90 ± 0.03	2.40 ± 0.20	95.20 ± 0.23	168.20 ± 0.14
OS2	2017	2.03 ± 0.02	1.83 ± 0.02	BDL	BDL	BDL	BDL	13.10 ± 0.07	17.07 ± 0.74
	2018	1.68 ± 0.06	2.35 ± 0.12	19.20 ± 0.12	5.50 ± 0.23	1.75 ± 0.10	3.30 ± 0.07	96.50 ± 0.19	161.40 ± 0.02
OS3	2017	6.48 ± 0.05	19.52 ± 0.28	5.05 ± 0.05	4.10 ± 0.04	3.93 ± 0.03	BDL	27.00 ± 0.91	43.00 ± 0.56
	2018	1.70 ± 0.12	2.30 ± 0.13	18.80 ± 0.88	5.30 ± 0.84	2.50 ± 0.09	2.70 ± 0.23	101.50 ± 0.31	184.00 ± 0.03

Table 4.9 (cont'd): Heavy metals concentration of sampled soils in Old Oyo National Park [Dry Seasons 2017 and 2018]

Soil Sample code	Sampling Year	Cu (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
TS1	2017	7.70 ± 0.01	8.08 ± 0.03	10.10 ± 0.19	5.05 ± 0.04	4.48 ± 0.03	BDL	7.54 ± 0.11	8.05 ± 0.08
	2018	5.25 ± 0.11	9.50 ± 0.18	11.40 ± 0.52	4.20 ± 0.04	3.20 ± 0.06	0.74 ± 0.11	11.40 ± 0.17	17.30 ± 0.25
TS2	2017	9.25 ± 0.04	9.90 ± 0.02	14.92 ± 0.27	BDL	9.25 ± 0.05	BDL	11.28 ± 0.43	6.88 ± 0.33
	2018	8.10 ± 0.27	7.14 ± 0.03	13.60 ± 0.44	3.90 ± 0.18	7.30 ± 0.41	0.52 ± 0.12	13.05 ± 0.03	16.70 ± 0.16
TS3	2017	6.45 ± 0.02	4.65 ± 0.04	11.36 ± 0.05	7.78 ± 0.05	3.55 ± 0.03	BDL	10.06 ± 0.22	11.34 ± 0.05
	2018	5.96 ± 0.22	6.20 ± 0.10	10.30 ± 0.13	4.60 ± 0.09	2.60 ± 0.13	0.95 ± 0.21	9.50 ± 0.33	19.10 ± 0.06

Note: Data are Means ± Standard Deviation of replicate (n = 3) analyses

BDL = Below detection limit; MS1 = Composited Soil Sample 1 in Marguba range; MS2 = Composited Soil Sample 2 in Marguba range; MS3 = Composited Soil Sample 3 in Marguba range; OS1 = Composited Soil Sample 1 in Oyo-Ile range; OS2 = Composited Soil Sample 2 in Oyo-Ile range; OS3 = Composited Soil Sample 3 in Oyo-Ile range; TS1 = Composited Soil Sample 1 in Tede range; TS2 = Composited Soil Sample 2 in Tede range; TS3 = Composited Soil Sample 3 in Tede range

Table 4.10: Heavy metals concentration of sampled soils in Old Oyo National Park [Wet Seasons 2017 and 2018]

Soil Sample code	Sampling Year	Cu (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
MS1	2017	0.76 ± 0.04	44.60 ± 0.47	5.30 ± 0.27	4.30 ± 0.11	3.18 ± 0.44	1.80 ± 0.16	14.80 ± 0.66	12.10 ± 0.36
	2018	0.42 ± 0.67	21.44 ± 1.56	2.48 ± 0.66	3.14 ± 0.71	4.43 ± 0.55	1.25 ± 0.07	28.33 ± 1.22	57.22 ± 1.36
MS2	2017	0.78 ± 0.12	44.00 ± 0.39	5.60 ± 0.03	4.10 ± 0.09	3.30 ± 0.31	1.50 ± 0.09	14.30 ± 0.35	12.10 ± 0.23
	2018	0.56 ± 0.72	17.82 ± 1.22	8.12 ± 0.98	2.94 ± 0.69	2.96 ± 0.82	1.81± 0.17	12.53 ± 0.69	48.91± 0.93
MS3	2017	0.78 ± 0.08	44.03 ± 0.92	5.00 ± 0.22	4.00 ± 0.73	3.30 ± 0.07	1.80 ± 0.27	14.92 ± 0.12	12.00 ± 0.04
	2018	0.61 ± 0.13	36.27 ± 1.78	9.10 ± 0.18	4.52 ± 0.96	1.08 ± 0.22	1.04 ± 0.20	19.56 ± 1.71	45.03 ± 0.78
OS1	2017	0.73 ± 0.03	13.97 ± 0.03	25.55 ± 0.21	BDL	BDL	BDL	63.30 ± 0.32	109.00 ± 0.07
	2018	0.84 ± 0.21	21.50 ± 0.93	31.07 ± 1.51	BDL	0.76 ± 0.31	0.66 ± 0.28	72.61 ± 2.34	87.42 ± 3.24
OS2	2017	1.05 ± 0.01	52.60 ± 0.92	13.00 ± 0.08	BDL	BDL	BDL	70.80 ± 0.28	57.20 ± 0.04
	2018	0.96 ± 0.58	49.03 ± 2.06	8.62 ± 0.69	1.56 ± 0.57	BDL	0.44 ± 0.16	64.11 ± 2.04	96.72 ± 2.68
OS3	2017	1.57 ± 0.07	8.60 ± 0.05	31.45 ± 1.23	BDL	0.50 ± 0.03	BDL	80.80 ± 0.29	158.00 ± 0.08
	2018	1.69 ± 0.81	16.51 ± 0.87	28.32 ± 1.14	BDL	1.32 ± 0.46	BDL	86.50 ± 1.87	94.49 ± 1.98

Table 4.10 (cont'd): Heavy metals concentration of sampled soils in Old Oyo National Park [Wet Seasons 2017 and 2018]

Soil Sample code	Sampling Year	Cu (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
TS1	2017	0.77 ± 0.21	6.45 ± 0.71	7.80 ± 0.67	3.15 ± 0.18	2.10 ± 0.02	1.10 ± 0.33	16.30 ± 0.37	19.90 ± 0.19
	2018	1.12 ± 0.93	5.94 ± 0.61	6.77 ± 0.88	0.82 ± 0.15	1.23 ± 0.38	0.53 ± 0.46	9.12 ± 0.33	11.52 ± 0.53
TS2	2017	0.79 ± 0.38	6.50 ± 0.04	7.60 ± 0.52	3.20 ± 0.25	2.00 ± 0.14	1.20 ± 0.26	16.00 ± 0.08	20.00 ± 0.26
	2018	0.68 ± 0.14	7.26 ± 0.85	4.06 ± 1.01	BDL	3.36 ± 0.51	BDL	11.45 ± 0.96	18.77 ± 1.26
TS3	2017	0.81 ± 0.29	6.44 ± 0.76	7.80 ± 0.18	3.40 ± 0.65	2.16 ± 0.26	1.10 ± 0.24	16.50 ± 0.22	19.70 ± 0.56
	2018	1.03 ± 0.72	3.71 ± 0.43	8.11 ± 0.92	2.31 ± 0.34	2.08 ± 0.11	1.29 ± 0.41	13.24 ± 1.02	14.20 ± 0.89

Note: Data are Means ± Standard Deviation of replicate (n = 3) analyses
BDL = Below detection limit; MS1 = Composited Soil Sample 1 in Marguba range; MS2 = Composited Soil Sample 2 in Marguba range; MS3 = Composited Soil Sample 3 in Marguba range; OS1 = Composited Soil Sample 1 in Oyo-Ile range; OS2 = Composited Soil Sample 2 in Oyo-Ile range; OS3 = Composited Soil Sample 3 in Oyo-Ile range; TS1 = Composited Soil Sample 1 in Tede range; TS2 = Composited Soil Sample 2 in Tede range; TS3 = Composited Soil Sample 3 in Tede range

The concentration of heavy metals in soils across the sampled ranges of Old Oyo National Park are shown in Tables 4.11 – 4.13. In Marguba range, the highest concentration of Cu [10.40 (in MS1 during the dry season of 2017)], Zn [44.60 (in MS1 during the wet season of 2017)], Cr [28.70 (in MS1 during the dry season of 2018)], Pb [4.52 (in MS3 during the wet season of 2018)], Ni [4.43 (in MS1 during the wet season of 2018)], Cd [2.90 (in MS1 during the dry season of 2018)], Fe [98.80 (in MS3 during the dry season of 2018)], Mn [105.50 (in MS3 during the dry season of 2018)] were observed as shown in Table 4.11.

In Tede range, the highest concentration of Cu [9.25 (in TS2 during the dry season of 2017)], Zn [9.90 (in TS2 during the dry season of 2017)], Cr [14.92 (in TS2 during the dry season of 2017)], Pb [7.78 (in TS3 during the dry season of 2017)], Ni [9.25 (in TS2 during the dry season of 2017)], Cd [1.29 (in TS3 during the wet season of 2018)], Fe [16.50 (in TS3 during the wet season of 2017)], Mn [20.00 (in TS2 during the wet season of 2017)] were observed as shown in Table 4.12.

In Oyo-Ile range, the highest concentration of Cu [6.48 (in OS3 during the dry season of 2017)], Zn [52.60 (in OS2 during the wet season of 2017)], Cr [31.45 (in OS3 during the wet season of 2017)], Pb [5.50 (in OS2 during the dry season of 2018)], Ni [3.93 (in OS3 during the dry season of 2017)], Cd [3.30 (in OS2 during the dry season of 2018)], Fe [101.50 (in OS3 during the dry season of 2018)], Mn [184.00 (in OS3 during the dry season of 2018)] were observed as shown in Table 4.13.

Across the ranges, Marguba had the highest mean concentration of Zn (22.96±17.58) and Cd (1.47±1.07), Tede had the highest mean concentration of Cu (3.99±3.42), Pb (3.20±2.23) and Ni (3.61±2.38) while Oyo-Ile had the highest mean concentration of Cr (17.22±10.97), Fe (66.12±30.17) and Mn (100.94±56.66).

Table 4.11: Concentration of heavy metals in all the sampled soils in Marguba range of Old Oyo National Park

Sample Code / Season and Year	Cu (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
MS1 (D_{17})	10.40	27.20	6.08	BDL	2.95	BDL	9.31	10.44
MS2 (D_{17})	3.45	13.60	5.33	BDL	BDL	BDL	8.37	10.12
MS3 (D_{17})	BDL	BDL	2.58	BDL	BDL	BDL	9.04	7.55
MS1 (W_{17})	0.76	44.60	5.30	4.30	3.18	1.80	14.80	12.10
MS2 (W_{17})	0.78	44.00	5.60	4.10	3.30	1.50	14.30	12.10
MS3 (W_{17})	0.78	44.03	5.00	4.00	3.30	1.80	14.92	12.00
MS1 (D_{18})	1.58	1..90	28.70	3.90	1.80	2.90	88.80	97.00
MS2 (D_{18})	1.63	1.80	26.50	4.30	2.90	2.85	87.00	104.00
MS3 (D_{18})	1.74	1.75	26.90	4.10	1.95	2.70	98.80	105.50
MS1 (W_{18})	0.42	21.44	2.48	3.14	4.43	1.25	28.33	57.22
MS2 (W_{18})	0.56	17.82	8.12	2.94	2.96	1.81	12.53	48.91
MS3 (W_{18})	0.61	36.27	9.10	4.52	1.08	1.04	19.56	45.03
Mean	**1.89**	**22.96**	**10.97**	**2.94**	**2.32**	**1.47**	**33.81**	**43.50**
Std	**2.83**	**17.58**	**10.07**	**1.83**	**1.38**	**1.07**	**35.32**	**39.37**

Note: Std = Standard Deviation; BDL = Below Detection Limit; MS1 (D_{17}) = Composited Soil Sample 1 in Marguba range in Dry season 2017; MS2 (D_{17}) = Composited Soil Sample 2 in Marguba range in Dry season 2017; MS3 (D_{17}) = Composited Soil Sample 3 in Marguba range in Dry season 2017;MS1 (W_{17}) = Composited Soil Sample 1 in Marguba range in Wet season 2017; MS2 (W_{17}) = Composited Soil Sample 2 in Marguba range in Wet season 2017; MS3 (W_{17}) = Composited Soil Sample 3 in Marguba range in Wet season 2017; MS1 (D_{18}) = Composited Soil Sample 1 in Marguba range in Dry season 2018; MS2 (D_{18}) = Composited Soil Sample 2 in Marguba range in Dry season 2018; MS3 (D_{18}) = Composited Soil Sample 3 in Marguba range in Dry season 2018; MS1 (W_{18}) = Composited Soil Sample 1 in Marguba range in Wet season 2018; MS2 (W_{18}) = Composited Soil Sample 2 in Marguba range in Wet season 2018; MS3 (W_{18}) = Composited Soil Sample 3 in Marguba range in Wet season 2018

Table 4.12: Concentration of heavy metals in all the sampled soils in Tede range of Old Oyo National Park

Sample Code / Season and Year	Cu (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
TS1 (D_{17})	7.70	8.08	10.10	5.05	4.48	BDL	7.54	8.05
TS2 (D_{17})	9.25	9.90	14.92	BDL	9.25	BDL	11.28	6.88
TS3 (D_{17})	6.45	4.65	11.36	7.78	3.55	BDL	10.06	11.34
TS1(W_{17})	0.77	6.45	7.80	3.15	2.10	1.10	16.30	19.90
TS2 (W_{17})	0.79	6.50	7.60	3.20	2.00	1.20	16.00	20.00
TS3 (W_{17})	0.81	6.44	7.80	3.40	2.16	1.10	16.50	19.70
TS1 (D_{18})	5.25	9.50	11.40	4.20	3.20	0.74	11.40	17.30
TS2 (D_{18})	8.10	7.14	13.60	3.90	7.30	0.52	13.05	16.70
TS3 (D_{18})	5.96	6.20	10.30	4.60	2.60	0.95	9.50	19.10
TS1 (W_{18})	1.12	5.94	6.77	0.82	1.23	0.53	9.12	11.52
TS2 (W_{18})	0.68	7.26	4.06	BDL	3.36	BDL	11.45	18.77
TS3 (W_{18})	1.03	3.71	8.11	2.31	2.08	1.29	13.24	14.20
Mean	**3.99**	**6.81**	**9.49**	**3.20**	**3.61**	**0.62**	**12.12**	**15.29**
Std	**3.42**	**1.77**	**3.05**	**2.23**	**2.38**	**0.52**	**2.96**	**4.76**

Note:
Std = Standard Deviation; BDL = Below detection limit; TS1 (D_{17}) = Composited Soil Sample 1 in Tede range in Dry season 2017; TS2 (D_{17}) = Composited Soil Sample 2 in Tede range in Dry season 2017; TS3 (D_{17}) = Composited Soil Sample 3 in Tede range in Dry season 2017; TS1 (W_{17}) = Composited Soil Sample 1 in Tede range in Wet season 2017; TS2 (W_{17}) = Composited Soil Sample 2 in Tede range in Wet season 2017; TS3 (W_{17}) = Composited Soil Sample 3 in Tede range in Wet season 2017; TS1 (D_{18}) = Composited Soil Sample 1 in Tede range in Dry season 2018; TS2 (D_{18}) = Composited Soil Sample 2 in Tede range in Dry season 2018; TS3 (D_{18}) = Composited Soil Sample 3 in Tede range in Dry season 2018; TS1 (W_{18}) = Composited Soil Sample 1 in Tede range in Wet season 2018; TS2 (W_{18}) = Composited Soil Sample 2 in Tede range in Wet season 2018; TS3 (W_{18}) = Composited Soil Sample 3 in Tede range in Wet season 2018

Table 4.13: Concentration of heavy metals in all the sampled soils in Oyo-Ile range of Old Oyo National Park

Sample Code / Season and Year	Cu (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
OS1 (D_{17})	0.28	BDL	3.98	BDL	BDL	BDL	22.04	34.82
OS2 (D_{17})	2.03	1.83	BDL	BDL	BDL	BDL	13.10	17.07
OS3 (D_{17})	6.48	19.52	5.05	4.10	3.93	BDL	27.00	43.00
OS1(W_{17})	0.73	13.97	25.55	BDL	BDL	BDL	63.30	109.00
OS2 (W_{17})	1.05	52.60	13.00	BDL	BDL	BDL	70.80	57.20
OS3 (W_{17})	1.57	8.60	31.45	BDL	0.50	BDL	80.80	158.00
OS1 (D_{18})	1.30	3.50	21.60	4.30	1.90	2.40	95.20	168.20
OS2 (D_{18})	1.68	2.35	19.20	5.50	1.75	3.30	96.50	161.40
OS3 (D_{18})	1.70	2.30	18.80	5.30	2.50	2.70	101.50	184.00
OS1 (W_{18})	0.84	21.50	31.07	BDL	0.76	0.66	72.61	87.42
OS2 (W_{18})	0.96	49.03	8.62	1.56	BDL	0.44	64.11	96.72
OS3 (W_{18})	1.69	16.51	28.32	BDL	1.32	BDL	86.50	94.49
Mean	**1.69**	**15.98**	**17.22**	**1.73**	**1.06**	**0.79**	**66.12**	**100.94**
Std	**1.59**	**17.89**	**10.97**	**2.34**	**1.26**	**1.24**	**30.17**	**56.66**

Note:
Std = Standard Deviation; BDL = Below detection limit; OS1 (D_{17}) = Composited Soil Sample 1 in Oyo-Ile range in Dry season 2017; OS2 (D_{17}) = Composited Soil Sample 2 in Oyo-Ile range in Dry season 2017; OS3 (D_{17}) = Composited Soil Sample 3 in Oyo-Ile range in Dry season 2017; OS1 (W_{17}) = Composited Soil Sample 1 in Oyo-Ile range in Wet season 2017; OS2 (W_{17}) = Composited Soil Sample 2 in Oyo-Ile range in Wet season 2017; OS3 (W_{17}) = Composited Soil Sample 3 in Oyo-Ile range in Wet season 2017; OS1 (D_{18}) = Composited Soil Sample 1 in Oyo-Ile range in Dry season 2018; OS2 (D_{18}) = Composited Soil Sample 2 in Oyo-Ile range in Dry season 2018; OS3 (D_{18}) = Composited Soil Sample 3 in Oyo-Ile range in Dry season 2018; OS1 (W_{18}) = Composited Soil Sample 1 in Oyo-Ile range in Wet season 2018; OS2 (W_{18}) = Composited Soil Sample 2 in Oyo-Ile range in Wet season 2018; OS3 (W_{18}) = Composited Soil Sample 3 in Oyo-Ile range in Wet season 2018

The concentrations of heavy metals in sampled soils of Old Oyo National Park across the seasons of sampling [dry (combined 2017 & 2018) and wet (combined 2017 & 2018)] are shown in Tables 4.14 and 4.15, respectively. The result showed that the dry seasons had the highest mean concentration of Cu (4.17±03.30), Cr (13.13±8.82), Pb (3.17±2.47), Ni (2.78±2.45), Cd (1.06±1.31), Fe (39.97±40.17) and Mn (56.80±62.44) while the mean concentrations of Zn (22.59±17.44) was highest during the wet seasons. This shows that the sampled soils were more contaminated with heavy metals during the dry season than the wet season.

The mean values of all the analysed heavy metals in the sampled soils across the four seasons of sampling (dry season 2017, wet season 2017, dry season 2018 and wet season 2018) revealed that only the concentration of Cd was higher than the maximum allowable limit (for Sweden and Denmark) across the four seasons of sampling except in dry season 2017 where it was below detection limit (BDL). Also, the mean levels of Cr, Ni, Cd and Cu (only dry season, 2017) were higher in comparison with a control as shown in Table 4.16. Statistically, there were significant differences in the values of Cu, Zn, Cr, Fe, Pb, Cd and Mn in the soil samples while there was no significant difference in the values of Ni in the soil samples across the four seasons (Appendix: Table II).

Table 4.14: Concentration of heavy metals in the sampled soils of Old Oyo National Park in the two Dry Seasons (2017 & 2018)

Sample Code / Season and Year	Cu (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
MS1 (D_{17})	10.40	27.20	6.08	BDL	2.95	BDL	9.31	10.44
MS2 (D_{17})	3.45	13.60	5.33	BDL	BDL	BDL	8.37	10.12
MS3 (D_{17})	BDL	BDL	2.58	BDL	BDL	BDL	9.04	7.55
OS1 (D_{17})	0.28	BDL	3.98	BDL	BDL	BDL	22.04	34.82
OS2 (D_{17})	2.03	1.83	BDL	BDL	BDL	BDL	13.10	17.07
OS3 (D_{17})	6.48	19.52	5.05	4.10	3.93	BDL	27.00	43.00
TS1 (D_{17})	7.70	8.08	10.10	5.05	4.48	BDL	7.54	8.05
TS2 (D_{17})	9.25	9.90	14.92	BDL	9.25	BDL	11.28	6.88
TS3 (D_{17})	6.45	4.65	11.36	7.78	3.55	BDL	10.06	11.34
MS1 (D_{18})	1.58	1..90	28.70	3.90	1.80	2.90	88.8	97.00
MS2 (D_{18})	1.63	1.80	26.50	4.30	2.90	2.85	87.00	104.00
MS3 (D_{18})	1.74	1.75	26.90	4.10	1.95	2.70	98.80	105.50
OS1 (D_{18})	1.30	3.50	21.60	4.30	1.90	2.40	95.20	168.20
OS2 (D_{18})	1.68	2.35	19.20	5.50	1.75	3.30	96.50	161.40
OS3 (D_{18})	1.70	2.30	18.80	5.30	2.50	2.70	101.50	184.00
TS1 (D_{18})	5.25	9.50	11.40	4.20	3.20	0.74	11.40	17.30
TS2 (D_{18})	8.10	7.14	13.60	3.90	7.30	0.52	13.05	16.70
TS3 (D_{18})	5.96	6.20	10.30	4.60	2.60	0.95	9.50	19.10
Mean	**4.17**	**7.02**	**13.13**	**3.17**	**2.78**	**1.06**	**39.97**	**56.80**
Std	**3.30**	**7.36**	**8.82**	**2.47**	**2.45**	**1.31**	**40.17**	**62.44**

Note: Std = Standard Deviation; BDL = Below detection limit; MS1 (D_{17}) = Composited Soil Sample 1 in Marguba range in Dry season 2017; MS2 (D_{17}) = Composited Soil Sample 2 in Marguba range in Dry season 2017; MS3 (D_{17}) = Composited Soil Sample 3 in Marguba range in Dry season 2017; OS1 (D_{17}) = Composited Soil Sample 1 in Oyo-Ile range in Dry season 2017; OS2 (D_{17}) = Composited Soil Sample 2 in Oyo-Ile range in Dry season 2017; OS3(D_{17}) = Composited Soil Sample 3 in Oyo-Ile range in Dry season 2017; TS1 (D_{17}) = Composited Soil Sample 1 in Tede range in Dry season 2017; TS2 (D_{17}) = Composited Soil Sample 2 in Tede range in Dry season 2017; TS3 (D_{17}) = Composited Soil Sample 3 in Tede range in Dry season 2017; MS1 (D_{18}) = Composited Soil Sample 1 in Marguba range in Dry season 2018;MS2 (D_{18}) = Composited Soil Sample 2 in Marguba range in Dry season 2018; MS3 (D_{18}) = Composited Soil Sample 3 in Marguba range in Dry season 2018; OS1 (D_{18}) = Composited Soil Sample 1 in Oyo-Ile range in Dry season 2018; OS2 (D_{18}) = Composited Soil Sample 2 in Oyo-Ile range in Dry season 2018; OS3 (D_{18}) = Composited Soil Sample 3 in Oyo-Ile range in Dry season 2018; TS1 (D_{18}) = Composited Soil Sample 1 in Tede range in Dry season 2018; TS2 (D_{18}) = Composited Soil Sample 2 in Tede range in Dry season 2018; TS3 (D_{18}) = Composited Soil Sample 3 in Tede range in Dry season 2018

Table 4.15: Concentration of heavy metals in the sampled soils of Old Oyo National Park in the two Wet Seasons

Sample Code / Season and Year	Cu (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
MS1 (W_{17})	0.76	44.60	5.30	4.30	3.18	1.80	14.80	12..10
MS2 (W_{17})	0.78	44.00	5.60	4.10	3.30	1.50	14.30	12.10
MS3 (W_{17})	0.78	44.03	5.00	4.00	3.30	1.80	14.92	12.00
OS1 (W_{17})	0.73	13.97	25.55	BDL	BDL	BDL	63.30	109.00
OS2 (W_{17})	1.05	52.60	13.00	BDL	BDL	BDL	70.80	57.20
OS3 (W_{17})	1.57	8.60	31.45	BDL	0.50	BDL	80.80	158.00
TS1 (W_{17})	0.77	6.45	7.80	3.15	2.10	1.10	16.30	19.90
TS2 (W_{17})	0.79	6.50	7.60	3.20	2.00	1.20	16.00	20.00
TS3 (W_{17})	0.81	6.44	7.80	3.40	2.16	1.10	16.50	19.70
MS1 (W_{18})	0.42	21.44	2.48	3.14	4.43	1.25	28.33	57.22
MS2 (W_{18})	0.56	17.82	8.12	2.94	2.96	1.81	12.53	48.91
MS3 (W_{18})	0.61	36.27	9.10	4.52	1.08	1.04	19.56	45.03
OS1 (W_{18})	0.84	21.50	31.07	BDL	0.76	0.66	72.61	87.42
OS2 (W_{18})	0.96	49.03	8.62	1.56	BDL	0.44	64.11	96.72
OS3 (W_{18})	1.69	16.51	28.32	BDL	1.32	BDL	86.50	94.49
TS1 (W_{18})	1.12	5.94	6.77	0.82	1.23	0.53	9.12	11.52
TS2 (W_{18})	0.68	7.26	4.06	BDL	3.36	BDL	11.45	18.77
TS3 (W_{18})	1.03	3.71	8.11	2.31	2.08	1.29	13.24	14.20
Mean	**0.89**	**22.59**	**11.99**	**2.08**	**1.88**	**0.86**	**34.73**	**49.68**
Std	**0.32**	**17.44**	**9.74**	**1.76**	**1.35**	**0.67**	**28.57**	**43.12**

Note: Std = Standard Deviation; BDL = Below detection limit; MS1 (W_{17}) = Composited Soil Sample 1 in Marguba range in Wet season 2017; MS2 (W_{17}) = Composited Soil Sample 2 in Marguba range in Wet season 2017; MS3 (W_{17}) = Composited Soil Sample 3 in Marguba range in Wet season 2017; OS1 (W_{17}) = Composited Soil Sample 1 in Oyo-Ile range in Wet season 2017; OS2 ($_{17}$) = Composited Soil Sample 2 in Oyo-Ile range in Wet season 2017; OS3 (W_{17}) = Composited Soil Sample 3 in Oyo-Ile range in Wet season 2017; TS1 (W_{17}) = Composited Soil Sample 1 in Tede range in Wet season 2017; TS2 (W_{17}) = Composited Soil Sample 2 in Tede range in Wet season 2017; TS3 (W_{17}) = Composited Soil Sample 3 in Tede range in Wet season 2017; MS1 (W_{18}) = Composited Soil Sample 1 in Marguba range in Wet season 2018; MS2 (W_{18}) = Composited Soil Sample 2 in Marguba range in Wet season 2018; MS3 (W_{18}) = Composited Soil Sample 3 in Marguba range in Wet season 2018; OS1 (W_{18}) = Composited Soil Sample 1 in Oyo-Ile range in Wet season 2018; OS2 (W_{18}) = Composited Soil Sample 2 in Oyo-Ile range in Wet season 2018; OS3 (W_{18}) = Composited Soil Sample 3 in Oyo-Ile range in Wet season 2018; TS1 (W_{18}) = Composited Soil Sample 1 in Tede range in Wet season 2018; TS2 (W_{18}) = Composited Soil Sample 2 in Tede range in Wet season 2018; TS3 (W_{18}) = Composited Soil Sample 3 in Tede range in Wet season 2018

Table 4.16: Mean values of heavy metals in soil samples of Old Oyo National Park

Heavy metals	Mean Values ± Standard Deviation				Maximum Allowable Levels (MAL) in Different Countries	Control [U.I Botanical Garden (Adeyi and Oyeleke, 2017)]
	Dry Season (2017)	Wet Season (2017)	Dry Season (2018)	Wet Season (2018)		
Cu (mg/kg)	5.76 ± 3.54^{abc}	0.89 ± 0.27^{ab}	3.22 ± 2.53^{abc}	0.88 ± 0.38^{ac}	Less than allowable levels	3.98
Zn (mg/kg)	12.11 ± 8.83^{abd}	25.24 ± 20.30^{abc}	4.05 ± 2.83^{bcd}	19.94 ± 14.81^{acd}	Less than allowable levels	47.40
Cr (mg/kg)	7.43 ± 4.24^{abc}	12.12 ± 9.70^{ab}	19.67 ± 6.88^{abc}	11.85 ± 10.37^{ac}	Less than allowable levels	3.95
Pb (mg/kg)	5.64 ± 1.91^{ac}	3.69 ± 0.50^{bc}	4.46 ± 0.58^{abcd}	2.55 ± 1.30^{cd}	Less than allowable levels	6.25
Ni (mg/kg)	4.83 ± 2.53	2.36 ± 1.01^{a}	2.88 ± 1.74^{a}	2.15 ± 1.31	Less than allowable levels	0.33
Cd (mg/kg)	BDL	1.42 ± 0.33^{ab}	2.12 ± 1.07^{abc}	1.00 ± 0.49^{ac}	Higher than MAL in Sweden and Denmark	0.35
Fe (mg/kg)	13.08 ± 6.80^{abc}	34.19 ± 28.43^{ab}	66.86 ± 41.91^{abc}	35.27 ± 30.41^{ac}	NAS	NAV
Mn (mg/kg)	16.59 ± 13.16^{abc}	46.67 ± 52.60^{ab}	97.02 ± 66.87^{abc}	52.70 ± 34.12^{ac}	NAS	NAV

Note: BDL - Below Detection Limit; NAV - Not available; NAS – Not accessible; Means having the same alphabets are significantly different at $P<0.05$

Table 4.17: Maximum Allowable Levels of Heavy metals in soils

Element	UK	Canada	Australia	Netherlands	Sweden	Denmark	Germany	France
As	20	12	100	55	15	-	50	37
Cd	1 – 8	10	20	12	0.4	0.5	20	20
Cr	130	64	-	380	120	500	400	150
Cu	130	63	1000	190	100	500	-	190
Pb	450	140	300	530	80	40	400	40
Ni	50	50	600	210	35	30	140	140
Zn	130	200	7000	720	350	500	-	9000
Fe	NA	NA	NA	NA	NA	NA	NA	NA
Mn	NA	NA	NA	NA	NA	NA	NA	NA

Note: NA – Not accessible

Source: Papapreponis *et al*., 2006

4.3 Assessment of contamination status of heavy metals in sampled soils of Old Oyo National Park

4.3.1 Contamination Assessment based on Contamination Factors

The calculated contamination factors for analysed heavy metals in the sampled soils are illustrated in Table 4.18. The result showed that Cu (except TS2), Zn, Pb, Fe and Mn in all the sampled ranges posed low contamination (<1) while Cr (except OS1 and OS3) showed moderate contamination (1-3). Cd (except TS1 and TS2) showed moderate contamination (3-6) while Ni (except OS1 and OS2) showed very high contamination (>6).

4.3.2 Contamination Assessment based on the Degree of contamination

The degree of contamination of the sampled soils as shown in Table 4.19 indicates that sampled soils (OS1, OS2, TS1 and TS3) fell within the moderate degree of contamination (8-16) while over 50% of the sampled soils (MS1, MS2, MS3, OS3 and TS2) fell within the considerable degree of contamination (16-32).

4.3.3 Contamination Assessment based on Geo-accumulation Index (*Igeo*)

The *Igeo* was also used to assess the heavy metal contamination sampled soil as shown in Table 4.20. The *Igeo* values for Cd fell within the moderately to strongly contaminated category (2 - 3) for OS1, TS1, TS2 and TS3 while MS1, MS2, MS3, OS2 and OS3 fell within the strongly contaminated category (3 - 4). The *Igeo* values for other heavy metals fell within the practically uncontaminated category (<0).

Table 4.18: Contamination Factor for heavy metals in sampled soil of Old Oyo National Park

Soil Samples	Cu	Zn	Cr	Pb	Ni	Cd	Fe	Mn
MS1	0.827	0.502	2.691	0.605	9.364	5.657	0.035	0.044
MS2	0.404	0.407	2.883	0.605	9.242	5.857	0.031	0.043
MS3	0.261	0.577	2.759	0.674	6.394	5.286	0.036	0.042
OS1	0.198	0.274	5.202	0.688	4.030	4.371	0.063	0.100
OS2	0.359	0.558	3.446	0.565	5.303	5.343	0.061	0.083
OS3	0.719	0.247	5.294	0.752	6.242	7.714	0.074	0.120
TS1	0.932	0.158	2.284	0.530	8.333	2.257	0.011	0.014
TS2	1.183	0.162	2.544	0.568	16.606	2.457	0.013	0.016
TS3	0.894	0.111	2.377	0.723	7.879	3.171	0.012	0.016

Table 4.19: Degree of contamination (C_{deg}) of sampled soils of OONP

Soil Samples	C_{deg}	Interpretation
MS1	19.725	considerable degree of contamination
MS2	19.472	considerable degree of contamination
MS3	16.029	considerable degree of contamination
OS1	14.926	moderate degree of contamination
OS2	15.718	moderate degree of contamination
OS3	21.162	considerable degree of contamination
TS1	14.519	moderate degree of contamination
TS2	23.549	considerable degree of contamination
TS3	15.183	moderate degree of contamination

Table 4.20: Geo-accumulation Index (Igeo) of heavy metals in sampled soils of OONP

Soil Samples	Cu	Zn	Cr	Pb	Ni	Cd	Fe	Mn
MS1	-4.411	-2.388	-3.549	-2.667	-4.815	3.343	-5.409	-5.085
MS2	-5.452	-2.689	-3.450	-2.667	-4.834	3.394	-5.618	-5.098
MS3	-6.083	-2.187	-3.514	-2.511	-5.366	3.246	-5.398	-5.141
OS1	-6.479	-3.261	-2.599	-2.481	-6.032	2.972	-4.567	-3.909
OS2	-5.623	-2.235	-3.193	-2.765	-5.635	3.261	-4.617	-4.174
OS3	-4.623	-3.408	-2.574	-2.352	-5.400	3.791	-4.342	-3.645
TS1	-4.248	-4.055	-3.787	-2.858	-4.983	2.018	-7.079	-6.724
TS2	-3.904	-4.015	-3.631	-2.757	-3.989	2.141	-6.856	-6.588
TS3	-4.308	-4.567	-3.729	-2.409	-5.064	2.509	-6.927	-6.543

4.4 Heavy metals concentration in plant (leaves) samples of Old Oyo National Park

The heavy metal concentration in plant samples (leaves) from Old Oyo National Park during the dry seasons of sample collection (2017 & 2018) are shown in Table 4.21. The result showed that in the dry season of 2017, the concentrations of Pb, Ni and Cd were below the detection limit in all the plant samples while Cr (2.88±0.02) in *Afzelia africana* was above WHO recommended level. In the dry season of 2018, Furthermore, in the dry season of 2018, Cr (in *Terminalia glaucescens, Vitellaria paradoxa, Burkea africana*), Cd (in all sampled plants except *Blighia sapida*, *Khaya grandifoliola*, *Daniella oliverii*) and Fe (except *Terminalia glaucescens, Pterocarpus erinaceus, Khaya grandifoliola, Afzelia africana, Daniella oliverii, Brachystegia euryloma*) were above the comparable recommended levels.

Similarly, the heavy metal concentration in plant samples (leaves) from Old Oyo National Park during the wet seasons of sample collection (2017 & 2018) are shown in Table 4.22. The result showed that the concentrations of Pb, Ni and Cd in *Blighia sapida*, *Khaya grandifoliola*, and *Daniella oliverii* were found to be below detection limit in 2017 as well as 2018. In the wet season of 2017, the concentrations of Cr in all the sampled plants (except *Blighia sapida*, *Kigelia africana*, *Khaya grandifoliola*, *Daniella oliverii*), Cd (in *Pterocarpus erinaceus*, *Vitellaria paradoxa*, *Anogeissus leiocarpus*, *Isoberlinia doka*) and Fe (in all the sampled plants) were above the recommended levels. During the wet season of 2018, the levels of Cr (in *Vitellaria paradoxa, Afzelia africana, Anogeissus leiocarpus*), Cd (in *Kigelia africana, Pterocarpus erinaceus, Afzelia africana, Anogeissus leiocarpus, Isoberlinia doka*) and Fe (in *Terminalia glaucescens, Kigelia africana, Vitellaria*

paradoxa, Afzelia africana, Isoberlinia doka) were above the comparable recommended level.

Table 4.21: Heavy metals concentration of plant samples in Old Oyo National Park [Dry Seasons 2017 & 2018]

S/N	Plant Samples	Sampling Year	Cu (mg/kg) 10*	Zn (mg/kg) 50*	Cr (mg/kg) 1.50*	Pb (mg/kg) 2.0*	Ni (mg/kg) 1.5*	Cd (mg/kg) 0.3*	Fe (mg/kg) 20*	Mn (mg/kg) 200*
1	*Blighia sapida*	2017	6.43 ± 0.02	29.10 ± 0.07	BDL	BDL	BDL	BDL	12.81 ± 0.24	1.22 ± 0.79
		2018	5.37 ± 0.16	30.05 ± 0.03	BDL	BDL	BDL	BDL	21.63 ± 0.38	2.89 ± 0.35
2	*Terminalia glaucescens*	2017	5.28 ± 0.03	8.48 ± 0.08	BDL	BDL	BDL	BDL	14.66 ± 0.71	1.10 ± 0.35
		2018	1.41 ± 0.09	2.40 ± 0.10	1.69 ± 0.04	1.21 ± 0.11	0.50 ± 0.08	0.65 ± 0.02	20.00 ± 0.10	8.00 ± 0.06
3	*Kigelia africana*	2017	3.03 ± 0.03	7.60 ± 0.08	BDL	BDL	BDL	BDL	9.21 ± 0.11	2.23 ± 0.29
		2018	1.69 ± 0.12	2.19 ± 0.09	0.98 ± 0.05	1.30 ± 0.10	0.40 ± 0.11	0.70 ± 0.17	22.00 ± 0.07	10.20 ± 0.02
4	*Pterocarpus erinaceus*	2017	4.15 ± 0.02	14.60 ± 0.03	BDL	BDL	BDL	BDL	11.72 ± 0.26	0.87 ± 0.12
		2018	2.10 ± 0.18	7.22 ± 0.16	1.23 ± 0.11	0.92 ± 0.03	1.02 ± 0.13	0.44 ± 0.02	16.10 ± 0.19	3.04 ± 0.07
5	*Vitellaria paradoxa*	2017	0.96 ± 0.06	10.20 ± 0.09	BDL	BDL	BDL	BDL	12.04± 0.98	1.34 ± 0.31
		2018	1.50 ± 0.06	2.53 ± 0.13	1.75 ± 0.10	1.24 ± 0.12	0.58 ± 0.14	0.68 ± 0.07	20.81 ± 0.26	8.30 ± 0.02
6	*Khaya grandifoliola*	2017	4.18 ± 0.01	11.80 ± 0.09	BDL	BDL	BDL	BDL	13.45 ± 0.60	2.79 ± 0.03
		2018	0.85 ± 0.01	7.12 ± 0.05	0.71 ± 0.41	BDL	BDL	BDL	17.01 ± 0.21	1.53 ± 0.13
7	*Afzelia africana*	2017	6.00 ± 0.04	20.10 ± 1.02	2.88 ± 0.02	BDL	BDL	BDL	11.12 ± 0.83	3.32 ± 0.42
		2018	3.98 ± 0.08	8.98 ± 0.28	1.04 ± 0.31	1.62 ± 0.06	0.43 ± 0.12	0.47 ± 0.01	18.50 ± 0.16	2.67 ± 0.03

Table 4.21 (cont'd): Heavy metals concentration of plant samples in Old Oyo National Park [Dry Seasons 2017 & 2018]

S/N	Plant Samples	Sampling Year	Cu (mg/kg) 10*	Zn (mg/kg) 50*	Cr (mg/kg) 1.50*	Pb (mg/kg) 2.0*	Ni (mg/kg) 1.5*	Cd (mg/kg) 0.3*	Fe (mg/kg) 20*	Mn (mg/kg) 200*
8	*Daniellia oliveri*	2017	6.53 ± 0.11	14.00 ± 0.87	BDL	BDL	BDL	BDL	9.56 ± 0.44	2.41 ± 0.18
		2018	4.07 ± 0.01	9.18 ± 0.82	0.36 ± 0.09	BDL	BDL	BDL	11.08 ± 0.12	1.96 ± 0.14
9	*Anogeissus leiocapus*	2017	3.71 ± 0.41	5.88 ± 0.01	BDL	BDL	BDL	BDL	10.53 ± 0.77	6.10 ± 0.22
		2018	1.70 ± 0.17	2.30 ± 0.21	1.21 ± 0.12	1.33 ± 0.04	0.46 ± 0.13	0.74 ± 0.19	22.10 ± 0.16	10.25± 0.06
10	*Brachystegia euryloma*	2017	0.35 ± 0.03	2.94 ± 1.72	BDL	BDL	BDL	BDL	9.98 ± 0.23	4.07 ± 0.01
		2018	0.73 ± 0.01	1.44 ± 0.14	1.20 ± 0.05	0.84 ± 0.04	0.22 ± 0.05	0.31 ± 0.02	13.10 ± 0.27	3.10 ± 0.13
11	*Isoberlinia doka*	2017	2.62 ± 0.78	4.21 ± 0.85	0.92 ± 0.03	BDL	BDL	BDL	12.24 ± 0.16	3.86 ± 0.37
		2018	1.69 ± 0.23	2.19 ± 0.18	1.19 ± 0.10	1.30 ± 0.03	0.40 ± 0.08	0.68 ± 0.11	21.50 ± 0.16	10.00 ±0.11
12	*Burkea africana*	2017	1.20 ± 0.33	5.34 ± 0.27	0.27 ± 0.34	BDL	0.16 ± 0.87	BDL	7.37 ± 0.94	2.82 ± 0.05
		2018	1.48 ± 0.02	2.48 ± 0.19	1.70 ± 0.05	1.21 ± 0.12	0.52 ± 0.11	0.66 ± 0.03	20.10 ± 0.13	8.10 ± 0.04

Note: * - Recommended Level for medicinal plant; BDL- Below detection limit;
Marguba Range = 1 – 4; **Tede Range** = 5 – 8; **Oyo-Ile Range** = 9 - 12

Table 4.22: Heavy metals concentration of plant samples in Old Oyo National Park [Wet Seasons 2017 & 2018]

S/N	Plant Samples	Sampling Year	Cu (mg/kg) 10*	Zn (mg/kg) 50*	Cr (mg/kg) 1.50*	Pb (mg/kg) 2.0*	Ni (mg/kg) 1.5*	Cd (mg/kg) 0.3*	Fe (mg/kg) 20*	Mn (mg/kg) 200*
1	*Blighia sapida*	2017	9.23 ± 0.14	36.06 ± 0.10	0.24 ± 0.03	BDL	BDL	BDL	34.54 ± 0.12	7.22 ± 0.21
		2018	6.82 ± 0.64	18.02 ± 0.67	0.29 ± 0.13	BDL	BDL	BDL	17.08 ± 0.91	9.54 ± 0.55
2	*Terminalia glaucescens*	2017	3.71 ± 0.41	5.88 ± 0.01	2.85 ± 0.04	BDL	BDL	BDL	24.8 ± 0.09	9.10 ± 0.27
		2018	3.04 ± 0.81	7.24 ± 0.28	0.79 ± 0.08	BDL	0.21 ± 0.09	BDL	22.13 ± 0.83	12.16 ± 0.69
3	*Kigelia africana*	2017	5.28 ± 0.02	8.48 ± 0.06	1.12 ± 0.58	BDL	BDL	BDL	41.24 ± 0.78	7.04 ± 0.11
		2018	3.52 ± 0.19	4.66 ± 0.33	0.83 ± 0.27	0.32 ± 0.16	0.32 ± 0.15	0.62 ± 0.18	31.25 ± 1.02	5.51 ± 0.36
4	*Pterocarpus erinaceus*	2017	3.07 ± 0.32	9.43 ± 0.05	2.23 ± 0.07	1.08 ± 0.08	1.16 ± 0.04	0.79 ± 0.04	24.20 ± 0.17	5.17 ± 0.15
		2018	3.07 ± 0.32	8.31 ± 0.45	1.14 ± 0.18	0.28 ± 0.13	1.19 ± 0.54	0.36 ± 0.21	18.44 ± 0.94	2.88 ± 0.22
5	*Vitellaria paradoxa*	2017	4.15 ± 0.02	16.60 ± 0.02	1.92 ± 0.33	0.52 ± 0.53	0.88 ± 0.32	0.28 ± 0.28	31.84 ± 0.89	3.02 ± 0.91
		2018	5.78 ± 0.73	18.11 ± 0.96	1.96 ± 0.49	1.26 ± 0.83	0.62 ± 0.14	BDL	25.19 ± 0.85	6.41 ± 0.73
6	*Khaya grandifoliola*	2017	1.82 ± 0.07	10.20 ± 0.09	0.92 ± 0.49	BDL	BDL	BDL	36.06 ± 1.12	3.76 ± 0.33
		2018	1.26 ± 0.16	12.58 ± 0.63	BDL	BDL	BDL	BDL	13.56 ± 1.30	4.21 ± 0.66
7	*Afzelia africana*	2017	5.12 ± 0.10	11.80 ± 0.09	3.70 ± 0.03	1.81 ± 0.04	0.75 ± 0.07	BDL	33.93 ± 0.50	6.73 ± 0.05
		2018	2.48 ± 0.27	6.40 ± 0.12	3.70 ± 0.03	1.17 ± 0.35	0.47 ± 0.16	0.29 ± 0.13	26.17 ± 1.82	5.92 ± 0.46

Table 4.22 (cont'd): Heavy metals concentration of plant samples in Old Oyo National Park [Wet Seasons 2017 & 2018]

S/N	Plant Samples	Sampling Year	Cu (mg/kg) 10*	Zn (mg/kg) 50*	Cr (mg/kg) 1.50*	Pb (mg/kg) 2.0*	Ni (mg/kg) 1.5*	Cd (mg/kg) 0.3*	Fe (mg/kg) 20*	Mn (mg/kg) 200*
8	*Daniellia oliveri*	2017	6.00 ± 0.04	20.10 ± 1.02	0.87 ± 0.02	BDL	BDL	BDL	26.44 ± 0.21	4.32 ± 0.46
		2018	3.91 ± 0.44	12.70 ± 0.89	BDL	BDL	BDL	BDL	18.90 ± 1.64	3.14 ± 0.62
9	*Anogeissus leiocapus*	2017	6.53 ± 0.11	14.00 ± 0.87	1.88 ± 0.06	1.00 ± 0.03	1.36 ± 0.09	0.43 ± 0.02	26.02 ± 0.20	4.43 ± 0.14
		2018	4.23 ± 0.18	9.33 ± 0.61	1.62 ± 0.88	0.82 ± 0.31	0.38 ± 0.12	0.58 ± 0.24	14.57 ± 0.92	7.25 ± 0.39
10	*Brachystegia euryloma*	2017	4.14 ± 0.08	10.14 ± 0.32	3.28 ± 0.12	BDL	0.66 ± 0.03	BDL	32.1 ± 1.32	6.50 ± 0.03
		2018	2.97 ± 0.88	6.61 ± 0.71	0.44 ± 0.10	BDL	0.41 ± 0.81	BDL	18.11 ± 0.72	4.42 ± 0.47
11	*Isoberlinia doka*	2017	4.36 ± 0.24	9.15 ± 0.15	5.22 ± 0.06	1.28 ± 0.04	1.07 ± 0.06	0.54 ± 0.14	37.67 ± 0.51	6.17 ± 0.05
		2018	3.61 ± 0.42	2.51 ± 0.39	0.74 ± 0.23	1.06 ± 0.12	0.52 ± 0.11	0.41 ± 0.32	22.13 ± 0.69	5.61 ± 0.72
12	*Burkea africana*	2017	4.31 ± 0.09	4.23 ± 0.11	5.28 ± 0.13	BDL	0.22 ± 0.24	BDL	22.21 ± 0.67	3.12 ± 0.04
		2018	6.56 ± 0.77	7.41 ± 0.52	1.32 ± 0.55	BDL	0.46 ± 0.71	BDL	12.50 ± 0.18	6.43 ± 0.56

Note: * - Recommended Level for medicinal plant; BDL- Below detection limit;
Marguba Range = 1 – 4; **Tede Range** = 5 – 8; **Oyo-Ile Range** = 9 - 12

The concentration of heavy metals in plant (leaves) samples across the sampled ranges of Old Oyo National Park are shown in Tables 4.23 – 4.25. In Marguba range, the highest concentration of Cu [9.23 (in *Blighia sapida* during wet season 2017)], Zn [36.06 (in *Blighia sapida* during wet season 2017)], Cr [2.85 (in *Terminalia glaucescens* during wet season 2017)], Pb [1.30 (in *Kigelia africana* during dry season 2018)], Ni [1.19 (in *Pterocarpus erinaceus* during wet season 2018)], Cd [0.79 (in *Pterocarpus erinaceus* during wet season 2017)], Fe [41.24 (in *Kigelia africana* during wet season 2017)] and Mn [12.16 (in *Terminalia glaucescens* during wet season 2018)] were observed as shown in Table 4.23.

In Tede range, the highest concentration of Cu [6.53 (in *Daniella oliverii* during dry season 2017)], Zn [20.10 (in *Afzelia africana* during dry season 2017 and in *Daniella oliverii* during wet season 2017)], Cr [3.70 (in *Afzelia africana* during wet season 2017 and wet season 2018)], Pb [1.81 (in *Afzelia africana* during wet season 2017)], Ni [0.88 (in *Vitellaria paradoxa* during wet season 2017)], Cd [0.68 (in *Vitellaria paradoxa* during dry season 2018)], Fe [36.06 (in *Khaya grandifoliola* during wet season 2017)] and Mn [8.30 (in *Vitellaria paradoxa* during dry season 2018)] were observed as shown in Table 4.24

In Oyo-Ile range, the highest concentration of Cu [6.56 (in *Burkea africana* during wet season 2018)], Zn [14.00 (in *Anogeissus leiocapus* during wet season 2017)], Cr [5.28 (in *Burkea africana* during wet season 2017)], Pb [1.33 (in *Anogeissus leiocapus* during dry season 2018)], Ni [1.36 (in *Anogeissus leiocapus* during wet season 2017)], Cd [0.74 (in *Anogeissus leiocapus* during dry season 2018)], Fe [37.67 (in *Isoberlina doka* in wet season 2017)] and Mn [10.25 (in *Anogeissus leiocapus* in dry season 2018)] were observed as shown in Table 4.25.

Table 4.23: Concentration of heavy metals in all the sampled plants in Marguba range of Old Oyo National Park

Plant Samples / Season and Year	Cu (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
Blighia sapida (D_{17})	6.43	29.10	BDL	BDL	BDL	BDL	12.81	1.22
Terminalia glaucescens (D_{17})	5.28	8.48	BDL	BDL	BDL	BDL	14/66	1.10
Kigelia africana (D_{17})	3.03	7.60	BDL	BDL	BDL	BDL	9.21	2.23
Pterocarpus erinaceus (D_{17})	4.15	14.60	BDL	BDL	BDL	BDL	11.72	0.87
Blighia sapida (W_{17})	9.23	36.06	0.24	BDL	BDL	BDL	34.54	7.22
Terminalia glaucescens (W_{17})	3.71	5.88	2.85	BDL	BDL	BDL	24.80	9.10
Kigelia africana (W_{17})	5.28	8.48	1.12	BDL	BDL	BDL	41.24	7.04
Pterocarpus erinaceus (W_{17})	3.07	9.43	2.23	1.08	1.16	0.79	24.20	5.17
Blighia sapida (D_{18})	5.37	30.05	BDL	BDL	BDL	BDL	21.63	2.89
Terminalia glaucescens (D_{18})	1.41	2.40	1.69	1.21	0.50	0.65	20.00	8.00
Kigelia africana (D_{18})	1.69	2.19	0.98	1.30	0.40	0.70	22.00	10.20
Pterocarpus erinaceus (D_{18})	2.10	7.22	1.23	0.92	1.02	0.44	16.10	3.04
Blighia sapida (W_{18})	6.82	18.02	0.29	BDL	BDL	BDL	17.08	9.54
Terminalia glaucescens (W_{18})	3.04	7.24	0.79	BDL	0.21	BDL	22.13	12.16
Kigelia africana (W_{18})	3.52	4.66	0.83	0.32	0.32	0.62	31.25	5.51
Pterocarpus erinaceus (W_{18})	3.07	8.31	1.14	1.19	1.19	0.36	18.44	2.88
Mean	**4.20**	**12.48**	**0.84**	**0.32**	**0.30**	**0.22**	**21.36**	**5.51**
Standard Deviation	**2.09**	**10.41**	**0.87**	**0.50**	**0.44**	**0.31**	**8.57**	**3.62**

Note: D_{17} = Dry season in 2017; W_{17} = Wet season in 2017; D_{18} = Dry season in 2018; W_{18} = Wet season in 2018

Table 4.24: Concentration of heavy metals in all the sampled plants in Tede range of Old Oyo National Park

Plant Samples / Season and Year	Cu (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
Vitellaria paradoxa (D_{17})	0.96	10.20	BDL	BDL	BDL	BDL	12.04	1.34
Khaya grandifoliola (D_{17})	4.18	11.80	BDL	BDL	BDL	BDL	13.45	2.79
Afzelia africana (D_{17})	6.00	20.10	2.88	BDL	BDL	BDL	11.12	3.32
Daniella oliverii (D_{17})	6.53	14.00	BDL	BDL	BDL	BDL	9.56	2.41
Vitellaria paradoxa (W_{17})	4.15	16.60	1.92	0.52	0.88	0.28	31.84	3.02
Khaya grandifoliola (W_{17})	1.82	10.20	0.92	BDL	BDL	BDL	36.06	3.76
Afzelia africana (W_{17})	5.12	11.80	3.70	1.81	0.75	BDL	33.93	6.73
Daniella oliverii (W_{17})	6.00	20.10	0.87	BDL	BDL	BDL	26.44	4.32
Vitellaria paradoxa (D_{18})	1.50	2.53	1.75	1.24	0.58	0.68	20.81	8.30
Khaya grandifoliola (D_{18})	0.85	7.12	0.71	BDL	BDL	BDL	17.01	1.53
Afzelia africana (D_{18})	3.98	8.98	1.04	1.62	0.43	0.47	18.50	2.67
Daniella oliverii (D_{18})	4.07	9.18	0.36	BDL	BDL	BDL	11.08	1.96
Vitellaria paradoxa (W_{18})	5.78	18.11	1.96	1.26	0.62	BDL	25.19	6.41
Khaya grandifoliola (W_{18})	1.26	12.58	BDL	BDL	BDL	BDL	13.56	4.21
Afzelia africana (W_{18})	2.48	6.40	3.70	1.17	0.47	0.29	26.17	5.92
Daniella oliverii (W_{18})	3.91	12.7	BDL	BDL	BDL	BDL	18.90	3.14
Mean	**3.66**	**12.03**	**1.24**	**0.48**	**0.23**	**0.11**	**20.35**	**3.86**
Standard Deviation	**1.95**	**4.92**	**1.29**	**0.68**	**0.33**	**0.21**	**8.66**	**2.01**

Note: D_{17} = Dry season in 2017; W_{17} = Wet season in 2017; D_{18} = Dry season in 2018; W_{18} = Wet season in 2018

Table 4.25: Concentration of heavy metals in all the sampled plants in Oyo-Ile range of Old Oyo National Park

Plant Samples / Season and Year	Cu (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
Anogeissus leiocapus (D_{17})	3.71	5.88	BDL	BDL	BDL	BDL	10.53	6.10
Brachystegia euryloma (D_{17})	0.35	2.94	BDL	BDL	BDL	BDL	9.98	4.07
Isoberlinia doka (D_{17})	2.62	4.21	0.92	BDL	BDL	BDL	12.24	3.86
Burkea africana (D_{17})	1.20	5.34	0.27	BDL	0.16	BDL	7.37	2.82
Anogeissus leiocapus (W_{17})	6.53	14.00	1.88	1.00	1.36	0.43	26.02	4.43
Brachystegia euryloma (W_{17})	4.14	10.14	3.28	BDL	0.66	BDL	32.10	6.50
Isoberlinia doka (W_{17})	4.36	9.15	5.22	1.28	1.07	0.54	37.67	6.17
Burkea africana (W_{17})	4.31	4.23	5.28	BDL	0.22	BDL	22.21	3.12
Anogeissus leiocapus (D_{18})	1.70	2.30	1.21	1.33	0.46	0.74	22.10	10.25
Brachystegia euryloma (D_{18})	0.73	1.44	1.20	0.84	0.22	0.31	13.10	3.10
Isoberlinia doka (D_{18})	1.69	2.19	1.19	1.30	0.40	0.68	21.50	10.00
Burkea Africana (D_{18})	1.48	2.48	1.70	1.21	0.52	0.66	20.10	8.10
Anogeissus leiocapus (W_{18})	4.23	9.33	1.62	0.82	0.38	0.58	14.57	7.25
Brachystegia euryloma (W_{18})	2.97	6.61	0.44	BDL	0.41	BDL	18.11	4.42
Isoberlinia doka (W_{18})	3.61	2.51	0.74	1.06	0.52	0.41	22.13	5.61
Burkea africana (W_{18})	6.56	7.41	1.32	BDL	0.46	BDL	12.50	6.43
Mean	**3.14**	**5.64**	**1.64**	**0.55**	**0.43**	**0.27**	**18.89**	**5.76**
Standard Deviation	**1.89**	**3.58**	**1.62**	**0.59**	**0.37**	**0.30**	**8.32**	**2.31**

Note: D_{17} = Dry season in 2017; W_{17} = Wet season in 2017; D_{18} = Dry season in 2018; W_{18} = Wet season in 2018

The concentrations of heavy metals in sampled plant (leaves) of Old Oyo National Park across the seasons of sampling [dry (combined 2017 & 2018) and wet (combined 2017 & 2018)] are shown in Tables 4.26 and 4.27, respectively. The result showed that the wet seasons had the highest mean concentration of Cu (4.37±1.79), Zn (11.25±7.01), Cr (11.25±7.01), Fe (25.46±7.98) and Mn (5.84±2.25), while the highest mean concentration of Pb (1.22±0.23), Ni (0.47±0.23) and Cd (0.59±0.15) were observed in the dry seasons. The mean concentrations of Zn were both highest in the wet (0.16±0.06) and dry (0.16±0.17) seasons. This shows that the sampled plants were contaminated more with heavy metals during the wet season than the dry season.

The mean values of all the analysed heavy metals in the sampled plant species across the four seasons of sampling (dry season 2017, wet season 2017, dry season 2018 and wet season 2018) revealed that the concentration of Cr (in wet season, 2017), Cd (all seasons except dry season 2017) and Fe (in wet seasons 2017 and 2018)were above the WHO recommended levels (in medicinal plant) as shown in Table 4.28. Statistically, there were significant differences in the values of all the analysed heavy metals in the plant samples across the four seasons at $P<0.05$ (Appendix: Table III).

Table 4.26: Concentration of heavy metals in the sampled plants of Old Oyo National Park in the two Dry Seasons (2017 & 2018)

Sample Code / Season and Year	Cu (mg/kg)	Zn(mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Ni(mg/kg)	Cd (mg/kg)	Fe(mg/kg)	Mn(mg/kg)
Blighia sapida (D_{17})	6.43	29.10	BDL	BDL	BDL	BDL	12.81	1.22
Terminalia glaucescens (D_{17})	5.28	8.48	BDL	BDL	BDL	BDL	14.66	1.10
Kigelia africana (D_{17})	3.03	7.60	BDL	BDL	BDL	BDL	9.21	2.23
Pterocarpus erinaceus (D_{17})	4.15	14.60	BDL	BDL	BDL	BDL	11.72	0.87
Vitellaria paradoxa (D_{17})	0.96	10.20	BDL	BDL	BDL	BDL	12.04	1.34
Khaya grandifoliola (D_{17})	4.18	11.80	BDL	BDL	BDL	BDL	13.45	2.79
Afzelia africana (D_{17})	6.00	20.10	2.88	BDL	BDL	BDL	11.12	3.32
Daniella oliverii (D_{17})	6.53	14.00	BDL	BDL	BDL	BDL	9.56	2.41
Anogeissus leiocapus (D_{17})	3.71	5.88	BDL	BDL	BDL	BDL	10.53	6.10
Brachystegia euryloma (D_{17})	0.35	2.94	BDL	BDL	BDL	BDL	9.98	4.07
Isoberlinia doka (D_{17})	2.62	4.21	0.92	BDL	BDL	BDL	12.24	3.86
Burkea africana (D_{17})	1.20	5.34	0.27	BDL	0.16	BDL	7.37	2.82
Blighia sapida (D_{18})	5.37	30.05	BDL	BDL	BDL	BDL	21.63	2.89
Terminalia glaucescens (D_{18})	1.41	2.40	1.69	1.21	0.50	0.65	20.00	8.00
Kigelia africana (D_{18})	1.69	2.19	0.98	1.30	0.40	0.70	22.00	10.20
Pterocarpus erinaceus (D_{18})	2.10	7.22	1.23	0.92	1.02	0.44	16.10	3.04
Vitellaria paradoxa (D_{18})	1.50	2.53	1.75	1.24	0.58	0.68	20.81	8.30
Khaya grandifoliola (D_{18})	0.85	7.12	0.71	BDL	BDL	BDL	17.01	1.53
Afzelia africana (D_{18})	3.98	8.98	1.04	1.62	0.43	0.47	18.50	2.67
Daniella oliverii (D_{18})	4.07	9.18	0.36	BDL	BDL	BDL	11.08	1.96
Anogeissus leiocapus (D_{18})	1.70	2.30	1.21	1.33	0.46	0.74	22.10	10.25
Brachystegia euryloma (D_{18})	0.73	1.44	1.20	0.84	0.22	0.31	13.10	3.10
Isoberlinia doka (D_{18})	1.69	2.19	1.19	1.30	0.40	0.68	21.50	10.00
Burkea africana (D_{18})	1.48	2.48	1.70	1.21	0.52	0.66	20.10	8.10
Mean	**2.96**	**8.85**	**1.22**	**1.22**	**0.47**	**0.59**	**14.94**	**4.26**
Standard Deviation	**1.94**	**7.94**	**0.65**	**0.23**	**0.23**	**0.15**	**4.77**	**3.13**

Note: D_{17} = Dry season in 2017; D_{18} = Dry season in 2018;

Table 4.27: Concentration of heavy metals in the sampled plants of Old Oyo National Park in the two Wet Seasons (2017 & 2018)

Sample Code / Season and Year	Cu (mg/kg)	Zn(mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Ni(mg/kg)	Cd (mg/kg)	Fe(mg/kg)	Mn(mg/kg)
Blighia sapida (W_{17})	9.23	36.06	0.24	BDL	BDL	BDL	34.54	7.22
Terminalia glaucescens (W_{17})	3.71	5.88	2.85	BDL	BDL	BDL	24.80	9.10
Kigelia africana (W_{17})	5.28	8.48	1.12	BDL	BDL	BDL	41.24	7.04
Pterocarpus erinaceus (W_{17})	3.07	9.43	2.23	1.08	1.16	0.79	24.20	5.17
Vitellaria paradoxa (W_{17})	4.15	16.60	1.92	0.52	0.88	0.28	31.84	3.02
Khaya grandifoliola (W_{17})	1.82	10.20	0.92	BDL	BDL	BDL	36.06	3.76
Afzelia africana (W_{17})	5.12	11.80	3.70	1.81	0.75	BDL	33.93	6.73
Daniella oliverii (W_{17})	6.00	20.10	0.87	BDL	BDL	BDL	26.44	4.32
Anogeissus leiocapus (W_{17})	6.53	14.00	1.88	1.00	1.36	0.43	26.02	4.43
Brachystegia euryloma (W_{17})	4.14	10.14	3.28	BDL	0.66	BDL	32.10	6.50
Isoberlinia doka (W_{17})	4.36	9.15	5.22	1.28	1.07	0.54	37.67	6.17
Burkea africana (W_{17})	4.31	4.23	5.28	BDL	0.22	BDL	22.21	3.12
Blighia sapida (W_{18})	6.82	18.02	0.29	BDL	BDL	BDL	17.08	9.54
Terminalia glaucescens (W_{18})	3.04	7.24	0.79	BDL	0.21	BDL	22.13	12.16
Kigelia africana (W_{18})	3.52	4.66	0.83	0.32	0.32	0.62	31.25	5.51
Pterocarpus erinaceus (W_{18})	3.07	8.31	1.14	0.28	1.19	0.36	18.44	2.88
Vitellaria paradoxa (W_{18})	5.78	18.11	1.96	1.26	0.62	BDL	25.19	6.41
Khaya grandifoliola (W_{18})	1.26	12.58	BDL	BDL	BDL	BDL	13.56	4.21
Afzelia africana (W_{18})	2.48	6.40	3.70	1.17	0.47	0.29	26.17	5.92
Daniella oliverii (W_{18})	3.91	12.70	BDL	BDL	BDL	BDL	18.90	3.14
Anogeissus leiocapus (W_{18})	4.23	9.33	1.62	0.82	0.38	0.58	14.57	7.25
Brachystegia euryloma (W_{18})	2.97	6.61	0.44	BDL	0.41	BDL	18.11	4.42
Isoberlinia doka (W_{18})	3.61	2.51	0.74	1.06	0.52	0.41	22.13	5.61
Burkea africana (W_{18})	6.56	7.41	1.32	BDL	0.46	BDL	12.50	6.43
Mean	**4.37**	**11.25**	**1.76**	**0.44**	**0.45**	**0.18**	**25.46**	**5.84**
Standard Deviation	**1.79**	**7.01**	**1.52**	**0.57**	**0.44**	**0.26**	**7.98**	**2.25**

Note: W_{17} = Wet season in 2017; W_{18} = Wet season in 2018

Table 4.28: Mean values of heavy metals in plant samples of Old Oyo National Park

Heavy metals	Mean Values ± Standard Deviation				Recommended Level (in medicinal plant)	References
	Dry Season (2017)	Wet Season (2017)	Dry Season (2018)	Wet Season (2018)		
Cu (mg/kg)	3.70 ± 2.14^{abc}	4.81 ± 1.88^{acd}	2.21 ± 1.45^{bce}	3.94 ± 1.67^{cde}	10	WHO, 2005
Zn (mg/kg)	11.19 ± 7.51^{ad}	13.00 ± 8.47^{bce}	6.51 ± 7.97^{abde}	9.49 ± 4.93^{c}	50	Khan *et al*., 2008
Cr (mg/kg)	1.36 ± 1.36^{ab}	2.46 ± 1.66^{ac}	1.19 ± 0.43^{ab}	1.28 ± 0.99^{ac}	1.50	WHO, 1998
Pb (mg/kg)	BDL	1.14 ± 0.47^{ab}	1.22 ± 0.23^{abc}	0.81 ± 0.43^{ac}	2.0	WHO, 1998
Ni (mg/kg)	0.16 ± 0.00^{abd}	0.87 ± 0.38^{abc}	0.50 ± 0.22^{ace}	0.51 ± 0.28^{ade}	1.5	WHO, 2005
Cd (mg/kg)	BDL	0.51 ± 0.21^{ab}	0.59 ± 0.15^{abc}	0.45 ± 0.14^{ac}	0.3	WHO, 2005
Fe (mg/kg)	11.22 ± 2.02^{ab}	30.92 ± 6.07^{ac}	18.66 ± 3.64^{abc}	20.00 ± 5.59^{a}	20	WHO, 1998
Mn (mg/kg)	2.68 ± 1.52^{abcd}	5.55 ± 1.88^{ab}	5.84 ± 3.56^{ac}	6.12 ± 2.63^{ad}	200	WHO, 1998

Note: BDL- Below detection limit; Means with the same alphabets are significantly different at $P \leq 0.05$

4.5 Heavy metals concentration in wild animals' faecal samples of Old Oyo National Park

The heavy metal concentration in faecal samples of wild animal species from Old Oyo National Park collected during the period of study is presented in Table 4.29. The result showed that Zn (123.0 ± 0.63) in the faeces of Mongoose (*Atilax paludinosus*) was the highest in all the wild animals' faecal samples analysed, followed by Fe (74.40 ± 2.52) in the faeces of Olive baboon (*Papio anubis*) while Cu (3.38 ± 0.26) in the faeces of African Civet cat (*Civettictis civetta*) was the lowest. The concentrations of Cr, Pb, Ni and Cd were below detection limits in all the faecal samples analysed.

Table 4.29: Heavy metals concentration in wild animals' faecal samples in Old Oyo National Park

Faecal Sample	Animal Species	Total Number of samples	Cu (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
F1	Mongoose (*Atilax paludinosus*)	4	8.83 ± 0.07	123.0 ± 2.63	BDL	BDL	BDL	BDL	63.20 ± 1.36	58.72 ± 1.68
F2	Olive baboon (*Papio anubis*)	12	3.40 ± 0.19	6.35 ± 0.44	BDL	BDL	BDL	BDL	74.40 ± 2.52	12.10 ± 0.27
F3	African Civet cat (*Civettictis civetta*)	3	3.38 ± 0.26	17.3 ± 0.31	BDL	BDL	BDL	BDL	11.82 ± 0.56	7.22 ± 0.20
F4	Kob (*Kobus kob*)	8	6.75 ± 0.11	23.7 ± 0.16	BDL	BDL	BDL	BDL	28.50 ± 1.19	15.30 ± 0.28
F5	Maxwell duiker (*Philantoba maxwelli*)	6	8.28 ± 0.24	31.9 ± 0.53	BDL	BDL	BDL	BDL	56.81 ± 2.31	38.24 ± 1.23
F6	Western hartebeest (*Alcelaphus buselaphus*)	4	10.60 ± 0.18	BDL	BDL	BDL	BDL	BDL	7.64 ± 0.41	52.05 ± 3.48
F7	Patas Monkey (*Erythrocebus patas*)	6	4.41 ± 0.13	10.62 ± 0.33	BDL	BDL	BDL	BDL	16.32 ± 0.35	8.18 ± 0.17

Note: BDL- Below detection limit

4.6 Physicochemical Characteristics of Water Samples in Old Oyo National Park

The physicochemical characteristics of water samples (rivers) of Old Oyo National Park collected for two years (2017 and 2018) are presented in Tables 4.30 to 4.33. The result showed that in the dry season of 2017, the sampled rivers' temperatures (except River Ogun) were below the range specified by WHO (2011) guidelines. Also, the sulphate levels in all the rivers (except Rivers Oopo and Owu) and the electrical conductivity (in River Ogun) were above the WHO permissible limit as shown in Table 4.30. In the wet season of 2017, only the pH of River Sooro was below the range specified by WHO guidelines (Table 4.31). The result of dry season, 2018 showed that the sampled rivers' temperatures (except River Ogun) were below the range specified by WHO (2011) guidelines. Furthermore, the total suspended solids [TSS] (in Rivers Oopo, Tessi and Sooro) as well as the total solids [TS] (in Rivers Oopo, Tessi and Sooro) were above the WHO (2011) permissible limits as shown in Table 4.32 while during the wet season of 2018, only the total solids [TS] in River Ogun was above the WHO (2011) permissible limit as shown in Table 4.33.

The mean values of all the analysed physicochemical characteristics in the sampled waterholes across the four seasons of sampling (dry season 2017, wet season 2017, dry season 2018 and wet season 2018) showed that the TSS (during dry season 2018), TS (during dry season 2018) and sulphate (during dry season 2017) levels were above the comparable WHO (2011) and NSDWQ (2007) guidelines for drinking water (Table 4.34 and Figure 4.2).

The comparison of water physicochemical parameters across the sampled ranges of Old Oyo National Park is shown in Table 4.35. The result shows that the highest mean level of

pH (6.83±0.08) and BOD (21.57±6.03) were observed in Oyo-Ile range while EC (151.52±63.77), Alkalinity (63.56±17.11), TDS (124.44±51.75), Chloride (17.41±8.25), DO (5.64±1.22) and COD (50.40±25.67) were noted to have had the highest mean level in Marguba range. Similarly, the mean level of TSS (371.58±318.73), TS (487.99±340.37), Nitrate (0.39±0.20), Phosphate (0.24±0.17) and Sulphate (194.58±346.11) were observed to be highest in Tede range.

Statistically, there were significant differences in all the physicochemical parameters of water sampled except pH, chloride and BOD that had no significant difference ($P<0.05$) as shown in Appendix: Table IV while sample temperature, TDS and Cl^- positively correlated with the heavy metals above permissible limit (Appendix: Table VI).

Table 4.30: Physicochemical Parameters of selected waterholes in Old Oyo National Park [Dry Season, 2017]

Water Holes	A Temp (^oC) Ambient	S. Temp (^oC) 25-30*	pH 6.5-8.5*	EC (µS/cm) 250*	Alkal. (mg/l) 100*	TDS (mg/l) 500*	TSS (mg/l) 500*	TS (mg/l) 500*	NO_3^- (mg/l) 10*	PO_4^{3-} (mg/l) 5.0*	SO_4^{2-} (mg/l) 400*	Cl^- (mg/l) 200*	DO (mg/) 7.5*	BOD (mg/l) NV*	COD (mg/l) NV*
River Ogun (MW_1)	28.22	25.32	7.10	270.00	71.20	173.0	112.0	285.0	0.19	0.005	789.12	16.34	7.44	5.43	36.14
River Oopo (MW_2)	23.81	20.46	6.51	150.00	54.14	147.4	158.0	305.4	0.07	0.004	102.11	26.08	7.22	23.76	48.26
River Ayinta (MW_3)	22.62	18.20	6.67	203.00	48.16	147.0	193.0	340.0	0.37	0.026	408.08	14.11	4.06	15.52	29.48
River Tessi (OW_1)	24.32	19.22	6.84	220.00	33.54	141.0	344.6	485.6	0.79	0.039	987.47	9.16	2.21	8.96	32.51
River Sooro (OW_2)	15.68	18.00	6.56	203.00	68.20	147.2	137.8	285.0	0.55	0.007	400.22	15.92	2.74	5.98	14.64
River Owu (TW_1)	27.30	24.10	6.87	80.10	52.04	51.2	33.2	84.4	0.05	0.003	129.04	2.64	4.12	24.67	48.11

Note: * WHO Permissible Limit (2011); NV – No value for surface water; A Temp = Ambient Temperature; S. Temp = Sample Temperature; EC = Electrical Conductivity; Alkal. = Alkalinity; TDS = Total Dissolved Solids; TSS = Total Suspended Solids; TS = Total Solids; NO_3^- = Nitrate; PO_4^{3-} = Phosphate; SO_4^{2-} = Sulphate; Cl^- = Chloride; DO = Dissolved Oxygen; BOD = Biological Oxygen Demand; COD = Chemical Oxygen Demand

Table 4.31: Physicochemical Parameters of selected waterholes in Old Oyo National Park [Wet Season, 2017]

Water Holes	A Temp (^oC) Ambient	S. Temp (^oC) 25-30*	pH 6.5-8.5*	EC (µS/cm) 250*	Alkal. (mg/l) 100*	TDS (mg/l) 500*	TSS (mg/l) 500*	TS (mg/l) 500*	NO_3^- (mg/l) 10*	PO_4^{3-} (mg/l) 5.0*	SO_4^{2-} (mg/l) 400*	Cl^- (mg/l) 200*	DO (mg/) 7.5*	BOD (mg/l) NV*	COD (mg/l) NV*
River Ogun (MW_1)	23.60	25.10	6.93	72.50	80.00	36.70	224.30	261.00	0.50	0.24	64.70	9.93	5.50	8.00	57.90
River Oopo (MW_2)	25.10	25.40	7.01	77.80	60.00	39.20	163.80	203.00	0.56	0.26	60.60	17.90	6.70	9.00	50.80
River Ayinta (MW_3)	27.50	26.20	6.47	82.40	70.00	46.00	218.00	264.00	0.43	0.27	82.40	16.20	6.54	8.00	56.20
River Tessi (OW_1)	28.10	28.10	6.53	48.80	50.00	24.90	103.10	128.00	0.31	0.28	54.10	15.90	6.90	16.00	43.80
River Sooro (OW_2)	28.10	27.05	6.43	75.00	80.00	38.10	130.90	169.00	0.50	0.29	28.40	21.80	6.40	24.00	87.70
River Owu (TW_1)	26.50	25.83	6.72	80.00	70.00	40.40	94.60	135.00	0.17	0.230	57.80	5.96	6.90	28.00	53.80

Note: * WHO Permissible Limit (2011); NV – No value for surface water; A Temp = Ambient Temperature; S. Temp = Sample Temperature; EC = Electrical Conductivity; Alkal. = Alkalinity; TDS = Total Dissolved Solids; TSS = Total Suspended Solids; TS = Total Solids; NO_3^- = Nitrate; PO_4^{3-} = Phosphate; SO_4^{2-} = Sulphate; Cl^- = Chloride; DO = Dissolved Oxygen; BOD = Biological Oxygen Demand; COD = Chemical Oxygen Demand

Table 4.32: Physicochemical Parameters of selected waterholes in Old Oyo National Park [Dry Season, 2018]

Water Holes	A Temp (^oC) Ambient	S. Temp (^oC) 25-30*	pH 6.5-8.5*	EC (µS/cm) 250*	Alkal. (mg/l) 100*	TDS (mg/l) 500*	TSS (mg/l) 500*	TS (mg/l) 500*	NO_3^- (mg/l) 10*	PO_4^{3-} (mg/l) 5.0*	SO_4^{2-} (mg/l) 400*	Cl^- (mg/l) 200*	DO (mg/) 7.5*	BOD (mg/l) NV*	COD (mg/l) NV*
River Ogun (MW_1)	25.50	26.12	6.82	210.26	86.56	163.00	340.34	503.34	0.23	0.063	14.33	10.90	5.90	8.05	28.20
River Oopo (MW_2)	24.44	22.20	6.74	174.15	43.38	152.23	1675.0	1827.0	0.01	0.217	85.72	37.71	5.30	30.20	120.14
River Ayinta (MW_3)	24.20	23.28	6.71	196.10	57.23	126.50	206.00	332.50	0.26	0.142	54.32	11.52	4.22	11.40	46.65
River Tessi (OW_1)	23.94	23.10	6.72	214.12	28.82	118.40	680.05	798.45	0.20	0.198	28.64	11.92	4.50	10.18	36.35
River Sooro (OW_2)	20.53	19.24	6.52	218.01	56.54	134.64	1015.0	1149.7	0.28	0.435	8.57	17.93	6.40	5.00	20.50
River Owu (TW_1)	25.10	23.14	6.91	88.42	64.32	63.10	122.42	185.52	0.11	0.160	37.24	3.22	5.27	19.31	43.26

Note: * WHO Permissible Limit (2011); NV – No value for surface water; A Temp = Ambient Temperature; S. Temp = Sample Temperature; EC = Electrical Conductivity; Alkal. = Alkalinity; TDS = Total Dissolved Solids; TSS = Total Suspended Solids; TS = Total Solids; NO_3^- = Nitrate; PO_4^{3-} = Phosphate; SO_4^{2-} = Sulphate; Cl^- = Chloride; DO = Dissolved Oxygen; BOD = Biological Oxygen Demand; COD = Chemical Oxygen Demand

Table 4.33: Physicochemical Parameters of selected waterholes in Old Oyo National Park [Wet Season, 2018]

Water Holes	A Temp (^oC) Ambient	S. Temp (^oC) 25-30*	pH 6.5-8.5*	EC (µS/cm) 250*	Alkal. (mg/l) 100*	TDS (mg/l) 500*	TSS (mg/l) 500*	TS (mg/l) 500*	NO_3^- (mg/l) 10*	PO_4^{3-} (mg/l) 5.0*	SO_4^{2-} (mg/l) 400*	Cl^- (mg/l) 200*	DO (mg/) 7.5*	BOD (mg/l) NV*	COD (mg/l) NV*
River Ogun (MW_1)	24.20	25.18	6.68	178.10	92.50	154.1	362.4	516.50	0.34	0.074	32.14	14.31	4.75	6.45	24.53
River Oopo (MW_2)	23.70	22.6	6.52	105.20	37.20	158.7	293.1	451.8	0.04	0.208	88.05	24.2	6.10	28.72	68.35
River Ayinta (MW_3)	25.40	25.05	6.54	98.72	62.30	149.4	304.5	453.95	0.32	0.161	62.50	9.68	3.92	7.54	38.12
River Tessi (OW_1)	21.50	23.25	6.70	128.30	48.40	174.2	282.0	456.20	0.26	0.196	36.80	17.22	4.52	12.44	25.62
River Sooro (OW_2)	22.10	23.07	6.48	96.50	68.30	152.8	279.2	432.0	0.26	0.473	12.42	19.1	5.53	9.41	24.74
River Owu (TW_1)	22.45	21.30	6.83	93.50	67.50	72.60	149.2	221.8	0.23	0.21	44.32	4.16	4.28	14.30	32.41

Note: * WHO Permissible Limit (2011); NV – No value for surface water; A Temp = Ambient Temperature; S. Temp = Sample Temperature; EC = Electrical Conductivity; Alkal. = Alkalinity; TDS = Total Dissolved Solids; TSS = Total Suspended Solids; TS = Total Solids; NO_3^- = Nitrate; PO_4^{3-} = Phosphate; SO_4^{2-} = Sulphate; Cl^- = Chloride; DO = Dissolved Oxygen; BOD = Biological Oxygen Demand; COD = Chemical Oxygen Demand

Table 4.34: Mean values of physicochemical parameters of the selected waterholes of Old Oyo National Park

Parameters	Mean Values ± Standard Deviation				WHO (2011) Guideline for Drinking water	NSDWQ (2007) Guideline for Drinking water
	Dry Season (Jan. 2017)	Wet Season (June, 2017)	Dry Season (Jan. 2018)	Wet Season (May, 2018)		
Ambient Temp (^oC)	23.67 ± 4.46^{ab}	26.48 ± 1.82^{abcd}	23.95 ± 1.77^{bc}	23.23 ± 1.47^{bd}	Ambient	Ambient
Sample Temp (^oC)	20.88 ± 3.11^{abc}	26.28 ± 1.12^{abc}	22.85 ± 2.21^{ab}	23.41 ± 1.49^{ac}	25 - 30	Ambient
pH	6.76 ± 0.22^{a}	6.68 ± 0.25	6.74 ± 0.13	6.63 ± 0.13^{a}	6.5 – 8.5	6.5 – 8.5
EC (µS/cm)	187.68 ± 65.24^{ab}	72.75 ± 12.25^{abc}	183.51 ± 49.26^{bc}	116.72 ± 32.58^{abc}	250	1000
Alkalinity (mg/l)	54.55 ± 13.80^{ab}	68.33 ± 11.69^{abc}	56.14 ± 19.51^{bc}	62.70 ± 18.96	100	100
TDS (mg/l)	134.47 ± 42.30^{ab}	37.55 ± 6.98^{abcd}	126.31 ± 35.06^{bc}	143.64 ± 35.87^{bd}	500	500
TSS (mg/l)	163.10 ± 103.91^{ac}	155.78 ± 56.16^{bc}	673.13 ± 592.10^{abcd}	278.40 ± 70.23^{cd}	500	-
TS (mg/l)	297.57 ± 128.82^{ac}	193.33 ± 59.88^{bcd}	799.37 ± 610.17^{abcd}	422.04 ± 102.16^{bc}	500	1500
NO_3^- (mg/l)	0.34 ± 0.29^{ac}	0.41 ± 0.15^{bcd}	0.18 ± 0.10^{abc}	0.24 ± 0.11^{bd}	10	50
PO_4^{3-} (mg/l)	0.01 ± 0.01^{abcd}	0.26 ± 0.02^{abc}	0.20 ± 0.13^{abc}	0.22 ± 0.14^{ad}	5.0	-
SO_4^{2-} (mg/l)	469.34 ± 354.94^{abcd}	58.00 ± 17.54^{ab}	38.14 ± 28.49^{ac}	46.04 ± 26.26^{ad}	400	100
Cl^- (mg/l)	14.04 ± 7.84	14.62 ± 5.72	15.53 ± 11.83	14.78 ± 7.10	200	250
DO (mg/l)	4.63 ± 2.22^{ab}	6.49 ± 0.52^{abcd}	5.27 ± 0.82^{bc}	4.85 ± 0.82^{bd}	7.5	-
BOD (mg/l)	14.05 ± 8.66	15.50 ± 8.76	14.02 ± 9.26	13.14 ± 8.18	NA	-
COD (mg/l)	34.86 ± 12.65^{abc}	58.37 ± 15.20^{abd}	49.18 ± 36.07^{ac}	35.63 ± 16.91^{bd}	Ambient	Ambient

Note: NA – Not available for surface water; Means having the same alphabets are significantly different at $P<0.05$

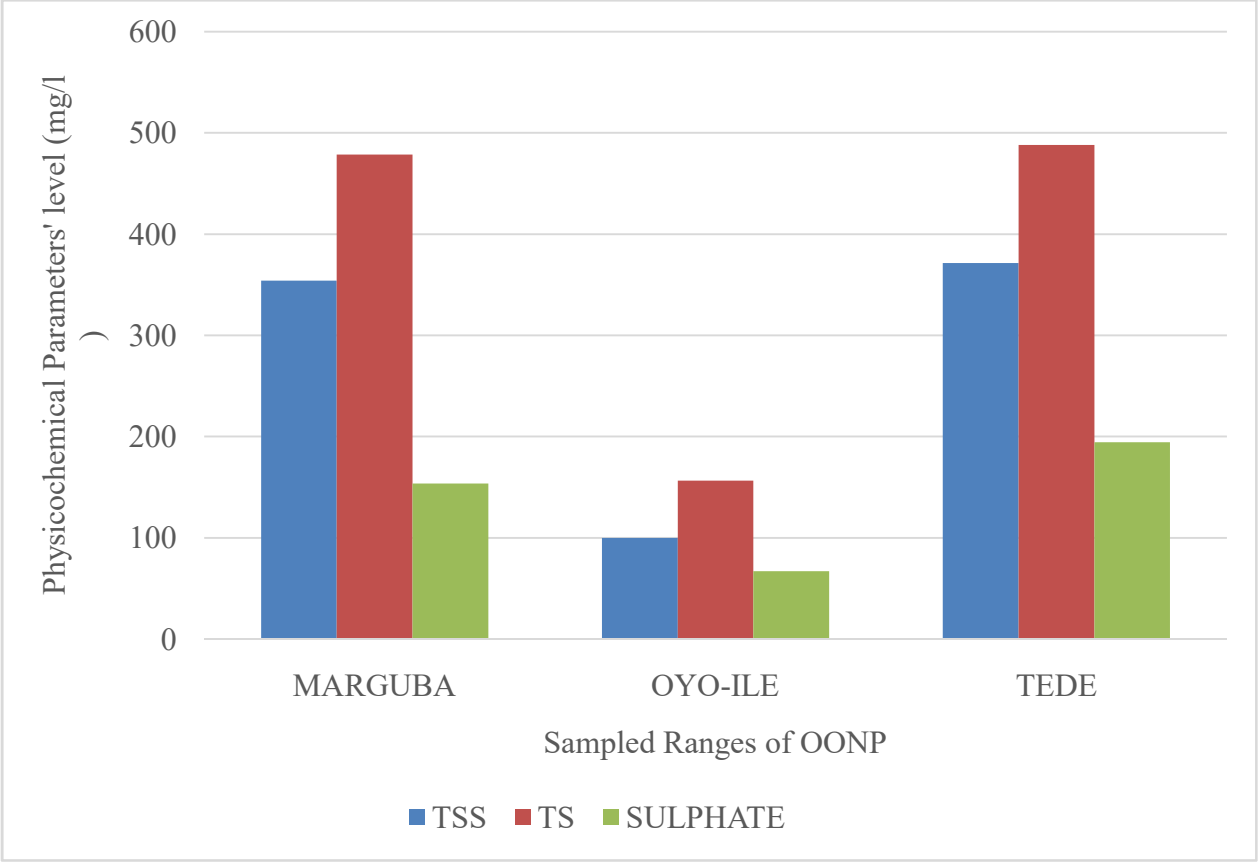

Figure 4.2: Mean plot of water physicochemical parameters (above permissible limit) among the selected ranges of Old Oyo National Park

Table 4.35: Comparison of water physicochemical parameters across the sampled ranges of Old Oyo National Park

Parameter	Range	Mean Level	Standard Deviation
Ambient Temperature	Oyo-Ile	25.34	2.13
	Marguba	24.86	1.63
	Tede	23.03	4.09
Sample Temperature	Oyo-Ile	23.59	1.89
	Marguba	23.76	2.49
	Tede	22.63	3.68
pH	Oyo-Ile	6.83	0.08
	Marguba	6.73	0.21
	Tede	6.60	0.14
EC	Oyo-Ile	85.51	6.63
	Marguba	151.52	63.77
	Tede	150.47	71.36
Alkalinity	Oyo-Ile	63.47	7.96
	Marguba	63.56	17.11
	Tede	54.23	17.68
TDS	Oyo-Ile	56.83	14.02
	Marguba	124.44	51.75
	Tede	116.41	54.85
TSS	Oyo-Ile	99.86	49.71
	Marguba	354.20	422.95
	Tede	371.58	318.73
TS	Oyo-Ile	156.61	59.86
	Marguba	478.62	436.82
	Tede	487.99	340.37

Note: EC = Electrical Conductivity; TDS = Total Dissolved Solids; TSS = Total Suspended Solids; TS = Total Solids

Table 4.35 (cont'd): Comparison of water physicochemical parameters among the ranges

Parameter	Range	Mean Concentration	Standard Deviation
Nitrate	Oyo-Ile	0.14	0.08
	Marguba	0.28	0.18
	Tede	0.39	0.20
Phosphate	Oyo-Ile	0.15	0.10
	Marguba	0.14	0.10
	Tede	0.24	0.17
Sulphate	Oyo-Ile	67.10	42.16
	Marguba	153.67	224.44
	Tede	194.58	346.11
Chloride	Oyo-Ile	4.00	1.45
	Marguba	17.41	8.25
	Tede	16.12	3.99
DO	Oyo-Ile	5.14	1.28
	Marguba	5.64	1.22
	Tede	4.90	1.74
BOD	Oyo-Ile	21.57	6.03
	Marguba	13.51	8.97
	Tede	11.50	6.13
COD	Oyo-Ile	44.40	9.08
	Marguba	50.40	25.67
	Tede	35.73	22.92

Note: DO = Dissolved Oxygen; BOD = Biological Oxygen Demand; COD = Chemical Oxygen Demand

4.7 Physicochemical Characteristics of Soil Samples in Old Oyo National Park

The physicochemical characteristics of soil samples of OONP collected for two years (2017 and 2018) are presented in Tables 4.36 to 4.39. The result showed that during the dry season of 2017, the % N (in MS1, OS3, TS1 and TS3), Mg (in all the samples) and K (in all the samples except OS3) were above the comparable critical limit as shown in Table 4.36. During the wet season of 2017, in all the soil samples, the % N (except OS3), Mg (in all the samples) as well as K (in all the samples except OS1, OS2 and OS3) were above the critical limit as shown in Table 4.37. In the dry season of 2018, in all the soil samples, % N (except in MS2, OS1, OS2, OS3) and exchangeable bases [Mg, K (except in OS3) were above the critical limit as shown in Table 4.38. During the wet season of 2018, in all the soil samples, the % N (except OS1, OS2, OS3) and exchangeable bases (Mg, K [except OS3]) as shown in Table 4.39 were above the critical limit. The mean values of most of the physicochemical parameters of soil samples from Old Oyo National Park across the four seasons of sampling are shown in Table 4.40 with % N (except dry season 2018), Mg (in all the seasons) and K (in all the seasons) were above the comparable critical limits.

Also, the concentration of soil physicochemical characteristics across the sampled ranges of Old Oyo National Park are presented in Table 4.41. The result shows that Available Phosphorus (3.56±6.07), Exchangeable Acidity (11.53±6.40), Ca (1.45±1.59), Mg (4.75±3.23), K (0.97±0.25), Na (0.59±0.18), ECEC (7.86±2.54) and Clay (121.92±38.80) in soils sampled from Marguba range had the highest mean level while pH (6.52±0.42) of sampled soils in Oyo-Ile range the highest mean level. Similarly, the sampled soils from Tede range had the highest mean level in SOC (222.75±17.73), SOM (2.44±0.48), Nitrogen (3.32±2.04), TEB (1.78±2.89), BS (29.83±40.72), Sand (273.29±318.17) and Silt

(658.83±316.77). Statistically, there were statistically significant differences in the levels of Soil Organic Carbon (P=0.047), Soil Organic Matter (P=0.041), Soil Nitrogen (P=0.020), Calcium (P=0.016), Total Exchangeable Bases (P=0.009) and Effective Cation Exchange Capacity (P=0.033) across the seasons of sampling at P≤0.05. [Appendix: Table V].

Table 4.36: Physicochemical Parameters of Soil Samples in Old Oyo National Park [Dry Season, 2017]

Soil Sample	pH (water)	Soil EC µS/cm)	SOC (%)	SOM (%)	% N	A. P (mg/kg)	Exch. Acidity (Cmol/kg)	Exchangeable bases (Cmol/kg)				TEB (Cmol/kg)	ECEC (Cmol/kg)	BS (%)	Particle Size (g/kg)			Textural Class
								Ca	Mg	K	Na				Sand	Silt	Clay	
MS1	6.6	108	2.54	4.02	0.26	12.90	1.60	3.70	0.95	0.68	0.36	5.69	7.29	78.05	762	156	82	Sandy Loam
MS2	6.1	112	0.82	1.64	0.14	13.95	1.90	3.73	0.98	0.52	0.34	5.57	7.47	74.56	824	110	66	Loamy Sand
MS3	6.0	190	2.12	3.71	0.12	14.00	0.14	4.45	0.96	0.74	0.36	6.51	6.65	97.89	846	56	98	Loamy Sand
OS1	6.0	118	0.59	0.71	0.08	12.40	1.75	2.68	0.72	0.82	0.52	4.74	6.49	73.04	842	56	102	Loamy Sand
OS2	6.3	131	0.56	0.95	0.10	12.20	1.68	2.82	0.85	0.64	0.38	4.69	6.37	73.63	844	62	94	Loamy Sand
OS3	6.9	58	1.19	1.93	0.16	8.45	0.25	1.19	0.88	0.22	0.23	2.52	2.77	90.97	754	160	86	Sandy Loam
TS1	6.3	210	2.16	3.79	0.24	15.94	0.19	3.96	0.68	0.56	0.19	5.39	5.58	96.59	750	158	92	Sandy Loam
TS2	5.5	216	2.08	3.41	0.14	13.06	0.12	4.09	0.82	0.50	0.16	5.57	5.69	97.89	818	132	50	Loamy Sand
TS3	5.4	208	2.22	3.69	0.19	11.20	0.22	7.04	0.62	0.44	0.24	8.34	8.56	97.43	832	118	50	Loamy Sand

Note: Soil EC - Electrical Conductivity; SOM – Soil Organic Matter; SOC – Soil Organic Carbon; % N – Total Nitrogen; A. P – Available phosphorus; Exch. Acidity – Exchangeable Acidity; ECEC – Effective Cation Exchange Capacity; Ca – Calcium; Mg – Magnesium; K – Potassium; Na – Sodium; TEB – Total Exchangeable Bases; BS – Basal Saturation; MS1 = Composited Soil Sample 1 in Marguba range; MS2 = Composited Soil Sample 2 in Marguba range; MS3 = Composited Soil Sample 3 in Marguba range; OS1 = Composited Soil Sample 1 in Oyo-Ile range; OS2 = Composited Soil Sample 2 in Oyo-Ile range; OS3 = Composited Soil Sample 3 in Oyo-Ile range; TS1 = Composited Soil Sample 1 in Tede range; TS2 = Composited Soil Sample 2 in Tede range; TS3 = Composited Soil Sample 3 in Tede range

Table 4.37: Physicochemical Parameters of Soil Samples in Old Oyo National Park [Wet Season, 2017]

Soil Sample	pH (water)	Soil EC (µS/cm)	SOC (%)	SOM (%)	% N	A. P (mg/kg)	Exch. Acidity (Cmol/kg)	Exchangeable bases (Cmol/kg)				TEB (Cmol/kg)	ECEC (Cmol/kg)	BS (%)	Particle Size (g/kg)			Textural Class
								Ca	Mg	K	Na				Sand	Silt	Clay	
MS1	5.3	250	2.50	4.31	0.23	17.1	0.20	9.53	1.19	0.81	0.38	11.91	12.11	98.35	780	150	70	Loamy Sand
MS2	5.3	250	2.60	4.48	0.24	16.9	0.20	9.50	1.21	0.84	0.34	11.89	12.09	98.35	752	152	96	Sandy Loam
MS3	6.3	260	2.50	4.31	0.23	16.2	0.20	9.50	1.21	0.80	0.30	11.81	12.01	98.33	770	164	66	Loamy Sand
OS1	6.6	62	1.62	2.79	0.17	9.2	0.30	1.60	0.80	0.24	0.36	3.00	3.30	90.91	872	34	94	Loamy Sand
OS2	7.2	308	1.75	3.02	0.19	16.5	0.40	7.91	1.70	0.37	0.58	10.56	10.96	96.35	892	54	54	Sand
OS3	7.1	67	1.58	2.72	0.13	7.4	0.30	1.33	0.95	0.38	0.38	3.04	3.34	91.02	752	114	134	Sandy Loam
TS1	5.2	224	3.12	5.38	0.29	18.3	0.20	5.97	0.78	0.60	0.28	7.63	7.83	97.45	830	120	50	Sandy Loam
TS2	5.3	250	3.04	5.24	0.29	16.0	0.20	5.91	0.80	0.58	0.29	7.58	7.78	97.43	842	114	44	Loamy Sand
TS3	5.3	260	3.03	5.22	0.29	15.2	0.20	8.90	0.80	0.62	0.29	10.61	10.81	98.15	876	97	27	Loamy Sand

Note: Soil EC- Electrical Conductivity; SOM – Soil Organic Matter; SOC – Soil Organic Carbon; % N – Total Nitrogen
A. P – Available Phosphorus; Exch. Acidity – Exchangeable Acidity; ECEC – Effective Cation Exchange Capacity
Ca – Calcium; Mg – Magnesium; K – Potassium; Na – Sodium; TEB – Total Exchangeable Bases; BS – Basal Saturation

Table 4.38: Physicochemical Parameters of Soil Samples in Old Oyo National Park [Dry Season, 2018]

Soil Sample	pH (water)	Soil EC µS/cm)	SOC (%)	SOM (%)	% N	A. P (mg/kg)	Exch. Acidity (Cmol/kg)	Exchangeable bases (Cmol/kg)				TEB (Cmol/kg)	ECEC (Cmol/kg)	BS (%)	Particle Size (g/kg)			Textural Class
								Ca	Mg	K	Na				Sand	Silt	Clay	
MS1	6.4	106	2.33	4.02	0.22	12.70	1.30	3.30	0.75	0.50	0.32	4.87	6.17	78.93	758	154	88	Sandy Loam
MS2	6.0	116	0.95	1.64	0.11	13.50	1.60	3.59	0.91	0.54	0.37	5.41	7.01	77.18	818	114	68	Loamy Sand
MS3	6.1	184	2.15	3.71	0.18	14.40	0.17	4.20	0.95	0.62	0.28	6.05	6.22	97.27	850	54	96	Loamy Sand
OS1	6.1	119	0.41	0.71	0.05	12.80	1.30	2.71	0.74	0.65	0.41	4.51	5.81	77.62	838	54	108	Loamy Sand
OS2	6.2	133	0.55	0.95	0.05	12.10	1.60	2.91	0.90	0.62	0.33	4.76	6.36	74.84	838	64	98	Loamy Sand
OS3	6.7	52	1.12	1.93	0.11	8.2	0.21	1.1	0.84	0.26	0.26	2.46	2.67	92.13	758	164	78	Sandy Loam
TS1	6.4	202	2.20	3.79	0.19	15.7	0.18	3.82	0.59	0.53	0.18	5.12	5.3	96.60	758	154	88	Sandy Loam
TS2	5.6	208	1.98	3.41	0.16	12.50	0.14	4.05	0.72	0.51	0.20	5.48	5.62	97.51	828	120	52	Loamy Sand
TS3	5.1	211	2.14	3.69	0.17	11.4	0.19	6.46	0.68	0.47	0.19	7.80	7.99	97.62	828	114	58	Loamy Sand

Note: Soil EC - Electrical Conductivity; SOM – Soil Organic Matter; SOC – Soil Organic Carbon; % N – Total Nitrogen; A. P – Available phosphorus; Exch. Acidity – Exchangeable Acidity; ECEC – Effective Cation Exchange Capacity; Ca – Calcium; Mg – Magnesium; K – Potassium; Na – Sodium; TEB – Total Exchangeable Bases; BS – Basal Saturation; MS1 = Composited Soil Sample 1 in Marguba range; MS2 = Composited Soil Sample 2 in Marguba range; MS3 = Composited Soil Sample 3 in Marguba range; OS1 = Composited Soil Sample 1 in Oyo-Ile range; OS2 = Composited Soil Sample 2 in Oyo-Ile range; OS3 = Composited Soil Sample 3 in Oyo-Ile range; TS1 = Composited Soil Sample 1 in Tede range; TS2 = Composited Soil Sample 2 in Tede range; TS3 = Composited Soil Sample 3 in Tede range

Table 4.39: Physicochemical Parameters of Soil Samples in Old Oyo National Park [Wet Season, 2018]

Soil Sample	pH (water)	Soil EC (µS/cm)	SOC (%)	SOM (%)	% N	A. P (mg/kg)	Exch. Acidity (Cmol/kg)	Exchangeable bases (Cmol/kg)				TEB (Cmol/kg)	ECEC	BS (%)	Particle Size (g/kg)			Textural Class
								Ca	Mg	K	Na				Sand	Silt	Clay	
MS1	5.8	260	2.12	3.65	0.28	13.40	0.60	5.24	0.94	0.61	0.44	7.23	7.83	92.34	748	124	128	Sandy Loam
MS2	5.6	258	1.90	3.28	0.21	14.05	0.90	4.68	1.22	0.65	0.41	6.96	7.86	88.55	768	163	69	Loamy Sand
MS3	6.0	270	2.62	4.52	0.18	16.50	0.32	4.51	1.28	0.68	0.35	6.82	7.14	95.52	782	142	76	Loamy Sand
OS1	6.2	164	1.40	2.41	0.12	11.40	1.20	2.79	0.82	0.72	0.43	4.76	5.96	79.87	794	56	150	Sandy Loam
OS2	6.1	210	1.52	2.62	0.13	12.70	0.96	.3.08	0.94	0.81	0.38	5.21	6.17	84.44	824	38	138	Sandy Loam
OS3	6.8	85	1.20	2.07	0.10	9.10	0.15	1.86	1.02	0.32	0.27	3.47	3.62	95.86	734	96	170	Sandy Loam
TS1	6.2	228	2.98	5.14	0.27	15.20	0.12	3.74	0.63	0.52	0.20	5.09	5.21	97.70	814	118	68	Loamy Sand
TS2	5.7	224	1.78	3.07	0.23	13.60	0.12	4.98	0.76	0.56	0.24	6.54	6.66	98.20	864	120	16	Loamy Sand
TS3	5.3	232	2.50	4.31	0.31	15.20	0.11	7.30	0.72	0.51	0.21	8.74	8.85	98.76	858	72	70	Loamy Sand

Note: Soil EC - Electrical Conductivity; SOM – Soil Organic Matter; SOC – Soil Organic Carbon; % N – Total Nitrogen; A. P – Available phosphorus; Exch. Acidity – Exchangeable Acidity; ECEC – Effective Cation Exchange Capacity; Ca – Calcium; Mg – Magnesium; K – Potassium; Na – Sodium; TEB – Total Exchangeable Bases; BS – Basal Saturation; MS1 = Composited Soil Sample 1 in Marguba range; MS2 = Composited Soil Sample 2 in Marguba range; MS3 = Composited Soil Sample 3 in Marguba range; OS1 = Composited Soil Sample 1 in Oyo-Ile range; OS2 = Composited Soil Sample 2 in Oyo-Ile range; OS3 = Composited Soil Sample 3 in Oyo-Ile range; TS1 = Composited Soil Sample 1 in Tede range; TS2 = Composited Soil Sample 2 in Tede range; TS3 = Composited Soil Sample 3 in Tede range

Table 4.40: Mean values of physicochemical parameters of soil samples of Old Oyo National Park

Parameters	Mean Values ± Standard Deviation				Critical Limi	Reference
	Dry Season (2017)	Wet Season (2017)	Dry Season (2018)	Wet Season (2018)		
pH	6.12 ± 0.48	5.96 ± 0.84	6.07 ± 0.47	5.97 ± 0.43	3.0 – 8.5	NMSU, 2000
Soil EC (µS/cm)	150.11 ± 56.98^{ab}	214.56 ± 87.87^{ac}	147.67 ± 55.93^{cd}	214.56 ± 58.05^{bd}	-	NMSU, 2000
SOC (%)	1.59 ± 0.79^{a}	2.42 ± 0.62^{ab}	1.54 ± 0.77^{b}	2.00 ± 0.60	-	-
% N	0.16 ± 0.06^{a}	0.23 ± 0.06^{ab}	0.14 ± 0.06^{bc}	0.20 ± 0.08^{c}	0.05 – 0.15	Tisdale *et al*., 1993
A.P (mg/kg)	12.68 ± 2.08	14.76 ± 3.78	12.59 ± 2.08	13.46 ± 2.22	8 – 20	Rankine and Fairhurst, 1999
E.A (cmol/kg)	0.87 ± 0.0.82^{a}	0.24 ± 0.07^{a}	0.74 ± 0.68	0.50 ± 0.43	-	-
Ca (cmol/kg)	3.74 ± 0.1.58^{a}	6.68 ± 3.28^{ab}	3.57 ± 1.43^{b}	4.24 ± 1.60	-	-
Mg (cmol/kg)	0.83 ± 0.13^{a}	1.05 ± 0.31^{ab}	0.79 ± 0.12^{b}	0.93 ± 0.22	0.08 – 0.25	Rankine and Fairhurst, 1999
K (cmol/kg)	0.57 ± 0.18	0.58 ± 0.22	0.52 ± 0.12	0.60 ± 0.14	0.20 – 0.40	Rankine and Fairhurst, 1999
Na (cmol/kg)	0.31 ± 0.11	0.36 ± 0.09	0.28 ± 0.08	0.33 ± 0.10	10 – 30	NMSU, 2000
TEB (cmol/kg)	5.45 ± 1.55^{a}	8.67 ± 3.61^{abc}	5.16 ± 1.41^{b}	6.09 ± 1.59^{c}	-	-
ECEC	6.32 ± 0.1.62^{a}	8.91 ± 3.58^{abc}	5.91 ± 1.45^{b}	6.59 ± 1.58^{c}	2 – 12	NMSU, 2000
BS (%)	86.67 ± 11.52^{a}	96.26 ± 3.07^{ab}	87.74 ± 10.24^{b}	92.36 ± 6.70	-	-
Sand (g/kg)	808.00 ± 40.66	818.44 ± 55.83	808.22 ± 38.67	798.44 ± 45.63	-	-
Silt (g/kg)	112.00 ± 44.11	111.00 ± 43.99	110.22 ± 43.74	103.22 ± 41.11	-	-
Clay (g/kg)	80.00 ± 19.95	70.56 ± 32.68	81.56 ± 18.99	98.33 ± 50.15	-	-

Note: Means with the same alphabets are significantly different at P≤0.05

Table 4.41: Comparison of soil physicochemical parameters across the selected ranges of OONP

Parameters	Ranges	Mean	Standard Deviation
pH	Marguba	5.95	0.40
	Oyo-Ile	6.52	0.42
	Tede	5.61	0.45
SOC	Marguba	196.83	69.53
	Oyo-Ile	125.58	74.57
	Tede	222.75	17.73
SOM	Marguba	2.10	0.61
	Oyo-Ile	1.12	0.48
	Tede	2.44	0.48
N	Marguba	2.87	1.80
	Oyo-Ile	1.63	1.15
	Tede	3.32	2.04
A.P	Marguba	3.56	6.07
	Oyo-Ile	2.84	5.02
	Tede	3.53	6.04
Exch. Acidity	Marguba	11.53	6.40
	Oyo-Ile	8.59	5.08
	Tede	11.14	6.83
Ca	Marguba	1.45	1.59
	Oyo-Ile	1.09	0.92
	Tede	1.38	2.32
Mg	Marguba	4.75	3.23
	Oyo-Ile	2.31	1.97
	Tede	4.44	2.69

Table 4.41 (cont'd): Comparison of soil physicochemical parameters among the selected ranges

Parameters	Ranges	Mean	Standard Deviation
K	Marguba	0.97	0.25
	Oyo-Ile	0.87	0.33
	Tede	0.67	0.12
Na	Marguba	0.59	0.18
	Oyo-Ile	0.46	0.20
	Tede	0.46	0.16
TEB	Marguba	1.75	2.53
	Oyo-Ile	1.28	1.72
	Tede	1.78	2.89
ECEC	Marguba	7.86	2.54
	Oyo-Ile	4.78	2.27
	Tede	7.04	1.74
BS	Marguba	27.41	34.32
	Oyo-Ile	23.82	33.76
	Tede	29.83	40.72
Sand	Marguba	271.40	325.80
	Oyo-Ile	268.59	329.30
	Tede	273.29	318.17
Silt	Marguba	612.33	306.59
	Oyo-Ile	631.67	329.37
	Tede	658.83	316.77
Clay	Marguba	121.92	38.80
	Oyo-Ile	79.67	37.23
	Tede	101.75	31.11

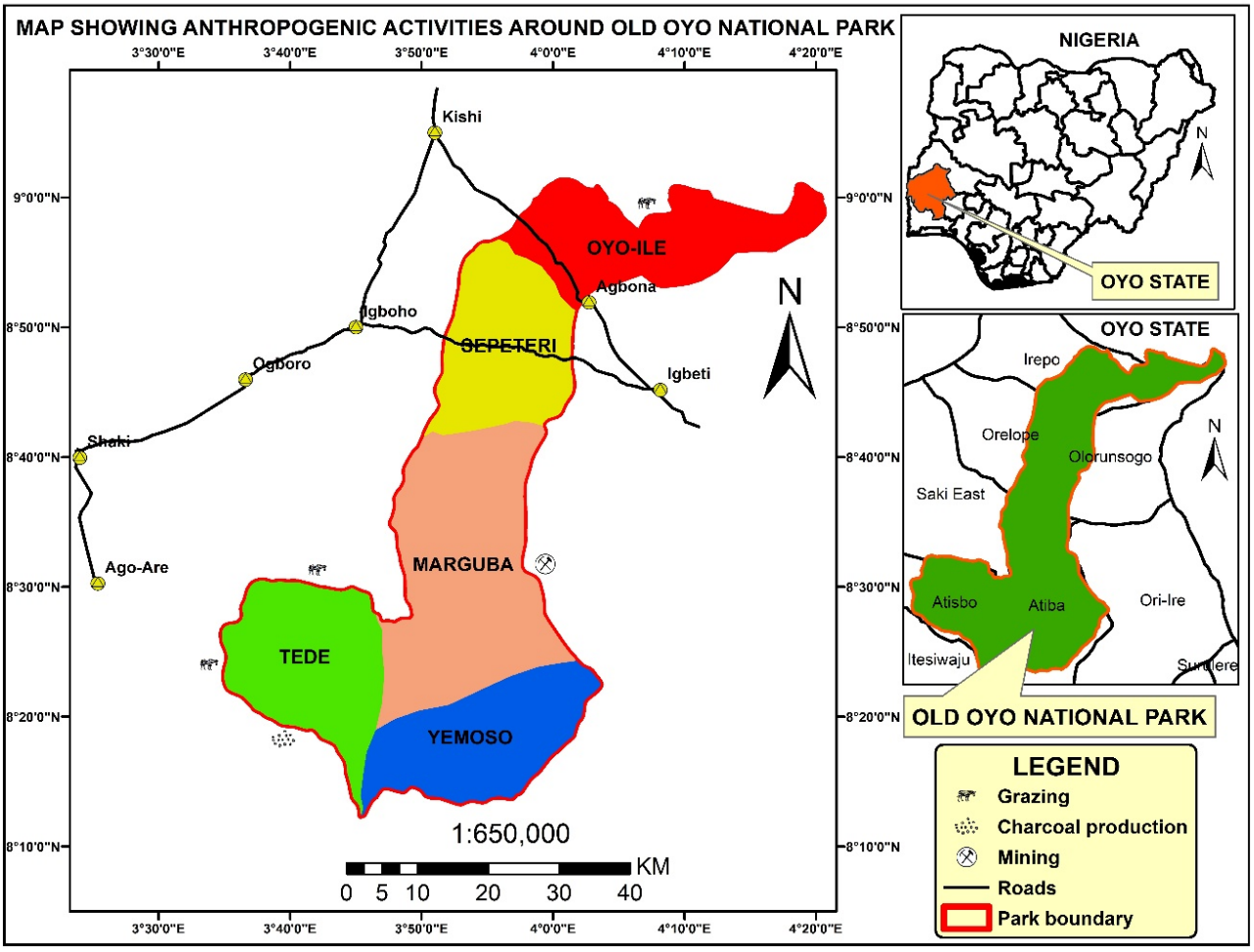

Figure 4.3: Map of Old Oyo National Park showing anthropogenic contacts

Source: Field Survey, 2016 – 2018

4.8 Microbial Characteristics of water samples (rivers) in Old Oyo National Park

The microbiological characteristics of sampled waterholes in Old Oyo National Park collected for two years (2017 and 2018) are presented in Tables 4.42 – 4.45. High heterotrophic bacteria count and *Salmonella* / *Shigella* spp. counts were recorded in the study with a total count of 26.05×10^5 cfu/ml and 58.30×103 cfu/ml, respectively recorded in River Ogun while *Staphylococcus aureus* was not detected in all the waterholes sampled in the dry season of 2017 (Table 4.42). In the wet season f 2017, total heterotrophic count was also highest in River Ogun with a count of 3.90×10^5 cfu/ml while *Staphylococcus aureus, Salmonella* / *Shigella* spp were not detected in the sampled waterholes (Table 4.43).

In the dry season of 2018, total heterotrophic count was highest in River Ayinta with a count of 4.62×10^5 cfu/ml while *Staphylococcus aureus, Salmonella* / *Shigella* spp. were also not detected in the sampled waterholes. The highest total fungi count was observed in River Owu with a count of 8.00×10^2 cfu/ml as shown in Table 4.44. In the wet season of 2018, total heterotrophic count was highest in River Ogun with a count of 4.05×10^5 cfu/ml while *Staphylococcus aureus,Salmonella* / *Shigella* spp. were also not detected in the sampled waterholes. The highest total fungi counts were observed in Rivers Oopo and Sooro with a count of 2.00×10^2 cfu/ml as shown in Table 4.45. The mean values of the microbial characteristics of waterholes in Old Oyo National Parkis presented in Table 4.46. The result showed that the total coliform counts observed in the study were discovered to be higher than the WHO permissible limit or guideline for drinking water while the other microbial characteristics were noted to be below the comparable permissible limit.

Table 4.42: Microbial Characteristics of selected waterholes in Old Oyo National Park [Dry Season, 2017]

Water Holes	Total Heterotrophic bacterial count ($x10^5$cfu/ml)	*Staphylococcus aureus* count ($x10^2$cfu/ml)	*Salmonella / Shigella* spp count ($x10^3$cfu/ml)	Fungi count ($x10^2$cfu/ml)	Total Coliform count ($x10^5$cfu/ml)/ (MPN/100ml)	Microflora Observed
River Owu (TW_1)	0.62	Nil	NG	10.00	3300	*Bacillus sp., E. coli Aspergillus flavus Penicillium* sp.
River Ogun (MW_1)	26.05	Nil	58.30	6.02	≥160000	*Bacillus sp., Shigella* sp. *Pseudomonas* sp., *E. coli, Enterobacter* sp., *Klebsiella* sp., *Penicillium* sp.,
River Oopo (MW_2)	5.07	Nil	1.50	2.00	17000	*Bacillus* sp., *Shigella* sp., *Pseudomonas sp., Enterobacter sp., Salmonella sp., Penicillium sp.,*
River Ayinta (MW_3)	6.41	Nil	0.97	2.03	≥160000	*Bacillus sp., Shigella sp., Pseudomonas sp., Enterobacter sp., Salmonella sp., Penicillium sp.,*
River Tessi (OW_1)	2.60	Nil	NG	NG	50	*Bacillus sp., Seratia sp.,*
River Sooro (OW_2)	1.84	Nil	NG	NG	4	*Bacillus sp.*

Note: NG = No growth; Nil = No growth of target organism

Table 4.43: Microbial Characteristics of selected waterholes in Old Oyo National Park [Wet Season, 2017]

Water Holes	Total Heterotrophic bacterial count ($x10^5$cfu/ml)	*Staphylococcus aureus* count ($x10^2$cfu/ml)	*Salmonella*/ *Shigella* spp count ($x10^3$cfu/ml)	Fungi count ($x10^2$cfu/ml)	Total Coliform count ($x10^5$cfu/ml)/ (MPN/100ml)	Microflora Observed
River Owu (TW_1)	0.1	0.00	0.00	0.00	11	*Bacillus sp., Penicillium sp.*
River Ogun (MW_1)	3.90	0.00	0.00	0.00	900	*Bacillus sp, Actinobacter sp, Enterobacter sp*
River Oopo (MW_2)	1.00	0.00	0.00	1.00	350	*Bacillus sp, Enterobacter sp*
River Ayinta (MW_3)	1.20	0.00	0.00	1.00	500	*Bacillus sp, Shigella sp. Pseudomonas sp Salmonella sp.*
River Tessi (OW_1)	0.40	0.00	0.00	0.00	26	*Bacillus sp.*
River Sooro (OW_2)	0.60	0.00	0.00	2.00	33	*Bacillus sp, Flavobacter sp, Enterobacter sp.*

Note: NG = No growth; Nil = No growth of target organism

Table 4.44: Microbial Characteristics of selected waterholes in Old Oyo National Park [Dry Season, 2018]

Water holes	Total Heterotrophic bacterial count ($x10^5$cfu/ml)	*Staphylococcus aureus* count ($x10^2$cfu/ml)	*Salmonella*/ *Shigella* spp count ($x10^3$cfu/ml)	Fungi count ($x10^2$cfu/ml)	Total Coliform count ($x10^5$cfu/ml)/ (MPN/100ml)	Microflora Observed
River Owu (TW_1)	1.6	Nil	NG	8.00	> 1600	*Bacillus* sp., *E. coli* *Penicillium* sp.
River Ogun (MW_1)	0.40	0.00	0.00	0.00	540	*Bacillus* sp., *Enterobacter* sp.
River Oopo (MW_2)	2.70	0.00	0.00	0.80	>1600	*Bacillus* sp., *Pseudomonas* sp., *Actinobacteria* sp., *Enterobacter* sp. *Flavobacterium* sp., *Aspergillus niger* *Penicillium* sp.
River Ayinta (MW_3)	4.62	Nil	0.00	1.80	≥160000	*Bacillus* sp., *Shigella* sp. *Pseudomonas* sp., *Enterobacter* sp., *Salmonella* sp.
River Tessi (OW_1)	0.40	0.00	0.00	0.10	>1600	*Bacillus* sp., *Pseudomonas* sp., *Actinobacteria* sp., *Enterobacter* sp., *Flavobacterium* sp., *Aspergillus niger*
River Sooro (OW_2)	3.50	0.00	0.00	0.30	>1600	*Bacillus*sp., *Pseudomonas*sp., *Flavobacterium* sp., *Aspergillus niger*

Note: NG = No growth; Nil = No growth of target organism

Table 4.45: Microbial Characteristics of selected waterholes in Old Oyo National Park [Wet Season, 2018]

Water Holes	Total Heterotrophic bacterial count ($x10^5$cfu/ml)	*Staphylococcus aureus* count ($x10^2$cfu/ml)	*Salmonella*/ *Shigella* spp count ($x10^3$cfu/ml)	Fungi count ($x10^2$cfu/ml)	Total Coliform count ($x10^5$cfu/ml)/ (MPN/100ml)	Microflora Observed
River Owu (TW_1)	0.3	0.00	0.00	0.00	18	*Bacillus* sp., *Penicillium* sp.
River Ogun (MW_1)	4.05	0.00	0.00	0.00	850	*Bacillus* sp., *Enterobacter* sp.
River Oopo (MW_2)	1.20	0.00	0.00	2.00	270	*Bacillus* sp., *Enterobacter* sp.
River Ayinta (MW_3)	1.00	0.00	0.00	1.00	400	*Bacillus* sp., *Pseudomonas* sp., *Shigella* sp., *Salmonella* sp.
River Tessi (OW_1)	0.82	0.00	0.00	1.00	33	*Bacillus* sp., *Enterobacter* sp.,
River Sooro (OW_2)	0.94	0.00	0.00	2.00	46	*Bacillus* sp., *Flavobacter* sp., *Enterobacter* sp.

Note: NG = No growth; Nil = No growth of target organism

Table 4.46: Mean values of Microbial Characteristics of waterholes in Old Oyo National Park

Microbial Parameters	Mean Values ± Standard Deviation				WHO PERMISSIBLE LIMIT
	Dry Season (2017)	Wet Season (2017)	Dry Season (2018)	Wet Season (2018)	
Total Heterotrophic Bacteria count ($x10^5$cfu/ml)	7.10 ± 8.95^{ab}	1.20 ± 1.29^{a}	2.20 ± 1.61^{ab}	1.39 ± 1.26^{a}	100 cfu/ml
Staphylococcus aureus Count ($x10^2$cfu/ml)	NIL	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	100 cfu/ml
Salmonella/Shigella count ($x10^3$cfu/ml)	10.13 ± 22.18	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	100 cfu/ml
Fungi Count ($x10^2$cfu/ml)	5.01 ± 3.82^{ab}	0.67 ± 0.76^{a}	1.83 ± 2.90	1.00 ± 0.84^{b}	100 cfu/ml
Total Coliform count ($x10^4$cfu/ml)/ (MPN/100ml)	5.67 ± 8.03^{a}	0.03 ± 0.04^{a}	2.78 ± 6.48^{a}	0.03 ± 0.03^{a}	0 per 100 ml

Note: Means having the same alphabets are significantly different at $P<0.05$

4.9 Microbial Characteristics of faecal samples in Old Oyo National Park

The microbiological characteristics of faecal samples in OONP is presented in Table 4.47. The result showed that the total heterotrophic bacteria count (59.20 x 10^5cfu/ml), total coliform count (49.55 x10^5cfu/ml) / (MPN/100 ml) and fungi count (3.80 x 10^2cfu/ml) observed in Olive baboon (*Papio anubis*) were seen to be highest of all the wild animals' faecal samples. *Salmonella* / *Shigella* count (72.44 x10^3cfu/ml) was highest in Maxwell duiker (*Philantoba maxwelli*) while no growth of *Staphylococcus aureus* was observed in all the faecal samples.

Table 4.47: Microbial Characteristics of Faecal Samples in Old Oyo National Park

Animal Species	Total bacterial count ($x10^5$cfu/ml)	Staphaureus. count ($x10^2$cfu/ml)	Salm/ Shig. Sp. count ($x10^3$cfu/ml)	Fungi count ($x10^2$cfu/ml)	Coliform count ($x10^5$CFU/ml)/ (MPN/100ml)	Microflora observed
Mongoose (*Atilax paludinosus*)	16.50	Nil	NG	0.22	12.40	*E. coli, Enterobacter* sp., *Klebsiella* sp., *Aspergillus fumigatus A. niger, Bacillus* sp., *Pseudomonas* sp.,
Olive baboon (*Papio anubis*)	59.20	Nil	68.01	3.80	49.55	*E. coli, Enterobacter* sp., *Klebsiella* sp., *A. fumigatus, A. niger Pseudomonas* sp., *Salmonella* sp., *Shigella* sp.,
African Civet cat (*Civettictis civetta*)	12.05	Nil	6.62	2.41	0.43	*E. coli, Enterobacter* sp., *Klebsiella* sp., *A. fumigatus, A. niger Pseudomonas* sp., *Salmonella* sp., *Shigella* sp.,
Kob (*Kobus kob*)	8.20	Nil	2.12	2.95	0.02	*Shigella* sp.,*Enterobacter* sp., *A. fumigatus, E. coli*
Maxwell duiker (*Philantoba maxwellii*)	37.60	Nil	72.44	3.34	24.12	*Shigella* sp., *Bacillus* sp., *A. fumigatus, E. coli Enterobacter* sp., *Flavobacteria* sp.,
Western hartebeest (*Alcelaphusbuselaphus*)	24.02	Nil	26.50	1.05	32.4	*Pseudomonas* sp., *Bacillus* sp., *Shigella* sp., *A. niger, E. coli Enterobacter* sp., *Klebsiella* sp.,

Note: NG = No growth; Nil = No growth of target organism

4.10 Principal Component Analysis Result

The Principal Component Analysis (PCA) of the data obtained in the water samples (Table 4.48), showed seven principal components (PCs) which explained 100% of the total variance. The first PC explained 26.1 % of the total variance and was best represented by Phosphate, Cu, Cr, Pb, Ni, Cd, Fe and Mn. The PC 2 was dominated by EC, TDS, Total Heterotrophic bacteria, Salmonella / Shigella and accounted for 17.1 % of the total variance. The PC 3 explained 13.1 % of the total variance and loaded by TSS, TS, Chloride, BOD and COD. PC 4 was dominated by DO and accounted for 9.78 % of the total variance. The PC 5 was dominated by nitrate and accounted for 6.8 % of the total variance. PC 6 explained 5.5 % of the total variance and loaded by pH and *Staphylococcus aureus*. The PCA result for only heavy metals in the sampled waterholes is shown in Table 4.49. Zinc had the highest contribution of total variability of identified components (Dimension 1 and Dimension 2) of waterholes, contributing about 50.97%. The scree plot and biplot displaying the dimensions are shown in Figures 4.4 and 4.5, respectively.

The PCA of the data obtained in the soil samples (Table 4.50), showed five PCs which explained 100% of the total variance. The first PC explained 55.6 % of the total variance and was best represented by pH, Soil EC, SOC, %N, A.P, Ca, Mg, K, Na, TEB, ECEC, BS, Sand, Silt, Clay and Cd. PC 2 explained 17.9 % of the total variance and loaded by Cr, Fe and Mn. PC 3 explained 7.9 % of the total variance and loaded by Pb and Ni. PC 4 was dominated by Zn and accounted for 4.9 % of the total variance. PC 5 explained 5.5 % of the total variance and loaded by Cu. The PCA result for only heavy metals in the sampled soils is shown in Table 4.51. Iron had the highest contribution of total variability of identified components in soils. The scree plot and biplot displaying the dimensions are shown in Figures 4.6 and 4.7, respectively.

The PCA of the data obtained in plant samples (Table 4.52), showed two PCs which explained 100% of the total variance. The first PC explained 41.9 % of the total variance and was best represented by Cr, Pb, Ni, Cd and Mn. PC 2 explained 23.7 % of the total variance and loaded by Cu, Zn and Fe. The Dimension 2 had the highest variability with Cu contributing about 42.1% as shown in Table 4.53. The scree plot and biplot displaying the dimensions are shown in Figures 4.8 and 4.9, respectively.

The PCA of the data obtained in faecal samples (Table 4.54), showed four PCs which explained 100% of the total variance. The first PC explained 35.7 % of the total variance and was best represented by Pb, Fe, Total Heterotrophic bacteria, Salmonella / Shigella, Fungi Count and Total Coliform Count. PC 2 explained 23.6 % of the total variance and loaded by Cu, Zn and Mn. PC 3 explained 17.4 % of the total variance and loaded by Ni and Cd. PC 4 was dominated by Cr and accounted for 10.7 % of the total variance. The PCA result for only heavy metals in the sampled wild animals' faeces is shown in Table 4.55. The scree plot and biplot displaying the dimensions are shown in Figures 4.10 and 4.11, respectively.

Table 4.48: Principal Component Analysis of the Water Samples

Component Matrix[a]

Parameters	Component						
	1	2	3	4	5	6	7
pH	-0.408	0.288	-0.150	0.227	-0.121	**0.561**	-0.506
EC	-0.197	**0.880**	0.114	-0.265	0.036	0.000	0.093
Alkalinity	0.147	-0.022	-0.553	0.384	0.311	0.317	0.314
TDS	0.121	**0.819**	0.144	-0.192	-0.106	-0.169	0.319
TSS	0.477	0.357	**0.664**	-0.171	-0.001	0.018	-0.245
TS	0.467	0.452	**0.646**	-0.189	-0.016	-0.007	-0.186
Nitrate	-0.105	-0.095	-0.465	-0.628	**0.501**	0.100	-0.175
Phosphate	**0.631**	-0.341	0.049	0.119	0.338	-0.276	-0.306
Sulphate	-0.681	0.400	0.015	-0.387	0.242	0.091	-0.056
Chloride	0.328	0.185	**0.675**	0.039	0.394	-0.202	0.175
DO	0.099	-0.144	0.184	**0.754**	0.404	-0.067	0.008
BOD	-0.035	-0.474	**0.684**	0.208	-0.263	0.192	0.268
COD	0.131	-0.356	**0.747**	0.176	0.214	0.356	-0.040
Cu	**0.781**	0.470	-0.151	0.071	-0.107	-0.030	0.154
Zn	0.478	-0.341	-0.003	-0.305	0.272	0.209	0.116
Cr	**0.569**	0.409	-0.366	0.118	-0.122	0.366	0.261
Pb	**0.814**	0.173	0.016	0.182	0.012	0.195	-0.275
Ni	**0.766**	0.154	-0.310	0.178	0.066	0.023	-0.315
Cd	**0.796**	0.438	-0.102	0.009	-0.124	-0.048	-0.050
Fe	**0.645**	-0.361	-0.190	-0.037	0.363	-0.081	0.290
Mn	**0.716**	0.390	-0.222	0.320	-0.195	0.004	0.043
Total Heterotrophic bacteria	-0.544	**0.615**	0.056	0.371	0.391	-0.022	-0.007
Staphylococcus aureus	0.134	0.020	0.301	-0.318	0.107	**0.671**	0.219
Salmonella / Shigella	-0.529	**0.513**	0.023	0.432	0.404	0.011	-0.024
Fungi Count	-0.510	-0.055	0.076	0.487	-0.381	0.013	0.022
Total Coliform Count	-0.512	0.471	0.042	0.161	0.168	-0.024	0.094
Eigen values	6.786	4.452	3.403	2.544	1.771	1.425	1.219
% Variance explained	26.100	17.123	13.089	9.783	6.813	5.480	4.689
% Cumulative	26.100	43.223	56.312	66.095	72.908	78.388	83.078

Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaiser Normalization. Bold figures indicate absolute values > 0.5 of parameters with strong loading values.

Table 4.49: Principal Component Analysis Results for Heavy metals in Sampled Waterholes

	Dimension 1	**Dimension 2**	**Dimension 3**	**Dimension 4**	**Dimension 5**
Cu	16.71	1.61	11.06	7.32	13.24
Zn	3.52	47.40	3.67	25.74	13.88
Cr	11.74	4.71	35.17	10.11	23.91
Pb	14.63	0.19	23.21	17.24	0.00
Ni	15.50	0.00	21.94	0.18	15.01
Cd	16.49	1.28	2.99	10.10	17.51
Fe	5.85	39.14	0.27	29.24	15.95
Mn	15.55	5.67	1.70	0.05	0.50

Note: Dimension = Principal Components

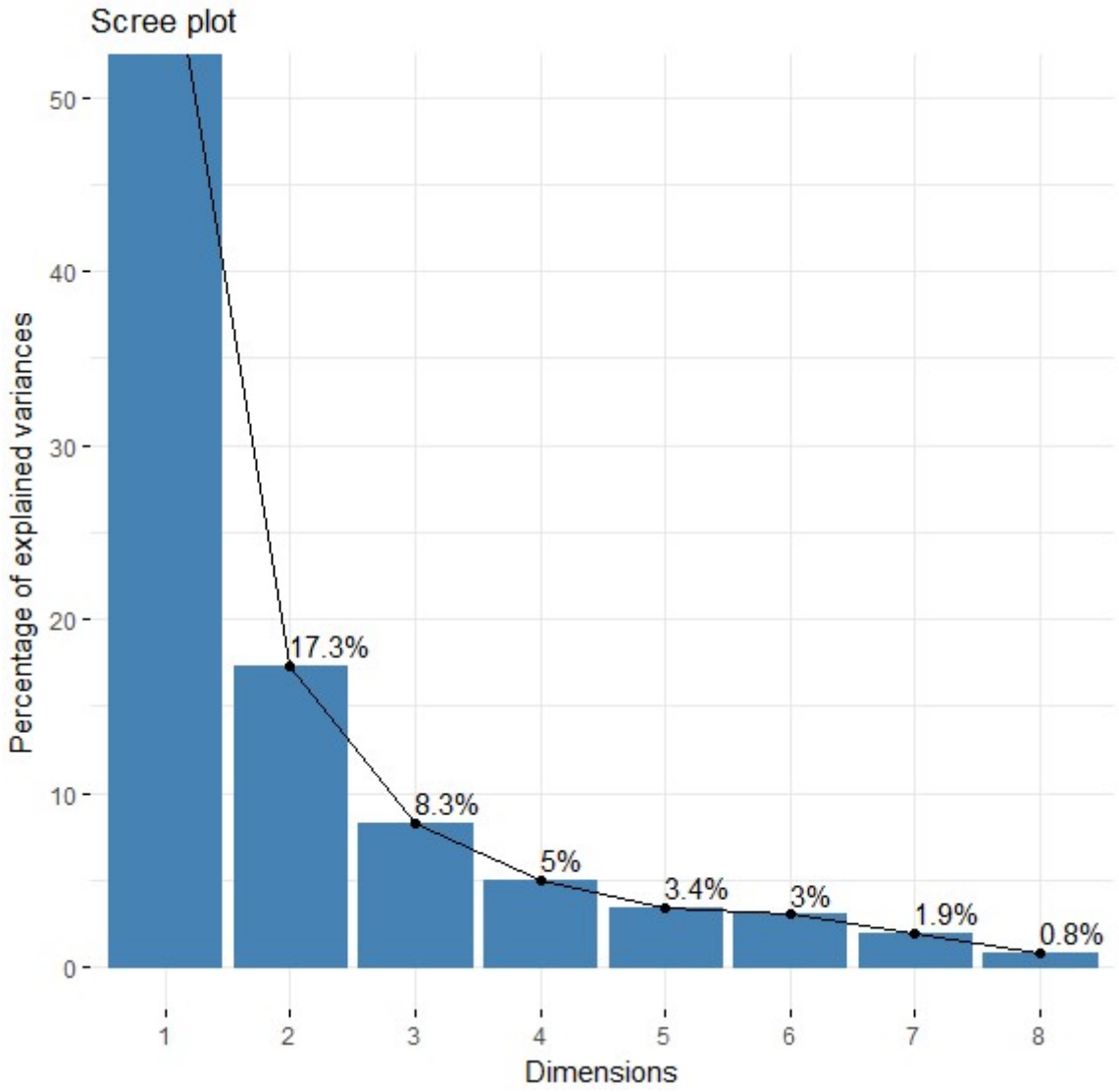

Figure 4.4: Scree plot displaying percentage total variance for heavy metals in sampled waterholes

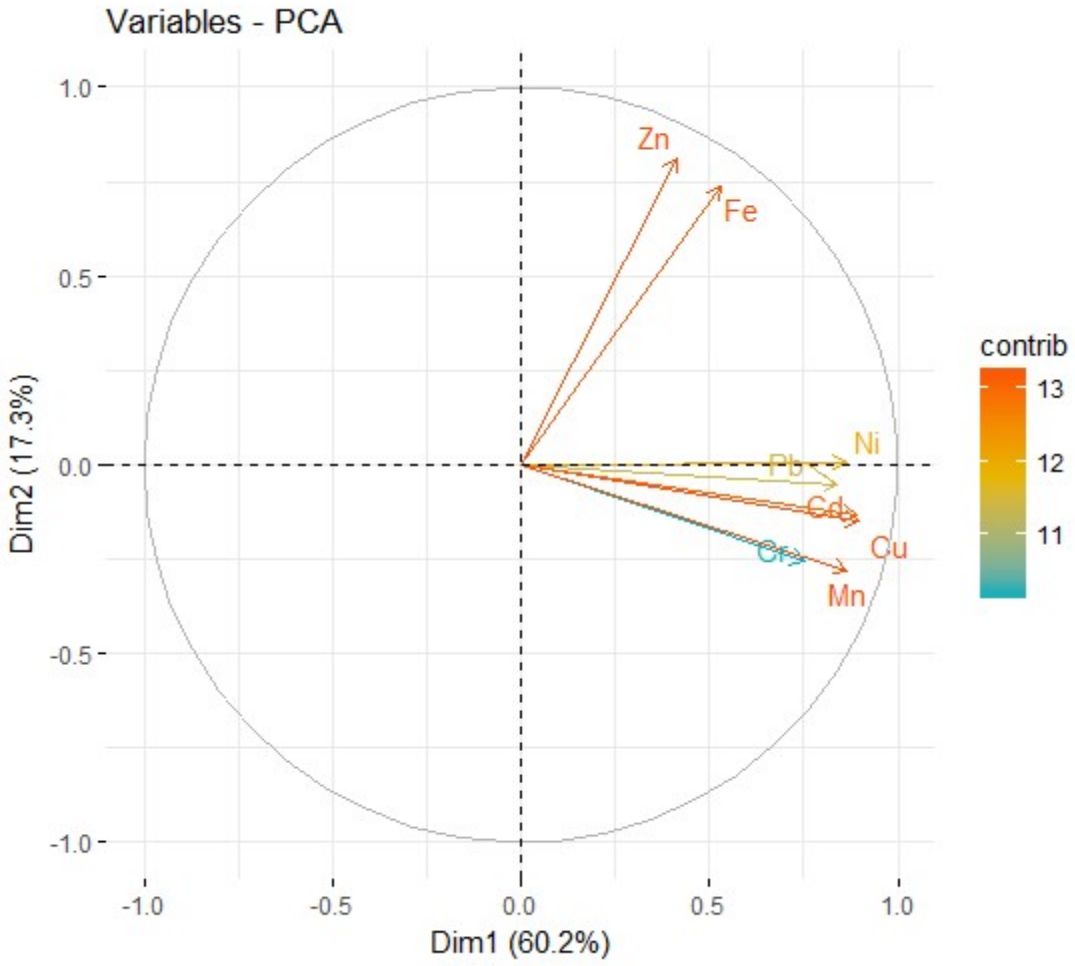

Figure 4.5: Biplot displaying the dimensions (components) of variables (heavy metals) in the sampled waterholes in rotated space

Note: The most important (or contributing) variables (heavy metals) are farther from the origin.

Table 4.50: Principal Component Analysis of the Soil Samples

Component Matrix[a]					
	Component				
Parameters	1	2	3	4	5
pH	**0.921**	0.283	-0.042	-0.114	0.175
Soil EC	**0.897**	-0.355	-0.038	0.074	-0.002
SOC	**0.871**	-0.342	-0.015	-0.282	0.064
SOM	**0.871**	-0.342	-0.015	-0.281	0.063
% N	**0.862**	-0.351	-0.033	-0.283	0.017
A.P	**0.974**	-0.108	0.043	-0.040	-0.020
Exch. Acidity	0.409	0.655	0.178	0.262	-0.240
Ca	**0.838**	-0.443	0.031	0.140	-0.095
Mg	**0.927**	0.105	-0.126	0.199	0.091
K	**0.931**	-0.020	0.074	0.133	-0.063
Na	**0.882**	0.299	-0.160	0.200	0.060
TEB	**0.902**	-0.336	0.008	0.156	-0.068
ECEC	**0.926**	-0.246	0.030	0.184	-0.096
BS	**0.960**	0.038	-0.005	-0.172	0.157
Sand	**0.951**	0.156	0.006	-0.139	0.101
Silt	**0.819**	-0.113	0.239	-0.165	0.049
Clay	**0.673**	0.521	-0.147	0.037	0.267
Cu	-0.586	-0.177	0.485	0.144	**0.513**
Zn	0.352	-0.270	-0.339	**0.753**	0.200
Cr	0.217	**0.809**	0.096	-0.150	0.358
Pb	0.242	-0.017	**0.793**	0.131	-0.260
Ni	-0.099	-0.320	**0.727**	0.129	0.447
Cd	**0.562**	0.369	0.532	0.035	-0.414
Fe	0.285	**0.914**	-0.008	0.046	0.035
Mn	0.250	**0.920**	0.030	0.002	-0.003
Eigen values	13.899	4.464	1.968	1.228	1.115
% Variance explained	55.597	17.857	7.871	4.911	4.461
% Cumulative	55.597	73.454	81.324	86.235	90.697

Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaiser Normalization. Bold figures indicate absolute values > 0.5 of parameters with strong loading values.

Table 4.51: Principal Component Analysis Results for Heavy metals in Sampled Soils

	Dimension 1	**Dimension 2**	**Dimension 3**	**Dimension 4**	**Dimension 5**
Cu	6.62	18.04	22.98	6.47	16.28
Zn	1.02	4.67	15.80	77.29	0.10
Cr	19.50	0.83	16.03	3.78	0.34
Pb	0.77	32.00	19.46	0.29	31.09
Ni	4.36	33.69	1.59	5.40	40.01
Cd	13.02	10.76	20.75	1.46	10.97
Fe	27.90	0.01	1.96	3.98	0.09
Mn	26.81	0.01	1.42	1.33	1.13

Note: Dimension = Principal Components

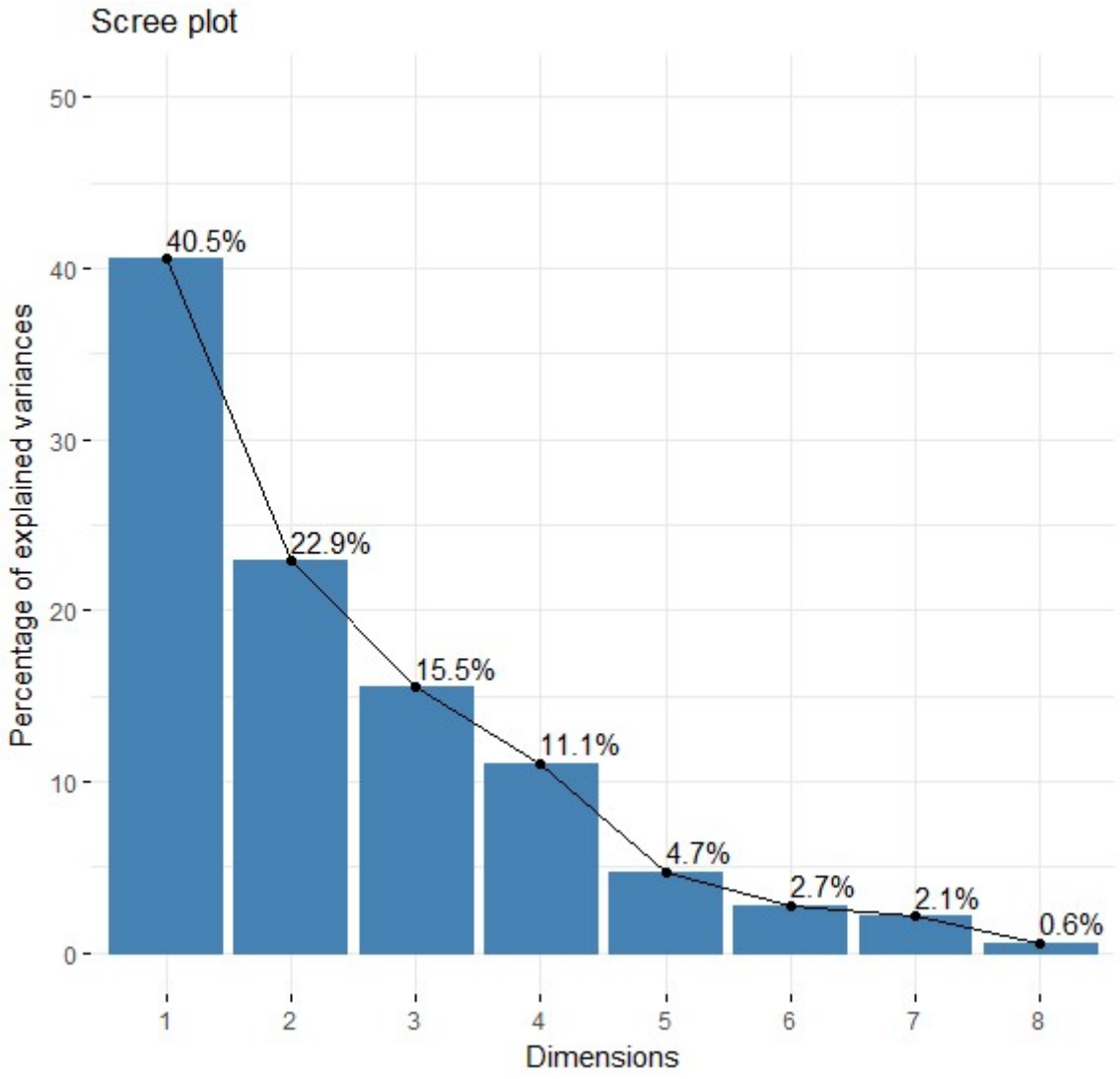

Figure 4.6: Scree plot displaying percentage total variance for heavy metals in sampled soils

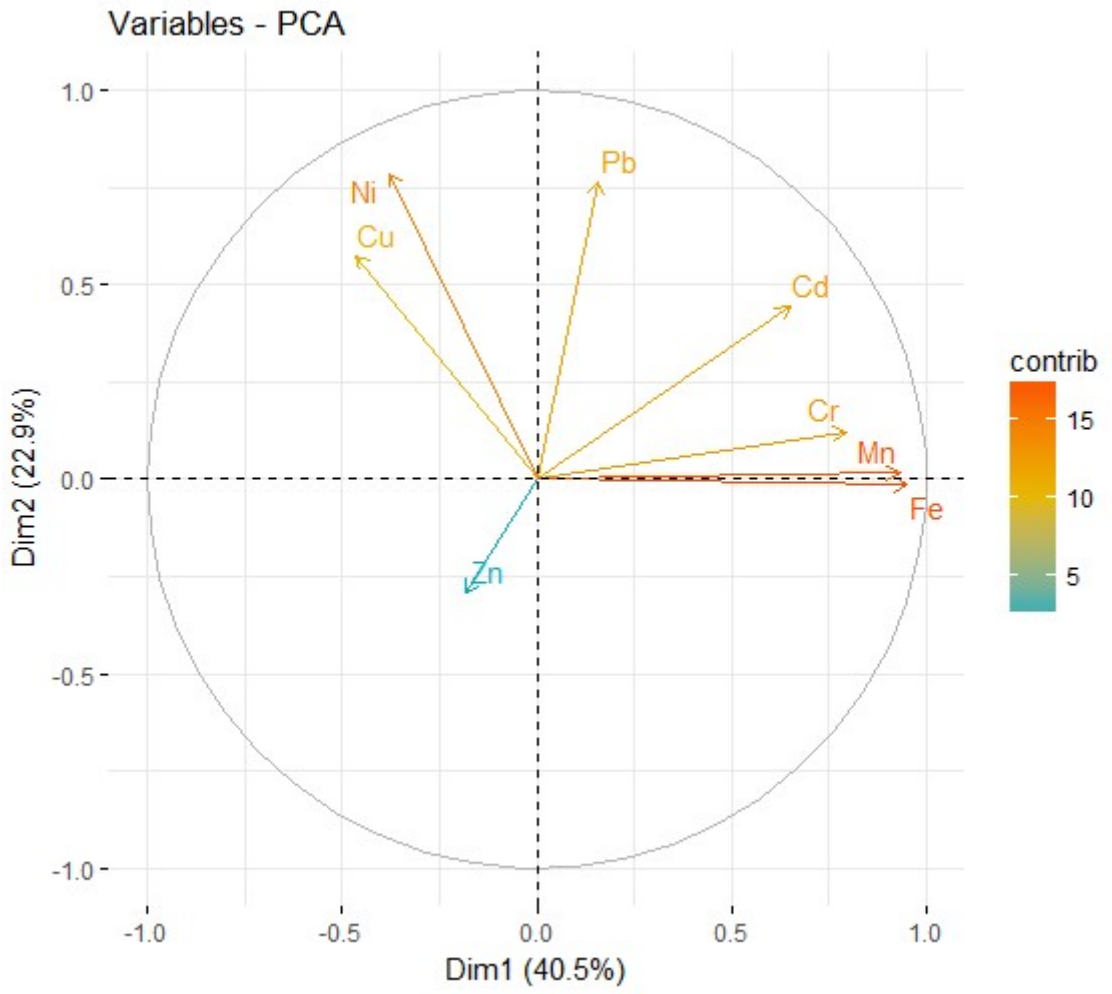

Figure 4.7: Biplot displaying the dimensions (components) of variables (heavy metals) in the sampled soils in rotated space

Note: The most important (or contributing) variables (heavy metals) are farther from the origin.

Table 4.52: Principal Component Analysis of the Plant Samples

Component Matrix[a]		
Parameters	Component	
	1	2
Cu	-0.329	**0.837**
Zn	-0.516	**0.717**
Cr	**0.621**	0.389
Pb	**0.864**	0.014
Ni	**0.768**	0.211
Cd	**0.838**	-0.186
Fe	0.474	**0.656**
Mn	**0.573**	0.128
Eigen values	3.352	1.892
% Variance explained	41.899	23.653
% Cumulative	41.899	65.552

Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaiser Normalization. Bold figures indicate absolute values > 0.5 of parameters with strong loading values.

Table 4.53: Principal Component Analysis Results for Heavy metals in the Plant Samples

	Dimension 1	Dimension 2	Dimension 3	Dimension 4	Dimension 5
Cu	3.25	36.82	0.70	5.44	18.37
Zn	7.85	26.81	3.95	11.32	2.04
Cr	11.48	8.09	0.05	43.31	19.47
Pb	22.41	0.01	3.98	7.23	0.16
Ni	17.60	2.38	23.16	0.01	0.06
Cd	21.28	1.87	2.74	16.63	0.41
Fe	6.39	23.13	8.75	4.85	51.30
Mn	9.74	0.91	56.67	11.20	8.19

Note: Dimension = Principal Components

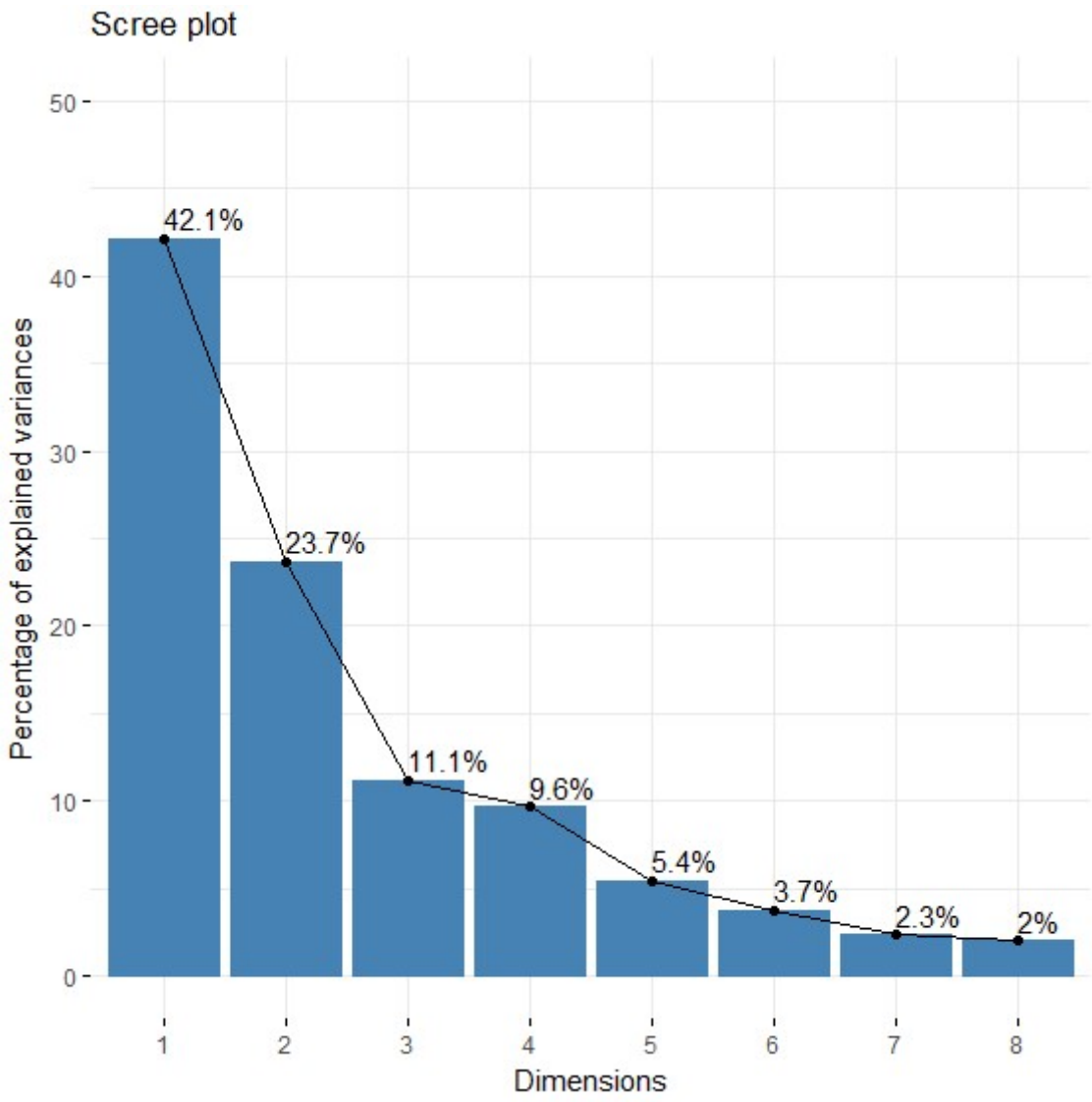

Figure 4.8: Scree plot displaying percentage total variance for heavy metals in the plant samples

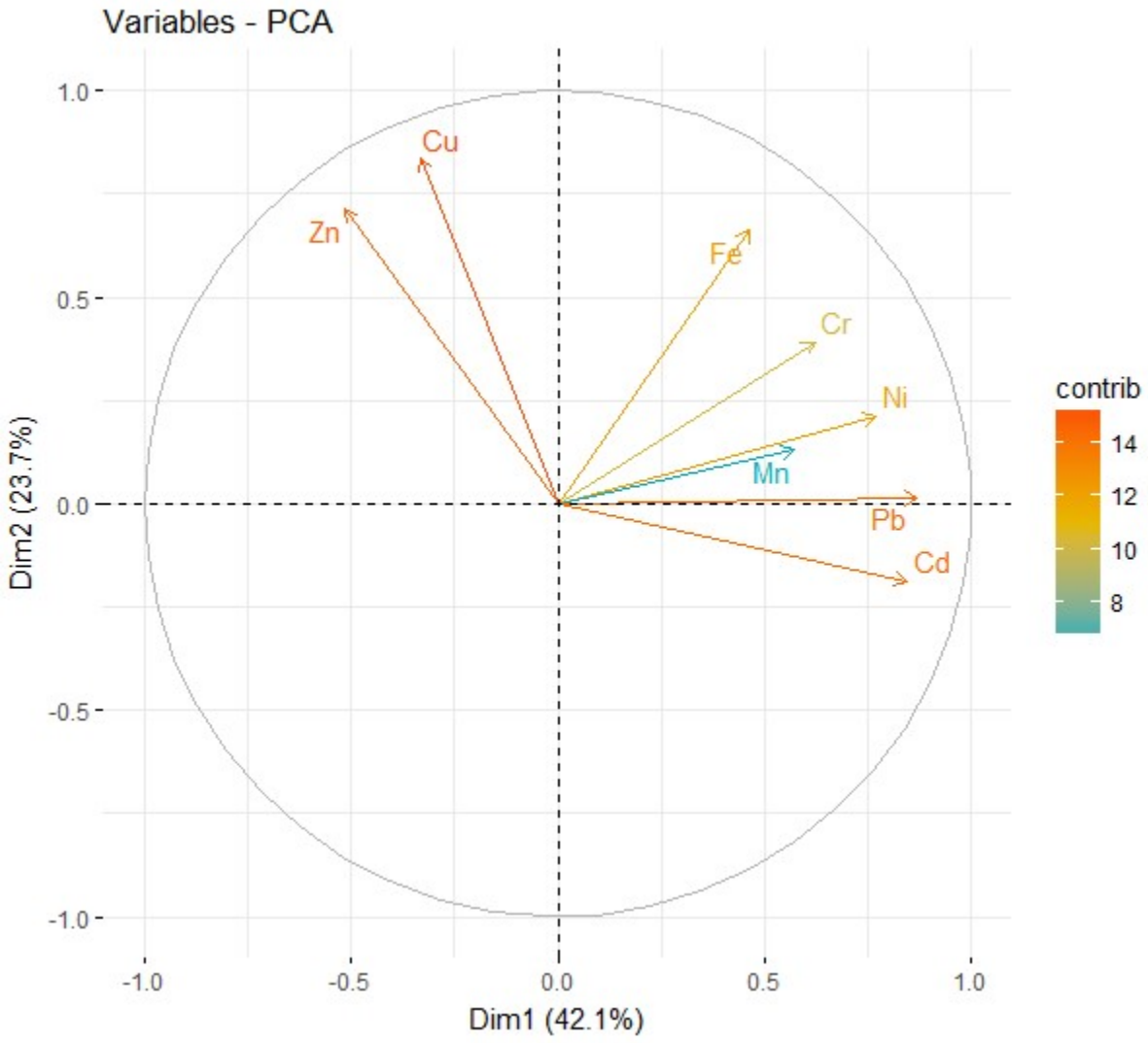

Figure 4.9: Biplot displaying the dimensions (components) of variables (heavy metals) in the plant samples in rotated space

Note: The most important (or contributing) variables (heavy metals) are farther from the origin.

Table 4.54: Principal Component Analysis of the Faecal Samples

Component Matrix[a]				
Parameters	Component			
	1	2	3	4
Cu	-0.383	**0.707**	0.262	0.301
Zn	-0.378	**0.614**	0.204	-0.513
Cr	0.324	0.342	0.423	**0.649**
Pb	**0.817**	-0.188	0.102	-0.483
Ni	-0.458	-0.575	**0.576**	-0.031
Cd	-0.458	-0.575	**0.576**	-0.031
Fe	**0.560**	0.348	0.487	-0.470
Mn	-0.249	**0.913**	0.184	0.017
Total Heterotrophic bacteria	**0.977**	0.129	0.050	-0.069
Staphylococcus aureus	0.008	-0.242	-0.748	0.138
Salmonella / Shigella	**0.906**	0.159	0.230	0.316
Fungi Count	**0.623**	-0.546	0.502	0.195
Total Coliform Count	**0.784**	0.158	-0.391	0.005
Eigen values	4.636	3.069	2.256	1.392
% Variance explained	35.667	23.613	17.355	10.714
% Cumulative	35.667	59.280	76.636	87.350

Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaiser Normalization. Bold figures indicate absolute values > 0.5 of parameters with strong loading values.

Table 4.55: Principal Component Analysis Results for Heavy metals in the Faecal Samples

	Dimension 1	**Dimension 2**	**Dimension 3**	**Dimension 4**
Cu	29.36	22.03	7.24	41.37
Zn	25.10	14.37	57.57	2.96
Cr	0.00	0.00	0.00	0.00
Pb	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00
Cd	0.00	0.00	0.00	0.00
Fe	6.47	59.19	33.22	1.12
Mn	39.07	4.42	1.97	54.55

Note: Dimension = Principal Components

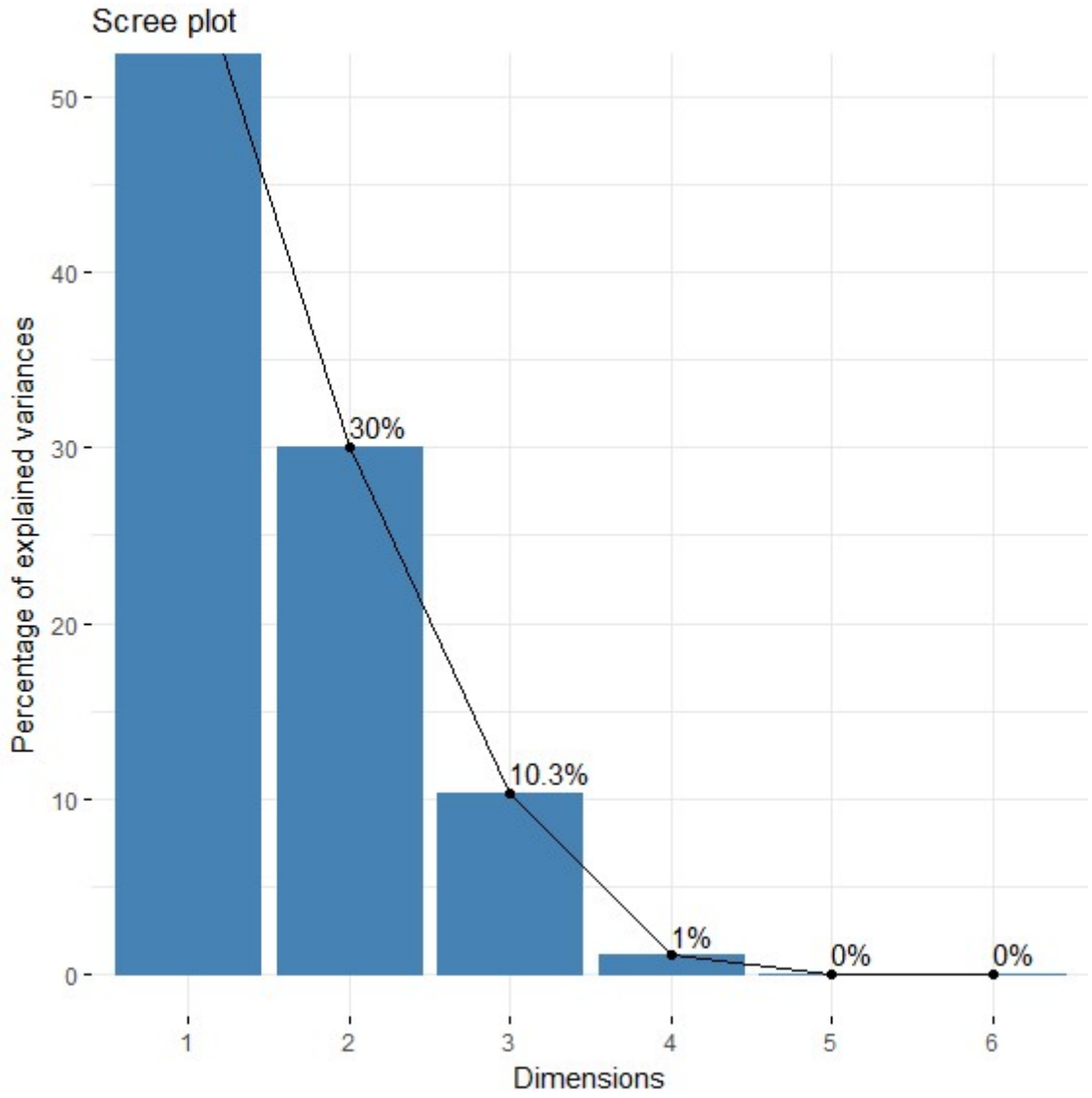

Figure 4.10: Scree plot displaying percentage total variance for heavy metals in the faecal samples

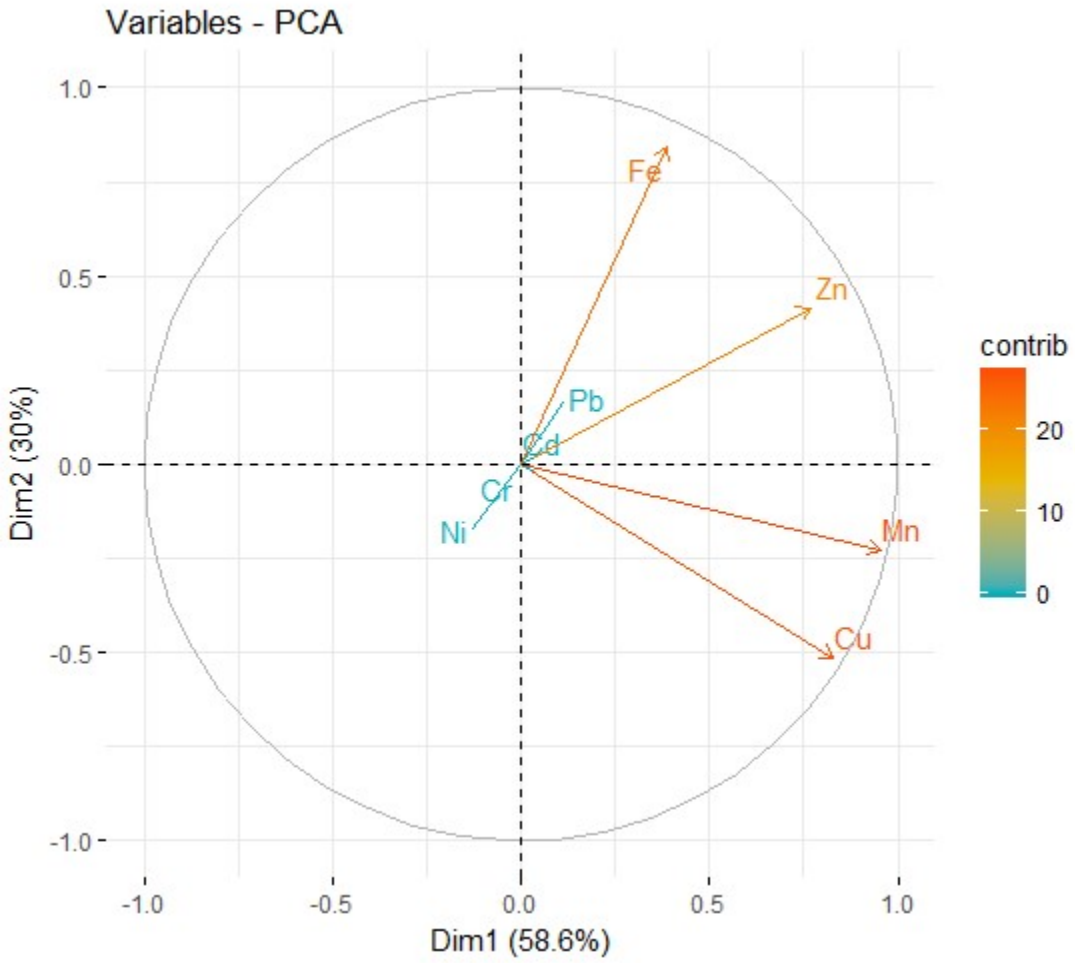

Figure 4.11: Biplot displaying the dimensions (components) of variables (heavy metals) in the faecal samples in rotated space

Note: The most important (or contributing) variables (heavy metals) are farther from the origin.

CHAPTER FIVE

DISCUSSION OF FINDINGS

5.1. Heavy metals concentration in selected waterholes of Old Oyo National Park

Water has unique chemical properties due to its polarity and hydrogen bonds which make it able to dissolve, absorb, adsorb or suspend many different compounds (WHO, 2007). In nature, water is not pure as it acquires contaminants from its surrounding and those arising from humans and animals as well as other biological activities (Mendie, 2005). There is an increasing concern about heavy metal contamination in river systems (Ahmad *et al.,* 2009). Wastewaters carry toxic heavy metals that get introduced into the aquatic system through various processes (Khan *et al.,* 2008). Sewage and industrial disposal have greatly increased the concentration of heavy metals in the aquatic ecosystems (Rai, 2008).Through rivers and streams, metals are transported as either dissolved species in water or as an integral part of suspended sediments (Duruibe *et al.,* 2007).

The result obtained from this study showed that the mean concentration of Fe was highest throughout the four seasons of sampling. This may be as a result of surface run-off into the water bodies with effluents and anthropogenic discharge of wastewaters from the surrounding communities. This agrees with the findings of Omonona *et al*. (2019). The iron transport capacity of a river has also been reported to be closely related to the vegetation types in its watershed (Krachler *et al.,* 2005). The mean concentration of Cd was discovered to be the lowest in the sampled rivers. The water samples (rivers) of Old Oyo National Park were more contaminated with heavy metals during the wet season than the dry season throughout the period of study. This is may be due to agricultural run-off, leaching of fertilizers and effluent discharges into the sampled rivers from the surrounding

communities. There were significant differences in the values of Cu, Zn, Cr, Fe, Pb, Ni, Cd and Mn in the water samples across the four seasons ($P<0.05$).

The mean concentration of all the heavy metals analysed (excluding Cu and Zn) were found to be above the NSDWQ (2007) and WHO (2011) permissible limits. This implies that the sampled rivers are not potable or safe for drinking. When animals drink from these water bodies, they bioaccumulate metals in their tissues and this could lead to behavioural alteration and lowering disease resistance and affect other physiological processes (Dauwe *et al.,* 2006). It could also cause teratogenic, mutagenic or carcinogenic effects in their biological systems resulting into threats to species perpetuation and decline in species population. Contamination with heavy metals is a serious threat to wildlife due to their toxicity, bioaccumulation and biomagnifications within the food chain (Demirezen and Uruc, 2006).

5.2 Heavy metals concentration in soil samples of Old Oyo National Park

Soil contamination by heavy metals is a major environmental concern. Soils are important sinks of heavy metals that could be inhaled, ingested, or absorbed, thereby entering the biosphere (Banat *et al.,* 2005). It is a major threat to soil due to the xenobiotic (human-made), industrial, agricultural chemicals and other improper waste disposal causing the alternation in the natural soil mechanism, environment of the soil and the soil micro-biota involved in the plant metabolic activities. With the aid of rapid urbanization and industrialization, heavy metals are continually being introduced into soils and biota through different pathways that includes but not limited to: fertilization, irrigation, rivers run-off, atmospheric deposition and mining (Emmanuel *et al.,* 2014). The application of numerous biosolids (livestock manures, composts, and municipal sewage sludge) to land inadvertently

leads to the accumulation of heavy metals in the soil (Basta *et al*., 2005). The environmental issues related to heavy-metal contamination are becoming serious in developing countries (Wei and Yang, 2010). The toxicity and mobility of heavy metals in soils is not only based on their total levels but also on their precise chemical form, bonding state, metal properties, environmental factors, soil properties and organic matter content (Osu and Okoro, 2011).

The results from the study showed that Mn had the highest mean concentration in the soil samples across the four seasons of sampling while Cd had the lowest mean concentration. The high concentration of Mn observed in the sampled soils may be attributed to the acidic nature and redox conditions of the soils as corroborated by Porter *et al*. (2004) and Millaleo *et al.* (2010) and a contribution from atmospheric deposition. When absorbed by plants from the soil, excessive Mn concentration can change varying processes such as enzyme activity, absorption, translocation and utilization of other mineral elements and cause oxidative stress in plant tissues (Lei *et al.,* 2007). This finding is contrary to Omonona *et al.* (2019) who found Fe to be highest in the soil samples of Omo Forest Reserve. The mean concentration of Fe was found to be higher (next to Mn) in the soil samples. The implication of this is that there is enough Fe concentration for plant uptake in maintaining proper metabolic and physiological cellular processes such as chlorophyll biosynthesis, nitrogen fixation, DNA replication and reactive oxygen species (ROS) scavenging (Yruela, 2013). Adefemi *et al.* (2007) also posited that Fe occurs at high concentrations in Nigeria soils.

All the soil samples were averagely contaminated more during the dry season than the wet season except for Zn and Cd. This may be due to higher evaporation rate with consequent concentration of materials in the soils. It might also be due to run-off effect that is capable

of leaching heavy metals in the sampled top soils and the impact of rainfall which may expedite the dilution of soil solution during wet season (Yahaya *et al.,* 2009). It could also be linked to differences in individual metal solubility, pH, leaching and topography of the sampling area (Iwegbue *et al.,* 2006b). This outcome also agrees with the findings of Oluyemi *et al.* (2008) but disagrees with Omonona *et al.* (2019) who reported more contamination during the wet season in the soil samples of Omo Forest Reserve. Metal-soil interaction is such that, when metals are introduced at the soil surface, downward transportation does not occur to any great extent unless the metal retention capacity of the soil is overstretched, or the clay content is too low or metal interaction with the associated waste matrix enhances its mobility (Lee *et al*., 2006). Therefore, changes in soil environmental conditions over time, such as the degradation of organic waste, changes in pH, redox potential, or soil composition can also enhance metal mobility.

There were significant differences in the values of Cu, Zn, Cr, Fe, Pb, Cd and Mn in the soil samples while there was no significant difference in the values of Ni in the soil samples across the four seasons ($P<0.05$). Addition of environmental pollutants (such as heavy metals) to soil may influence microbial proliferation and enzymatic activities, probably leading to a declining rate of biochemical process within the soil environment (Filazi *et al*., 2003). Assessing the concentration of heavy metals in the soil of national parks is imperative in order to evaluate the potential risks to both flora and fauna. Heavy metal concentration in the soil solution plays an important role in controlling metal bioavailability to plants (Nazir *et al.,* 2015).

5.3 Assessment of contamination status of heavy metals in sampled soils of Old Oyo National Park

5.3.1 Contamination Assessment based on Contamination Factors

The calculated contamination factors for analysed heavy metals in the sampled soils showed that Ni (except OS1 and OS2) showed very high contamination (>6). The highest contamination factor of 16.606 (Ni) was observed in TS2 and least contamination factor of < 0.9 (Cu, Zn, Pb, Fe, Mn) were observed in most sampled soils implying low influences from anthropogenic sources (Taylor and McLennan, 1985).

5.3.2 Contamination Assessment based on the Degree of contamination

The degree of contamination of the sampled soils indicates that 50% of the sampled soils (MS3, OS1, OS2, and TS1) fell within the moderate degree of contamination (8-12) while sampled soils (MS1, MS2, OS3 and TS2) fell within the considerable degree of contamination (16-32). The contamination assessment based on the degree of contamination results indicate that soil pollution by heavy metals were classified as contaminated soils (Kumar *et al*., 2012).

5.3.3 Contamination Assessment based on Geo-accumulation Index (Igeo)

The Geo-accumulation Index (Igeo) has been widely used to evaluate the degree of heavy metal contamination or pollution in terrestrial, aquatic and marine environment (Tijani and Onodera, 2009). The Igeo was also used to evaluate the heavy metal contamination sampled soils in Old Oyo National Park. The *Igeo* values for Cd fell within the moderately to strongly contaminated category (2 - 3) while the other heavy metals, having negative values, fell within the practically uncontaminated category (<0).

5.4 Heavy metals concentration in plant samples of Old Oyo National Park

Heavy metals contamination is a global challenge as heavy metals are not destructible and majority have impacts on life forms especially when permissible limits are exceeded (Emmanuel *et al.,* 2014). Trace metals accumulation in plants from anthropogenic sources has been reported to have drawn greater attention to inorganic pollution, and established plants as passive bio-monitors, since plants respond directly to the state of soil and air (Divan *et al.,* 2009). Plants growing in polluted areas show symptoms of accumulation of heavy metals in different parts of them (Kulshreshtha *et al.,* 2010) though some plants have the ability to absorb heavy elements in different plant tissues more than others (Aksoy *et al.,* 2012). The larger portion of the concentration of iron (highest) obtained from the study may have been obtained from the soil. Stihi *et al.* (2011) reported that increased soil heavy metal levels have proportional influence on the concentration absorbed by plants while Adefemi *et al.* (2007) earlier posited that iron (Fe) occurs at high concentrations in Nigeria soils. Parzych (2014) noted that the specific sensitivity of some plant species to the presence of heavy metals in soil allows for the determination of the degree, range and structure of environmental changes. The implication of this high iron level is that there is availability of Fe for the plant species uptake to maintain normal cellular activities such as DNA replication, nitrogen fixation, reactive oxygen species (ROS) scavenging and chlorophyll biosynthesis (Yruela, 2013). Even though cadmium (Cd) had the lowest mean concentration in the plant samples across the seasons of sampling, it is of ecotoxicological concern. When biomagnified in animal tissues, cadmium possesses inhibitory capabilities, that is, it can block calcium channels or metabolism thereby disrupting the electrolyte balance and causing the excretion of calcium, which can lead to brittle bones (Larison, 2001). In mammals, cadmium has been reported to induce not only acute renal and liver failures but

also pneumonitis and pulmonary oedema in mammals (Annabi *et al.,* 2013). The high values of Zn obtained from the study may be from effluents eliciting from human activities such as illegal metal smelting and mining from outside the boundaries of the park. Huseyinova *et al.* (2009) asserted that heavy metals spread as a result of human activities, leading to an excess accumulation that exceeds the permissible limits causing serious environmental disaster. Specifically, very high concentration of Zinc can cause injury to the pancreas and distort metabolism of protein and leading to arteriosclerosis when bioaccumulated in animals or humans (Sinha *et al.,* 2010). Despite the fact that the concentrations of copper, lead, nickel and manganese obtained in this study were relatively low when compared with the recommended levels, their bioaccumulative tendencies and biomagnification potential along the food chain cannot be jettisoned. This is because the intensity of heavy metal uptake can change the overall elemental composition of the plants in its entirety (Vaikosen and Alade, 2017). Also, consumption of medicinal or wild plant and their products contaminated with toxic substances like these heavy metals, have been reported to elicit deleterious health effects on living organisms (Sethy and Ghosh, 2013). The plant samples of Old Oyo National Park on the average, were more contaminated with heavy metals during the wet season compared to the dry season. This may be accredited to run-off as averred by Jung (2001) and atmospheric deposition. Barbes *et al.* (2014) also opined that the concentrations of major and trace metals in plants depend on root uptake as well as accumulation of dry and wet deposition on outer plant organs, such as leaves or bark. The presence of these heavy metals and their toxicity may have an inhibitory impact on the growth of plant species, photosynthetic activity, enzymatic activity, and build-up of other nutrient elements, as well as disrupting the root system (Gune *et al*., 2004) since

certain plants have the ability to uptake and accumulate metallic contaminants via the root system and store them in various plant compartments (Tangahu *et al*., 2011).

5.5 Heavy metals concentration in faecal samples from Old Oyo National Park

The nature of metals from both natural and anthropogenic sources combined with their necessity in biological processes produces a multifaceted system for assessment (Ferreira, 2011). Environmental changes can be examined biologically and non-biologically, *in-situ* or using field samples in laboratory (Gupta, 2012). The degree to which animal species (domesticated or wild) are exposed to metal contamination can therefore be assessed using faecal samples as bio-indicator (Gaumat and Bakre, 1998). High concentrations of metals were observed in the faecal samples of Western hartebeest (*Philantoba maxwelli*), Olive baboon (*Papio anubis*) and Mongoose (*Atilax paludinosus*) respectively.

The range of concentration of Zn in this study is similar to those reported by Gupta (2012) and Gupta and Bakre (2013), and was found to be highest in the faecal sample of Mongoose (*Atilax paludinosus*). Metal concentration in faeces often equals that in food (Leonzio and Massi, 1989) with additional concentration plausible through other routes of exposure such as inhalation, dermal contact. The addition exposure or highest concentration of Zn in the faecal samples therefore might have come through inhalation though the uptake of micronutrients like Zn and Cu is dependent on the animal's demands. Generally, there are no enough recent data on wildlife as regards zinc contamination which necessitates further research in this area but secondary toxicities have been recorded in birds, carnivores and other mammals.

5.6 Physicochemical Characteristics of selected waterholes in Old Oyo National Park

Water is one of the most important and essential natural resources that exists on our planet and is essential for survival of both aquatic and terrestrial organisms (Swaleh and Usmani, 2016). Rapid industrialization is responsible for increasing water pollution as the untreated excessive waste thrown in the water bodies has dreadful effects on its physiochemical properties. The industrial pollutants associated with organic matter, inorganic dissolved solids and other unwanted chemicals cause serious problems in the water quality (Radha *et al.,* 2007). Physicochemical characteristics are known to affect the biotic components of an aquatic system in different ways (Ayoade *et al.,* 2006) and pollutants generally have been known to affect the physicochemical characteristics of water (Singh *et al.,* 2006). Assessment of the adequacy of the physicochemical quality of water often relies on the comparison of the results of water quality analysis with guideline values or permissible limits (WHO, 2017).

The physicochemical characteristics of water samples observed from this study are comparable with those of typical tropical surface waters. The temperature range observed in the study falls within the recommended rangefor aquatic life in the tropical environment (Ayodele and Ajani, 1999; Olukunle, 2000). Temperature is one of the major factors influencing spatial and temporal distributions of organisms in ecosystems (Masood *et al.,* 2015). The feeding, reproduction, growth and migratory behaviour of aquatic species is greatly influenced by the temperature of water (Crillet and Quetin, 2006). The lower values recorded in the dry season could be due to the period / time of sampling which was early in the morning. Water temperature influences many physical, chemical and biological processes and the rate of chemical reactions generally increases at higher temperatures

(Suleiman and Audu, 2014). Seasonal variations in water temperature depend on where they are located (Perlman, 2013) though the increase in water temperature is directly related to total dissolved or suspended solids (Martinez *et al.,* 2011). The mean temperature values recorded across the four seasons were significantly different ($P<0.05$) and are within the WHO (2011) permissible limit.

The mean pH values observed in the study were not significantly different ($P<0.05$) and are within the NSDWQ (2007) and WHO (2011) permissible limits which indicate the productive nature of the rivers sampled. Any change in pH in water outside the permissible limits may hold dire consequences for the health of aquatic organisms since most of their metabolic activities are pH dependent (Chen and Lin, 1995). Higher values were observed in the dry seasons as compared with the wet season and this is contrary to the findings of Ajibade *et al.* (2008a) and Omonona *et al.* (2019). The mean pH values across the four seasons imply that the water samples (rivers) are acidic and may therefore not be potable or safe for drinking. The slight acidity observed in the study may be as a result of increased carbon dioxide concentration eliciting from organic decomposition (Mustapha, 2008). The mean values of EC of the water samples were higher during the dry season. This is contrary to Ajibade *et al*. (2008a) who reported higher values during the wet season due to the leaching of the mineral salt from the bedrock and re-suspension of solids. This may have been due to increased water concentration due to low water level (Samuel *et al.,* 2015). The high EC recorded in the water samples indicates high dissolved salts (Keke *et al.,* 2015) and could be linked to discharge of sewage materials and leaching of inorganic contaminants. The mean EC values recorded across the four seasons were significantly different ($P<0.05$) and below the WHO (2011) permissible limit.

The alkalinity of water is a quality parameter that describes its acid neutralizing capacity. The alkalinity values obtained from this study are higher than those reported by Omonona *et al*. (2019) at Omo Forest Reserve. The mean values of alkalinity observed in this study are higher during the wet season. The mean alkalinity values recorded across the four seasons were significantly different ($P<0.05$) and the mean values are below the WHO (2011) permissible limit.The quantity of TDS is often proportional to the degree of pollution and further indicates the salinity behaviour of river water (Masood *et al.,* 2015). The mean values of TDS of the water samples in this study were higher during the dry season. This could be as a result of the tidal influence of the rivers during the wet season. The low TDS values observed during the wet season of 2017 may be due to dilution and usage by phytoplankton (Adakole *et al.,* 2008). Higher TDS in water system increases the chemical and biological oxygen demand and ultimately depletes the dissolved oxygen level in water (Ugwu and Wakawa, 2012). It also reduces water clarity, which could contribute to the decrease in photosynthetic activities and might lead to an increase in water temperature. The mean TDS values obtained across the four seasons were significantly different ($P<0.05$) and the mean values were below the WHO (2011) permissible limit. Olabaniyi and Owoyemi (2006) earlier reported that TDS varies considerably in different geological regions owing to differences in their solubility of minerals.

The mean values of TSS of the water samples were higher during the dry season. The very high values recorded from Rivers Oopo and Sooro in the dry season of 2018 may be attributed to atmospheric particle deposits and storm water run-off. The mean TSS values obtained across the four seasons were significantly different ($P<0.05$) and the mean values were below the WHO (2011) permissible limit.The mean values of nitrate in the water

samples were higher during the wet seasons as compared with the dry seasons. This may be due to contributory run-off of chemical fertilizers and from oxidation of nitrogenous waste products in human and animal faeces into the rivers sampled as corroborated by Dami *et al*. (2013). The low nitrate concentration recorded in this study may be attributed to the fact that uncontaminated natural waters often contain only trace amounts of nitrate (Jaji *et al*., 2007) and probably due to its utilization as nutrient by the algal community. Low concentration level of nitrate in the sampled rivers might also be due to the dearth of significant consequences of farming activities into the rivers as corroborated by Yakubu *et al.* (2014). The mean nitrate values obtained across the four seasons were significantly different ($P<0.05$) and the mean values were below the NSDWQ (2007) and WHO (2011) permissible limits. The mean values of phosphate in the water samples were higher during the wet seasons when compared with the dry seasons. This may be due to run-off or leaching of fertilizer residues from agricultural farms in the surrounding communities and other phosphate sources. Wetzel (2001) posited that the rate of phosphorus release into the water can double when sediments are frequently disturbed. The low phosphate concentration recorded in this study may be attributed to dilution and movement of water which could not allow aquatic sedimentation and decay of organic matter (Ojutiku and Kolo, 2011; Keke *et al.,* 2015). Increased levels of phosphorus may result in fouling of natural water and production of toxic cyanobacteria (Omaka, 2007). The mean phosphate values obtained across the four seasons were significantly different ($P<0.05$) and the mean values were below the NSDWQ (2007) and WHO (2011) permissible limits.

The mean values of sulphate in the water samples were higher during the dry seasons. The values obtained during the dry season of 2017 showed that the sulphate content of all the

rivers sampled were above the NSDWQ (2007) permissible limit while those of Rivers Ogun, Ayinta, Tessi and Sooro were above the WHO (2011) permissible limit. The presence of sulphate in the sampled rivers may be attributed to the washing activities from surrounding communities and discharge of house hold effluents into the rivers. Sources of sulphate in the water could also be associated with soil mineralogy with possible contribution from other plethora of anthropogenic activities (Oyhakilome *et al.,* (2012). The mean sulphate values obtained across the four seasons were significantly different ($P<0.05$) and the mean value (dry season 2017) was above the NSDWQ (2007) and WHO (2011) permissible limits. Furthermore, the mean values of chloride in the water samples were slightly higher during the dry seasons when compared with the wet seasons. This may be due to the concentration of this anion from excessive water evaporation from the rivers as corroborated by Oyhakilome *et al.* (2012). The mean chloride values obtained across the four seasons were not significantly different ($P<0.05$) and the mean values were below the NSDWQ (2007) and WHO (2011) permissible limits.

The mean values of the DO in the water samples were higher during the wet seasons when compared with the dry seasons. DO concentration in natural waters depends on the physical, chemical and biochemical activities in the water bodies. The lower values obtained during the dry seasons may be as a result of lower water depth and reduced agitation by wind current (Ajibade *et al.,* 2008a) and high levels of nutrients and TSS. DO is very crucial for the survival of aquatic life and it is also used to evaluate the degree of freshness of a river (Andem *et al.,* 2012). The DO recommended for the survival of aquatic species in tropical water is between 3 and 5 ppm (Ayodele and Ajani, 1999). It is known to affect such attributes as growth, survival, distribution, behaviour and physiology of aquatic organisms.

DO concentration in water has also been reported to tend to decrease as temperature of the water increases (Eze and Ogbaran; 2010). According to Srivastava *et al.* (2009), depletion of dissolved oxygen is the most frequent result of certain forms of water pollution. The mean DO values obtained across the four seasons were significantly different ($P<0.05$) and the mean values were below the WHO (2011) permissible limit.

The mean values of the BOD in the water samples were slightly higher during the wet seasons when compared with the dry seasons. This may be probably due to the increased input of decomposable organic matter (require oxygen for their biodegradation) into the rivers sampled through surface run-off. The high values recorded may be probably due to discharges from surrounding communities that empty into the rivers and other anthropogenic activities. High BOD is suggestive of poor water quality, and the lesser the BOD, the lower organic matter present in water (Samuel *et al.,* 2015). The mean BOD values obtained across the four seasons were not significantly different ($P<0.05$) and the mean values (which are > 10 mg/l) were above the WHO (2011) permissible limits. The implication of this is that the rivers sampled are heavily polluted (Emere and Nasiru, 2008; Abolude *et al.,* 2012). The mean values of the COD in the water samples were higher during the wet seasons when compared with the dry seasons. The high values of COD obtained from the study may be as a result of chemical oxidation of some organic substances which are oxidized biologically (Okoroafor *et al.,* 2013) due to discharges of domestic wastewater from nearby settlements, surface and ground water carrying chemicals directly from agricultural farms (Abolude *et al.,* 2012). It may also be as a result of high presence of inorganic substances in water and also the activities of micro- organisms which decomposes the massive inflow of organic waste brought about by wind and run-off (Meme

et al., 2014). The mean COD values obtained across the four seasons were significantly different ($P<0.05$) and the mean values were above the WHO (2011) permissible limits.

5.7 Physicochemical Characteristics of Sampled Soil in Old Oyo National Park

Soil is a natural sink for different environmental contaminants (Edori and Iyama, 2017). Once pollutants or contaminants find their way into the soil matrix, they interact with the soil and subsequently disrupts the chemical and physical properties of the soil (Edori and Iyama, 2017). Soil properties that are sensitive to the presence of contaminants or other changes can be used as indicators of natural or anthropogenic influence. The soil pH obtained from this study is higher than the 4.85 – 6.54 range reported by Alarape (2002). The higher values observed in the wet seasons may be due to the fact that the basic cations were forced off the soil colloids by the mass action of hydrogen ions from the rain as those attached to the colloids (Edori and Iyama, 2017). The mean range of soil pH across the seasons shows the soils were slightly acidic. This falls within the normal range of 4.5 – 7.5 as posited by Agbede (2008) though below the pH range of 6.8 to 8.0 recommended for optimum plant's growth (Jain *et al*., 2015). Soils with low pH have been reported to favour availability, mobility and redistribution of metals due to increased solubility of the ions in acidic environment (Oviasogie and Ndiokwere, 2008). The pH is one of the most important physicochemical parameter of soil. In the maintenance of soil fertility, type of organism found in the soil and nutrient availability to plants, pH has been reported to play a crucial role (Patil *et al*., 2014; Edori and Iyama, 2017) and is an indicative measurement of the chemical properties of soil.

The high conductivity values observed in the soil samples is an indication of anthropogenic interference and infer the availability of soluble salts in the soil samples as corroborated by

Arias *et al.* (2005)and Egbenda *et al.* (2015) though Jain *et al.* (2015) averred that low soil EC is often appropriate for plant growth. According to Wagh *et al*. (2013), soils with EC below 0.4mS/cm are considered marginal or non-saline, while soils above 0.8 mS/cm are considered severely saline. The soils in this study were therefore found to be highly saline. Suitable amount of soil pH and EC leads to optimum availability of nutrients, reduced accessibility of toxic elements and increased activity of micro-organisms (Raman and Sathiyanarayanan, 2009).The SOC (%) ranged from 1.20 to 3.12 in the wet season and 0.41 to 2.33 in the dry season. The mean range of SOC across the seasons is from 1.54 to 2.42. SOC has often been attributed to soil productivity and is of interest to researchers because of its role as a sequestration site for atmospheric carbon (West and Post, 2002). It plays a vital role in carbon cycle and nutrient availability. Soils have varying organic compounds in different degrees of decomposition.The SOC is obtained by decomposition of the plants, animals and from anthropogenic sources such as chemical contaminants, fertilizers or rich organic waste (Avramidisa *et al*., 2015). The presence of organic carbon raises the cation exchange capacity of the soil which retains nutrients absorbed by plants (Amos-Tautua *et al*., 2014).

The SOM (%) ranged from 2.07 to 5.38 in the wet seasons and 0.71 to 4.02 in the dry season. The mean range of SOM across the seasons is from 2.65 to 4.16. Ayolagha and Onwugbuta (2001) asserted that high SOM (>2.0%) in soils is conducive for heavy metal chelation formation. SOM is one of the most significant chemical parameter of soil quality as it affects soil porosity, and promotes gas exchange and water relations. Micheni *et al*. (2004) opined that in maintaining soil's physical, chemical and biological properties, SOM has a key role to play. It supplies the essential nutrients and has an excellent capacity to

hold water and absorb cations. Much of the soil organic matter (SOM) was composed of soil organic carbon (SOC). This may be due to the large percentage of carbon in plant tissues as corroborated by Havlin *et al.* (2005). Mandal *et al*. (2014) also reported that forest soil reserves much higher organic carbon including varying proportion of active organic carbon fractions and stable organic matter, referred to as humus in comparison to agriculture and other land use. The amount of SOM in any soil influences the nutrient content and any alteration will change the quality and quantity of soil fertility. Both SOC and SOM are used to predict the organic richness of the soil environment and have an exerting influence on soil development, fertility, and available moisture (Edori and Iyama, 2017).

The mean range of % N across the seasons is from 0.14 to 0.23. Nitrogen is often readily available to plants either as ammonium or nitrate. Once nitrogen is present in the soil, it undergoes different transformation which determines its availability to plants (Lamb *et al*., 2014). In addition, mineralization transforms organic nitrogen present in soil organic matter, crop residues, and manure to inorganic nitrogen. The soils of the park are considered very good since nitrogen value greater than 0.1% is rated good (Defoer *et al*., 2000). The A.P (mg/kg) ranged from 7.4 to 18.30 in the wet seasons and 8.2 to 15.7 in the dry season. The mean range of A.P across the seasons is from 12.59 to 14.76. The soil samples are not deficient in available phosphorus because the values were generally higher than 6.0 mg/kg (Defoer *et al*., 2000). This may be due to the availability of high amount of organic matter and plants decomposition (Ideriah *et al*., 2006) and leaching off of fertilizer nutrients from agricultural farms from the surrounding communities.Excess phosphorus in soil can turn out to be a point source of contamination, because the surplus not used by plants is wash away

by run-offs into ponds, lakes and rivers. Although phosphorus stimulates plant growth in soils, nonetheless its excess in water enhances algal growth, which if it persistently continues can result in algal bloom.

The exch. acidity (Cmol/kg) ranged from 0.11 to 1.20 in the wet seasons and 0.14 to 1.60 in the dry season. The mean range of exchangeable acidity across the seasons is from 0.24 to 0.74. The exchangeable bases Ca and Mg were found to be higher (respectively) in this study and this attest to the fact that they have been reported to be the most abundant minerals in the soil (Middha *et al*., 2015). They enhance soil structure and improve water penetration and supply favourable environment for the growth of plants and microorganisms (Jain *et al*., 2015). Na had the least concentration of the exchangeable bases in this study. High Na concentration has been reported to pose a threat on soil permeability, soil texture and also reduces the soil's water intake (Patil *et al*., 2014). Deficiency of potassium (K) in plants often leads to non-utilization of nitrogen and water efficiently, increasing the susceptibility of plants to diseases. The slight increase in K in the wet season of 2018 might be due to soil saturation which resulted in widening of clay minerals, releasing previously fixed K as agreed by Middha *et al.* (2015). Increased quantity of potassium in the soil leads to high osmotic pressure in the plant, thereby increasing its water absorptive capacity (Joseph, 2005). Generally, the values of Ca, Mg and K observed in this study attest to the fact their low values have been reported for most Nigerian soils (Uzoho *et al*., 2007)and this may be attributed to leaching of nutrients especially caused by high rainfall. Meanwhile, the TEB (Cmol/kg) ranged from 3.00 to 11.91 in the wet seasons and 2.46 to 7.80 in the dry season.

The mean range of TEB across the seasons is from 5.16 to 8.67. The increase in the TEB and organic matter may lead to plants absorbing nutrients more easily (Aydinalp and Marinova, 2003). The ECEC (Cmol/kg) ranged from 3.30 to 12.11 in the wet seasons while in the dry season, it ranged from 2.67 to 7.99. The mean range of ECEC across the seasons is from 5.91 to 8.91. The ECEC is dependent especially on the pH, clay and on the soil organic matter content.The mean range of BS across the seasons is from 87.74 to 96.26. This range is higher than the 72.32 – 97.35 reported by Alarape (2002). The soil samples analysed had high base saturation and were higher than the 60% permissible limit established for ecological zone (Holland *et al*., 1989). The textural class of the soil samples (determined by soil texture triangle) from the study showed that the soil samples from Marguba Range (MS1, MS2, MS3) of Old Oyo National Park were Loamy sand (LS) and Sandy loam (SL) while that of Tede Range (TS1, TS2, TS3) also were (LS) and Sandy loam (SL). These differences are due to micro heterogeneity that is typical of tropical soils (Oshunsanya, 2013). The textural class of soil samples from Oyo-Ile range (OS1, OS2, OS3) were Loamy sand (LS), Sandy loam (SL) and Sand (S). The soil texture (sand) observed in OS2 (in the wet season of 2017) might be attributed to the fact that tropical soils are highly heterogeneous and also possibly due to the length of transect or topographical sequence from which the soil samples were collected and composited. Sandy soils usually hold little water and percolation of water through it is invariably high and promoting ground water contamination. Nyles and Ray (1999) had earlier reported that soils possessing separate high sand and low clay content have high pollutant leaching potentials.

Significant differences were observed in all the physicochemical parameters of soil sampled except pH, K and textural class (Sand and Silt) that had no significant difference ($P<0.05$).

The physicochemical properties of soil, such as texture, cation exchange capacity, pH and the amount of organic matter within the soil, are important parameters that affect the heavy metal accumulation rate of soils (Wua and Zhang, 2011).

5.8 Microbial Characteristics of selected waterholes (rivers) in Old Oyo National Park

The discharge of contaminated water from domestic, industrial and agricultural sources into water bodies is one of the origins of the degradation of the quality of surface water. In fact, the quality of surface water like rivers rapidly change as a response to alteration within the surrounding environment. Also, water physicochemical parameters, such as pH, nutrients and presence of toxic compounds may influence the density of bacterial populations in surface waters. The assessment of the presence of bacteria and other microbes in water represents a major concern for human- and animal-health protection (Fey *et al.,* 2004).The result showed that the mean values of microbial counts of the water samples were higher during the dry season than the wet season. This agrees with the findings of Venkateesharaju *et al.* (2010) but disagrees with Nnane *et al*. (2011) who opined that greater incidence of pathogen loads is likely to occur when there is high rainfall and floods. Bacteria have been reported to be ideal markers of microbial pollution of surface waters because of their quick response to environmental changes (Pall *et al.,* 2013) and their distribution depends on changes in water temperature, salinity and physicochemical parameters (Igbinosa *et al.,* 2012). The total heterotrophic bacterial count provides an indication of the general load of aerobic and facultative anaerobic bacteria of a water sample. Its' frequency is commonly used as an indicator of comprehensive microbiological quality (Robertson and Brooks, 2003), and their presence in surface water has implications for animal and public health, especially pathogenic organisms.

The total heterotrophic bacteria count from this study was found to be highest during the dry season of 2017 and this reflects the contamination extent by the easily decomposable organic matters and also be due to waste disposal into the sampled rivers (Shekha *et al*., 2013). The total heterotrophic bacteria results from this study exceeded the World Health Organization (WHO) standard for heterotrophic bacteria in potable water. *Staphylococcus aureus*, regarded as important indicators of the whole aquatic ecosystem health (Kumar *et al*., 2010) was observed in no concentration in this study. Furthermore, the Salmonella / Shigella (enteric pathogens) were observed in the rivers sampled only during the dry season of 2017 with a mean value of 20.26. This is worrisome due to the fact that the genus *Salmonella* have been mostly considered as an endemic public health concern worldwide (Soto *et al.,* 2006). The sources of contamination are probably due to anthropogenic interferences and animal faeces and the introduction of microorganisms by birds and wild animals. The high prevalence of *Salmonella* observed in the study might not be unconnected to manure from free-grazing domestic animals and wild species as corroborated by Negera *et al.* (2017). The detection of these enteric pathogens from the sampled rivers implies that the surrounding communities of Old Oyo National Park can be put at high risk of diarrhoea disease when drunk. Majority of microbial pathogens are often excreted in faecal matter which contaminates the environment and then gain access to new hosts through ingestion (Toze, 1999). Although the indicators of faecal pollution used as sentinels in river monitoring to indicate the presence of faecal contamination are many, the favoured faecal indicator (especially in fresh waters including rivers) is the bacterium *E. coli* (Davies-Colley, 2013; McBride *et al.,* 2013).

The presence of *E. coli* in River Owu (dry seasons 2017 and 2018) and River Ogun (dry season 2017) indicated recent faecal contamination of the rivers and this could be attributed to animal faecal wastes (wild and livestock) and open defecation. This finding is in consonance with Ajibade *et al.* (2008b) who reported *E. coli* in the major rivers of Kainji Lake National Park, Nigeria and contrary to Sangodoyin and Opebiyi (2017) who had earlier reported the absence of *E. coli* in some rivers in Old Oyo National Park. *E. coli* has frequently been reported to be the causative agent of diarrhoea, urinary tract infection, haemorrhagic colitis, and haemolytic uraemic syndrome (Al-Otaibi, 2009). In fact, *Streptococcus faecalis* with *E. coli* are good indicators of gastrointestinal diseases (Shekha *et al*., 2013). The presence of thermo-tolerant coliform bacteria such as *Klebsiella sp.* and *Enterobacter sp.* in River Ogun further confirmed its faecal contamination (WHO, 2017). Though microbes such as *Pseudomonas sp.*, *Aspergillus sp.* and *Actinobacter sp.* observed in the rivers sampled may not appear to represent a health implication, they may be of concern for severely immune-suppressed persons (those with neutrophil counts below 500 per microliter) that drink from them (WHO, 2017). Other microbes such as *Bacillus sp., Flavobacterium sp. and Seratia sp.* observed in the waterholes have the tendency to cause disease in vulnerable subpopulations especially surrounding communities drinking them.

5.9 Microbial Characteristics of faecal samples in Old Oyo National Park

The current trend in minimizing pathogen health risks to water supplies is to make use of a risk management-based approach to ensure delivery of high-quality water (Cox *et al*., 2005). One potential source of these pathogens in rivers or water samples in national parks or other protected areas is the faeces of domestic (from surrounding communities) and wild animals. Pathogens from animal faeces may enter water bodies through direct deposition or as a result of overland run-off. There are several microorganisms present in animal faeces

including pathogenic and non-pathogenic species, the normal flora and the opportunistic ones (Adegunloye, 2006). The result from this study showed that faecal coliforms such as *E. coli* and thermo-tolerant bacteria such as *Enterobacter sp.* and *Klebsiella sp.* were observed.

Wild animals are susceptible to a wide range of infectious and non-infectious diseases caused by fungi. Fungal diseases are primarily associated with immunosuppression and inter-current illnesses (Mancianti *et al.,* 2002). Fungi are mainly opportunistic pathogens that invade the body if a severely weakened natural defense permits them to do so. Most factors facilitating an invasive fungal infection are often unavoidable because they are directly connected to the underlying diseases as well as to their treatment. The results obtained showed that *Aspergillus fumigatus* and *Aspergillus niger* were the only microflora fungal species from this study. Environmental contamination with toxigenic fungi under favorable conditions may lead to mycotoxin build-up reaching to injurious levels for animals and human health. The presence of the various microflora observed in the study pose a serious threat to both wildlife and environmental health.

5.10 Principal Component Analyses of Waterholes, Soil, Plant and Faecal Samples

Monitoring and assessment of heavy metal contamination has become a very critical area of study because of direct implications on environmental health. The Principal component Analyses (PCA), one of the multi-dimensional data analysis methods used to identify significant sources /components that explain the variations in heavy metal contamination and water quality, is gradually becoming very prevalent particularly in environmental assessment studies that have to do with monitoring and measurement (Oketola *et al*., 2013). The application of multivariate statistical technique assists to simplify and organize large

data sets by data reduction and interpretation of the variables (Cobbina *et al*., 2015). In order to evaluate the most significant metal in terms of contribution to toxicity in the samples, the PCA methodology was performed.

An eigenvalue gives a measure of the significance of the factor with the highest eigenvalues being the most significant (Nair *et al*., 2010). Eigenvalue should be one or greater for proper considerations during PCA. Factor loadings values of > 0.75, between 0.75 – 0.5 and 0.5 – 0.3 are classified as strong, moderate and weak based on their absolute loading values. From the study, Zinc had highest contribution of total variability of identified components (PC 1 and PC 2) of waterholes (50.97%), plants (34.66%) and faeces (39.47%) while lead (52.23%) had highest contribution of total variability of identified components in soils. These metals are most significant toxins and have been given special attention throughout the world basically due to their ubiquitous nature and toxic effects even at very concentrations (Ferner, 2001; Salinska *et al*., 2013). This PCA result also implies that Pb and Cd contamination in the samples were influenced by anthropogenic activities such as industrial effluents and domestic sewage discharges with more contributions from the non-point sources of heavy metal pollution, such as agriculture, surface runoff and soil erosion. Vystavna *et al*. (2012) reported that cadmium is an anthropogenic indicator of the industrial impact of an environment. The application of PCA eases the explanation of complex data matrices to better understand heavy metal contamination, water quality and ecological status of studied ecosystems (Varol *et al*., 2012).

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Heavy metal contamination of the environment is a global challenge because heavy metals are not destructible and majority of them possess toxic impacts on biological species particularly when permissible limits are surpassed, posing serious significant threats to wild flora and fauna. The levels of heavy metals analysed in the sampled rivers of Old Oyo National Park were above the permissible limits except for Cu and Zn. As such, the sampled rivers of Old Oyo National Park may not be potable and/or safe for drinking. The sampled soils of Old Oyo National Park were contaminated mostly with Mn with the highest concentration in the second dry season (January 2018). The heavy metals in the sampled plant species were mostly below the permissible limit except for cadmium. The faecal samples of mongoose (*Atilax paludinosus*) had the highest concentration of heavy metals while Cr, Pb, Ni, Cd were below detection limit in all the faecal samples analysed.

Water quality is of crucial concern for mankind since it is directly linked with human well-being. Particularly, river water quality is very important for ecological health. The high BOD and COD is an indication of the polluted nature of the rivers sampled with their poor quality and were above the WHO permissible limit. Meeting water quality expectations rivers in OONP is important and expected to guard drinking water resources, promote recreational activities and offer a good enabling environment for wildlife. There were significant differences in all the physicochemical parameters of soil sampled except pH, K and textural class (Sand and Silt) while seasonal variation was observed in the levels of heavy metals in the soil (Cu, Zn,), water (Zn, Ni, Fe) and plants (Cu, Ni, Fe). The

bacteriological and mycological analyses of the water and faecal samples from this study further confirmed that the water from the sampled waterholes are unsafe for consumption as coliform counts were above the permissible limits recommended by WHO.The trend of heavy metal levels, its anthropogenic relation, seasonal variation and related physicochemical parameters observed in this study is a pointer to contamination of studied ecosystem with possible health implication on wildlife. These findings are of ultimate importance to wildlife species perpetuation and tourism potentials of OONP.

6.2 Recommendations

a. There is need for further heavy metal contamination studies to be carried out in the ranges (Sepeteri and Yemoso) that were not covered in this study so as to have a holistic data on heavy metal contamination in Old Oyo National Park.

b. There is need to carry out the study over time (continuous assessment) so as to monitor heavy metal deposition, accumulation and contamination in the park.

c. There is need to conduct further studies on the sediments of the rivers sampled so as to be able to assess heavy metal deposition over time.

d. Other environmental contaminants' studies (pesticides, phthalates, and so on) should also be carried out in OONP so as to have a detailed environmental contamination status of the park.

e. There is need for the management of OONP to embark and intensify efforts on a holistic conservation education and enlightenment programmes for the local / surrounding communities of the park so as to intimate them on the consequential effects of their activities on the park's ecosystem.

f. The use of metal stabilization (adsorbents) and bioremediation (phytoremediation) methods to remediate heavy metals from water and soil in OONP is hereby proffered.

Contribution to Knowledge

a) Cadmium toxicity was most significant in Old Oyo National Park.

b) The study provided baseline information on heavy metals levels in plant (leaves) species in Old Oyo National Park.

c) The study provided additional information on the physicochemical characteristics of soil and waterholes in Old Oyo National Park.

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APPENDIX

Table I: ANOVA of the heavy metals in the sampled waterholes of Old Oyo National Park

		Sum of Squares	df	Mean Square	F	Sig.
Cu	Between Groups	1.623	3	.541	19.609	.000
	Within Groups	1.876	68	.028		
	Total	3.498	71			
Zn	Between Groups	.117	3	.039	10.780	.000
	Within Groups	.246	68	.004		
	Total	.362	71			
Cr	Between Groups	.956	3	.319	5.821	.001
	Within Groups	3.724	68	.055		
	Total	4.680	71			
Pb	Between Groups	.340	3	.113	21.242	.000
	Within Groups	.363	68	.005		
	Total	.703	71			
Ni	Between Groups	.115	3	.038	21.634	.000
	Within Groups	.121	68	.002		
	Total	.236	71			
Cd	Between Groups	.075	3	.025	33.489	.000
	Within Groups	.050	68	.001		
	Total	.125	71			
Fe	Between Groups	509.589	3	169.863	26.789	.000
	Within Groups	431.175	68	6.341		
	Total	940.764	71			
Mn	Between Groups	3.547	3	1.182	12.566	.000
	Within Groups	6.398	68	.094		
	Total	9.945	71			

Table II: ANOVA of the heavy metals in the sampled soils of Old Oyo National Park

		Sum of Squares	df	Mean Square	F	Sig.
Cu	Between Groups	157459.310	3	52486.437	3.495	.018
	Within Groups	1561934.660	104	15018.603		
	Total	1719393.970	107			
Zn	Between Groups	7541.854	3	2513.951	14.998	.000
	Within Groups	17432.209	104	167.617		
	Total	24974.063	107			
Cr	Between Groups	2341.496	3	780.499	12.490	.000
	Within Groups	6498.941	104	62.490		
	Total	8840.437	107			
Fe	Between Groups	39801.414	3	13267.138	16.260	.000
	Within Groups	84858.542	104	815.948		
	Total	124659.956	107			
Pb	Between Groups	129.299	3	43.100	12.090	.000
	Within Groups	370.753	104	3.565		
	Total	500.052	107			
Ni	Between Groups	18.595	3	6.198	1.549	.206
	Within Groups	416.104	104	4.001		
	Total	434.699	107			
Cd	Between Groups	61.957	3	20.652	42.873	.000
	Within Groups	50.098	104	.482		
	Total	112.054	107			
Mn	Between Groups	89204.017	3	29734.672	15.024	.000
	Within Groups	205837.645	104	1979.208		
	Total	295041.662	107			

Table III: ANOVA of the heavy metals in the sampled plants of Old Oyo National Park

		Sum of Squares	df	Mean Square	F	Sig.
Cu	Between Groups	125.700	3	41.900	13.687	.000
	Within Groups	428.590	140	3.061		
	Total	554.290	143			
Zn	Between Groups	824.387	3	274.796	5.399	.002
	Within Groups	7125.735	140	50.898		
	Total	7950.122	143			
Cr	Between Groups	84.602	3	28.201	24.928	.000
	Within Groups	158.378	140	1.131		
	Total	242.980	143			
Pb	Between Groups	15.127	3	5.042	20.750	.000
	Within Groups	34.021	140	.243		
	Total	49.148	143			
Ni	Between Groups	7.691	3	2.564	8.562	.000
	Within Groups	41.920	140	.299		
	Total	49.611	143			
Cd	Between Groups	3.623	3	1.208	22.793	.000
	Within Groups	7.419	140	.053		
	Total	11.042	143			
Fe	Between Groups	7124.755	3	2374.918	117.902	.000
	Within Groups	2820.045	140	20.143		
	Total	9944.801	143			
Mn	Between Groups	275.326	3	91.775	15.313	.000
	Within Groups	839.071	140	5.993		
	Total	1114.396	143			

Table IV: ANOVA of the physicochemical parameters of the sampled waterholes of Old Oyo National Park

		Sum of Squares	df	Mean Square	F	Sig.
Amb Tmp	Between Groups	116.139	3	38.713	6.170	.001
	Within Groups	426.673	68	6.275		
	Total	542.812	71			
Sam. Tmp	Between Groups	268.668	3	89.556	22.474	.000
	Within Groups	270.968	68	3.985		
	Total	539.636	71			
pH	Between Groups	.193	3	.064	2.018	.120
	Within Groups	2.165	68	.032		
	Total	2.358	71			
EC	Between Groups	166162.163	3	55387.388	31.807	.000
	Within Groups	118413.185	68	1741.370		
	Total	284575.348	71			
Alkali	Between Groups	2171.142	3	723.714	3.074	.033
	Within Groups	16007.327	68	235.402		
	Total	18178.468	71			
TDS	Between Groups	130400.681	3	43466.894	45.256	.000
	Within Groups	65311.800	68	960.468		
	Total	195712.481	71			
TSS	Between Groups	3204025.203	3	1068008.401	13.104	.000
	Within Groups	5542049.712	68	81500.731		
	Total	8746074.915	71			
TS	Between Groups	3781230.238	3	1260410.079	14.184	.000
	Within Groups	6042782.962	68	88864.455		
	Total	9824013.200	71			

Nitrate	Between Groups	.558	3	.186	6.551	.001
	Within Groups	1.932	68	.028		
	Total	2.490	71			
Phosphate	Between Groups	.652	3	.217	28.551	.000
	Within Groups	.518	68	.008		
	Total	1.170	71			
Sulphate	Between Groups	2407145.765	3	802381.922	28.464	.000
	Within Groups	1916862.966	68	28189.161		
	Total	4324008.731	71			
Chloride	Between Groups	20.414	3	6.805	.108	.955
	Within Groups	4269.503	68	62.787		
	Total	4289.917	71			
DO	Between Groups	37.191	3	12.397	8.595	.000
	Within Groups	98.077	68	1.442		
	Total	135.268	71			
BOD	Between Groups	51.438	3	17.146	.256	.857
	Within Groups	4563.166	68	67.105		
	Total	4614.604	71			
COD	Between Groups	6946.526	3	2315.509	5.307	.002
	Within Groups	29666.937	68	436.278		
	Total	36613.463	71			

Table V: Correlation between analysed heavy metals (above permissible limit) and physicochemical parameters of sampled waterholesin Old Oyo National Park

		Cr	Pb	Ni	Cd	Fe	Mn
Cr	Pearson Correlation	1					
	Sig. (2-tailed)						
	N	24					
Pb	Pearson Correlation	.533**	1				
	Sig. (2-tailed)	.007					
	N	24	24				
Ni	Pearson Correlation	.506*	.750**	1			
	Sig. (2-tailed)	.012	.000				
	N	24	24	24			
Cd	Pearson Correlation	.581**	.776**	.706**	1		
	Sig. (2-tailed)	.003	.000	.000			
	N	24	24	24	24		
Fe	Pearson Correlation	.213	.342	.454*	.395	1	
	Sig. (2-tailed)	.318	.101	.026	.056		
	N	24	24	24	24	24	
Mn	Pearson Correlation	.696**	.701**	.641**	.728**	.273	1
	Sig. (2-tailed)	.000	.000	.001	.000	.196	
	N	24	24	24	24	24	24
pH	Pearson Correlation	.066	-.001	.060	-.199	-.521**	-.105
	Sig. (2-tailed)	.760	.995	.780	.351	.009	.625
	N	24	24	24	24	24	24
EC	Pearson Correlation	.210	-.049	-.264	.180	-.424*	.081
	Sig. (2-tailed)	.324	.819	.212	.399	.039	.705
	N	24	24	24	24	24	24

Alkalinity	Pearson Correlation	.477*	.093	.213	-.028	.315	.288
	Sig. (2-tailed)	.018	.665	.317	.897	.134	.173
	N	24	24	24	24	24	24
TDS	Pearson Correlation	.462*	.359	.404	.623**	.243	.565**
	Sig. (2-tailed)	.023	.085	.051	.001	.253	.004
	N	24	24	24	24	24	24
TSS	Pearson Correlation	.124	.441*	.053	.403	-.018	.288
	Sig. (2-tailed)	.563	.031	.805	.051	.932	.173
	N	24	24	24	24	24	24
TS	Pearson Correlation	.163	.440*	.061	.447*	-.037	.319
	Sig. (2-tailed)	.446	.031	.778	.028	.864	.128
	N	24	24	24	24	24	24
Nitrate	Pearson Correlation	-.040	-.193	.054	-.188	.150	-.315
	Sig. (2-tailed)	.853	.367	.802	.379	.483	.133
	N	24	24	24	24	24	24
Phosphate	Pearson Correlation	-.070	.430*	.379	.364	.592**	.297
	Sig. (2-tailed)	.746	.036	.068	.080	.002	.159
	N	24	24	24	24	24	24
Sulphate	Pearson Correlation	-.277	-.489*	-.437*	-.447*	-.515*	-.444*
	Sig. (2-tailed)	.191	.015	.033	.029	.010	.030
	N	24	24	24	24	24	24
Chloride	Pearson Correlation	.008	.226	.092	.222	.214	.090
	Sig. (2-tailed)	.970	.288	.669	.297	.314	.677
	N	24	24	24	24	24	24
DO	Pearson Correlation	.038	.153	.057	-.060	.074	.124
	Sig. (2-tailed)	.861	.476	.791	.782	.732	.564
	N	24	24	24	24	24	24
BOD	Pearson Correlation	-.290	-.022	-.262	-.269	.011	-.157
	Sig. (2-tailed)	.169	.918	.216	.203	.958	.463

	N	24	24	24	24	24	24
	Pearson Correlation	-.225	.173	-.012	-.137	.144	-.170
COD	Sig. (2-tailed)	.292	.419	.956	.523	.503	.428
	N	24	24	24	24	24	24
	Pearson Correlation	.266	.210	.335	.085	.337	.074
Sample Temp	Sig. (2-tailed)	.209	.324	.110	.694	.108	.730
	N	24	24	24	24	24	24

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed)

Table VI: ANOVA of the physicochemical parameters of the sampled soils of Old Oyo National Park

		Sum of Squares	df	Mean Square	F	Sig.
pH	Between Groups	.174	3	.058	.172	.915
	Within Groups	10.818	32	.338		
	Total	10.992	35			
SOC	Between Groups	38835.889	3	12945.296	2.965	.047
	Within Groups	139727.333	32	4366.479		
	Total	178563.222	35			
SOM	Between Groups	4.550	3	1.517	3.089	.041
	Within Groups	15.710	32	.491		
	Total	20.260	35			
N	Between Groups	.046	3	.015	3.754	.020
	Within Groups	.132	32	.004		
	Total	.178	35			
A.P	Between Groups	27.156	3	9.052	1.297	.292
	Within Groups	223.338	32	6.979		
	Total	250.494	35			
EA	Between Groups	2.080	3	.693	2.095	.120
	Within Groups	10.587	32	.331		
	Total	12.666	35			
Ca	Between Groups	59.081	3	19.694	3.975	.016
	Within Groups	158.557	32	4.955		
	Total	217.638	35			
Mg	Between Groups	.366	3	.122	2.782	.057
	Within Groups	1.405	32	.044		
	Total	1.771	35			
K	Between Groups	.029	3	.010	.341	.796
	Within Groups	.896	32	.028		
	Total	.924	35			
Na	Between Groups	.025	3	.008	.904	.450
	Within Groups	.300	32	.009		
	Total	.326	35			
TEB	Between Groups	69.084	3	23.028	4.620	.009
	Within Groups	159.516	32	4.985		
	Total	228.600	35			
	Between Groups	49.296	3	16.432	3.278	.033

ECEC	Within Groups	160.414	32	5.013		
	Total	209.709	35			
	Between Groups	527.521	3	175.840	2.409	.085
BS	Within Groups	2335.366	32	72.980		
	Total	2862.887	35			
	Between Groups	1801.222	3	600.407	.288	.834
Sand	Within Groups	66776.000	32	2086.750		
	Total	68577.222	35			
	Between Groups	430.444	3	143.481	.077	.972
Silt	Within Groups	59879.111	32	1871.222		
	Total	60309.556	35			
	Between Groups	3604.111	3	1201.370	1.107	.361
Clay	Within Groups	34732.444	32	1085.389		
	Total	38336.556	35			