BEHAVIOUR OF MICROPOLLUTANTS IN SOILS AND THEIR INTERACTIONS WITH SOIL CONSTITUENTS IN THE VICINITY OF DYE PITS, ZARIA CITY, NIGERIA

BY

MURSHIDA ADEJOKE RAMADAN

DEPARTMENT OF BIOLOGICAL SCIENCES, FACULTY OF SCIENCE
AHMADU BELLO UNIVERSITY, ZARIA
NIGERIA

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BY

Murshida Adejoke RAMADAN (B.Sc A.B.U. 2009)
(M.Sc/Scie/12510/2010-2011)

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DEPARTMENT OF BIOLOGICAL SCIENCES, FACULTY OF SCIENCE
AHMADU BELLO UNIVERSITY, ZARIA
NIGERIA

MARCH, 2015.

DECLARATION

I hereby declare that the work in this thesis entitled "BEHAVIOUR OF MICRO POLLUTANTS IN SOILS AND THEIR INTERACTIONS WITH SOIL CONSTITUENTS IN THE VICINITY OF DYE PITS, ZARIA CITY, NIGERIA" was carried out by me in the Department of Biological Sciences under the supervision of Dr. Nafiu Abdu and Prof. S. A. Abdullahi . The information derived from the literature has been duly acknowledged in the text and list of references provided. No part of this thesis has previously been presented for another degree or diploma at this university or any other institution. All sources of information are specifically acknowledged by means of references.

Murshida Adejoke RAMADAN _____ _____

Signature Date

CERTIFICATION

This thesis entitled "BEHAVIOUR OF MICRO POLLUTANTS IN SOIL AND THEIR INTERACTION WITH SOIL CONSTITUENTS IN THE VICINITY OF DYE PITS, ZARIA CITY, NIGERIA" by Murshida Adejoke RAMADAN, meets the regulations governing the award of the degree of Master of science, Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literary presentation.

Dr. Nafiu Abdu Chairman, Supervisory Committee Department of Soil Science, Ahmadu Bello University, Zaria.	_____ Signature	_____ Date
Prof. S. A. Abdullahi Member, Supervisory Committee Department of Biological Sciences, Ahmadu Bello University, Zaria.	_____ Signature	_____ Date
Prof. A. K. Adamu Head, Department of Biological Sciences, Ahmadu Bello University, Zaria.	_____ Signature	_____ Date
Prof. A. Z. Hassan Dean, School of Postgraduate Studies, Ahmadu Bello University, Zaria.	_____ Signature	_____ Date

DEDICATION

I dedicate this thesis to Almighty Allah and also to the memory of my late parents Alhaji Ismail Ramadan Balogun and Hajia Aisha Ismail. May Allah grant them eternal rest amin.

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ABSTRACT

The behaviour of micropollutants in soil and their interactions with soil constituents was investigated under the influence of textile dye waste pits in Zaria city. A total of 90 soil samples were collected from six different dye sites. The physicochemical properties were analyzed by on standard analytical procedures. The soil microbial biomass carbon and nitrogen was estimated by the chloroform fumigation method, colony count was used for microbial enumeration, while the distribution of lead, cadmium, copper and chromium was determined after triple acid digestion. The sequential extraction procedure was used to fractionate the soil into six operationally defined species. The pH of the contaminated samples ranged from 8.59-9.98 which indicate alkalinity. Organic carbon ranged from 0.29 – 0.58 g/kg, total nitrogen ranged from 0.10 – 0.16 g/kg, available phosphorus ranged from 8.10 - 12.24 g/kg. Microbial biomass carbon and nitrogen ranged from 170.82 - 334.44 mg/kg, and 16.89 - 37.28 mg/kg respectively. Microbial enumeration showed the abundance of bacterial and fungal counts, this is an indication that soils with the highest alkalinity level had the lowest MBC, MBN, bacterial and fungal counts. The dominant genera of bacterial and fungal counts were *Bacillus* and *Aspergillus*. Total concentrations of Lead, Chromium and Cadmium recorded maximum values of 181.57, 228.57 and 40.55 mg kg^{-1}, respectively. However, the concentration of Copper was within acceptable limit of 63 mg kg^{-1} whereas concentrations of Pb, Cd, and Cr were above the threshold levels (70, 6.4 and1.4 mg kg^{-1}). No uniform trend was observed horizontally, although, metal concentrations increased down the soil profile; these were attributed to facilitated transport and ground-water enrichment. Speciation of the heavy metals constituted that 50-80% of the metals that were associated with the resistant soil fraction; thus represent heavy metals held in the crystal lattices of minerals with strong bindings affinity and consequently are not

easily released into the environment. However, the effect of chemicals in the dye effluent, under the influence of pH, could release these metals into the soil-exchange site thereby increasing the concentrations of labile Cd, Cr and Pb in soils and consequently aggravate the potential hazard for the redistribution and subsequent translocation of these metals into the food chain and aquifer. It can be concluded that soil from the dye pits in Zaria city are highly coloured, foul smelling, alkaline in nature and contained trace metal ions where concentrations were higher than minimum allowable contaminant levels. The effluents from the dye areas were the major source of pollutants impacting on the soil properties in the study area. Thus, there is need for treatment of dye effluent by the dyers before discharge into the environment.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Soil

Soil is a vital part of the natural environment. It is just as important as plants, animals, rocks, landforms, and rivers. It influences the distribution of plant species and provides a habitat for a wide range of organisms (Ashman and Puri, 2002). It controls the flow of water and chemical substances between the atmosphere and the earth, and acts as both a source and sink for contaminants and pollutants in the atmosphere (Ashman and Puri, 2002). Soil also acts as historical medium concealing archaeological artifacts and paleontological materials (Ashman and Puri, 2002). Soil is a complex ecosystem where living organisms play a key role in the maintenance of its properties. Soil biota comprises a huge diversity of organisms belonging to different taxonomic and physiologic groups, which interact at different levels within the community (Seklemova, E., Pavlova, A. and Kovacheva, K., 2001).

Soil contamination is a condition that occur when soil loses its biophysical and biochemical properties due to anthropogenic and/or natural influence in the soil environment. Anthropogenic influence includes chemical contaminants which adversely affect the soil by altering its physicochemical properties thereby making it imperfect for crop bearing. The excessive use of chemicals also adversely affects soil microbial diversity (Jessic*a*, F.C.L., Amvrossios, C. and Micheal, R. W., 2011). Contaminants in soil can easily be taken up by plants along with nutrients contained in the soil which when consume by man may pose a health hazard (Abdu, N., Abdukadir, A., Agbenin, J. O. and Buerkert, A., 2011a).

Increasing industrialization and urbanization leads to risk of environmental pollution. The discharge of toxic effluents from various industries adversely affects water

resources, soil fertility, aquatic organisms and ecosystem integrity. Activities by humans are greatly altering the ecosystem worldwide at unprecedented rates and leading to accelerated loss of biodiversity and environmental pollution (Raven, 2002). This was exactly the circumstance taking place in developing worlds. For instance, the mining industry, a primary contributor to the rapid economic boost, produced a huge area of wasteland and caused serious environmental problems in China (Li, 2006). In Africa, Over 50 percent of the population is rural and directly reliant on locally grown food (Brown, 2001). This farming can be sustainable if farmers invest in fertilizer, and in soil and water conservation, the persistent farmland usage further expose this valuable resource to degradation (Brown, 2001*).* In a developing country like Nigeria where there is often poor enforcement of waste treatment and disposal regulations, waste are disposed indiscriminately which increase the pollution level (Ogungbemi, 2002).

Intensification of agriculture and manufacturing industries has resulted in increased release of a wide range of xenobiotic compounds to the environment (Kamaludeen, S. P., Arunkumar, K. R., Avudainayagam, S., and Ramasamy, K., 2003). Excess loading of hazardous waste has led to scarcity of clean water and disturbances of soil thus limiting crop production and endangering human and animal survival (Kamaludeen *et al*., 2003).

Many substances are manufactured and used, and eventually find their way into the environment at very low concentrations, becoming organic micropollutants, of which there are now estimated to be 100,000, most of which are toxic to the environment. These include pesticides, medicines, cosmetics, flame retardants, perfumes, waterproofing and spot repelling treatments, plastifiers, insolating foams, etc. that do not degrade in the environment. A few persistent organic pollutants are now controlled or banned by international treaty, but most are still not regulated in any way. Dissolved

substances in industrial effluents alter the chemical and biological status of the soil and water, which may affect growth and productivity of plant. Effluents also affect the susceptibility of plant to various pathogens (Khan and Jain, 1995). Among various industries, the textile and dyeing industries discharge large volume of waste water after the dyeing process. Effluents from dyeing industries have been reported to alter the colour and qualities of soil and water body posing serious environmental problems (Khan and Jain, 1995). The industrial effluents consist of organic compounds along with inorganic complexes and other non biodegradable substances.

Heavy metals particularly, lead (Pb), chromium (Cr), cadmium (Cd) and copper (Cu) are widely used for the production of colour pigments in textile dyes. These heavy metals which are transferred to the environment are potentially toxic and can bio-accumulate in the human body, aquatic life, natural water-bodies and also possibly trapped in the soil (Mathur, N., Bhatnagar, P. and Bakre, P., 2005). Heavy metal concentrations in soil are associated with biological and geochemical cycles and are influenced by anthropogenic activities such as agricultural practices, industrial activities and waste disposal methods (Eja, M.E., Ogd, O.R. and Arikpo, O.E., 2003).

Dyeing is the process of imparting colors to a textile material through a dye (colour). Dyes are obtained from flowers, nuts, berries and other forms of vegetables and plants as well as from animal and mineral sources. These are known as natural dyes. They comprise one of the major groups of chemicals besides fertilizers, pharmaceuticals and petrochemicals. During ancient times, people used dyes from natural resources like Tesu flowers, to make their clothes bright and colorful. Likewise, indigo, logwood, madder, etc. are natural dyes originating from plants; while Tyrian purple, kermes, cochineal etc. are natural dyes of animal origin. Such dyes were almost biodegradable, therefore not hazardous. However, these dyes are very expensive and require a lot of

labour in their manufacture and use. This has led to the use of preferably cheaper and easily available dye sources, such as chemicals.

The other class of dyes is known as synthetic dyes. These are based on a particular type of chemical composition. Some of these dyes are- acid (Anionic) dyes, basic (Cationic) dyes, neutral- premetalized dyes, sulfur dyes, vat dyes, reactive dyes, pigment dyes etc. Textile industries are the major users of dyes in the world (Faraco *et al*., 2009). A huge fraction of dyes are discharged out from the textile industries, causing serious damage to the environment The wastewater effluent from the textile industry is considered as one of the most polluting among all industries. The environmental and health effects of wastewater from textile industry have been a subject of scientific scrutiny over a long time. The chemical nature of the waste from textile industry ranges from organochloride based waste pesticides to heavy metals associated with dyes and dying process (Faraco, V., Pezzella, C., Miele, A., Giardina and Sannia, G., 2009). For a given metal the toxicity varies widely depending on the allotrope or oxidation state of metal. The environmental risks of potentially toxic metals in soils are strongly determined by their most available fractions, rather than by the total amounts. These available fractions are often estimated by extraction with solutions of various abilities to dissolve the soil metals (Mathur *et al.,* 2005: Abdu, N., Abdukadir, A., Agbenin, J. O. and Buerkert, A., 2012).

1.2 Statement of Research Problem

Dyeing activity is commonly practiced in Zaria city and their method of discharge of effluents may have effects on the characteristics of surrounding soil. Dyeing and the indiscriminate disposal of dye waste into the environment has effects on both soil and groundwater quality. Leaching of pollutants through soil due to their vertical movement

in the soil and eventual contamination of groundwater is an environmental concern. Some heavy metals contained in these effluents from the dye and related industries have been reported to be carcinogenic (Tamburlini, G., Ehrenstein, O. V. and Bertollini, R., 2002).

1.3 Justification

Activities such as farming, dyeing, animal grazing, and indiscriminate waste disposal increases soil and environmental pollution. These factors may have a negative impact on the quality of soil and groundwater, thereby affecting the health status of the populace. Dyeing is a very important economic activity among Zaria city inhabitants, the improper disposal of dye waste would have adverse effects on the ecosystem because heavy metal and other chemical contaminants leach from these dye wastes into the soil. The activity of heavy metals in soil matrix and is dependent on the chemical species of the metals present. Thus, the knowledge of the chemical speciation of heavy metals provides information on the bioavailability and toxicity of such metals (Abdu, 2010). The data on the effects of dye waste on soil chemical indicators and micro pollutants in the soil of Zaria city, northern Nigeria is lacking or under reported. This research that was designed to provide such baseline data which would provide information that will ascertain the contamination problems associated with dye pits effluents that may confront the inhabitants surrounding dye pit and may be used for appropriate protection remedies.

1.4 Aim of the Research

This research was designed to ascertain the behaviour of micro pollutants in soil and their interaction with soil constituents in the vicinity of dye pits in Zaria City, Nigeria.

1.5 Objectives

To determine:

i. The physicochemical properties of the soil surrounding the dye pits

ii. Microbial enumeration and microbial biomass in the soil influenced by the dye waste.

iii. The spatial and geochemical distribution of Cr, Pb, Cu and Cd in the soil within the vicinity of a dye pits.

iv. The influence of dye waste on the horizontal and vertical distribution of heavy metals in the soil.

1.6 Research Hypotheses

i. Dye pits wastes have no significant effects on the physicochemical properties of the soil surroundings.

ii. Dye waste does not influence the microbial enumeration and microbial biomass of the soil significantly.

iii. The spatial distributions and geochemical species of heavy metals in the soil are not influenced by dye waste contamination.

iv. The influence of dye waste has no significant effect on the horizontal and Vertical distribution of these heavy metals constituents in the soil.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Environmental Pollution

Pollution is defined in various ways. It is considered as the release of unwanted substances to the environment by man in quantities that damage either the health or the resources itself (Varies, W., Romkens, P.F. and Schutze, G., 2007). Environmental protection and rational use of natural resources and other industrial raw materials has become an important sphere of mankind's advancement in the 20th century. Mankind's demand for resources and raw materials has intensified the ecological and economic contradictions in the industries. This wide spread industrialization in urban areas has drastically reduced land area for waste disposal. Soil and streams have been used for multifarious purposes including waste disposal. Our careless dumping of wastes has affected these precious resources. Environmental pollution has become a major concern of developing countries in the last few decades.

There is a growing sense of global urgency regarding the pollution of our environment by an array of chemicals used in various activities (Varies *et al*., 2007). Pollution of water and soils by heavy metals is an emerging problem in urban industrialized countries. Since the advent of development through mining and smelting, metallurgical industries, sewage, warfare, and tanning the survival of plants and animals are much affected. Soil, water and biodiversity are fundamental elements of ecosystem and are the subject of many agrarian, ecological, biological and hydrological studies. Large quantities of chemical elements infiltrate the water running off cultivated soils thereby entering the animal and human food chain. The quality of life on earth is inextricably linked to overall quality in the environment. Currently there are two fundamental pollution related problems, the disposal of large quantities of wastes that are continually

being produced and the removal of toxic compounds that have been accumulating at dump sites in the soils and in water system over the last few decades.

Industrial pollution is one of the problems presently facing Nigeria and several efforts are being vigorously pursued to control it in various industries spanning length and breadth of the country to see that Nigerians live is a disease free environment. Effluent generated by the industries is one of the sources of pollution.

Contaminated air, soil, and water by effluents from the industries are associated with heavy disease burden (WHO, 2002) and this could be part of the reasons for the current shorter life expectancy in the country (WHO, 2003) when compared to the developed nations. Environmental pollution caused by heavy metals is increasing along with the increase in the usage of chemicals in industry and agriculture. Such pollution is apparent in streams and lakes and in groundwater which is replenished directly from surface water (Huget, N. F., Bosch, C., Lourencetti, C., Nadal, M., Schumacher, M., Grimalt, J. O. and Domeingo, J. L., 2009).

2.2 Micropollutants in the Environment

Micro-pollutants are chemicals of great concern because of their ability to potentially cause adverse effects in organisms at concentrations as low as a few ng/L. Micro-pollutants are found almost everywhere on earth, including water bodies, soils and human food. The main groups of micro-pollutants are dyes, pharmaceuticals, personal care products, pesticides and industrial chemicals, released by industry, households, or agriculture. They enter the environment and spread throughout the water ecosystem. Although micro-pollutants may be partly degraded in the sewage treatment plant or in the water bodies, they are usually not completely removed. After being taken up by aquatic organisms or humans via contaminated water or food, they are transported to

different tissues within the organism. Depending on their properties and the biology of the target species, they may bio-accumulate, metabolize or cause adverse effects. These effects may translate into alterations on a higher biological level such as disruption of the hormone system, followed by impacts on reproduction, etc. Eventually, effects may translate into other compartments of the ecosystem.

In contrast, macropollutants are compounds occurring in greater amounts (μg/L-mg/L) and include acids, salts, nutrients, and organic matter. However, a clear distinction between 'macro' and 'micro' cannot be made since classification also depends on the actual site and situation.

Micropollutants have been detected in surface waters in several European countries (Kreuzinger, 2002; Andersen, H., Siegrist, H., Halling- Sorensen, B. and Ternes, T., 2003) and they are of increasing importance in water pollution control. In particular, the role of chemicals that are suspected of having an impact on the hormonal systems of humans and wildlife, i.e. endocrine-disrupting compounds (EDC) and other micro-pollutants such as pharmaceutical compounds has to be emphasized. It is thought that endocrine-disrupting compounds and pharmaceutical residues enter rivers, streams and surface waters through the effluents and residual sludge from wastewater treatment plants (WWTPs).

2.3 Industrialization

Since the beginning of the industrial evolution, pollution of the biosphere with toxic metals has accelerated dramatically. Increasing industrialization and population develops the standard of living, which results in highly contaminated atmosphere due to drainage and wastage from these industries (Tiwari, K. K., Dwivedi, S., Mishra, S., Srivastava, S., Tripathi, R.D., Singh, W.K. and Chakraborty, S., 2008). Rapid

industrialization plays an important role in polluting the environment and causes severe degradation in pedosphere, hydrosphere and atmosphere. Water used in industries creates a waste that has potential hazard for our environment because of the introduction of various contaminants such as heavy metals into soil and water resources (Azumi and Bichi, 2010).

Environmental contamination with metals through industrial wastes is one of the major health concerns of developing countries. Metal pollutants can easily enter the food chain if heavy metals contaminated soils are used for the production of crops (Principi, P., Villa, F., Bernasconi, M. and Zanardini, E., 2006). The accumulation of metals in an aquatic environment has direct consequences to man and ecosystem. The release of pollutants differs from industry to industry. The waste from the pulp industry mainly contain carbohydrates, textile industry contain dyes, plating industry contain nickel and leather tanning wastes contain mainly chromium, zinc, copper, suphides, carbonates, sodium and many other toxic organic compounds and inorganic compounds (Nouri, J., Khorasani, N., Lorestani, B., Karami, M., Hassani, A. H. and Yousefi, N., 2009). The process of tanning involves the use of large amounts of freshwater and various chemicals. Every 10 kg of raw skins tanned require about 350 litres of fresh water.

Various chemicals used in tanning are lime, sodium bicarbonate, common salt, sodium sulphate, chrome sulphate, fat liquors, vegetable oils and dyes. The wastewater discharged for 100 kg of skins and hides processing, varies from 3000 litres to 3200 litres. The largest polluting material in the tanning industry which was very difficult to rid off is common salt.

2.4 Concept of Dye Activities

Dyeing is a combined process of bleaching and colouring, which generates huge volumes of wastewaters and results in environmental degradation. More than 100,000 commercial dyes are available to textile industries worldwide with over 700,000 tons of commercial dyes being produced annually (Macmullan, G., Meehan, C., Conneely, A., Kirby, N., Robinson, T., Nigam, P., Banat, I. M., Marchant, R. and Smyth, W.F., 2001). Dyes containing azo groups are one of the largest classes of commercial dyes used in textile industry. Azo compounds are compounds bearing the functional group R-N=N-R', in which R and R' can be either aryl or alkyl. The N=N group is called an azo group. Therefore, they are used as dyes, and are commonly known as azo dyes, an example of which is Disperse Orange. Some azo compounds, such as methyl orange are used as acid-base indicators due to the different colors of their acid and salt forms. Azo dyes in purified form are seldom directly mutagenic or carcinogenic, except for some few with free amino groups (Sugumar and Sandhya, 2010).

Azo dyes represent the largest class of dyes applied in textile processing. The degree of fixation of dyes to fabrics is never complete, resulting in dye-bearing effluents. The removal of dyes from these effluents is desired, not only for aesthetic reasons, but also because many azo dyes and their breakdown products are toxic to aquatic life and are mutagenic to humans (Lazaridis and Keenan, 2010).

It is the largest group of dyes, with -N=N- as a chromophore in an aromatic system. Depending upon the number of azo-groups present they are called as monazo, disazo, trisazo, tetrakisazo and polyazo dyes. Diazotisation of a primary amine, in presence of HCl and $NaNO_2$ at freezing temperature, produces a diazonium salt which in turn coupled with aromatic compounds, produces an azo-dye. Azo pigments are colourless particles (typically earths or clays), which have been coloured using an azo compound

(Chaube, P., Indurkar, H. and Moghe, S., 2010). The problem of environmental pollution is increasing day by day due to the release of xenobiotic substances into water, soil and air. These substances include organic compounds (pesticides, dyes, polymers etc.) and heavy metal ions. The damage caused by these pollutants to plants, animals and humans cannot be neglected and hence strategies must be developed to solve the problem of environmental pollution on the priority basis. Removal of dyes from the effluents or their degradation before discharge is a great environmental challenge for the industries (Baldrian and Gabriel, 2003).

Zaria is a major city in Kaduna state which is one of the most developed states in northern Nigeria and dyeing activities are some of its dominating activities. It is on record that the first textile industry in Nigeria was established in Kaduna (Jibrin, 2004). This could be a reason why dyeing activities is also a very important economic activity among Zaria city inhabitants.

2.5 Effect of Heavy Metals in the Environment

Heavy metal contamination of soil results from anthropogenic activities such as mining, smelting procedures and agriculture as well as natural activities (Navarro, M.C., Perez-Sirvent, C., Martinez- Sanchez, M. J., Vidal, J., Tovar, P.J. and Bech, J., 2008). Chemical and metallurgical industries are the most important sources of heavy metals in the environment. The metals are classified as "heavy metals" if in their standard state they have a specific gravity of more than 5 g/cm^3. There are known sixty heavy metals. Heavy metals get accumulated in time in soils and plants and could have a negative influence on physiological activities of plants (e.g. photosynthesis, gaseous exchange, and nutrient absorption), determining the reductions in plant growth, dry matter accumulation and yield. In small concentrations, the traces of some heavy metals in

plants or animals are not toxic (Cortes, O. E. J., Barbosa, L. A. D., Kiperstok, A., 2003). The most commonly occurring metals at the discharge sites of textile industries in Tamil Nadu India are lead, chromium, arsenic, zinc, cadmium, copper, and mercury. Presence of these metals in the water and soil may cause serious threat to human health and ecological systems (Sundar, K., Vidya, R., Mukherjee, A. and Chandrasekara, M., 2010). Lead, cadmium and mercury are exceptions; they are toxic even in very low concentrations. Every 1000 kg of "normal soil" contains 200 g chromium, 80 g nickel, 16 g lead, 0.5 g mercury and 0.2 g cadmium, theoretically. Monitoring the endangerment of soil with heavy metals is of interest due to their influence on ground and surface water and also on plants, animals and humans (Korashy and Elkadi, 2008).

Some heavy metals such as Cu, Cd, Pd and Cr are important for proper functioning of biological systems but their deficiency or excess could lead to a number of disorders (Ward, 1995). Industrial effluents discharged from the textile and tannery industries contain a higher amount of metals especially chromium, copper and cadmium. These effluents released on the land as well as dumped in to the surface water which ultimately leaches to groundwater and lead to contamination due to accumulation of toxic metallic components and resulted in a series of well documented problems in living beings (Malarkodi, M., Krisnasamy, R. Kmaraperumal, R. and Chitdeshwari, T., 2007). Hence, industrial effluents offer a wide scope of environmental problems and health hazards are becoming more complex and critical not only in developing countries like India but also in developed countries.

The toxicity and potential mutagenity of heavy metals, such as arsenic, lead, chromium, cadmium, copper, nickel and zinc in the environment have been well established. According to the United States Environmental Protection Agency (USEPA, 2005). There are over 200,000 heavy-metal-contaminated sites in the United States that require

urgent cleanup to protect public health and the environment. Problem of pollution by metals have aggravated and affected the ecological balance and caused serious health hazards because of the release on land as well as dumping on the surface water.

Heavy metals used in various industrial activities find their way into the physiological system of the living being. Exposure to heavy metals results in acute and chronic toxicity. The functions of kidney, liver and lungs are mainly affected by these metals (Alsaleh, I., Shinwari, N., Mashhour, A., Mohamed, G.E.D., Ghosh, M.A., Shamonasi, Z. and AL Naseer, A., 2006). The presence of heavy metals in industrial and urban waste water is one of the main causes of water and soil pollution (Wang, H., Su, J. Q., Zheng, X. W., Tian, Y., Xiong, X. J.and Zheng, T. L., 2009).

Heavy metals are ubiquitous environmental contaminants in an industrialized society. Concern over the possible health and ecosystem effects of heavy metals has been increased in recent years. Tremendous increase in the use of heavy metals over the past decades has inevitability resulted in an increased flux of metallic substances in the environment. Some metal ions are cumulative poisons capable of being assimilated and stored in the tissues of organisms causing noticeable adverse physiological effects. Soil pollution by metals is essentially different from air or water pollution because the persistence of heavy metals in soil is reportedly much longer than in other compartments of the biosphere. Removal of heavy metals from polluted soil is difficult. Once deposited on the soil certain metals such as lead and chromium may be virtually permanent (Okeyode and Moshood, 2010). Heavy metals emitted either from anthropogenic or natural activities can disperse in environment and may ultimately get deposited in the soil. Plants growing in such areas may absorb heavy metals in their parts.

2.6 Health Risk Assessment from Heavy Metal

The release of these heavy metals poses a significant threat to the environment and public health because of their toxicity, bioaccumulation in the food chain and persistence in nature. Heavy metals can pose health hazards if their concentration exceeds allowable limits. The ever increasing pressure of over exploitation of natural resources has affected severely the quality of the environment. Environmental pollution is becoming the global problem in which pollution is an important issue as water is used directly for various purposes. The disposal of reactive dyes into the environment causes serious damage as they intensely affect the photosynthetic activity of hydrophytes by limiting the light penetration and their breakdown products may be toxic to some aquatic organisms (Wang *et al*., 2009). It also affects water bodies, ecosystem integrity, soil fertility and plant growth. The azo dyes are becoming a great concern due to their visible color, biorecalcitrance and toxicity to animals and humans.

The microbial metabolic cleavage of azo linkages in the azo dyes results in free aromatic amines that are possibly toxic, mutagenic or carcinogenic and causes serious health hazard in many life forms (He, Z. L., Zhang, M.K., Calvert, D.V., Stoffella, P.J., Yong, X. E. and Yu, S., 2004; Khadijah, 2009). During the past 20 years, a number of studies have examined the possibility that occupational exposure to hazardous chemical substances increases the risk for various diseases. The incidence of environmental exposures on the general status of health has been increasingly acknowledged for numerous diseases. The industrious\ hazardous waste may show effects in terms of death and morbidity. This may manifest as respiratory diseases, skin reactions, allergies, diminution of vision, corneal opacity, abortion, and malformation of pregnancy, stunted growth, neurological disorders, mental depression, psychiatric changes, altered immune response, chromosomal aberrations and cancer. Health related studies have shown that

excessive intake of toxic trace metals results in neurological and cardiovascular diseases as well as renal dysfunction (Mehra and Juneja, 2005). It is understood through documented evidence that the primary pathways of toxic metal accumulation in humans are through the ingestion of contaminated water and food. Wastes may pose a problem to human health either through drinking water or indirectly through food chain or via fish .Approximately 1.2 billion people in developing nations lack clean water because most household and industrial wastes are dumped into rivers and lakes without treatment contributing to many waterborne diseases in humans (Branco, R., Alpoin, M.C. and Morias, P.V., 2005). Environmental changes including increased water pollution have fostered much of the increase and high incidence of malaria (Branco *et al*., 2005).

Despite the toxicity of the effluents, the microbial flora of tannery wastes was relatively rich with the organisms such as bacteria, yeast, algae, protozoa and fungi causing irritation and corrosion of the skin and respiratory tract.

Hexavalent chromium is toxic and mutagenic to most organisms and is known to cause lung carcinoma in human beings. The exposure of chemicals like chromium, pentachlorophenol and other toxic pollutants increases the risk of dermatitis, ulcer, nasal septum, perforation and lung cancer (Branco *et al*., 2005).

2.7 Bioavailability and Mobility of Heavy Metal

Understanding the behaviour, movement, retention, mobilization and dynamic equilibria of heavy metals in a heterogeneous system like a soil is imperative to characterize its bioavailability and mobility and possible food chain contamination (Gomes, P. C., Fontes, M.P.F., da Silva, A.G., Mendonca, E.de S. and Netto, R.A., 2001). Trace metal transport and availability in a competitive heterogeneous system between different soil

components is a function of the interactions of the different chemical species of such metals present in the system, the soil conditions and the prevailing environmental conditions and not only a function of total metal content in the soil-solution or solid phase (He *et al*., 2004). Activity of heavy metals in a complex soil matrix is dependent on the chemical species of the metals present. Thus, knowledge about the chemical speciation of heavy metals provides information on the bioavailability and toxicity of such metals. The plant available heavy metals are the water soluble species which cause damage to human health through consumption of contaminated crops.

The total content of heavy metals is made up by their different forms (fractions), which can be related to chemical species, as well as to their different solubility and mobility in soil environment. Sequential extraction of elements is used to identify these fractions. The methods of sequential fractionation enable us to determine the geochemical species of these metals in soil and to estimate more precisely their availability and toxicity to trophic chain components. The geochemistry (solubility, mobility and availability) of heavy metals depend on: the value of pH, the content and type of iron and manganese compounds as well as the content of organic matter, carbonate content and clay minerals (He *et al*., 2004).

2.8 Microbial Biomass and Enumeration

The importance of microorganisms in ecosystem functioning has led to an increased interest in determining soil microbial biomass (Azam, F., Farooq, S. and Lodhi, V. A., 2003). Soil microorganisms constitute a source and sink for nutrients and are involved in numerous activities, such as transformation of Carbon (C), Nitrogen(N), Phosphorus(P) and Sulphur(S), degradation of xenobiotic organic compounds, formation of soil physical structure and enhancement of plants' nutrient uptake

(Seklemova *et al*., 2001). The soil microbial biomass is the active component of the soil organic pool, which is responsible for organic matter decomposition affecting soil nutrient content and, consequently, primary productivity in most biogeochemical processes in terrestrial ecosystems (Gregorich, E.G., Liang, B. C., Drury, C.F., Mackenzie, A.F., and McGill, W. B., 2000; Crecchio, C., Curci, M., Pellegrino, A., 2007; Haney, R. L., Franzluebbers, F. M., Hons, L.R., Hossner, A. J and Zuberer, D.A., 2001).

Soil microbial communities develop in response to constraints and pressures in their environment (physical, chemical, and biological). The chemical and biological constraints have been studied extensively (Bressan, M., Mougel, C., Dequiedt, S., 2008;Hackl, E., Zechmeister-Boltenstern, S., Bodrossy, L. and Sessitssch, A., 2004). In contrast, ways in which the physical environment of soil exerts control over community structure and diversity are more poorly understood. Non homogeneous distributions of bacteria are created by numerous environmental factors and have been observed at a range of spatial scales, from sub-centimeter to meter to kilometer or more (Fierer and Jackson, 2006; Cho and Tiedje, 2000). Micro-scale distribution is influenced by, among other factors, pore structure, chemical conditions and proximity to other bacterial taxa. Therefore, measuring microbial biomass is a valuable tool for understanding and predicting long-term effects on changes in land use and associated soil conditions (Sharma, P., Rai, S.C., Sharma, R. and Sharma, E., 2004).

2.9 Measures to Counter Dye Pollution

Textile industries are the major users of dyes in the world. A huge fraction of dyes are discharged from the textile industries, causing serious damage to the environment. Common treatment strategies of effluent waste generation and the disposal of waste

forms part of everyday lives which is more for industries especially tanneries because of the tremendous volume of waste and chemicals used. Remediation of these tannery wastes is of paramount importance since they damage the normal functioning of the ecosystem (Kirby, N., Marchant, R. and McMullan, G., 2000). To reduce the toxic effects of these chemical contaminants on soil, water, air and the atmosphere, various treatment procedures are widely employed.

These methods aim at reducing the toxicity of the metals before letting it into the land. The ability of the microorganisms to decolorize and metabolize dyes can be employed to treat the environment polluted by textile dyes. Most of the present research is focused on the degradation of azo dyes which is the most widely used. The biodegradation of other commercial dyes like phthalocyanines have also been recently addressed (Kirby *et al*., 2000). Nanotechnology, microbial technology, cycloning, flotation, micro flotation, electro flotation and filtration processes are some of the chemical methods for removing the toxic substances in the effluents to make them available for further practical uses. Continous flow and fixed film bioreactors were used for the reduction of chromium compounds. Batch reactors were also used to remove a particular metal from the effluent (Farooq, U., Kozinski, J. A., Khan, M. A. and Ather, M., 2010).

A modified batch reactor called sequencing batch reactor was also used for the purpose of contaminant removal. These conventional methods for removal of metal cause secondary and adverse effects on biological activities, soil structure and fertility. Biosorption is another effective and versatile method and can be easily adopted at low cost to remove heavy metals from large amount of industrial wastewaters. Recent studies have showed that heavy metals can be removed using biomaterials (Farooq *et al*., 2010). The use of plants for extraction of contaminants from the environment or for

lowering their toxicity defined as phytoremediation is yet another method for toxicity removal (Rai, 2010).

In the past few decades, there is an immense effort to develop a cost-effective and eco-friendly alternative to conventional waste treatment methods. Among all the technologies bioremediation has emerged as the most desirable approach to clean up the environment and to restore its original status (Rai, 2010).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Location and Description of Study Area

Zaria lies between latitude 11^{o} 03' 0" and 11^{o} 05' 0" N and longitude 7^{o} 41'0" and 7^{o} 42' 0" E and located on a plateau at altitude of about 2200 feet above sea level in center of Northern Nigeria and more than 400 miles (634.71km) away from the sea (Yahaya, O., Umoh, V.J., and Ameh, J.B., 2011).

It possesses a tropical continental climate with the tropical climate more pronounced during the dry season, especially in December and January. The city lies within a region which has a tropical savanna climate with distinct wet and dry seasons (Maiwada and Renne, 2007). The mean annual rainfall is 1060mm (Owonubi, J.J., Abdulmumin, S., Malgwi, B and Mu'azu, S.,1991).

The total population of Zaria region according to the 2006 population census was 408,198 (Maiwada and Renne, 2007). Not only is Zaria a market town for the surrounding area, it is also the home of numerous artisans, from traditional crafts like leather work, dyeing and cap making, to tinkers, print shops and furniture makers. Zaria city is also the center of textile activities for over 200 years and has made elaborately hand-embroidered robes that are worn by men throughout Nigeria and West Africa (Maiwada and Renne, 2007).

3.2 Sample Sites

A total of five locations were selected amongst the dyeing centres with one location selected from a non-dyeing centre which serves as a control. A purposive sampling method was used and the locations selected are Kofar Kuyanbana (11^{o} 04' 623"N, 007^{o} 68' 951"E), Kofar Jatau (11^{o} 03' 340"N, 007^{o} 70' 690"E), Kusfa (11^{o} 02' 359"N, 007^{o}

71’ 700”E), Mabuga (11^{o} 05’ 089”N, 007^{o} 69’ 759”E) , Angwan Iya (11^{o} 04’ 620”N, 007^{o} 68’ 951”E) and Kofar Gayan (11^{o} 03’ 349”N, 007^{o} 70’ 709”E) (the control). These locations represent the major dyeing centers in Zaria city. Figure 1 shows the sampling locations in a map of Zaria city.

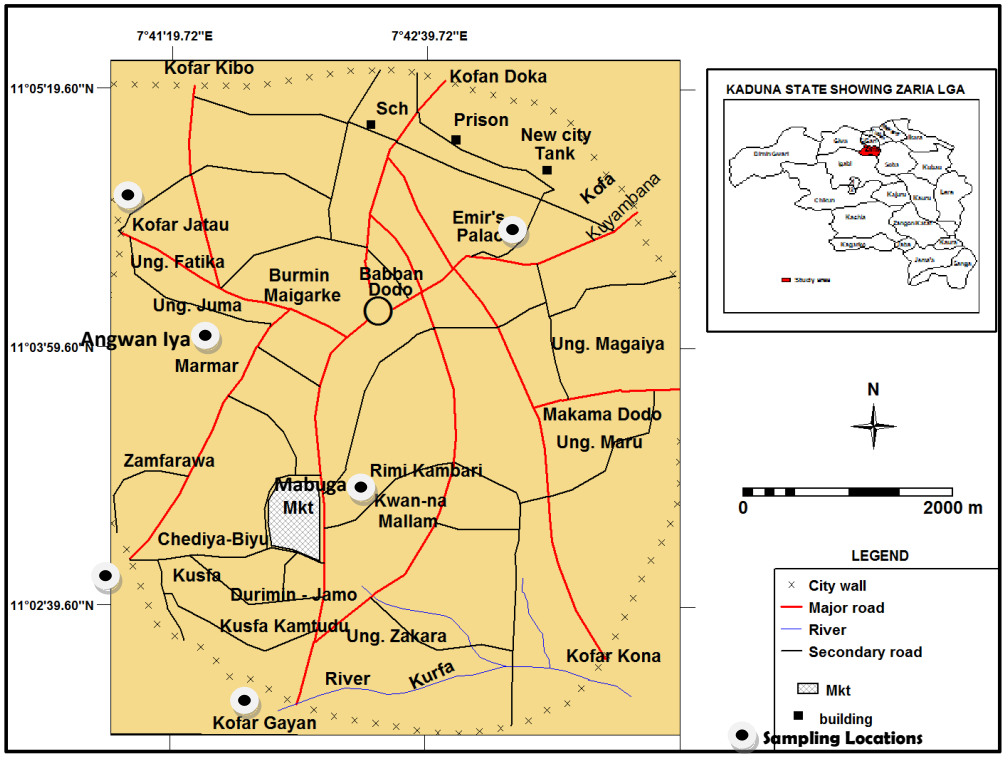


Figure 1: Map of Study Area Showing Sampling Locations

Source: Adapted and modified from Administrative Map of Kaduna State

3.3 Soil Sampling and Preparation

Soil samples were collected in the immediate vicinity of dye pits and dump sites of the dye waste. Composite samples consisting of 15 auger points were collected at three depths (0-15 cm, 15-30 and 30-45 cm). The samples were collected at five distances from the dye pit; immediately within the pit < 1 m, 5 m, 10 m, 20 m and 50 m from the dye pit. The soil samples were air dried, thoroughly homogenized, crushed with porcelain pestle and mortar and sieved through 2mm mesh for physicochemical analysis. Sampling was also done at a distance 1 km from the dye pits, to obtain additional control samples for comparism

3.4 Laboratory Analyses

3.4.1 Soil pH

Soil pH was determined in 1:2 soil-water suspension and in 0.01M $CaCl_2$ suspension using a glass electrode pH meter, Briefly, 10g of <2mm sieved soil was weighed into plastic beaker and 25ml of distilled water added gradually until the soil becomes wet. The soil suspension was then stirred thoroughly with a glass rod and the pH measured by inserting the glass electrode into the soil suspensions. The same procedure was repeated but using 0.01M $CaCl_2$ solution instead of water and the suspension was allowed to stand for 30 minutes with occasional stirring after the addition of $CaCl_2$.

3.4.2 Particle size analysis

The particle size distribution was determined by the standard hydrometer method as described by Gee and Bauder (1986).

Fifty grams (50g) of <2mm sieved soil samples was weighed into separate polythene bottle and 25 ml sodium hexametaphosphate (Calgon) solution and 400 ml tap water were added and shaken for 15 minutes on a mechanical shaker. The soil suspension was

transferred to a 1-L capacity cylinder and made up to the 1-L mark with distilled water. The suspension was stirred with a plunger. The temperature of the soil suspension was taken, then a hydrometer was inserted and measurement was taken after 40 seconds and after 2 hours for clay and silt respectively. Textural class calculation was made according to the relations below and the textural class obtained using the international soil Textural Triangle.

$$\% \, Clay = \frac{\text{corrected 2hrs reading} - \text{blank} \times 100}{weight}$$

$$\% \, Silt = \frac{\text{corrected 40 seconds reading} - \text{blank} \times 100}{weight} - (Clay)$$

$$\% \, Sand = \frac{100 - (\text{Clay} + \text{Silt})}{weight}$$

3.4.3 Organic carbon determination

The organic carbon of the dye pits soil was determined by the Walkley-Black dichromate wet oxidation method as described by Nelson and Sommers (1982).

One gram (1g) of finely soil sample was weighed into 250 ml conical flask then 10ml of 1N $K_2Cr_2O_7$ solution was added, the flask was swirled gently to disperse the soil. This was followed by addition of 20 ml concentrated sulphuric acid solution thoroughly mixed and the mixture was left for 30 minutes. The flask was allowed to cool down for two hours. 20ml of distilled water was then added and the whole suspension filtered through Whatman No. 1 filter paper after which three drops of ferroin indicator was added and titrated with 0.4N ferrous ammonium sulphate solution. When end point was reached, the colour change from green to red. Blank determination was made in the same manner without soil and the Organic carbon was calculated from the relationship below.

$$\%\ Organic\ carbon = \frac{(\text{blank titre} - \text{actual titre}) \times 0 \cdot 003 \times \text{m} \times \text{f}}{weight\ of\ soil\ sample}$$

Where m = concentration of ferrous ammonium sulphate, f = correction factor =

% OC×1·725 = % Organic matter.

3.4.4 Total nitrogen determination

The total nitrogen content of the soils was determined using the micro-Kjeldahl technique as described by Bremmer and Mulvaney (1982).

One gram of soil was weighed into 10ml of Kjeldahl digestion tube, 2-3 g of catalyst mixture (500g of $NaSO_4$ + 50g of $CuSO_4$ + few drops of selenium) was added, 10 ml concentrated H_2SO_4 was also added, the digestion tube was heated in a digesting block for 1-2 hours until frothing ceased and a clear digest was obtained. The digestion tube was allowed to cool and a little water was added with care and the content was washed into a 100 ml volumetric flask, after cooling it was made to mark. 10ml of the digest was pipetted into 250ml distillation flask. 10 milliliters of NaOH was added. The ammonia produced was trapped in 10ml of 2% boric acid and measured into a conical flask containing 2 drops of the indicator. The flask was introduced to the bottom of the distillation condenser in which 50 milliliters of the distillate was collected. The distillate was then titrated with 0·01N H_2SO_4 to an end point which turned from green to purple colour. Total Nitrogen was calculated from the relationship below

$$\%\ \text{N} = \frac{0 \cdot 014 \times (\text{T} - \text{B}) \times \text{NA} \times \text{Vol of digest}}{weight\ of\ soil \times aliqot\ distilled}$$

Where T = Actual titre, B= Blank titre, NA= Normality of the acid.

3.4.5 Available phosphorus determination

Available phosphorus was determined following the procedure described by IITA (1979) using the Bray- 1 extraction method (Bray and Kurtz, 1945). The phosphorus in

solution was determined colorimetrically by the modified single solution procedure using ascorbic acid (Murphy and Riley, 1962).

One gram of soil was weighed into a 5ml tube with stopper and 7 milliliters of P extractant (HCl and NH_4F) was added using pipette, the container was shaken for 3 minutes and the suspension was filtered into a dry 25 ml beaker followed by the addition of 10ml water and 4 ml of colour development solution which consist of ammonium molybdate, H_2SO_4 + potassium antimony tatarate, and ascorbic acid was added and mixed. After 10-15 minutes, reading was taken at 890 nm or 660 nm on a Spectronic 20 reader. The absorption was read off and standards were measured in the same way.

3.4.6 Exchange acidity (KCl – exchangeable Aluminuim)

Ten grams of soil was weighed in to a funnel fitted with a filter paper, 100 ml of 1N KCl was used to leach the soil gradually in not less than 2 hrs. The leachate was collected in 100 ml volumetric flask and made to volume with 1N KCl and mixed thoroughly. Total exchange acidity (H+Al) was determined by titration of the extract with standard NaOH solution using 3-4 drops phenolphthalein (Thomas, 1982).

3.4.7 Exchangeable bases determination

Ten grams of 2 mm sieved soil was weighed in to a 100 cm^3 volumetric flask; the soil in the funnel was leached with 1N ammonium acetate solution (pH 7) to a volume of 100 cm^3. Leaching was done for about 2 hours with about 10 ml at each washing, the funnel was removed after leaching with the filter paper ,the flask was corked and shaken ,the concentration of Na and K in the leachate was determined using flame emission photometer and AAS for Mg and Ca. Black (1965).

3.4.8 Available heavy metals (Cu, Cd, Pb and Cr) determination

The 0.1M HCl extraction method as described by IITA (1979) was used to determine available heavy metals. Five grams of soil sample was shaken in 50 ml of 0.1M HCl for 30 minutes and centrifuged. The concentration of Cu, Cd, Pb and Cr was determined in Atomic Absorption Spectrophotometer (AAS), model AA 6680, Shimadzu, Kyoto, Japan.

3.4.9 Total heavy metals determination

This was determined after triple acid digestion (HNO_3, HF and HCl) (Lim and Jackson, 1986). 0.2 gram of air-dried and finely ground soil was weighed into a teflon beaker and digested with a 2:3:2 mixtures of HNO_3, HF and HCl at 80°C. The beaker was swirled gently and digested on a digestion block until brown fumes appeared which subsequently turned white indicating full digestion. The digested soil samples was set aside to cool and filtered through Whatman No. 42 filter paper and diluted to 50 ml with distilled water in clean plastic vials prior to analysis. Concentration of Cr, Cd, Pb and Cu in the digest was determined with in Atomic Absorption Spectrophotometer (AAS) : Model AA 6680, Shimadzu, Kyoto, Japan.

3.5 Fractionation of Heavy Metals

The sequential extraction procedure modified from Tessier, A., Campbell, P.G.C. and Bisson, M., 1979) was used to fractionate the soil into six operationally defined species as follows:

(i) Water soluble (WS): Two grams of air-dried soil was weighed into plastic bottle, 25 ml of distilled water was added and extracted at room temperature for 2 hrs. The mixture was centrifuged, decanted and filter to get the supernatant into a clean plastic vial and the concentration of Cu, Pb, Cr and Cd was determined in AAS.

(ii) Exchangeable (EXCH)*:* The residue from (i) above was extracted at room temperature for 30 minutes with 20 ml 1M NH_4OAC Solution (pH 7.0) with continuous agitation. The filtrate was decanted into clean plastic vial and the concentration of Cu, Pb, Cr and Cd was determined in AAS.

(iii) Bound to carbonates (CARB)*:* The residue from (ii) above was extracted by adding 20 ml 1M NaOAC at room temperature adjusted to pH 5.0 with acetic acid (HOAC). Continuous agitation was maintained for about 5 hours. The mixture was centrifuged, decanted and filtered and the supernatant obtained was poured into a clean plastic vial and the concentration of Cu, Pb, Cr and Cd was determined in AAS.

(iv) Bound to Fe and Mn Oxide (Fe-MnO): The residue from (iii) above was extracted with 20 ml of 0.04 M NH_2OH-HCl in acetic acid. The experiment was performed at 96 ^oC by heating in water bath for 6 hours with occasional agitation. The mixture was centrifuged, decanted and filtered to get the supernatant into a clean plastic vial and the concentration of Cu, Pb, Cr and Cd was determined in AAS.

(v) Bound to organic matter (OM)*:* Five milliliters of 0.1 N HNO_3 and ten milliliters of 30% H_2O_2 was added to the residue from (iv) above, and the mixture was heated to 85^oC for 5 hrs with occasional agitation. After cooling, 15ml of 3.2 M NH_4OAC in 20% (v/v) HNO_3 was added and agitated continuously for 30 min. The addition of NH_4OAC was designed to prevent adsorption of extracted metals onto the oxidized sediment. The mixture was centrifuged, decanted and filter to get the supernatant into a clean plastic vial and the concentration of Cu, Pb, Cr and Cd was determined in AAS.

(vi) Residual fraction (RES): The residual fraction was calculated by subtracting the sum of the fractions (i-v) from the total determined above.

$$RES = MT - (WS + EXCH + CARB + Fe - MnO + OM)$$

$$MT = TOTAL\ METAL\ CONCENTRATION$$

3.6 Soil Microbial Biomass Carbon and Nitrogen

The soil microbial biomass C and N was estimated by the fumigation-extraction method (Brookes, P. C., Landman, A., Pruden, G. and Jenkinson, D.S., 1985; Sparling and West, 1988), using freshly collected moist soil samples. Ten grams of fresh soil sample was extracted immediately after collection, with 50 ml of 0.5M K_2SO_4. A second subsample (10g) was extracted and immediately fumigated in an incubator using reagent-grade ethanol-free chloroform. Ethanol was removed from the chloroform by washing the chloroform with about 5% by volume concentrated sulphuric acid (H_2SO_4) by shaking in a separating funnel and after separating the acid, the chloroform was washed with 10 rinses of distilled water. Water – saturated filter paper was placed in the incubator to keep the samples moist. After 5 days, the incubator was opened and after allowing the chloroform to dissipate, the soil was removed and immediately extracted with 0.5M K_2SO_4 as done for the unfumigated sample.

The extractable C and N in both fumigated and unfumigated samples were determined. Microbial biomass C was estimated by multiplying the difference in extractable C between fumigated and unfumigated samples by a conversion factor of 2.64 (Vance, E. D., Brookes, P.C. and Jenkinson, D.S., 1987). Microbial biomass N was calculated by multiplying the difference in extractable N between fumigated and unfumigated sample by a conversion factor of 1.46 (Brookes *et al*., 1985).

$$\text{Microbial biomass carbon} = (\text{ExtractedCt1} - \text{ExtractedCt0}) \times 2.64$$

$$\text{Microbial biomass nitrogen} = (\text{Extracted Nt1} - \text{ExtractedNt0}) \times 1.46$$

3.7 Microbial Enumeration (Bacteria and Fungi)

The procedure of Prescott, L.M., Harley, J.P. and Klen, D.A., 2005) was used as follows:

(i) Preparation of media

For bacteria 22.5 g of plate count agar was weighed and dissolved in one litre of distilled water, heated to dissolution and sterilized by autoclaving at 121^{o}C for 15 minutes. For fungi 39 grams of saborand dextrose agar was done in the same manner.

(ii) Preparation of serial dilution for isolation of microorganism

One gram soil sample was weighed into universal bottle containing 9 ml of sterile distilled water (stock solution) shake thoroughly to mix. 1 ml was taken into another 9 ml of sterile distilled water in the universal bottle this gave 10^1 dilutions, this process continued until 10^4 dilutions were obtained. 1ml of 10^4 dilutions was transfer into sterile Petri dish. A 15 ml of molten agar cooled to 45^{o}C was added and swirled to mixed completely. The plate was then allowed to solidify before incubation at 37^{o}C for bacteria and 25^{o}C for fungi. After the incubation period the isolated colonies was counted using a counter and result was expressed as the colony forming unit per gram (Cfu/g). For bacteria incubation was done for three days and fungi for about a weak. The result was expressed using the following relation:

$$\frac{Total\ no\ of\ colony\ counted \times dilution\ factor}{Volume\ of\ inoculum}$$

(iii) Preparation of smear for bacteria

A smear was prepared in a clean glass slide. A drop of water was placed on a clean glass slide with the aid of a sterile wire loop; a bacterial colony was picked from the petri dish and (cultured plate) and emulsified with the wire on the slide to obtain a thin film. A smear was allowed to air dry and fixed by heating over the Bunsen burner flame by passing the slide trice with the smear facing upward.

(iv) Gram staining of fixed bacteria

The smear was stained with crystal violet and allowed to stand for 1 minute, and later washed with water and further flooded with grams iodine for 1 minute and again washed with water. It was decolorized with acetone and immediately washed with water and counter stained with safranine and allowed to stand for 1 minute, washed again and finally air dried. It was then examined under the microscope using × 100 objectives to view the bacterial present.

3.8 Statistical Analyses

Statistical analyses were performed using Excel and SAS statistical package version 9. Analysis of Variance (ANOVA) was carried out to compare the difference of means from various sampling sites, and the means were separated by Duncan Multiple Range Test (DMRT) when difference was significant. P - values <0.05 was taken for significant difference. Correlation analysis was carried out to determine relationship between heavy metals in soil and soil physicochemical and biological properties. The mobility index of Lead, Cadmium, Chromium and Copper was assessed according to the relationship below (MI) (Liu, J., Duan C-Q, Zhu, Y., Zhang, X., and Wang, C., 2007)

$$\sum_{i=1}^{n} \frac{Fi}{\frac{Ti}{n}}$$

Where F_i is the metal concentration in the mobile fractions, T_i, the total concentration of the metals, and n is the number of the soil samples. Descriptive statistics technique was used to summarize the data of the various metal fractions with respect to locations. The pollution index (Pi) and geo-accumulation index (I-geo) was employed to assess the pollution of individual metals. Pollution index was calculated using the formula:

EF = Ci/Si; where Ci represents the concentration of heavy metal *i* in soil while Si indicates the relevant standard value for this metal. EF values close to unity (1) indicate that the metal is of crusted origin while, values <1 indicates mobilization or depletion of the metal, and those values >1 suggests anthropogenic enrichment (Bhuiyan, M.A.H., Parvez, L., Islam, M.A., Dampare, S.B. and Suzuki, S., 2010). The geoaccumulation index (I-geo) as proposed by Muller (1969) was calculated by computing the base 2 logarithm of the measured total concentration of the metal over its background concentration using the mathematical relation (Muller, 1969):

$$\text{I-geo} = \log_2 (Cn/1.5Bn)$$

Where Cn is the concentration of metal n in the soil, Bn is the soil background concentration of heavy metal n and 1.5 is a factor compensating the background data (correction factor) due to lithogenic effects. Muller (1981) report distinguished the following seven classes or grades of the geoaccumulation index:

Class 0; Igeo $\leq$ 0 = unpolluted

Class 1; 0 < Igeo < 1 = unpolluted to moderately polluted

Class 2; 1 < Igeo < 2 = moderately polluted

Class 3; 2 < Igeo < 3 = moderately to highly polluted

Class 4; 3 < Igeo < 4 = highly polluted

Class 5; 4 < Igeo < 5 = highly to extremely polluted

Class 6; 5 < Igeo < 6 = extremely polluted.

CHAPTER FOUR

4.0 RESULTS

4.1 Soil Characterization

4.1.1 Soil Physicochemical Properties

The soil samples taken from all dye and non-dye locations have sandy loam texture using the USDA classification system (Table 4.1). The soil samples from the non-dye areas had the lowest pH (H_2O) of 5.42 slightly acidic which is significantly lower ($P<0.05$) than soil samples from dye pits which ranged from 9.35 to 9.98 alkaline. Similar trend was observed for pH in $CaCl_2$ (Table 4.1). The Organic carbon of the soils ranged from 0.29 to 0.58 gkg^{-1}. Total nitrogen values ranged from 0.10 to 0.16 gkg^{-1}. Available phosphorus values ranged from 8.10 to 18.73 gkg^{-1}(Table 4.1) for both dye and non dye areas.

There were significant differences along the locations for all parameters measured. Mabuga had the highest pH in both H_2O (9.98) and $CaCl_2$ (9.61) while Kofar Gayan had the lowest values for pH (H_2O) and pH ($CaCl_2$) which were 5.42 and 4.70 respectively. Angwan Iya had the highest value for organic carbon (0.58 gkg^{-1}), while Kofar Gayan had the lowest OC content (0.29 gkg^{-1}). But for total nitrogen, the highest value was found in Kofar Kuyanbana (0.16 gkg^{-1}) and the lowest was in Angwan Iya and Kofar Gayan (0.10gkg^{-1}). For available phosphorus (AP) Kusfa had the highest value of 18.73 gkg^{-1}, while Kofar Gayan had the lowest value of 8.10 gkg^{-1} (Table 4.1).

4.2 Concentration of Exchangeable Bases and Acidity in Soils Collected From Dye Areas in Zaria City

The acidity values ranged from 0.47 to 0.81, while for exchangeable bases, potassium (K) ranged from 0.37 to 3.32 cmol/kg , sodium (Na) ranged from 1.70 to 12.90 cmol/kg,

Table 4.1: Physicochemical properties of soils collected from dye areas in Zaria city (Mean±SD)

Location	Sand (g/kg)	Silt (g/kg)	Clay (g/kg)	Textural class	pH (H_2O)	pH ($CaCl_2$)	OC (g/kg)	TN (g/kg)	AP (g/kg)
KG	700	200	100	Sandy loam	5.42 ± 0.31^{c}	4.70 ± 0.35^{d}	0.29 ± 0.08^{c}	0.10 ± 0.04^{ab}	8.10 ± 2.10^{c}
Kusfa	722	170	108	Sandy loam	9.44 ± 0.72^{b}	8.80 ± 0.57^{c}	0.51 ± 0.29^{ab}	0.12 ± 0.02^{ab}	18.7 ± 3.50^{3a}
KJ	701	201	98	Sandy loam	9.64 ± 0.68^{a}	9.04 ± 0.40^{b}	0.46 ± 0.26^{b}	0.11 ± 0.14^{ab}	12.24 ± 5.05^{b}
Mabuga	721	170	109	Sandy loam	9.98 ± 0.21^{a}	9.61 ± 0.30^{a}	0.54 ± 0.28^{ab}	0.11 ± 0.05^{ab}	12.15 ± 4.13^{b}
AI	699	171	130	Sandy loam	9.78 ± 0.32^{a}	8.63 ± 0.45^{c}	0.58 ± 0.46^{a}	0.10 ± 0.04^{ab}	9.37 ± 3.11^{bc}
KK	746	140	114	Sandy loam	9.35 ± 0.58^{b}	8.59 ± 0.42^{c}	0.48 ± 0.15^{b}	0.16 ± 0.07^{a}	9.49 ± 2.52^{bc}

Note: Means with the same alphabets along a column are not significantly different at P≥0.05

AP= Available Phosphorus, OC= Organic Carbon and TN= Total NitrogenPotassium

KG= Kofar Gayan, KJ= Kofar Jatau, AI= Angwan Iya AND KK= Kofar Kuyanbana

calcium (Ca) ranged from 1.81 to 7.40 cmol/kg and magnesium (Mg) ranged from 1.95 to 6.06 cmol/kg (Table 4.2). The highest exchangeable acidity of 0.81 was recorded at Kofar Gayan, while the lowest (0.47) was recorded at Angwan Iya. The exchangeable bases Mabuga had the highest values for both K (3.32 cmol/kg) and Ca (7.40 cmol/kg), while Kofar Gayan had the lowest values of 0.37 cmol/kg and 1.81 cmol/kg for K and Ca respectively. For Na and Mg, highest values were recorded at Kofar Jatau which were 12.90 cmol/kg and 6.06 cmol/kg, while the lowest Na and Mg concentrations were recorded at Kofar Gayan with a value of 1.70 and 1.95cmol/kg respectively (Table 4.2)

4.3 Soil Physicochemical Properties Based on Distance Along The Dye Pit

There were variations in the physicochemical parameters with variation with the distances from the dye pits. These values did not significantly ($p>0.5$) vary with distance from dye source (Table 4.3, 4.4, 4.5, 4.6, 4.7 and 4.8).

4.4 Vertical Distribution of Soil Physicochemical Properties

Table 4.9 – 4.14 shows the vertical distribution of the measured soil properties. Some of the values were higher at 0-15 for the variables measured and lower values were observed at lower depths. Organic carbon, AP, TN, acidity and Na showed the lowest values at 30-45 (Table 4.9). Down the profile, pH and Mg concentrations increased but OC and Na decreased. Also, highest values were observed at 0-15cm depth for OC, Na and Ca and lower values were observed for pH, AP, TN and Mg (Table 4.10). In Table 4.11, K, Ca and Mg decreases down the soil profile while OC increase with profile depth.

Table 4.2: Concentration of exchangeable bases (cmol/kg) and exchange acidy in soils collected from dye areas in Zaria city (Mean±SD)

Location	Acidity	K	Na	Ca	Mg
KG	0.81±0.11^{a}	0.37±0.03^{d}	1.70±0.40^{c}	1.81±0.25^{d}	1.95±0.85^{d}
Kusfa	0.73±0.20^{ab}	3.28±0.41^{a}	9.98±2.00^{b}	5.17±1.70^{b}	4.33±1.55^{b}
KJ	0.55±0.35^{bc}	0.88±0.49^{c}	12.90±3.92^{a}	3.66±1.71^{c}	6.06±1.91^{a}
Mabuga	0.67±0.11^{b}	3.32±0.28^{a}	8.41±2.93^{b}	7.40±1.01^{a}	2.93±1.96^{c}
AI	0.47±0.33^{c}	1.57±0.38^{b}	9.24±3.21^{b}	6.95±3.38^{ab}	2.14±1.10^{c}
KK	0.73±0.20^{ab}	0.78±0.52^{c}	9.43±2.33^{b}	3.42±0.31^{c}	2.65±1.40^{c}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

K=Potassium, Na=Sodium, Calcium and Mg= Magnessium

Table 4.3: Physicochemical properties of soil under the influence of dye effluents based on distance from Kofar Gayan dye pit in Zaria city (Mean±SD)

Distance from dye pit (m)	pH (H_2O)	pH $CaCl_2$	OC (g/kg)	AP (g/kg)	TN (g/kg)	Acidity	K (cmol/kg)	Na (cmol/kg)	Ca (cmol/kg)	Mg (cmol/kg)
< 1	5.56±0.47^{a}	4.71±0.35^{a}	0.34±0.10^{a}	8.63±2.19^{b}	0.13±0.04^{a}	0.87±0.12^{a}	0.36±0.09^{b}	1.85±0.20^{a}	1.70±0.10^{a}	2.47±1.46^{a}
5	5.27±0.31^{a}	4.61±0.26^{a}	0.29±0.08^{a}	4.38±0.70^{bc}	0.14±0.07^{a}	0.80±0.20^{a}	0.32±0.03^{b}	1.74±0.30^{a}	1.90±0.10^{a}	1.43±0.38^{ab}
10	5.54±0.35^{a}	4.62±0.26^{a}	0.34±0.10^{a}	10.33±4.75^{ab}	0.16±0.10^{a}	0.80±0.32^{a}	0.32±0.03^{b}	1.62±0.10^{a}	1.63±0.25^{a}	0.93±0.25^{b}
20	5.42±0.24^{a}	4.87±0.31^{a}	0.24±0.13^{a}	13.77±4.86^{a}	0.18±0.04^{a}	0.73±0.12^{b}	0.38±0.03^{b}	1.63±0.20^{a}	1.87±0.25^{a}	2.70±0.29^{a}
50	5.31±0.08^{a}	4.67±0.18^{a}	0.23±0.07^{a}	3.79±0.99^{c}	0.13±0.04^{a}	0.87±0.12^{a}	0.46±0.00^{a}	1.68±0.40^{a}	1.93±0.61^{a}	2.23±0.30^{a}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.4: Physicochemical properties of soil under the influence of dye effluents based on distance from Kusfa dye pit in Zaria city (Mean±SD)

Distance from dye pit (m)	pH (H_2O)	pH $CaCl_2$	OC (g/kg)	AP (g/kg)	TN (g/kg)	Acidity	K (cmol/kg)	Na (cmol/kg)	Ca (cmol/kg)	Mg (cmol/kg)
< 1	9.30±0.61[a]	8.70±0.61[a]	0.66±0.51[a]	4.38±2.63[c]	0.13±0.04[a]	0.60±0.20[a]	2.77±0.49[b]	9.97±1.35[a]	6.10±3.00[a]	3.70±1.80[b]
5	9.47±0.72[a]	8.93±0.93[a]	0.66±0.29[a]	6.71±2.20[b]	0.11±0.04a	0.87±0.20[a]	2.92±0.65[b]	10.09±1.31[a]	5.40±1.70[a]	4.77±1.89[a]
10	9.30±0.82[a]	8.57±0.64[a]	0.33±0.23[a]	13.58±3.00[b]	0.12±0.05[a]	0.67±0.12[a]	3.76±0.41[a]	9.68±1.28[a]	4.50±1.71[a]	2.30±1.55[c]
20	9.57±0.45[a]	8.87±0.57[a]	0.45±0.12[a]	13.71±3.01[b]	0.12±0.53[a]	0.67±0.23[a]	2.96±0.92[b]	10.26±1.48[a]	4.70±1.05[a]	5.43±2.00[a]
50	9.57±0.57[a]	8.93±0.84[a]	0.43±0.34[a]	15.75±3.50[a]	0.12±0.20[a]	0.87±0.23[a]	3.97±1.08[a]	9.91±2.00[a]	5.13±2.61[a]	5.47±2.10[a]

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.5: Physicochemical properties of soil under the influence of dye effluents based on distance from Kofar Jatau dye pit in Zaria city (Mean±SD)

Distance from dye pit (m)	pH(H_2O)	pH $CaCl_2$	OC (g/kg)	AP (g/kg)	TN (g/kg)	Acidity	K (cmol/kg)	Na (cmol/kg)	Ca (cmol/kg)	Mg (cmol/kg)
< 1	9.80±0.10^{a}	9.13±0.21^{a}	0.51±0.26^{a}	16.63±4.00^{a}	0.12±0.07^{a}	0.33±0.02^{c}	0.94±0.26^{a}	13.85±1.65^{a}	3.50±1.9^{a}	7.83±3.6^{a}
5	9.67±0.68^{a}	9.13±0.67^{a}	0.46±0.13^{a}	14.00±5.13^{ab}	0.14±0.02^{a}	0.60±0.20^{a}	0.84±0.48^{a}	13.56±3.02^{a}	3.20±1.6^{a}	7.67±3.5^{a}
10	9.77±0.40^{a}	9.03±0.40^{a}	0.45±0.25^{a}	11.26±4.89^{b}	0.12±0.02^{a}	0.93±0.28^{a}	0.60±0.08^{ab}	12.98±3.00^{a}	3.47±2.1^{a}	6.97±4.2^{a}
20	9.43±0.72^{a}	8.93±0.55^{a}	0.36±0.13^{b}	11.67±4.05^{b}	0.07±0.00^{b}	0.40±0.08^{b}	0.68±0.25^{ab}	11.88±2.11^{a}	3.80±1.0^{a}	4.63±1.4^{b}
50	9.57±0.45^{a}	8.97±0.65^{a}	0.51±0.25^{a}	7.64±3.14^{c}	0.12±0.04^{a}	0.47±0.10^{b}	1.32±1.04^{b}	12.23±2.99^{a}	4.33±1.6^{a}	3.20±1.2^{b}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.6: Physicochemical properties of soil under the influence of dye effluents based on distance from Mabuga dye pit in Zaria city (Mean±SD)

Distance from dye pit (m)	pH (H_2O)	pH $CaCl_2$	OC (g/kg)	AP (g/kg)	TN (g/kg)	Acidity	K (cmol/kg)	Na (cmol/kg)	Ca (cmol/kg)	Mg (cmol/kg)
< 1	10.03±0.25^{a}	9.73±0.25^{a}	0.83±0.19^{a}	14.41±2.44^{a}	0.13±0.05^{a}	0.73±0.42^{a}	3.61±1.19^{a}	10.38±2.2^{a}	7.43±1.0^{a}	1.07±0.4^{b}
5	10.07±0.12^{a}	9.60±0.30^{a}	0.59±0.28^{a}	15.46±2.94^{a}	0.15±0.11^{a}	0.93±0.31^{a}	3.42±0.87^{a}	7.83±0.92^{b}	8.17±1.9^{a}	3.30±0.5^{a}
10	10.03±0.15^{a}	9.73±0.15^{a}	0.49±0.26^{a}	13.13±1.76^{a}	0.08±0.02^{b}	0.67±0.12^{a}	3.37±0.28^{a}	8.58±0.78^{b}	7.30±0.5^{a}	2.33±0.4^{a}
20	9.97±0.21^{a}	9.60±0.20^{a}	0.34±0.14^{b}	6.71±0.82^{b}	0.09±0.02^{b}	0.34±0.15^{b}	3.18±0.71^{a}	7.30±0.90^{b}	6.90±0.8^{a}	2.57±0.3^{a}
50	9.80±0.40^{a}	9.40±0.20^{a}	0.46±0.15^{a}	11.03±4.13^{ab}	0.07±0.04^{b}	0.46±0.25^{ab}	3.01±0.70^{a}	7.94±0.9^{3b}	7.20±0.6^{a}	0.37±0.1^{c}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.7: Physicochemical properties of soil under the influence of dye effluents based on distance from Angwan Iya dye pit in Zaria city (Mean±SD)

Distance from dye pit (m)	pH (H_2O)	pH $CaCl_2$	OC (g/kg)	AP (g/kg)	TN (g/kg)	Acidity	K (cmol/kg)	Na (cmol/kg)	Ca (cmol/kg)	Mg (cmol/kg)
< 1	9.70±0.4^{a}	8.73±0.1^{a}	0.46±^{a}	6.77±2.7^{b}	0.08±0.1^{b}	0.01±0.0^{b}	1.57±0.6^{a}	8.35±0.3^{ab}	7.97±0.4^{a}	2.03±0.9^{a}
5	9.73±0.3^{a}	8.67±0.1^{a}	0.51±^{a}	6.01±1.4^{b}	0.11±0.1^{ab}	0.01±0.0^{b}	1.39±0.1^{a}	8.41±0.2^{ab}	6.40±0.3^{ab}	1.70±0.7^{ab}
10	9.73±0.3^{a}	8.67±0.2^{a}	0.77±^{a}	7.64±1.5^{b}	0.08±0.2^{b}	0.02±0.0^{b}	1.57±0.4^{a}	99.33±2.3^{a}	6.80±0.2^{a}	1.80±0.8^{ab}
20	9.87±0.3^{a}	8.57±0.2^{a}	0.70±^{a}	7.58±2.0^{b}	0.09±0.3^{b}	0.03±0.0^{b}	1.57±0.4^{a}	9.85±3.2^{a}	6.00±0.2^{ab}	3.50±0.9^{a}
50	9.87±0.3^{a}	8.53±0.4^{a}	0.71±^{a}	8.84±2.4^{a}	0.14±0.4^{a}	0.33±0.0^{a}	1.73±0.3^{a}	10.26±3.2^{a}	7.60±0.3^{a}	1.67±0.3^{ab}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.8: Physicochemical properties of soil under the influence of dye effluents based on distance from Kofar Kuyanbana dye pit in Zaria city (Mean±SD)

Distance from dye pit (m)	pH (H_2O)	pH $CaCl_2$	OC (g/kg)	AP (g/kg)	TN (g/kg)	Acidity	K (cmol/kg)	Na (cmol/kg[1]	Ca (cmol/kg)	Mg (cmol/kg)
< 1	9.80±0.36[a]	8.73±0.47[a]	0.18±0.04[a]	4.03±1.32[a]	0.18±0.09[a]	1.13±0.50[a]	0.87±0.51[a]	9.85±2.39[a]	3.23±1.75[a]	3.53±1.05[a]
5	9.57±0.78[a]	8.57±0.42[a]	0.32±0.16[a]	4.55±1.97[a]	0.09±0.02[b]	0.80±0.60[a]	0.74±0.46[a]	10.96±3.70[a]	3.43±0.31[a]	2.97±0.70[ab]
10	9.04±0.29[a]	8.34±0.25[a]	0.33±0.15[a]	3.27±1.05[a]	0.16±0.07[a]	0.73±0.46[a]	0.74±0.52[a]	7.54±0.80[ab]	3.37±0.31[a]	2.83±0.31[ab]
20	9.33±0.59[a]	8.87±0.80[a]	0.26±0.14[a]	2.92±1.43[ab]	0.14±0.12[a]	0.87±0.12[a]	0.82±0.57[a]	8.35±0.56[ab]	3.83±0.40[a]	3.10±1.00[a]
50	9.03±0.15[a]	8.40±0.26[a]	0.32±0.13[a]	2.68±1.31[ab]	0.21±0.11[a]	0.60±0.20[a]	0.74±0.56[a]	10.43±4.34[a]	3.23±1.12[a]	0.80±0.01[b]

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.9: Effect of soil depth on physicochemical properties of soil under the influence of dye effluents in Kofar Gayan, Zaria city (Mean±SD)

Auger depth (cm)	pH (H_2O)	pH ($CaCl_2$)	OC (g/kg)	AP (g/kg)	TN (g/kg)	Acidity	K (cmol/kg)	Na (cmol/kg)	Ca (cmol/kg)	Mg (cmol/kg)
0-15	5.70±0.31^{a}	4.96±0.19^{a}	0.37±0.06^{a}	14.21±2.69^{a}	0.15±0.05^{a}	0.92±0.30^{a}	0.35±0.07^{a}	1.70±0.15^{ab}	1.72±0.11^{a}	1.48±0.71^{ab}
15-30	5.24±0.20^{b}	4.52±0.08^{b}	0.31±0.06^{ab}	5.78±1.19^{b}	0.16±0.08^{a}	0.80±0.24^{a}	0.39±0.07^{a}	1.88±0.23^{a}	1.92±0.46^{a}	2.02±0.12^{a}
30-45	5.32±0.13^{b}	4.60±0.20^{b}	0.19±0.06^{b}	4.55±1.00^{b}	0.13±0.05^{a}	0.72±0.11^{a}	0.37±0.07^{a}	1.35±0.23^{b}	1.78±0.23^{a}	2.36±0.13^{a}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.10: Effect of soil depth on physicochemical properties of soil under the influence of dye effluents in Kusfa, Zaria city (Mean±SD)

Auger depth (cm)	pH (H_2O)	pH ($CaCl_2$)	OC (g/kg)	AP (g/kg)	TN (g/kg)	Acidity	K (cmol/kg)	Na (cmol/kg)	Ca (cmol/kg)	Mg (cmol/kg)
0-15	9.18±0.26^{a}	8.36±0.09^{b}	0.58±0.11^{a}	11.73±2.89^{b}	0.11±0.02^{a}	0.72±0.08^{a}	3.41±1.09^{a}	10.43±1.24^{a}	5.58±1.43^{a}	2.46±0.09^{b}
15-30	9.40±0.43^{a}	8.42±0.22^{b}	0.56±0.21^{a}	25.55±4.34^{a}	0.13±0.03^{a}	0.84±0.04^{a}	2.90±0.49^{ab}	9.95±1.47^{a}	4.64±0.98^{a}	4.82±0.12^{a}
30-45	10.10±0.14^{a}	9.62±0.31^{a}	0.38±0.01^{b}	18.90±3.21^{ab}	0.11±0.05^{a}	0.64±0.02^{a}	3.49±0.71^{a}	9.56±0.98^{a}	5.28±1.37^{a}	5.72±1.00^{a}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.11: Effect of soil depth on physicochemical properties of soil under the influence of dye effluents in Kofar Jatau, Zaria city (Mean±SD)

Auger depth (cm)	pH (H_2O)	pH ($CaCl_2$)	OC (g/kg)	AP (g/kg)	TN (g/kg)	Acidity	K (cmol/kg)	Na (cmol/kg)	Ca (cmol/kg)	Mg (cmol/kg)
0-15	9.12±0.41[b]	8.50±0.25[b]	0.43±0.22[a]	13.79±3.60[a]	0.18±0.09[a]	0.56±0.32[a]	0.76±0.23[ab]	13.04±2.05[a]	3.96±1.12[a]	8.78±2.34[a]
15-30	10.00±0.12[a]	9.46±0.18[a]	0.44±0.23[a]	12.60±1.98[a]	0.07±0.03[ab]	0.44±0.23[a]	0.74±0.20[ab]	14.19±3.21[a]	3.64±1.42[a]	6.58±1.95[a]
30-45	9.82±0.41a	9.16±0.11[b]	0.51±0.20[a]	10.33±2.11[a]	0.08±0.04[ab]	0.64±0.51[a]	1.13±0.81[a]	11.48±3.76[a]	3.38±1.60[a]	2.82±1.86[b]

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.12 shows no significant difference for all the parameter measured down the depth except for Ca and Mg. Down the soil profile, pH Mg and acidity decreases but AP and K increases. From Table 4.13 pH, TN, Acidity, K and Mg increases, while Na and Ca decreases. Available P, acidity, K and Ca concentrations decreased down the soil profile (Table 4.14).

4.5 Soil Microbial Properties

Soil microbial biomass Carbon and Nitrogen showed significant differences in soil samples of dye and the non-dye areas (Table 4.15). However, microbial biomass C ranged from 170.82 mg/kg to 334.44 mg/kg, while microbial biomass N ranged from 16.89 mg/kg to 37.28 mg/kg. The highest was observed at Kofar Gayan for both MBC and MBN, while the lowest value was observed at Kusfa and Mabuga for both MBC and MBN respectively. The total bacterial counts (TBC) of the soil sample ranged from 3.60×10^{4} to 1.29×10^{7} cfu/g. The total fungi counts (TFC) of the soil ranged from 1.46 to 8.74×10^{6}cfu/g (Table 4.15).

Although there were differences in the total bacteria and fungi counts of the different sampling locations, these differences were not significant ($p>0.05$). Kofar Gayan showed highest count for bacteria and fungi while, Mabuga showed the lowest for both (Table 4.15). Along the horizontal distance, there was no significant difference ($p>0.05$), although their values differed from one location to another. Although down the soil profile, a significant variation ($p>0.05$) was observed (Table 4.16 -4.27). The concentration of microbial organisms was highest at surface soil depth in most of the locations under study.

Table 4.12: Effect of soil depth on physicochemical properties of soil under the influence of dye effluents in Mabuga, Zaria city (Mean±SD)

Auger depth (cm)	pH (H_2O)	pH ($CaCl_2$)	OC (g/kg)	AP (g/kg)	TN (g/kg)	Acidity	K (cmol/kg)	Na (cmol/kg)	Ca (cmol/kg)	Mg (cmol/kg)
0-15	10.04±0.20^{a}	9.68±0.22^{a}	0.77±0.16^{a}	10.33±3.22^{a}	0.13±0.06^{a}	0.76±0.32^{a}	3.07±0.48^{a}	8.70±1.85^{a}	8.36±1.22^{a}	4.38±1.36^{a}
15-30	10.02±0.17^{a}	9.66±0.15^{a}	0.41±0.13^{ab}	12.99±4.23^{a}	0.08±0.05^{b}	0.68±0.21^{a}	3.42±0.62^{a}	9.18±3.57^{a}	6.84±0.68^{b}	0.58±0.11^{b}
30-45	9.88±0.30^{a}	9.50±0.29^{a}	0.45±0.14^{ab}	13.13±5.22^{a}	0.11±0.05^{ab}	0.56±0.16^{a}	3.47±0.42^{a}	7.34±0.59^{ab}	7.00±1.00^{b}	0.82±0.12^{b}

Note: Means with the same alphabets along the column are not significantly different at P<0.05.

Table 4.13: Effect of soil depth on physicochemical properties of soil under the influence of dye effluents in Angwan Iya, Zaria city (Mean±SD)

Auger depth (cm)	pH (H_2O)	PH ($CaCl_{2)}$	OC (g/kg)	AP (g/kg)	TN ((g/kg)	Acidity	K (cmol/kg)	Na (cmol/kg)	Ca (cmol/kg)	Mg (cmol/kg)
0-15	9.54±0.11[a]	8.62±0.08[a]	0.59±0.04[a]	6.09±2.71[b]	0.07±0.00[b]	0.02±0.00[b]	1.53±0.31[b]	8.35±0.25[b]	8.38±1.14[a]	1.26±0.85[ab]
15-30	9.73±0.22[a]	8.72±0.19[a]	0.88±0.04[a]	9.46±3.11[a]	0.11±0.01[a]	0.02±0.00[b]	1.86±0.27[a]	8.21±0.47[b]	7.40±0.29[a]	2.28±0.91[a]
30-45	10.10±0.07[a]	8.76±0.29[a]	0.44±0.02[a]	7.56±3.00[b]	0.12±0.11[a]	0.20±0.00[a]	1.86±0.33[ab]	11.16±2.91[a]	5.08±2.20[b]	2.88±1.00[a]

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.14: Effect of soil depth on physicochemical properties of soil under the influence of dye effluents in Kofar Kuyanbana, Zaria city (Mean±SD)

Auger depth(cm)	pH (H_2O)	pH ($CaCl_2$)	OC (g/kg)	AP (g/kg)	TN (g/kg)	Acidity	K (cmol/kg)	Na (cmol/kg)	Ca (cmol/kg)	Mg (cmol/kg)
0-15	9.38±0.75^{a}	8.42±0.08^{a}	0.27±0.15^{a}	4.52±0.19^{a}	0.13±0.04^{a}	1.16±0.03^{a}	1.37±0.09^{a}	9.77±2.19^{a}	4.12±1.11^{a}	2.80±0.7^{a}
15-30	9.58±0.36^{a}	8.94±0.19^{a}	0.23±0.17^{a}	3.57±0.16^{ab}	0.21±0.09^{a}	0.72±0.01^{ab}	0.57±0.02^{b}	8.73±1.98^{a}	3.42±1.04^{a}	3.36±1.0^{a}
30-45	9.10±0.29^{a}	8.40±0.29^{a}	0.36±0.18^{a}	2.38±0.80^{b}	0.13±0.06^{a}	0.60±0.02^{ab}	0.39±0.01^{c}	9.77±2.00^{a}	2.72±0.91^{b}	1.78±0.1^{ab}

Note: Means with the same alphabets along the column are not significantly different at P<0.05.

Table 4.15: Microbial properties of soils under the influence of dye effluents in Zaria city

Location	MBC(mg/kg)	MBN(mg/kg)	BC(cfu/g)	FC(cfu/g)
KG	334.44^{a}	37.28^{a}	1.29×10^{7a}	8.74×10^{6a}
Kusfa	170.82^{d}	22.89^{b}	2.23×10^{5a}	2.53×10^{4a}
KJ	259.48^{b}	28.67^{b}	4.83×10^{5a}	4.70×10^{4a}
Mabuga	195.94^{d}	16.89^{c}	3.60×10^{4a}	1.46×10^{4a}
AI	215.28^{c}	23.78^{b}	4.17×10^{4a}.	8.06×10^{4a}
KK	203.32^{cd}	19.66^{b}	1.40×10^{5a}	5.53×10^{4a}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

KG = Control, MBC = Microbial biomass carbon, MBN = Microbial biomass nitrogen, BC = Bacterial carbon, FC= Fungal count

Table 4.16: Horizontal distribution of microbial properties of soils under the influence of dye effluents Kofar Gayan, in Zaria city

Distance from dye pit (m)	MBC (mg/kg)	MBN (mg/kg)	BC (cfu/g)	FC (cfu/g)
< 1	273.00[a]	28.22[a]	4.40×10^{5a}	1.56×10^{5a}
5	278.20[a]	29.91[a]	6.37×10^{7a}	6.33×10^{4a}
10	362.70[a]	32.30[a]	2.16×10^{5a}	3.6×10^{4a}
20	364.00[a]	33.22[a]	2.13×10^{5a}	4.34×10^{7a}
50	404.30[a]	35.21[a]	3.50×10^{5a}	1.27×10^{5a}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.17: Horizontal distribution of microbial properties of soils under the influence of dye effluents in Kusfa, Zaria city

Distance from dye pit (m)	MBC (mg/kg)	MBN (mg/kg)	BC (cfu/g)	FC (cfu/g)
< 1	165.10^{a}	18.23^{a}	3.60×10^{5a}	3.33×10^{4a}
5	158.60^{a}	17.10^{a}	2.40×10^{5a}	3.33×10^{4a}
10	150.80^{a}	16.67^{a}	3.06×10^{5a}	1.33×10^{4a}
20	206.70^{a}	22.78^{a}	7.00×10^{4a}	3.33×10^{4a}
50	172.90^{a}	19.00^{a}	1.40×10^{5a}	1.33×10^{4a}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.18: Horizontal distribution of microbial properties of soils under the influence of dye effluents in Kofar Jatau, Zaria city

Distance from dye pit (m)	MBC (mg/kg)	MBN (mg/kg)	BC (cfu/g)	FC (cfu/g)
< 1	266.50^{a}	29.46^{a}	8.13×10^{5a}	1.00×10^{4a}
5	276.90^{a}	30.17^{a}	1.36×10^{5a}	1.00×10^{4a}
10	289.90^{a}	32.11^{a}	7.20×10^{5a}	2.00×10^{4a}
20	237.90^{a}	26.22^{a}	7.06×10^{5a}	6.66×10^{4a}
50	226.20^{a}	25.00^{a}	3.90×10^{4a}	2.66×10^{4a}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.19: Horizontal distribution of microbial properties of soils under the influence of dye effluents in Mabuga, Zaria city

Distance from dye pit (m)	MBC (mg/kg)	MBN (mg/kg)	BC (cfu/g)	FC (cfu/g)
< 1	97.50[a]	19.40[a]	3.00×10^{4a}	2.66×10^{4a}
5	76.70[a]	8.50[a]	1.53×10^{5a}	3.33×10^{4a}
10	111.80[a]	12.44[a]	1.23×10^{5a}	7.00×10^{4a}
20	106.60[a]	11.78[a]	1.23×10^{5a}	7.66×10^{4a}
50	87.10[a]	9.60[a]	2.73×10^{5a}	7.00×10^{4a}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.20: Horizontal distribution of microbial properties of soils under the influence of dye effluents in Angwan Iya, Zaria city

Distance from dye pit (m)	MBC (mg/kg)	MBN (mg/kg)	BC (cfu/g)	FC (cfu/g)
< 1	226.20[a]	25.01[a]	1.33×10^{4b}	1.36×10^{4a}
5	230.10[a]	25.16[a]	1.66×10^{4b}	3.33×10^{4a}
10	175.50[a]	19.30[a]	4.00×10^{4ab}	3.33×10^{3a}
20	221.00[a]	24.45[a]	1.70×10^{4b}	1.33×10^{4a}
50	223.60[a]	24.66[a]	9.33×10^{4a}	6.66×10^{3a}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.21: Horizontal distribution of microbial properties of soils under the influence of dye effluents in Kofar Kuyambana, Zaria city

Distance from dye pit (m)	MBC (mg/kg)	MBN (mg/kg)	BC (cfu/g)	FC (cfu/g)
< 1	235.30[a]	26.00[a]	2.60×10^{5a}	4.33×10^{4a}
5	176.80[a]	19.34[a]	2.00×10^{4a}	7.80×10^{4a}
10	183.30[a]	20.16[a]	1.12×10^{6a}	7.00×10^{4a}
20	196.30[a]	21.56[a]	2.20×10^{5a}	2.70×10^{4a}
50	224.90[a]	24.76[a]	4.63×10^{5a}	1.66×10^{4a}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.22: Effect of soil depth on microbial biomass, bacteria and fungi count of soil under the influence of dye effluents in Kofar Gayan, Zaria city

Auger depth (cm)	MBC (mg/kg)	MBN (mg/kg)	BC (cfu/g)	FC (cfu/g)
0-15	405.60^{a}	45.10^{a}	7.60×10^{4a}	8.40×10^{4a}
15-30	370.50^{a}	41.00^{a}	1.06×10^{5a}	4.20×10^{4a}
30-45	233.22^{b}	25.65^{a}	2.40×10^{5a}	4.00×10^{4a}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.23: Effect of soil depth on microbial biomass, bacteria and fungi count of soil under the influence of dye effluents in Kusfa, Zaria city

Auger depth (cm)	MBC (mg/kg)	MBN (mg/kg)	BC (cfu/g)	FC (cfu/g)
0-15	216.12^{a}	24.12^{a}	3.26×10^{5a}	8.20×10^{4a}
15-30	120.84^{b}	13.00^{b}	3.02×10^{5a}	1.60×10^{4b}
30-45	175.50^{a}	19.02^{a}	1.42×10^{5a}	2.00×10^{3b}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.24: Effect of soil depth on microbial biomass, bacteria and fungi count of soil under the influence of dye effluents in Kofar Jatau, Zaria city

Auger depth (cm)	MBC (mg/kg)	MBN (mg/kg)	BC (cfu/g)	FC (cfu/g)
0-15	284.92^{a}	37.12^{a}	8.40×10^{5a}	8.00×10^{5a}
15-30	253.50^{a}	28.61^{a}	3.57×10^{5a}	2.60×10^{4a}
30-45	280.02^{a}	31.00^{a}	2.25×10^{5a}	1.60×10^{3a}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.25: Effect of soil depth on microbial biomass, bacteria and fungi count of soil under the influence of dye effluents in Mabuga, Zaria city

Auger depth (cm)	MBC (mg/kg)	MBN (mg/kg)	BC (cfu/g)	FC (cfu/g)
0-15	225.40^{a}	25.00^{a}	9.28×10^{5a}	2.04×10^{5a}
15-30	213.72^{ab}	22.11^{ab}	1.76×10^{5a}	1.20×104^{b}
30-45	170.82^{b}	18.65^{b}	1.48×10^{5a}	1.50×10^{4b}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.26: Effect of soil depth on microbial biomass, bacteria and fungi count of soil under the influence of dye effluents in Angwan Iya, Zaria city

Auger depth (cm)	MBC (mg/kg)	MBN (mg/kg)	BC (cfu/g)	FC (cfu/g)
0-15	220.60^{a}	25.00^{a}	4.8×10^{4a}	8.21×10^{3a}
15-30	216.86^{a}	24.07^{a}	3.20×10^{5a}	8.00×10^{3a}
30-45	218.40^{a}	24.22^{a}	2.80×10^{4a}	8.20×10^{3a}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.27: Effect of soil depth on microbial biomass, bacteria and fungi count of soil under the influence of dye effluents in Zaria, Kofar Kuyanbana, Zaria city

Auger depth (cm)	MBC (mg/kg)	MBN (mg/kg)	BC (cfu/g)	FC (cfu/g)
0-15	188.14^{a}	16.79^{a}	4.82×10^{5a}	6.80×10^{4a}
15-30	122.26^{a}	10.80^{a}	2.22×10^{5a}	6.00×10^{4a}
30-45	108.42^{a}	12.07^{a}	4.74×10^{5a}	2.61×10^{5a}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

4.6 Variations in Bacteria Types in Sampling Locations

Throughout the sampling locations, a total of six (6) distinct genera of bacteria were observed, these were *Bacillus, Lactobacillus, Escherichia, Pseudomonas, Salmonella and Staphylococcus* (Table 4.28). Kusfa had all the six (6) genera with *Bacillus* being the most dominant. The fewer genera were *Lactobacillus* and *Escherichia.* In Kofar Jatau, six (6) genera were also observed, *Bacillus, Pseudomonas* and *Escherichia* genera were the most dominant while *Lactobacillus* and *Salmonella* were less dominant.

Likewise in Mabuga six (6) genera were also recorded and the most dominant genera were *Bacillus* and the least is *Escherichia*. In Angwan Iya four (4) genera were recorded and *Bacillus* was the most dominant and *Escherichia* was the least. At Kofar Kuyanbana, five (5) genera were recorded and *Escherichia* was the most dominant, while *Pseudomonas* was the least; and finally six (6) genera were recorded in Kofar Gayan which is the control, *Lactobacillus* was dominant, while *Escherichia* and *Salmonella* were the less dominant genera as shown in Table 4.28.

4.7 Variations in Fungi Genera in Sampling Locations

A total of nineteen (19) distinct genera of fungi were recorded throughout the sampling locations, (Table 4.29). In Kusfa eight (8) genera were recorded with *Aspergillus* being the most dominant while the less dominant genera were *Rhizopus, Trichoderma* and *Sclerotium.* Similarly in Kofar Jatau twelve (12) genera were recorded, *Aspergillus* genera was the most dominant, while *Candida* and *Fusarium* were less dominant. At Mabuga eight (8) genera were also recorded and the dominant genera were *Aspergillus, Genicularia and Fusarium*, while the less dominant genera were *Vulvularia and Gleosporium.* As observed in Angwan Iya, seven (7) genera were recorded and *Aspergillus* been the most dominant, while *Vulvularia, Sclerotium and Gleosporium* were the less dominant. At Kofar Kuyanbana, ten (10) genera were recorded and *Aspergillus* was the dominant, while *Alternaria* and *Rhizoctonia* were the less dominant

and finally fourteen (14) genera were recorded in Kofar Gayan which is the control with *Fusarium* as the dominant genera. *Candida* and *Penicillium* were the less dominant as shown in Table 4.29.

Table 4.28: Occurrence of some genera of aerobic heterotrophic bacteria within the vicinity of dye pits in Zaria city

Bacteria	Kusfa	KJ	Mabuga	AI	KK	KG
Bacillus	+	+	+	+	+	+
Lactobacillus	+	+	+	+	+	+
Staphylococcus	+	+	+	-	-	+
Salmonella	+	+	+	-	+	+
Pseudomonas	+	+	+	+	+	+
Escherichia	+	+	+	+	+	+

KK and KG; Kofar Kuyanbana and Kofar Gayan respectively, + = present; - = absent.

4.8 Total Cu, Cr, Pb and Cd Concentrations in The Soil

The total heavy metals concentration showed wide variations. There were significant differences in all the locations. The lowest concentration of Cu (27.29 $mgkg^{-1}$) was recorded at Kofar Gayan, while the highest concentration of 42.47 $mgkg^{-1}$ was recorded at Angwan Iya (Table 4.30). Chromium concentration showed very wide variation. The values ranged from 21.10 $mgkg^{-1}$ to 228.57 $mgkg^{-1}$ at Kofar Gayan and Mabuga respectively. These values are very much high when compared with standard thresholds for arable soils.

However, the highest Pb concentration (Pb 181.57 $mgkg^{-1}$) was recorded at Kofar Kuyanbana, the lowest concentration of 120.60 $mgkg^{-1}$ was recorded along Kofar Gayan. Surprisingly, Cd had the highest concentration of 40.55 $mgkg^{-1}$ at Kofar Gayan, while the lowest concentration of 13.07 $mgkg^{-1}$ was recorded at Kusfa (4.30) these values are extremely higher than the 3.0 $mgkg^{-1}$ acceptable Cd concentrations in arable lands.

4.9 Horizontal Distribution of Total Cu, Cr, Pb and Cd in The Vicinity of Dye Pits in Zaria City

The variations in the concentration of Cu, Cr, Pb and Cd with sampling distance are presented in Figures. There was no significant variation ($p>0.05$) in their concentration with distance from the dye pits. There was no uniform trend observed in the heavy metals concentration with distance in Kofar Gayan (Figure 4.1), but Pb and Cd showed highest and lowest concentration along the distance in Kusfa (Figure 4. 2). Figure 4.3 showed no significant difference for the heavy metals measured across the distance at Kofar Jatau along the distance.

Table 4.29: Occurrence of some aerobic heterotrophic fungi within the vicinity of dye pits in Zaria city

Fungi	Kusfa	KJ	Mabuga	AI	KK	KG
Aspergillus	+	+	+	+	+	+
Rhizoctonia	+	+	+	-	+	+
Neurospora	+	+	+	-	-	-
Rhizopus	+	-	-	-	-	+
Fusarium	+	+	+	+	+	+
Cephallospora	+	+	+	-	-	-
Trichoderma	+	-	-	-	+	+
Alternaria	-	+	-	-	+	-
Cladosporium	-	+	-	-	-	+
Phoma	-	-	-	+	+	+
Genicularia	-	-	+	+	-	+
Vulvularia	-	-	-	+	+	+
Monilla	-	-	+	-	+	+
Cheatomilla	-	+	+	-	-	-
Candida	-	+	-	-	+	+
Canoplea	-	+	-	-	-	-
Sclerotium	+	+	-	+	+	+
Penicillium	-	-	-	-	-	+
Gleosporium	-	+	-	+	-	+

+ indicate present, - indicates absent

Table 4.30: Concentration of total heavy metals in soils receiving dye effluents in Zaria city (Mean±SD)

Location	Cu (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Cd (mg/kg)
KG	27.29±1.18^{b}	21.10±7.00^{d}	120.60±23.00^{c}	40.55±5.17^{a}
Kusfa	29.04±5.17^{b}	47.22±9.23^{c}	127.37±23.01^{c}	13.07±2.45^{f}
KJ	32.20±4.27^{ab}	181.43±42.5^{ab}	181.52±32.21^{a}	19.45±5.67^{d}
Mabuga	31.24±7.27^{ab}	228.57±18.4^{a}	158.54±35.23^{b}	23.56±6.34^{c}
AI	42.47±9.10^{a}	154.65±47.2^{ab}	155.83±32.11^{b}	31.24±7.23^{bc}
KK	34.25±8.20^{ab}	99.95±23.4^{b}	181.57±20.23^{a}	35.48±9.34^{b}

Note: Means with the same alphabets along the column are not different at P≥0.05.

Figure 4.4 showed no significant difference for heavy metals along the distance at Mabuga, but a rapid increase was observed for Cr at <1m. No uniform distribution of heavy metals observed across the distance at Angwan Iya. The highest concentration was recorded when distance was lowest at 10 m for Cr (Figure 4.5). Figure 4.6 showed no significant difference for the heavy metals measured across the distance at Kofar Kuyanbana. The highest concentration was recorded at 20m for Pb while Cr concentrations was highest at <1m from the dye pit respectively.

4.10 Vertical Distribution of Total Cu, Cr, Pb and Cd

There was a significant variation in heavy metal concentration with soil depth for Pb (Figure 4.7) Pb increased with profile depth in Angwan Iya and Kofar Jatau .For Cd, there was increased down the depth in Kofar Gayan and Mabuga (Figure 4.8). A rapidly increased in Kofar Jatau was observed and a uniformly deseccnable trend was observed for Cu (Figure 4.9). Chromium concentration was high at 0-15cm (Figure 4.10).

4.11 Concentration of Available Cu, Cr, Pb and Cd in The Soil

The amounts of heavy metals extractable represent quantities that are mobile and readily available in the soil for plant uptake. Significant difference ($p<0.05$) was observed along the locations for all the metals. Kofar Gayan has the lowest concentrations of 1.54 $mgkg^{-1}$, 0.84 $mgkg^{-1}$ and 8.88 $mgkg^{-1}$ for Cu, Cr and Pb respectively. Cadmium was not detected at Kofar Gayan. Kusfa recorded highest concentration of 12.39 $mgkg^{-1}$, 18.00 $mgkg^{-1}$and 0.08 $mgkg^{-1}$ for Cu, Pb and Cd respectively. Although highest value of 9.14 $mgkg^{-1}$ was recorded at Mabuga (Table 4.31).

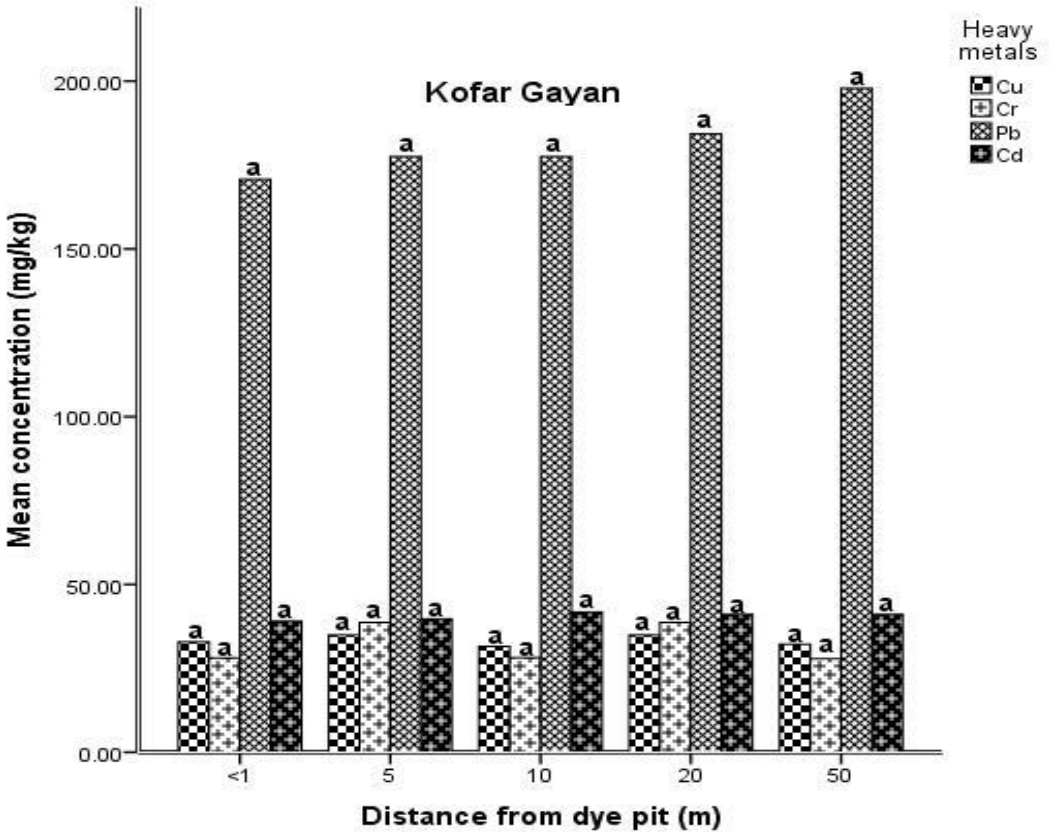


Figure 4.1: Horizontal distribution of total Cu, Cr, Pb and Cd in soils in Kofar Gayan

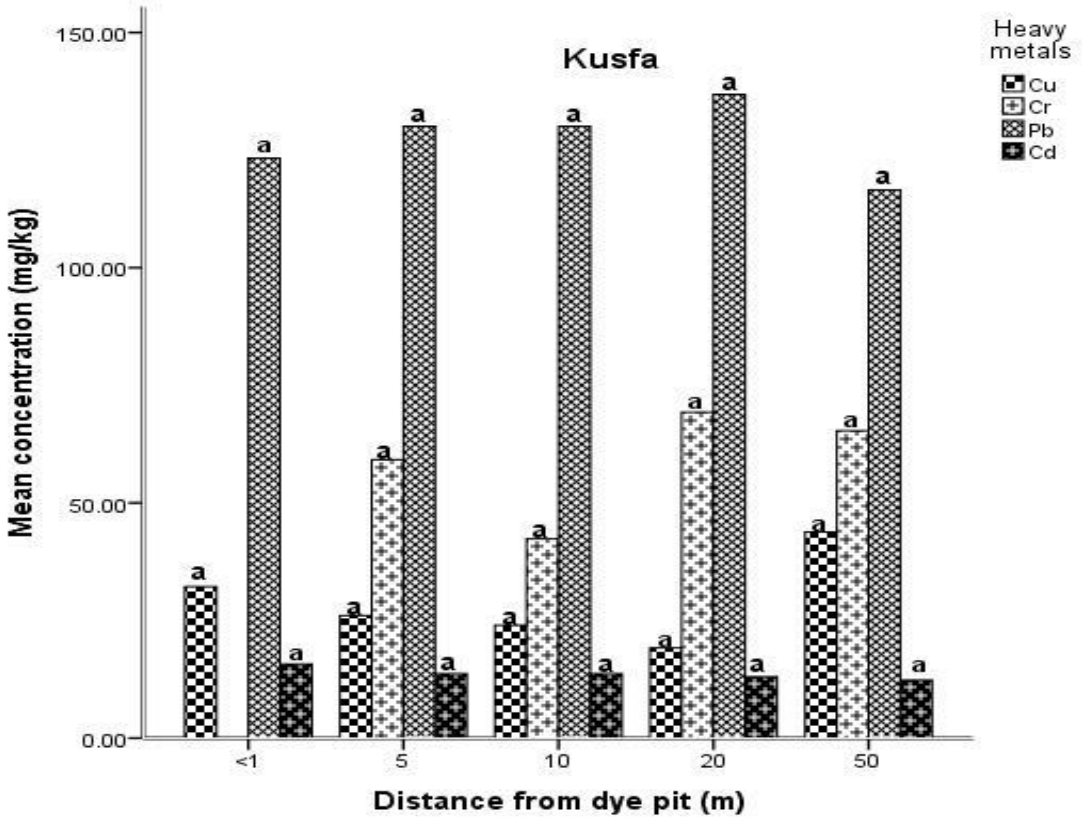


Figure 4.2: Horizontal distribution of total Cu, Cr, Pb and Cd in soils receiving dye effluents in Kusfa

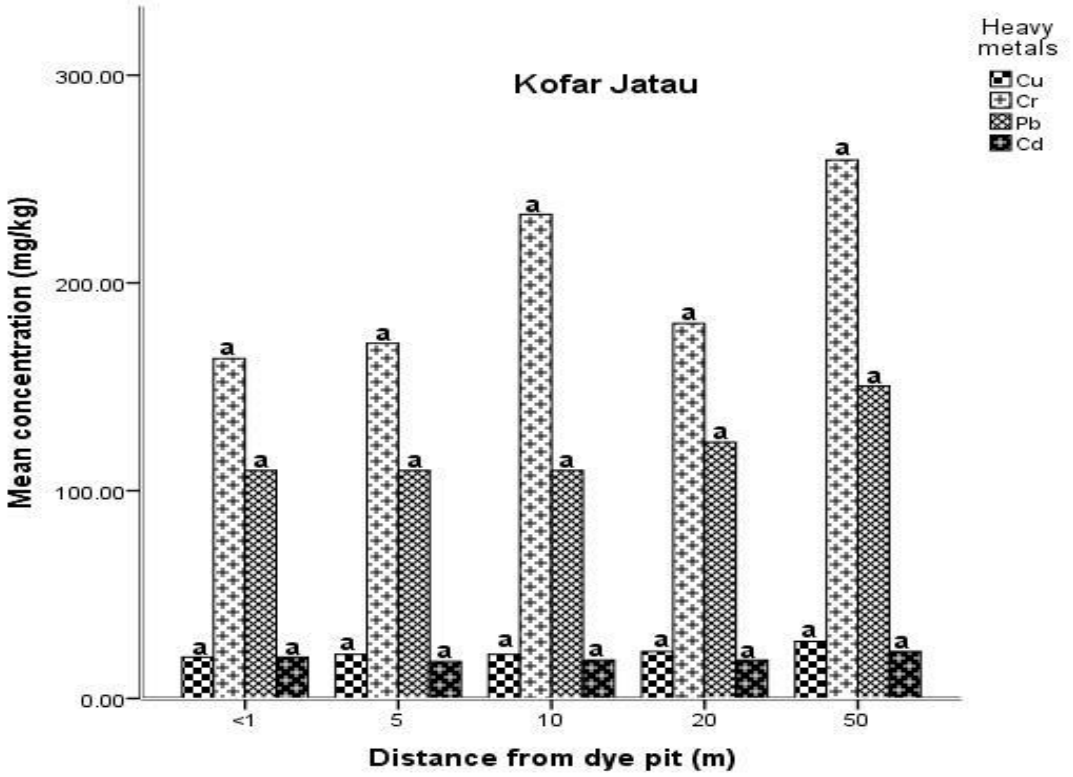


Figure 4.3: Horizontal distribution of total Cu, Cr, Pb and Cd in soils receiving dye effluents in Kofar Jatau

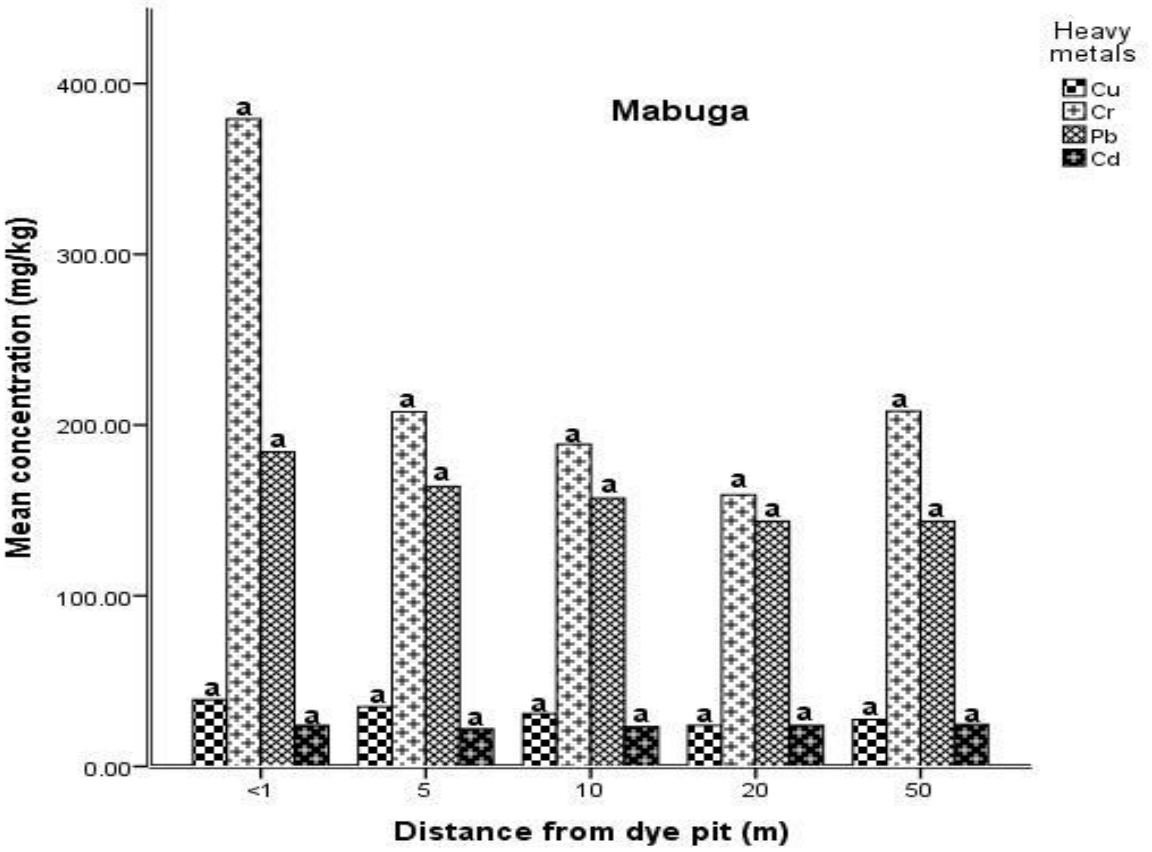


Figure 4.4: Horizontal distribution of total Cu, Cr, Pb and Cd in soils receiving dye effluents in Mabuga

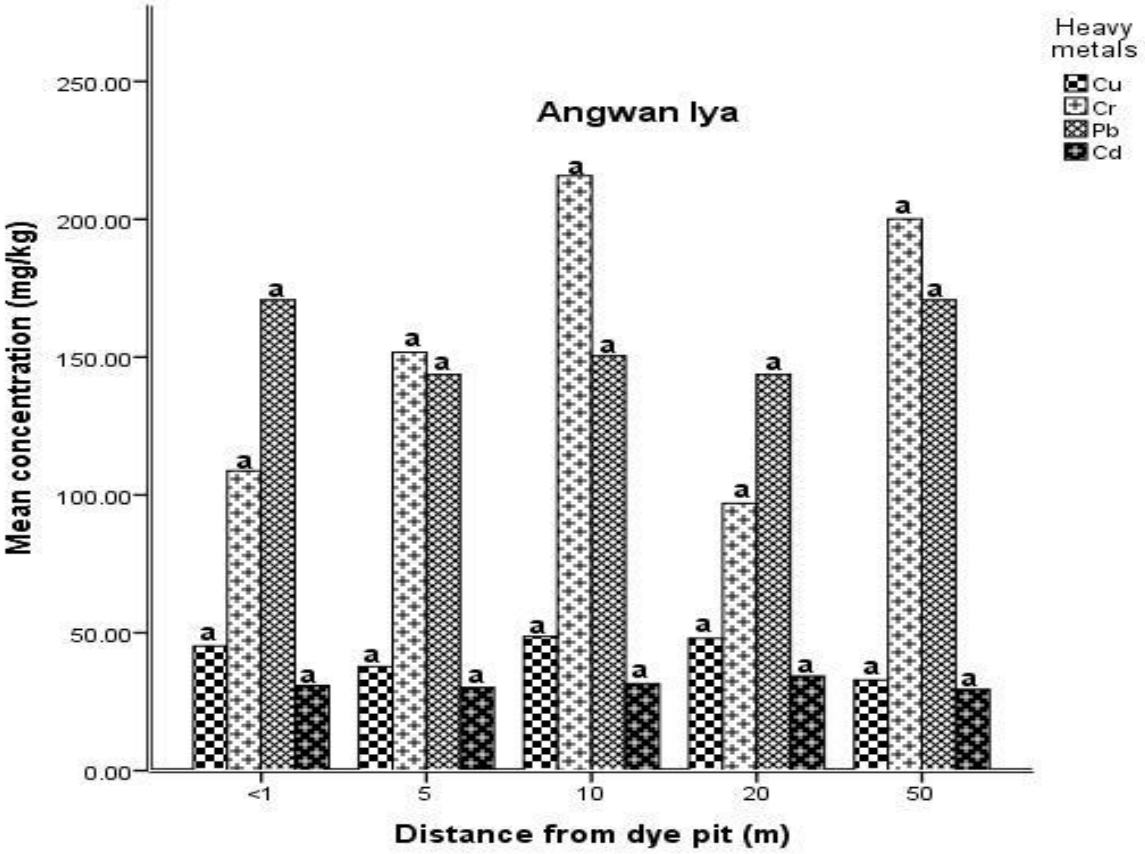


Figure 4.5: Horizontal distribution of total Cu, Cr, Pb and Cd in soils receiving dye effluents in Angwan Iya

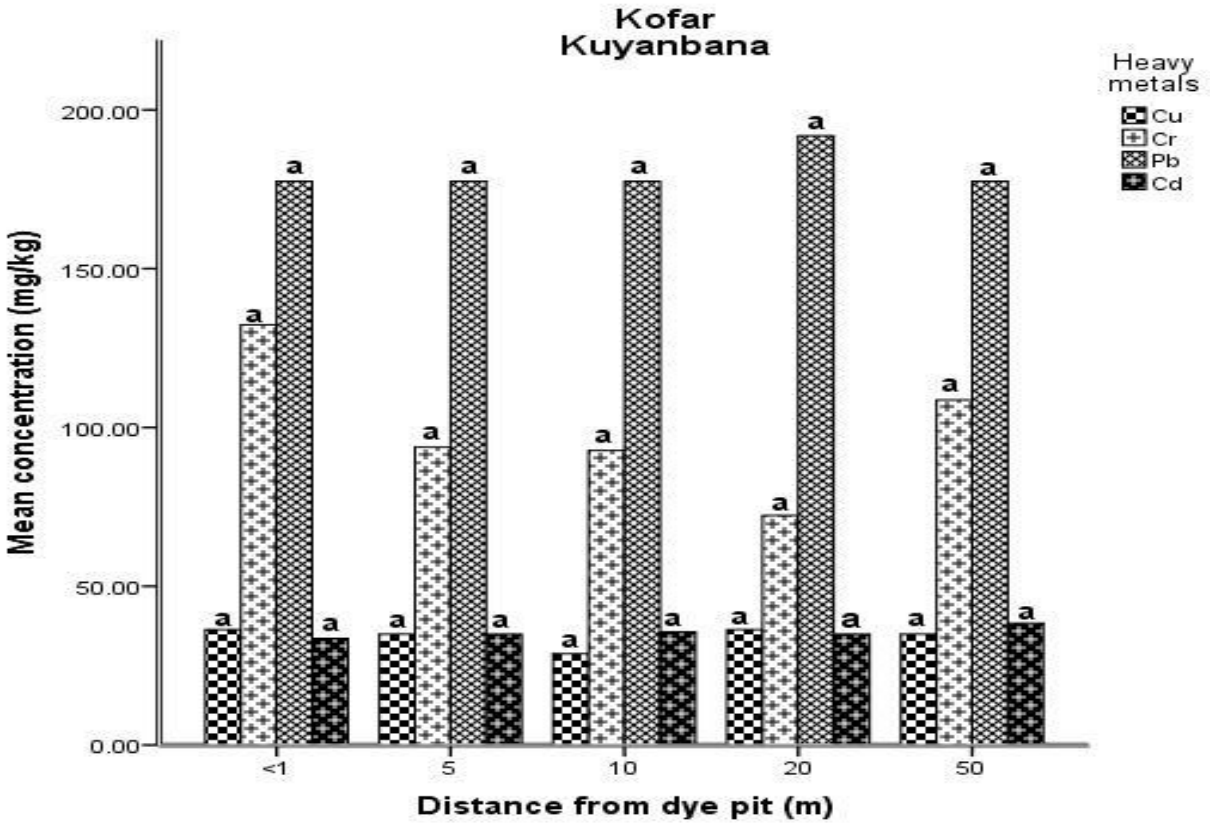


Figure 4.6: Horizontal distribution of total Cu, Cr, Pb and Cd in soils receiving dye effluents in Kofar Kuyanbana

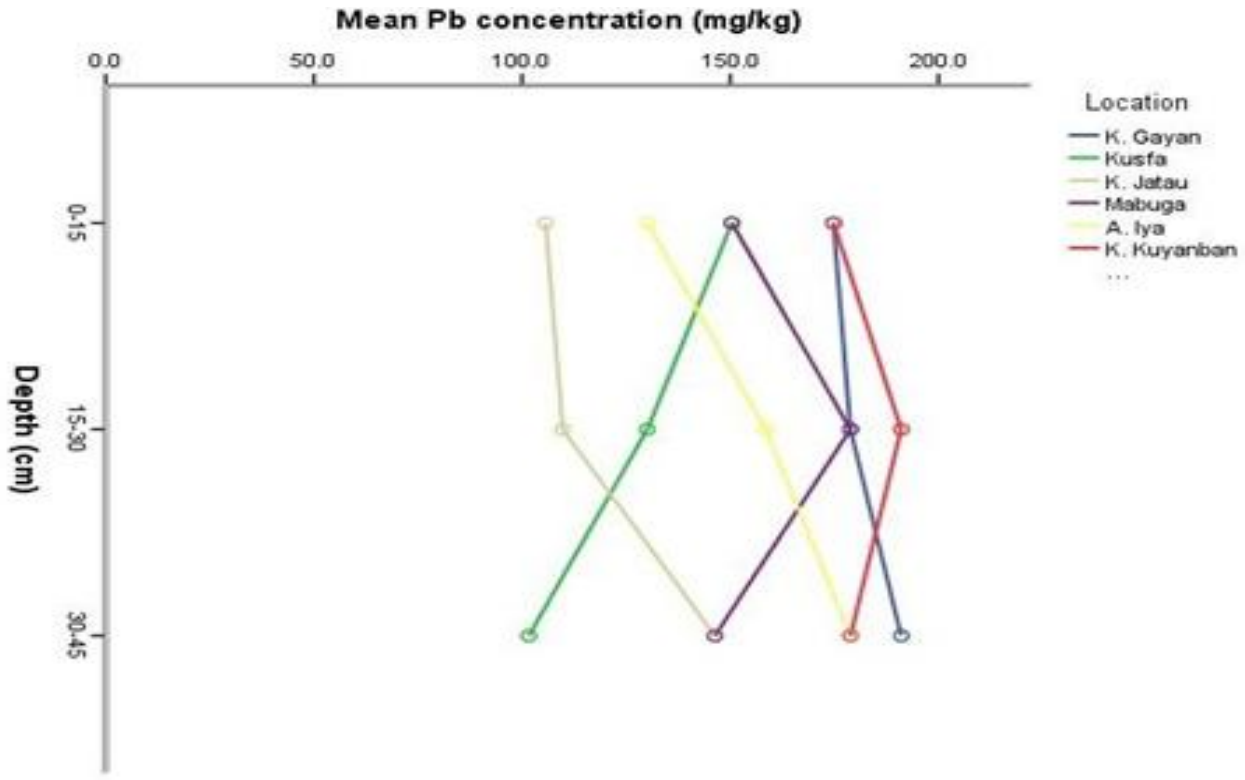


Figure 4.7: Vertical distribution of Pb (mg/kg) in soil under the influence of dye effluents

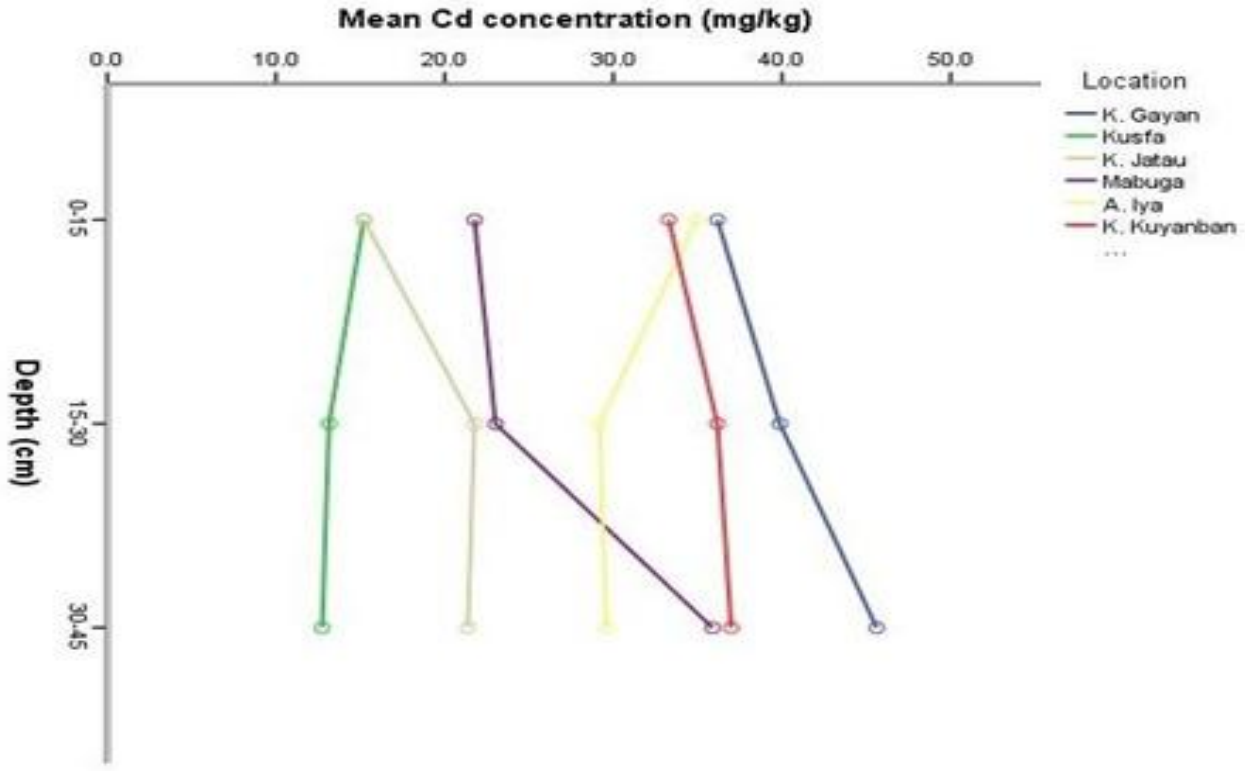


Figure 4.8: Vertical distribution of Cd(mg/kg) in soil under the influence of dye effluents

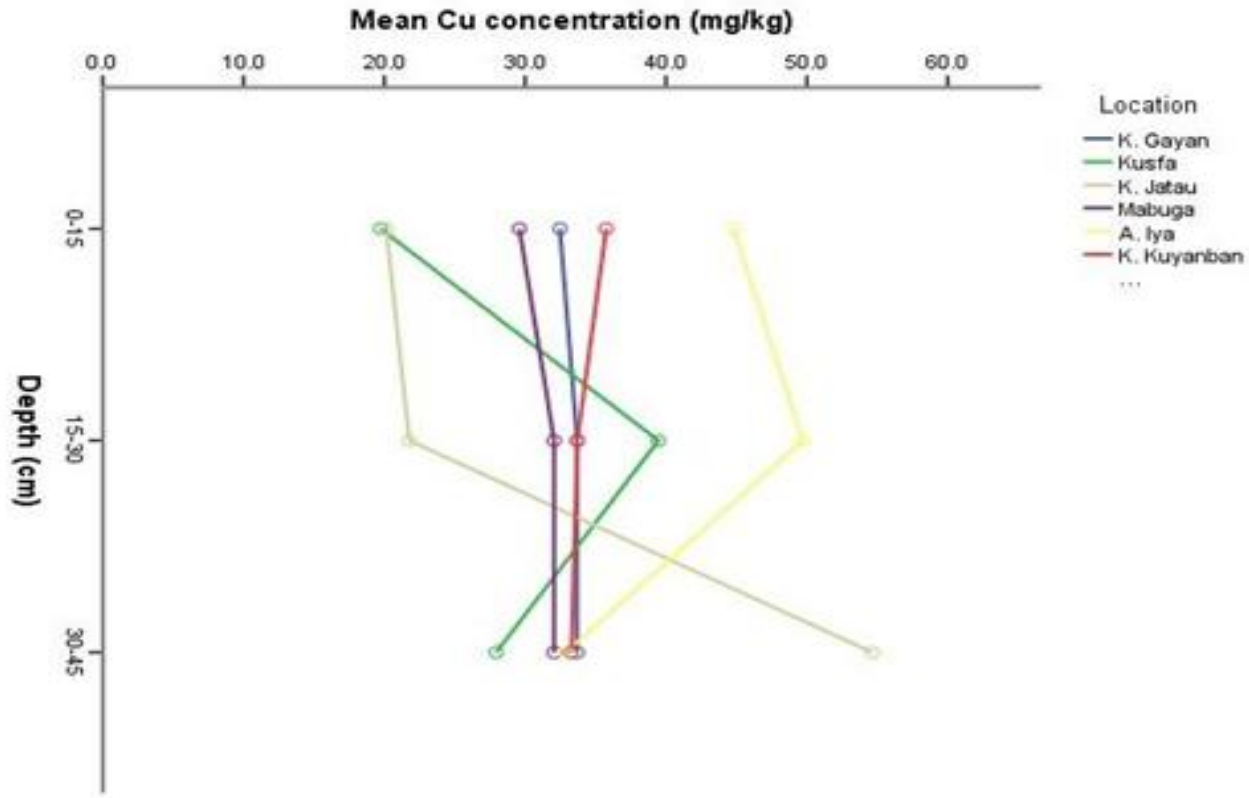


Figure 4.9: Vertical distribution of Cu (mg/kg) in soil under the influence of dye effluents

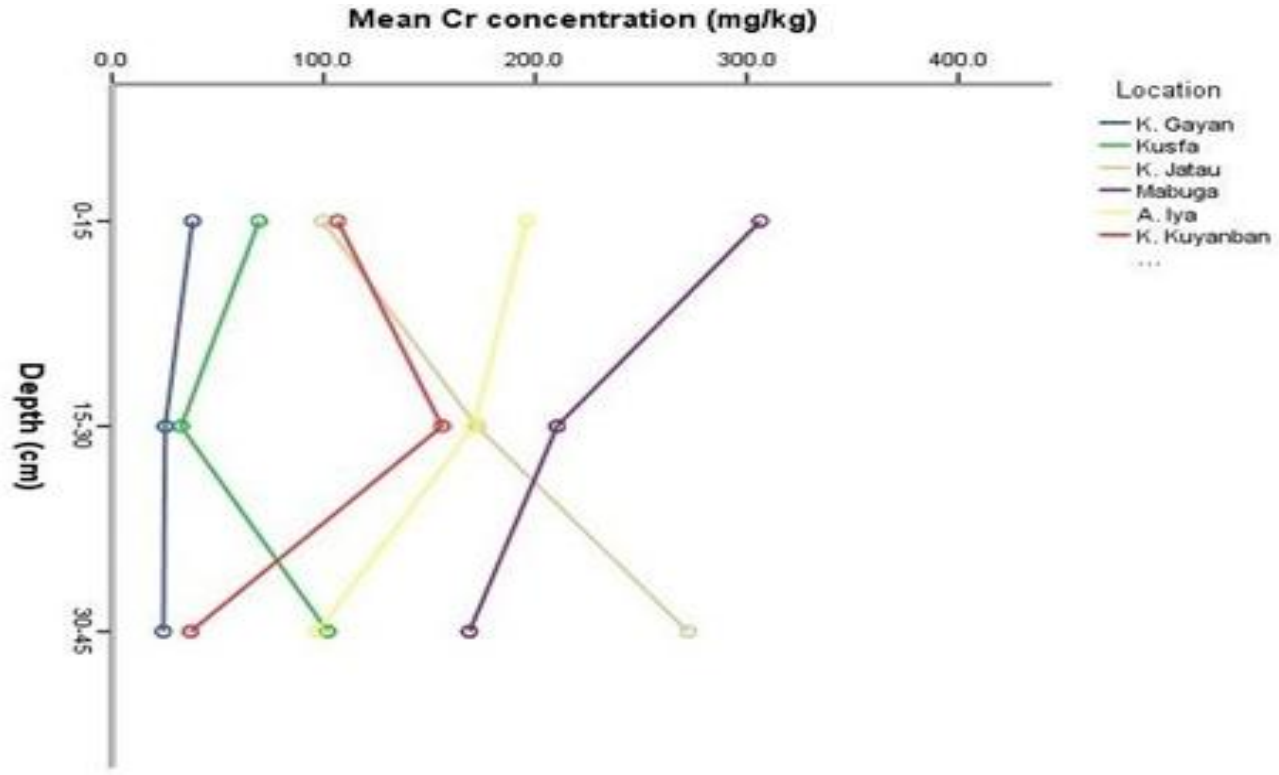


Figure 4.10: Vertical distribution of Cr(mg/kg) in soil under the influence of dye effluents

4.12 Horizontal Distribution of Available Cu, Cr, Pb and Cd as Influenced By Dye Effluents

The concentration of available Cu, Cr, Pb and Cd did not vary significantly ($p>0.05$) with distance from the dye pit. There were differences in their mean concentrations (Table 4.32). The highest concentration of Pb (10.98 mg/kg) was observed at 10 m away from the dye point. Similar observation was made at Kusfa where there is no significant difference in the concentration of the metals studied (Table 4.33). Cadmium concentration was the lowest with values ranging from 0.00-0.29 mg/kg, while the highest Pb concentration was 22.65 mg /kg at a distance of 20 m from the dye pit.

Kofar Jatau showed no uniform trend in the distribution of the metals. The highest value was observed at a distance of 5 m for Cu, 20 m for Pb and at 50 m for Cr (Table 4.34). Table 4.35 showed no significance differences in the concentration of heavy metals along the distances in Mabuga. Highest concentration of Cu was observed at 20 m, Cr at 50m while Pb was observed at < 1 m from the dye source. However, Angwan Iya showed significant difference in the concentration of the heavy metals. Cadmium concentrations were not detected except at 20 m which is 0.01 mg/kg (Table 4.36).

At Kofar Kuyanbana, there is no significant difference along the distance, although their values differ slightly at varying distances. Highest Cr and Cd concentration was observed at < 1 m from the dye pits (Table 4.37).

4.13: Vertical Distribution of Available Cu, Cr, Pb and Cd

There is no significant variation with auger depth in the concentrations of available Cu, Cr, Pb and Cd. Chromium and Pb decreases down the soil profile at Kofar Gayan. Significant concentrations were observed at 0-15 cm for Cu, Cr and Pb at this location (Table 4.38). Kusfa showed significant variation with auger depth for the heavy metals.

Table 4.31: Concentration of available Cu, Cr, Pb and Cd (mg/kg) in soil under the influence of dye effluents in Zaria city (Mean±SD)

Location	Cu	Cr	Pb	Cd
KG	1.54±0.10^{c}	0.84±0.01^{d}	7.72±3.00^{b}	0.00±0.00^{c}
Kusfa	12.39±3.44^{a}	1.89±0.02^{cd}	18.00±4.23^{a}	0.08±0.04^{a}
KJ	4.00±0.43^{bc}	7.26±2.33^{a}	9.66±0.78^{b}	0.03±0.01^{b}
Mabuga	6.05±1.23^{b}	9.14±2.22^{a}	9.61±0.67^{b}	0.07±0.00^{b}
AI	3.04±0.23^{bc}	6.19±2.11^{ab}	8.88±5.23^{b}	0.02±0.00^{bc}
KK	6.10±0.88^{b}	4.00±1.19^{bc}	15.06±5.32^{a}	0.04±0.01^{b}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.32: Horizontal distribution of available Cu, Cr, Pb and Cd in soils receiving dye effluents in Kofar Gayan, Zaria city (Mean±SD)

Distance from dye pit (m)	Cu (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Cd (mg/kg)
< 1	2.54±1.94[a]	1.20±0.01[a]	9.63±2.38[a]	0.02±0.00[a]
5	1.87±1.15[a]	1.55±1.01[a]	9.14±1.19[a]	0.10±0.01[a]
10	1.11±0.19[a]	1.13±0.34[a]	10.98±4.67[a]	0.01±0.00a
20	1.13±0.22[a]	1.55±0.35[a]	7.36±1.19[a]	0.01±0.00a
50	1.05±0.22[a]	1.10±0.32[a]	7.28±1.52[a]	0.01±0.00a

Note: Means with the same alphabets along the column are not significantly different at P<0.05.

Table 4.33: Horizontal distribution of available Cu, Cr, Pb and Cd in soils receiving dye effluents in Kusfa, Zaria city (Mean±SD)

Distance from dye pit (m)	Cu (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Cd (mg/kg)
< 1	13.68±5.65^{ab}	0.20±0.00^{b}	12.57±3.77^{b}	0.09±0.02^{a}
5	10.02±6.08^{ab}	2.37±0.76^{a}	20.90±5.85^{a}	0.03±0.01^{a}
10	10.71±6.01^{ab}	1.69±0.45^{a}	21.36±3.20^{a}	0.06±0.02^{a}
20	7.17±1.04^{ab}	2.77±0.76^{a}	22.65±8.75^{a}	0.01±0.00^{a}
50	20.37±7.54^{a}	2.61±0.92^{a}	12.51±2.47^{a}	0.03±0.01^{a}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.34: Horizontal distribution of available Cu, Cr, Pb and Cd in soils receiving dye effluents in Kofar Jatau, Zaria city

Distance from dye pit (m)	Cu (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Cd (mg/kg)
< 1	4.09±1.75[a]	6.54±2.77[a]	8.33±2.45[b]	0.05±0.01[a]
5	4.49±0.53[a]	2.84±0.38[ab]	10.81±0.55[a]	0.03±0.01[a]
10	3.97±2.04[a]	9.32±2.45[a]	7.75±1.96[b]	0.01±0.00[a]
20	3.81±1.23[a]	7.22±1.02[a]	12.37±3.29[a]	0.07±0.03[a]
50	3.66±1.54[a]	10.37±1.15[a]	9.01±1.06[a]	0.01±0.00[a]

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.35: Horizontal distribution of available Cu, Cr, Pb and Cd in soils receiving dye effluents in Mabuga, Zaria city (Mean±SD)

Distance from dye pit (m)	Cu (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Cd (mg/kg)
< 1	8.12±0.79[a]	15.17±5.18[a]	13.53±2.67[a]	0.09±0.04[a]
5	6.05±2.22[a]	8.31±3.68[ab]	10.04±5.61[a]	0.01±0.00[b]
10	3.03±1.69[ab]	7.55±2.76[ab]	4.39±0.93[b]	0.01±0.00[b]
20	8.29±1.17[a]	6.36±2.98[ab]	12.04±8.04[a]	0.09±0.01[a]
50	4.75±1.59[a]	8.32±0.46[ab]	7.78±2.43[ab]	0.14±0.02[a]

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.36: Horizontal distribution of available Cu, Cr, Pb and Cd in soils receiving dye effluents in Angwan Iya, Zaria city (Mean±SD)

Distance from dye pit (m)	Cu (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Cd (mg/kg)
< 1	2.75±0.38^{ab}	4.35±1.04^{a}	6.65±0.29^{a}	0.00±0.00^{a}
5	1.67±0.29^{b}	6.07±1.39^{a}	8.66±0.66^{a}	0.01±0.00^{a}
10	1.25±0.80^{b}	8.63±3.27^{a}	7.51±2.65^{a}	0.02±0.00^{a}
20	1.99±0.68^{b}	3.88±0.36^{a}	6.38±2.57^{a}	0.01±0.00^{a}
50	7.52±3.00^{a}	8.00±5.07^{a}	9.38±2.38^{a}	0.01±0.00^{a}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.37: Horizontal distribution of available Cu, Cr, Pb and Cd in soils receiving dye effluents in Kofar Kuyanbana, Zaria city (Mean±SD)

Distance from dye pit (m)	Cu (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Cd (mg/kg)
< 1	6.66±2.34[a]	5.29±3.51[a]	12.96±0.67[a]	1.86±0.02[a]
5	5.27±1.27[a]	3.75±0.54[a]	15.07±1.22[a]	0.02±0.00[ab]
10	6.51±0.89[a]	3.71±0.54[a]	14.10±5.75[a]	0.00±0.00[ab]
20	5.29±0.48[a]	2.89±1.64[a]	17.75±3.98[a]	0.02±0.00[ab]
50	6.75±4.02[a]	4.35±0.12[a]	15.41±0.84[a]	0.00±0.00[b]

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.38: Effect of soil depth on available Cu, Cr, Pb and Cd (mg/kg) in soil under the influence of dye effluents in Kofar Gayan, Zaria city (Mean±SD)

Auger depth (cm)	Cu	Cr	Pb	Cd
0-15	1.93±1.59[a]	1.52±1.49[a]	9.82±1.33[a]	0.01±0.00[a]
15-30	1.20±0.16[a]	1.01±0.38[a]	9.81±3.89[a]	0.00±0.00[a]
30-45	1.49±0.98[a]	0.00±0.00[b]	7.03±0.60[a]	0.06±0.00[a]

Note: Means with the same alphabets along the column are not significantly different at P<0.05.

Table 4.39: Effect of soil depth on available Cu, Cr, Pb and Cd (mg/kg) in soil under the influence of dye effluents in Kusfa, Zaria city (Mean±SD)

Auger depth (cm)	Cu	Cr	Pb	Cd
0-15	6.33±0.92^{ab}	0.28±0.62^{b}	10.51±1.90^{b}	0.04±0.02^{ab}
15-30	17.33±5.94^{a}	1.31±0.40^{ab}	17.02±10.07^{ab}	0.16±0..08^{a}
30-45	13.51±9.01^{a}	4.08±1.04^{a}	26.47±14.27^{a}	0.05±0.01^{ab}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.40: Effect of soil depth on available Cu, Cr, Pb and Cd (mg/kg) in soil under the influence of dye effluents in Kofar Jatau, Zaria city (Mean±SD)

Auger depth (cm)	Cu	Cr	Pb	Cd
0-15	4.39±1.35[a]	3.99±1.74[b]	10.08±2.20[a]	0.05±0.02[a]
15-30	3.74±1.42[a]	6.90±2.85[ab]	8.70±1.63[a]	0.02±0.00[a]
30-45	3.87±1.37[a]	10.89±3.06[a]	10.18±3.56[a]	0.03±0.01[a]

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.41: Effect of soil depth on available Cu, Cr, Pb and Cd (mg/kg) in soil under the influence of dye effluents in Mabuga, Zaria city (Mean±SD)

Auger depth (cm)	Cu	Cr	Pb	Cd
0-15	10.92±1.93[a]	12.26±2.79[a]	13.79±2.33[a]	0.11±0.01[a]
15-30	5.16±0.12[ab]	8.41±2.13[a]	9.68±1.43[ab]	0.07±0.01[a]
30-45	2.06±0.01[b]	6.76±0.36[a]	5.35±0.97[b]	0.03±0.00[b]

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Down the soil profile, Cr and Pb increases (Table 4.39). Similarly, there is significant difference with depth in this location but only Cr concentration increases down the profile (Table 4.40).

At Mabuga, the concentration of the four metals decreases down the soil profile. The highest concentration was observed at 0-15cm (Table 4.41). There was significant difference in the concentration of the metals at this location. At Angwan Iya, Cu and Pb increases, while Cr concentration decreases with depth. Cadmium concentrations were not detected at this location (Table 4.42). Table 4.43 showed significant difference down the soil profile at Kofar Kuyanbana. Copper, Pb and Cd increases down the profile, while Cr concentration decreases at this depth.

4.14 Metal Fractionation in Soil

4.14.1 Chromium fractions

Chromium is mostly abundant in the residual fraction in all the locations. Up to 70% of Cr was in the residual fraction in Kofar Gayan (Figure 4.11). Chromium in the water soluble fractions ranged from 2-4% across the locations with Kofar Gayan having the lowest value and Kusfa having the highest value.

The exchangeable fractions ranged from 2-10% with the lowest percentage observed at Kofar Gayan, while Kofar Jatau and Kofar Kuyanbana both had the highest value. Carbonate-bound fraction had the highest percentage of 9% in Mabuga and Angwan Iya, while the highest percentage of organic matter-bound fraction (19%) was found at Kusfa and the lowest fraction was found at Mabuga.

4.14.2 Copper fractions

Figure 4.12 shows that Copper was mainly found in the residual fraction (68%) in Kofar Gayan, relatively higher amounts of this metal were bound to organic matter (22%) and oxides of iron and manganese (3%). Low concentrations were obtained in the other fractions. Similarly, Kusfa, Kofar Jatau, Kuyanbana and Angwan Iya have a significantly high concentration of Cu fraction held unto the Organic Matter which ranged from 20-27% (Figure 4.12). At Angwan Iya, carbonate-bound fraction was the next most important fraction after the residual. The carbonate bound fractions obtained was up to 16% of the total Cu concentration. Mabuga has 8% of the exchangeable bound fraction of the total Cu in the study area.

4.14.3 Lead fractions

Figure 4.13 shows that soil from Kusfa, Pb was found mostly in the residual fraction (77%), although a significant amount was also in the fraction bound to carbonate (12%), the other fractions were in smaller concentrations (Figure 4.13).

In contrast, Mabuga and Kofar Jatau, have the organically bound fraction as the most important (12-14%), after residual, followed by that bound to carbonate (9-10%). Mabuga has the least value in the exchangeable fraction (1%), while that bound to oxide fraction (3%) was found in Kusfa and Kofar Kuyanbana. The exchangeable fraction had the least value of the total Pb from all the locations.

4.14.4 Cadmium fractions

In Kofar Gayan, the bulk of the total Cd concentration was partitioned to the residual fraction (80 %) of the total Cd, followed by the organically bound fraction (20%). In Kusfa, the exchangeable fraction held as high as 12% of the total Cd (Figure 4.14). However, the distributions of Cd among the oxide, OM and carbonate fractions were

Table 4.42: Effect of soil depth on available Cu, Cr, Pb and Cd (mg/kg) in soil under the influence of dye effluents in Angwan Iya, Zaria city (Mean±SD)

Auger depth (cm)	Cu	Cr	Pb	Cd
0-15	1.46±0.30^{b}	7.84±1.20^{a}	4.71±0.10^{b}	0.20±0.01^{a}
15-30	1.57±0.20^{b}	6.84±1.30^{a}	5.08±0.20^{b}	0.40±0.01^{a}
30-45	6.07±0.60^{a}	3.88±0.01^{ab}	13.37±2.00^{a}	0.30±0.00^{a}

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

Table 4.43: Effect of soil depth on available Cu, Cr, Pb and Cd (mg/kg) in soil under the influence of dye effluents in Kofar Kuyanbana, Zaria city (Mean±SD)

Auger depth (cm)	Cu	Cr	Pb	Cd
0-15	5.10±1.57[a]	4.27±0.32[ab]	12.69±2.56[b]	0.00±0.00[b]
15-30	6.49±1.51[a]	6.24±1.23[a]	15.21±3.45[ab]	0.00±0.00[b]
30-45	6.70±1.64[a]	1.49±0.23[b]	17.27±4.54[a]	1.14±0.01[a]

Note: Means with the same alphabets along the column are not significantly different at P≥0.05.

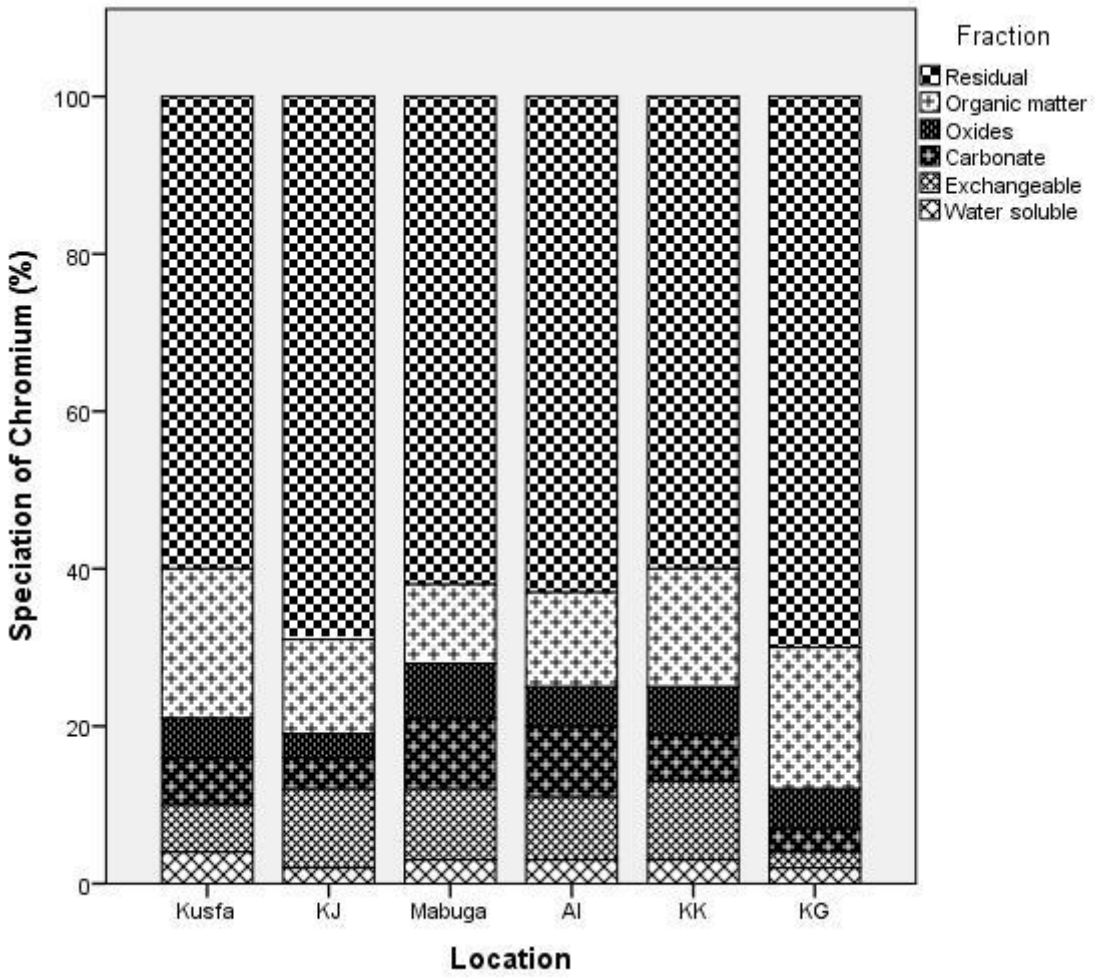


Figure 4.11: Distribution of Cr in different geochemical fractions of soil in six locations in Zaria city

smaller concentrations. In the Kofar Jatau and Mabuga soils, the residual fraction was the most important, this was followed by the organically bound fraction which ranged from 18-20%. Water soluble fraction held the least with a percentage range of 2-3 of the total Cd concentration. Similar trend was observed at Angwan Iya and Kofar Kuyanbana. Fractionation results partitioned the bulk of the total concentration of Cd to the residual fractions (Figure 4.14).

4.15 Potential Mobility of Heavy Metals in Soil

The mobility index was used as a more accurate methods of predicting the risk of contaminant transfer to food chain or groundwater. The calculated mobility indices for the metals under study ranged from 0.76-3.39 for Cd; 3.00-8.35 for Pb; 3.34-17.41 for Cr and 3.46-17.59 for Cu (Figure 4.15). These values showed that Cu was the most mobile in the soil followed by Cr, while Cd was the least mobile of the four studied metals.

4.16 Evaluation of Degree of Soil Contamination with Cu, Cr, Pb and Cd

The calculated average metal Enrichment Factor was obtained across the six locations. For Cd, the enrichment factors were Kusfa 68.5%, Kofar Jatau 97.3%, Mabuga 117.8%, Angwan Iya 156.2%, Kofar Kuyanbana 177.4% and Kofar Gayan 202.8%. Lead showed EF of 8.5% for Kusfa, 8.04% for Kofar Jatau, 10.57% for Mabuga, 10.39% for Angwan Iya and 12.10% for both Kofar Kuyanbana and Kofar Gayan.

Also Cr gave EFs of 0.9% for Kusfa, 2.5% for Kofra Jatau, 3.2% for Mabuga, 2.2% for Angwan Iya, 1.4% for Kofar Kuyanbana and 0.4% for Kofar Gayan. This only indicated some low level of enrichment compared to the average rock (parent material).

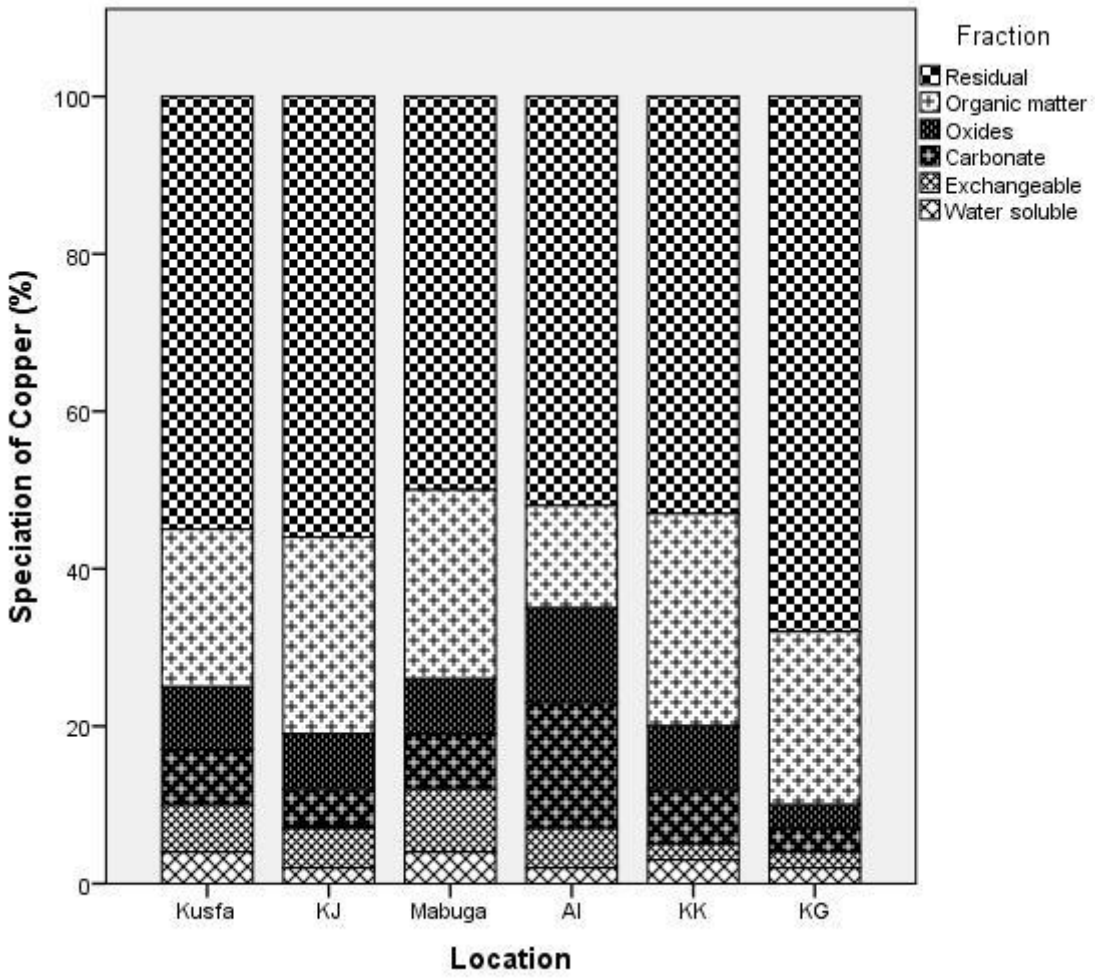


Figure 4.12: Distribution of Cu in different geochemical fractions of soil in six locations in Zaria city

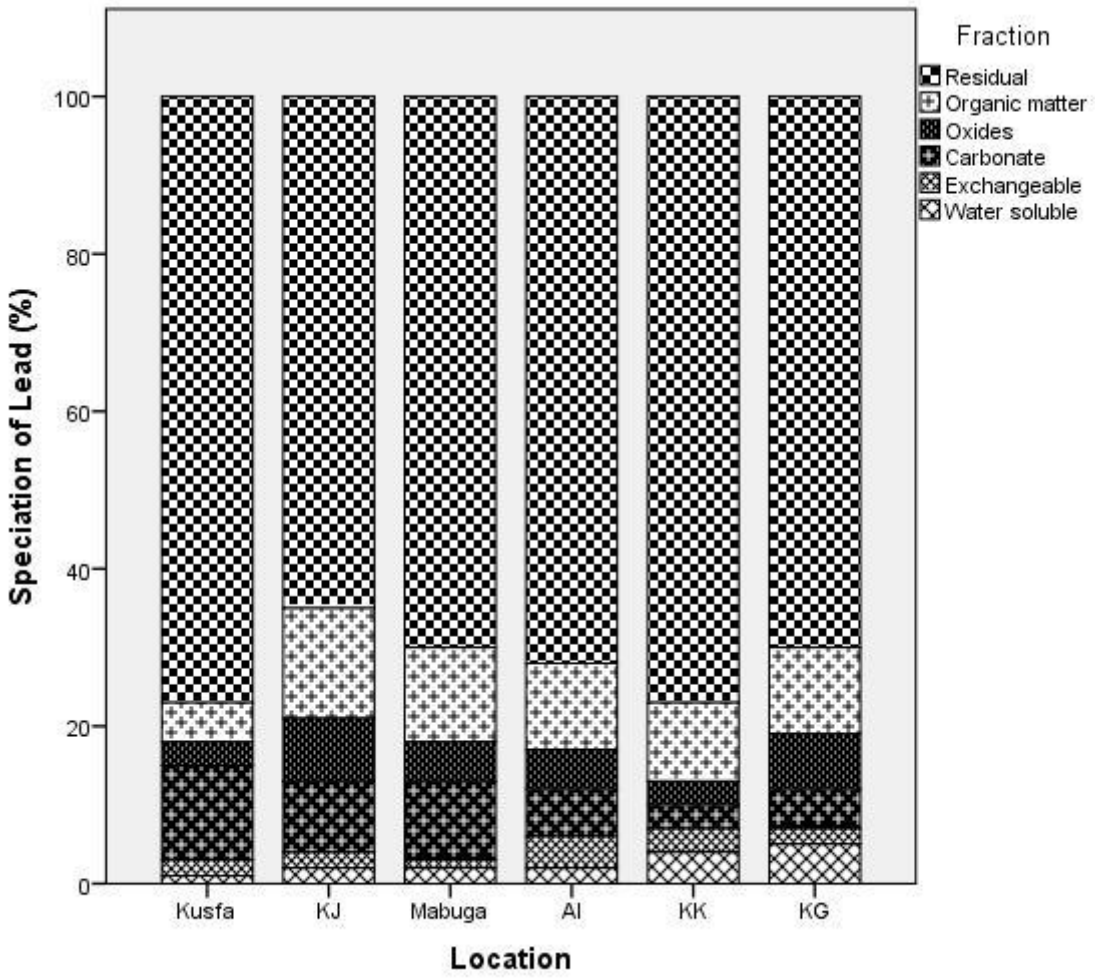


Figure 4.13: Distribution of Pb in different geochemical fractions of soil in six locations in Zaria city

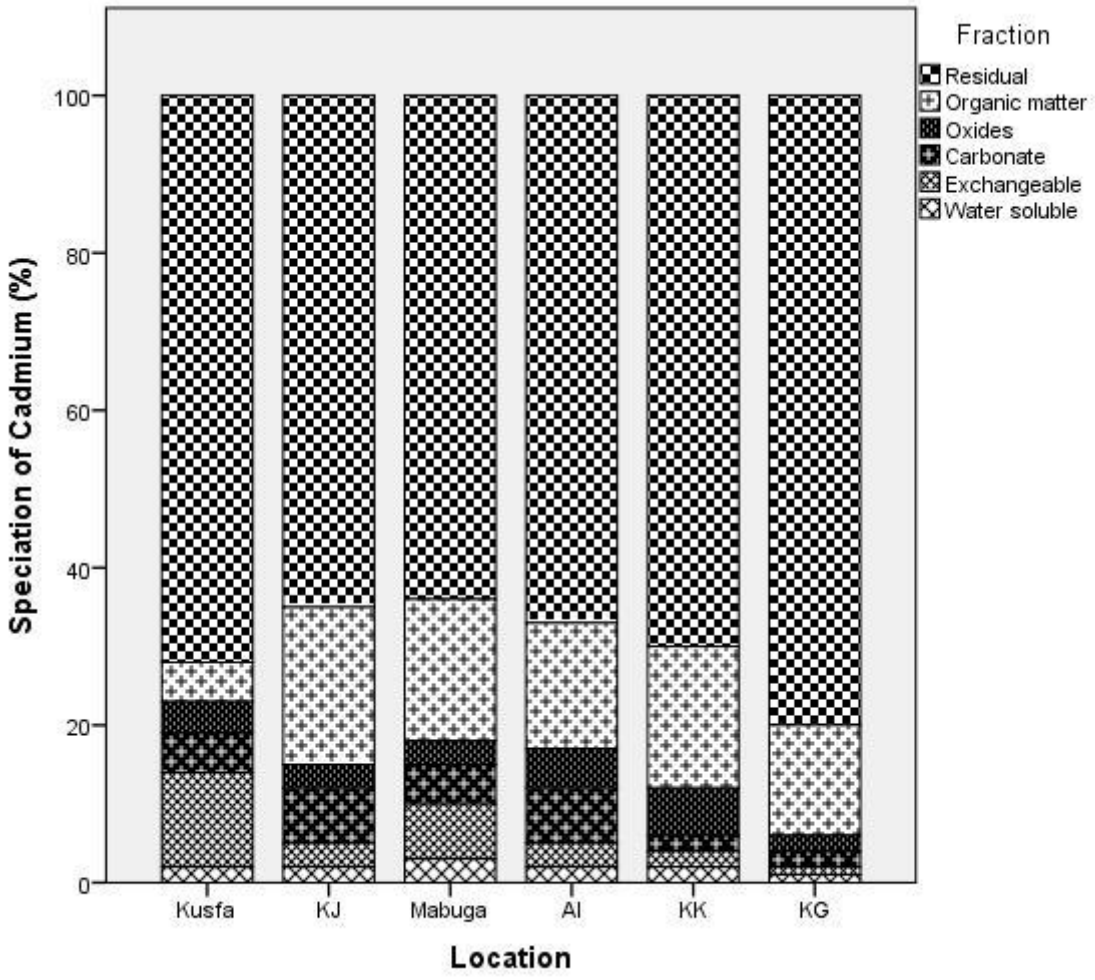


Figure 4.14: Distribution of Cd in different geochemical fractions of soil in six locations in Zaria city

Copper showed the lowest values for the EF studied. Kusfa, Mabuga and Kofar Jatau all had 0.9%, Angwan Iya had 1.3%, Kofar Kuyanbana and Kofar Gayan had 1.0%.

The average contamination factor for Cu from all the locations was below 2, while some were below 1 indicating no to medium contamination (Table 4.44; Muller, 1969).

The calculated average I-geo was obtained across the sites. For Cd, Kusfa showed 5.5%, Kofar Jatau showed 6%, Mabuga showed 6.3%, Angwan Iya showed 6.7%, Kofar Kuyanbana showed 6.9% and Kofar Gayan showed 7.1%. For Pb, Kusfa showed 2.5%, Kofar Jatau showed 2.4%, Mabuga and Angwan Iya showed 2.8%, Kofar Kuyanbana and Kofar Gayan showed 3%. The geoaccumulation index also showed that the concentrations of Cd and Pb where above the critical levels, however, Cr and Cu values were below the threshold value (Table 4.45). Two of the geoaccumulation indices for Cr approached 1, the rest were below 1. For Cu, the geoaccumulation factors were below 1 across all locations (Table 4.45). These indices were interpreted according to Appendix 1. (Abdu, N., Agbenin, J. O., and Buerkert, A., 2011c).

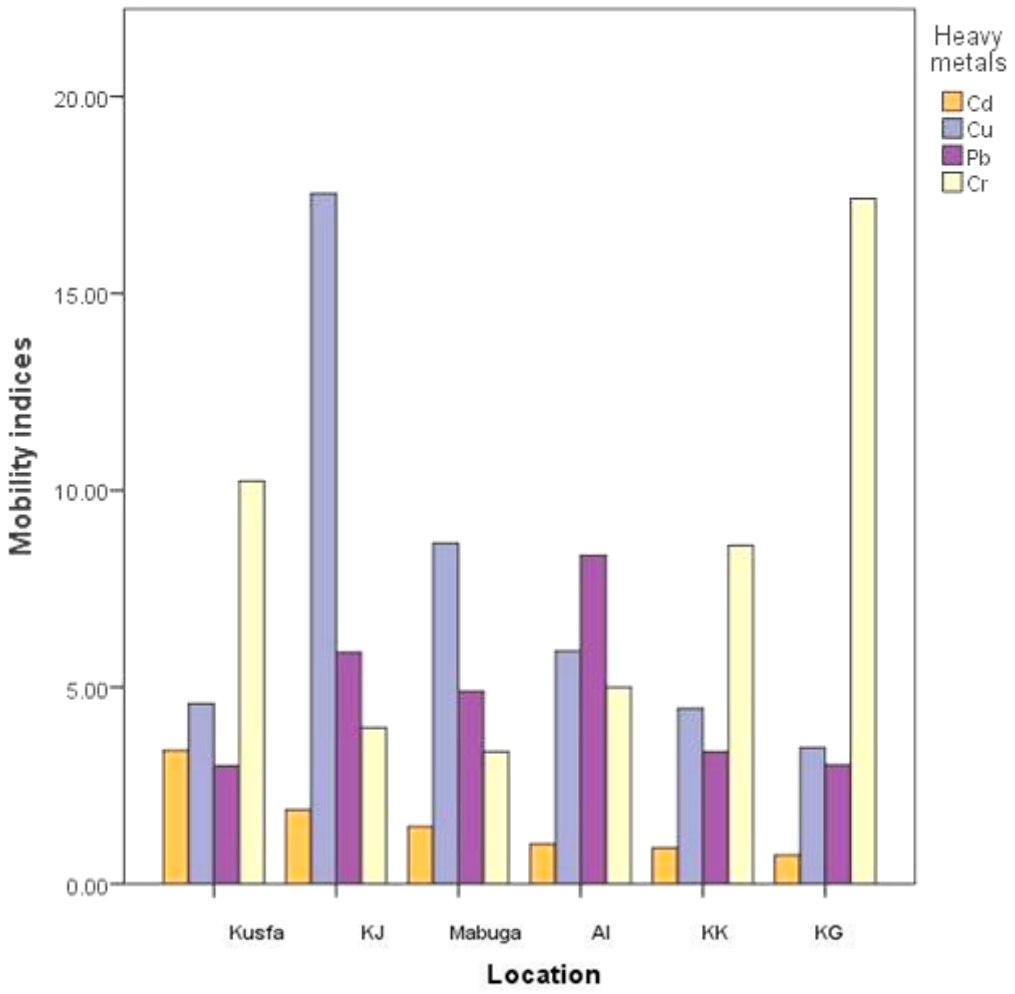


Figure 4.15: Mobility indices for Cd, Cu, Pb and Cr across the study area in Zaria city

Table 4.44: Calculated Enrichment Factors (EF) for Cu, Cr, Pb and Cd in six locations under the influence of dye effluents in Zaria city

Location	Depth	Cd	Cu	Pb	Cr
Kusfa	0-15	76.05	0.60	10.03	0.78
	15-30	65.75	1.20	8.67	0.45
	30-45	63.70	0.85	6.78	1.42
KJ	0-15	76.05	0.61	7.05	1.38
	15-30	108.90	0.66	7.32	2.39
	30-45	106.85	1.66	9.76	3.78
Mabuga	0-15	108.90	0.90	10.03	4.26
	15-30	115.10	0.97	11.92	2.92
	30-45	129.45	0.97	9.76	2.35
AI	0-15	174.70	1.36	8.67	2.72
	15-30	145.90	1.51	10.57	2.37
	30-45	147.95	1.00	11.92	1.35
KK	0-15	166.45	1.08	11.65	1.48
	15-30	180.85	1.02	12.74	2.17
	30-45	184.95	1.01	11.92	0.52
KG	0-15	180.85	0.98	11.65	0.53
	15-30	199.35	1.02	11.92	0.35
	30-45	228.10	1.02	12.74	0.42

Table 4.45: Calculated Geoaccumulation Factor (I-geo) for Cu, Cr, Pb and Cd in six locations under the influence of dye effluents in Zaria city

Location	Depth	Cd	Cu	Pb	Cr
Kusfa	0-15	5.66	-1.33	2.74	-0.95
	15-30	5.45	-0.33	2.53	-1.72
	30-45	5.41	-0.82	2.18	-0.08
KJ	0-15	5.66	-1.30	2.23	-0.12
	15-30	6.18	-1.18	2.29	0.67
	30-45	6.15	0.14	2.70	1.33
Mabuga	0-15	6.18	-0.74	2.74	1.50
	15-30	6.26	-0.63	2.99	0.96
	30-45	6.43	-0.63	2.70	0.65
AI	0-15	6.86	-0.14	2.53	0.86
	15-30	6.60	0.01	2.82	0.66
	30-45	6.62	-0.59	2.99	-0.15
KK	0-15	6.79	-0.47	2.96	-0.02
	15-30	6.91	-0.55	3.09	0.53
	30-45	6.95	-0.57	2.99	-1.54
KG	0-15	6.91	-0.61	2.96	-1.51
	15-30	7.05	-0.55	2.99	-2.10
	30-45	7.25	-0.55	3.09	-1.85

CHAPTER FIVE

5.0 DISCUSSIONS

5.1 Soil Characterization

The physicochemical characteristics of the soil in the various study locations in Zaria city differed substantially from one another due to wide use of dyes and chemical in the textile effluent. The soil samples taken from all dye and non-dye locations have similar sandy loam texture in all the locations, according to the USDA classification system (Table 4.1). Across the distances and down the soil profile, there was no change in the textural class of the soils indicating that dye effluent has no impact on the distribution of soil particle sizes. Soil pH affects the soil's physical, chemical, and biological properties and processes, as well as plant growth. The nutrition, growth, and yields of most crops decrease where pH is low and increase as pH rises to an optimum level. The pH of soils from the dye areas is alkaline in nature (8.59 -9.98) which is significantly different ($P<0.05$) from the pH of soils from non-dye areas which is moderately acidic (Table 4.1).

Mabuga showed highest pH value, this may be due to frequent effluent discharge of the dye chemicals in those areas. The control site, Kofar Gayan where dye activities does not take place had the lowest pH value. The increase in soil pH in the dye areas may be attributed to accumulation of various soluble salts in the dye effluent. Similar result was also obtained in the work of Ahmad *et al.* (2012) on the influence of dye effluent in the soil of Indian. The results obtained also were in agreement with the results of the survey conducted by Joshi and Kumar (2011).

Although the values were considerably higher in the dye areas than the non-dye areas, Organic Carbon (OC) content of the soils were generally low. Addition of dye effluent may be responsible for the increase in OC due to several organic substances present in

the dye chemicals. Available P values were low which is characteristic of a typical savanna soil of northern Nigeria. Soil available phosphorus was relatively higher in the dye area when compared to the control. Similar reason as in the case of OC might be responsible for the observed increase in available P. Soil in this area generally have low total N contents due to their sandy texture. This is similar to what was reported by Ahmad, M. T., Manderia, S. and Manderia, K., 2012) on the influence of dye effluent on the soil of Indian.

The acidity value in the contaminated soil is relatively lower than the uncontaminated soil. This confirms the influence of dye waste on increasing the soil pH. The higher concentration of exchangeable cations such as Na, K, Ca and Mg in the soil samples taken from the dye areas (Tables 4.2) comparable to the soil samples taken from non-dye areas is due to the discharge of dye effluents containing various excess soluble salts used in the dye process. The contamination of soils around dye areas increased the available sodium in such soils when compared to soils taken from non-dye area as shown in (Table 4.2). Increase in the sodium ion concentration of soils can be attributed to Na-containing minerals in the wastewater (Mojiri, 2011).

High amounts of sodium ions can result in precipitation of calcium and magnesium ions from the soil thus affecting their effectiveness in enhancing physical internal drainage (Ishaya, K.S., Maracus, D. N., Kukwi, 2011) thus damaging the soil structure. Along the distances, there are virtually no significant differences and no uniform trend in the distribution of the physicochemical parameters measured in all the locations. But there were more concentration of some of the variables at < 1m while some were further away from the dye source. This may be due to nearness to the dye pit.

5.2 Soil Microbial Properties

Bacterial and fungal populations were relatively greater in soil samples collected from non-dye areas when compared to soil samples from dye areas. Differences in bacteria and fungi counts between the different samples were not significant in all the location, although bacteria count was more than that of fungi. This is may be due to the fact that most soil bacteria prefer a slightly alkaline reaction while fungi grow in acidic medium. This finding corroborates with that of Ogunmwonyi, I. N., Igbinosa, O., Aiyegoro, O. A. and Odjadjare, E. E., 2008) on the microbial analysis of different top soil samples. Soil reactions also influence the type of the bacteria and fungi present in soil. Even though more strains of fungi was observed than that of bacteria, but total bacterial counts were generally higher than that of fungi, irrespective of sampling locations. The predominance of bacteria over fungi observed throughout the sampling time has been reported by other workers (Ogunmwonyi *et al*., 2008; Pandey, A., Singh, P., Iyengar, L., 2007). *Bacillus and Aspergillus* were the dominant bacteria and fungi genera found in the soil samples from all the location.

The observed difference in chemical properties of soils such as pH, organic carbon, total nitrogen and cations may have led to differences in microbial properties in soil samples from dye and non-dye areas. Horizontally, no uniform trend is observed in all the locations. Relative microbial biomass decreased exponentially with depth. More bacteria and fungi counts were recorded most especially at 0-15cm. It is widely presumed that the number of heterotrophic bacteria changes with depth. Fierer, N., Schimel., J., Holden, P., 2003) and Hartman, M., Lee, S., Hallam, S.I. and Mohn, W.W., 2009) also reported that microbial biomass often exhibits exponential decreases with depth. However, even the deepest soils had microbial biomass levels that were measurable. This may be due to bacterial and fungal species having the ability to absorb

and/or degrade textile dyes. It could also be attributed to spatial and resource factors such as nutrients that can influence the microbial diversity of the soil (Zhou, J., Xia, B., Treves, D.S., Wu, L.Y., Marsh, T.L., O'Neill, R.V., Palumbo, A.V. and Tiedje, J.M., 2002). The soil microbial biomass itself is an important pool of readily mineralizable organic N in soils and therefore, low potentially mineralizable N may be linked to low microbial biomass N due to saline environment. The control had the highest counts and highest microbial biomass C and N. This indicates that soils with the highest salinity level showed the lowest soil microbial biomass and activities while soils with low salinity levels showed no effect on soil microbial indices.

The soil microbial biomass is the active component of the soil organic pool, which is responsible for organic matter decomposition affecting soil nutrient content and, consequently, primary productivity in most biogeochemical processes in terrestrial ecosystems (Gregorich *et al*., 2000; Haney *et al*., 2001). Therefore, measuring microbial biomass is a valuable tool for understanding and predicting long-term effects on changes in land use and associated soil conditions (Sharma *et al*., 2004). Even at the dye areas, there were measurable numbers of bacteria and fungi. This is because under osmotic stress, microorganisms enhance their survival by channeling the consumed C and N into biomass production or cell proliferation, which naturally results in a decline in the rate of C and N mineralization. Furthermore, N mineralization may be affected by species composition of soil microorganisms, as species differ in their ability to degrade various organic compounds. Low average soil MBN content was also reported by Muhammad, S., Muller, T. and Joergensen, R G., 2008) in saline and alkaline soils from the Pakistani Punjab. Microbial biomass decreased with increasing level of salinity, underlying the detrimental effect of salinity on soil microorganisms. Reduction in soil microbial biomass due to increased salinity caused a substantial exponential decline in

potentially mineralizable N. Osmotic stress usually limits microbial growth and activity in saline soil, while under sodic condition, ion toxicities and adverse pH conditions may also inhibit microbial growth (Rietz and Haynes, 2003). While a number of factors may concomitantly cause the differentiation of soil microbial communities, this result suggest that pH and nutrients availability is the primary control on microbial community composition within the soil profiles.

5.3 Total Concentration of Cu, Cr, Pb and Cd

The concentration of Cu was below the threshold levels, where as those of Pb, Cd and Cr were all above the threshold levels (181.57, 228.57 and 40.55) given from all the regulatory bodies, Appendix 2: CCME, 2001).

The concentration of Cd was far above the limit even at the control site. Cadmium concentration recorded was worrisome. The effluents released on the surrounding soils were responsible for these high Cd and Cr concentrations corroborating the findings of Mariappan and Rajan (2004). However, Kashem and Singh (1999) reported low Cd concentrations in textile effluent contaminated soils from Bangladesh. Also the values are also far beyond that reported by Malarkodi *et al*. (2007) in the soils contaminated with textile effluent in Tamil Nadu. The observed Cd contents in our case may be attributed to the diversity and the chemical composition of dye material used in Zaria. Metal concentration was high, but might not be phyto-toxic, because at alkaline pH some metals are not mobile and bio-available. The very high concentration of Cd observed in the control suggests that dye effluent was not the primary source of Cd contamination in this soil. This might be as a result of other anthropogenic activities taking place in the study sites. There was no significant difference in the values of Cu from dye and non dye areas. The copper values for both contaminated and

uncontaminated soil samples fall below maximum permissible limit (Appendix 2). The low Cu concentration in all the sites is an indication of minimal Cu concentration in the dye chemical composition. Despite the low concentration, this was still higher than that values reported by Abdu (2010) in wastewater irrigated vegetable garden soils in Kano, Nigeria and some of the values reported by Adelekan, B. A. and Abegunde, K. D., 2011) in soil and groundwater. The values also vary from one location to another. The results from this study did not find Cu to be a contaminant in the soils of Zaria City. Therefore, no possible health risk of contamination.

Although Cr concentration was above the threshold levels given by EU and UK (Appendix 2), Mabuga recorded the highest concentration of Cr while the lowest concentration was recorded at Kofar Gayan. This shows that more dye activities occurs mostly at Mabuga. Most of the Cr values obtained were higher than that reported by Abdu (2010) in vegetable garden soils in Kano and Adelekan *et al.* (2011) on heavy metal contamination of soil and groundwater. The result obtained shows the possibility of Cr contamination in the study areas except in the control which has the lowest Cr value. Since Cr is one of the constituent of dye chemicals and about 2-10% of the effluent is loss to the soil (Welham, 2000). Chromium is one of those heavy metals which are steadily increasing due to industrial growth, especially the development of chemical and tanning industry and municipal waste. As observed by Ghosh and Singh (2005) non biodegradability of Cr is responsible for its persistence in the environment; once mixed in soil, it undergoes transformation into various mobile forms before ending into the environmental sink.

Lead concentration was above the threshold level given by regulatory bodies in Canada and UK (Appendix 2). Lead was observes to be relatively high in soil samples from non-dye and dye areas. The highest concentration was found at Kofar Kuyanbana while

the lowest was found at Kofar Gayan. The Pb values obtained are also higher than that reported by Abdu (2010) in vegetable garden soil and Ilemobayo and Kolade (2008); Ipeayeida and Dawodu (2008) and Nwachukwu, M.A, Feng, H. and Achilike, K., 2010) in soil samples collected from auto-mechanic sites.

5.4 Horizontal Distribution of Total Cu, Cr, Pb and Cd in Zaria City

The non-discernible trend observed in metal concentrations with distance indicates that there is no movement of some of these metals along the horizontal pathway. The highest concentration of Cu observed at < 1m away from the dye pit in Mabuga and Kofar Kuyanbana indicates the presence of Cu in the dye component.

5.5 Vertical Distribution of Total Cu, Cr, Pb and Cd in Zaria City

The observed decrease in the concentration of heavy metals down the depth may be related to the higher concentration of OM in the top horizon since OM has high affinity for heavy metals. However, the observed increase in heavy metal concentration with profile depth may be attributed to leaching-related translocation. The trend of a higher concentration of heavy metals in the subsoil can be attributed to superficial enrichment through human activities. Higher concentrations of Cu, Cd and Pb at lower depths likely shows the effects of leaching as the soils are mainly sandy in texture which allows easy infiltration and percolation of surface water. The high concentration of Cd observed in the control soil, Kofar Kuyanbana and Angwan Iya likely reflects its association with the soil parent materials. Kofar Gayan showed increase in Cu, Pb and Cd down the depth, Cd concentration decreases, likely shows effects of leaching.

5.6 Extractable Concentration of Cu, Cr, Pb and Cd

The amounts of metals extractable represent the available quantities that can be taken up. These forms of metals are mobile and readily available for soil and plant uptake. Although their values were very low compare to the total. These low levels of extractable heavy metals in the soils indicate high insolubility of the metal. Even though the total concentration was extremely high, only a small fraction of it was labile and readily available. Therefore, accumulation in the food chain is relatively low and the leaching of potential uptake of the metal by plants is limited. Among the metals, Pb had the highest percentage of extracted concentration while Cd generally has the least and was not detected at some point. The trend observed for this study is Pb > Cr > Cu > Cd.

5.7 Metal Fractionation of Soil

Fractionation results partitioned the bulk of the total concentration of Pb, Cd, Cr and Cu to the residual fractions (50- 80%) (Figure 4.11- 4.14). The residual fraction represents metals associated with silicate clay minerals (Hlavay *et al.*, 2004). Highest concentration of the total Pb was bound to the residual fractions in Kusfa and Kofar Kuyanbana while the exchangeable fraction of the soil in both locations held the least percentages of the total Pb concentration recorded.

Similarly, In Kofar Gayan, high percentage of the total Cd was also bound to the residual fractions, the water soluble fractions and exchangeable fractions held the least percentage. The exchangeable metal ions measure those trace metals that are released most readily into the environment; this fraction corresponds to the form of metals most available for plant uptake and could be easily released following any change in the ionic strength of the soil solution medium (Filguerias *et al.*, 2002). Elements held unto the

exchange fraction are easily exchangeable by other cations due to the weak electrostatic force of attraction in operation. The low proportion of metals held on this fraction in these soils is an indication of a low risk of Pb and Cd being released into the environment and also a low potential of food chain contamination.

Fractionation results reported by Krishnamurti *et al*. (2003) also observed that the exchangeable fraction usually represented a small fraction of the total metal content in unpolluted soils.

A significantly high concentration of the heavy metals fraction was held unto the OM fraction, especially for soils sampled at Kofar Kuyanbana for Cu. Organic matter has a high affinity for heavy metals, forming stable complexes with them; especially the divalent ions, for which organic matter exhibits a high degree of selectivity compared to monovalent ions (Filguerias *et al*., 2002). Kennedy *et al*. (2002) observed that metallic pollutants associated with this phase remains in the soil for longer periods but may be mobilized by decomposition processes (because they are oxidizable). Hence, the degradation of OM under oxidizing conditions would facilitate the release of Pb bound to this fraction (Filguerias *et al*., 2002). The organic bound fractions were the next most important fractions controlling Cr, Cd, Pb and Cu availability in these soils. The percentage of Pb partitioned to OM fraction is higher especially in Kofar Jatau.

In Angwan Iya and Kusfa, carbonate bound fractions were more for both Cu and Pb from the whole sampling locations. Carbonate could be an important adsorbent for many metals when OM and Fe-Mn oxides are less abundant (Stone and Droppo, 1996). The metal bound to carbonate is sensitive to pH and is mobilizable when pH is lowered. Generally, heavy metals in the exchangeable and carbonate fractions are readily and potentially bioavailable (Filguerias *et al.* 2002). The relatively high value of Cr in the

exchangeable fractions at Kofar Kuyanbana and Kofar Jatau (10%) in both locations shows that there is possibility of Cr being mobile in this environment.

Although Cd and Pb showed the highest concentration in the residual fractions followed by Cr and Cu from all the locations, indicates a lithogenic origin of the metal contaminants (McLean and Bledsoe, 1992). More metals were present in the residual fraction than in the other fractions which showed that the degree of pollution in the environment is presently low However, most of Cr, Cd, Cu and Pb are strongly retained in the residual phase in all soils held in the crystal lattices of minerals with strong bindings and consequently they will not be released into the environment.

5.8 Potential Mobility of Heavy Metals in Soil

The mobility index (Liu *et al*., 2007; Banat *et al.*, 2003) was used as a more accurate prediction of the risk of contaminant transfer to the food chain or ground water .The observed order of mobility was Cu > Cr > Pb >Cd. Although low concentration of Cu was observed to be associated with the available heavy metals, the high mobility index may reflect potential risk of pollution through leaching and plant uptake of metals. This could be further aggravated by the predominantly sandy texture of the studied soils. Cadmium had the least potential mobility. These results largely indicate anthropogenic origin of the metals which were attributed to the dyeing activities. Although lead recorded the highest total metal concentration, this element was comparatively the less mobile.

5.9 Evaluation of Contamination of Cu, Cr, Pb and Cd

The contamination factor of Cu and Cr indicates low contamination while Cd and Pb have very high contamination factor (> 3) indicating moderate to strong contamination

(Muller, 1969). The higher contamination factors were all observed at lower profile depths which preclude anthropogenic input from the surface. However, the EF > 100 and the I-geo grade (6) of Cd in the soil is strong indication of superficial enrichment of the metal. Although the Cd contents of the parent material of the study sites were not determined, the high Cd concentration could also be related to lithogenic origin of the soil.

The geoaccumulation index also showed that concentrations of Cd and Pb were above critical levels. For Cu and Cr, the geoaccumulation factor was below zero across locations and depths indicating no case of contamination. The enrichment factor calculated for this element, however, suggests level of contamination for Cd and Pb. The EF suggests that these elements originated mainly from the parent rock in the earth's crust. Values <1 indicate mobilization or depletion of an element whereas EF >1 indicate effects of anthropogenic inputs (Bhuiyan *et al*., 2010) which may only have been the case for Cd and Pb.

Although EF and I-geo allow for quick inferences on the status of a metal relative to mean soil and lithosphere concentration, it is important to point out that these indices are based mainly on total concentration of a metal in the environment. EF and I-geo factors revealed highest grades for Pb and Cd.

5.10 Correlation Matrix of Bacterial Counts, Fungal Counts, Microbial Biomass and Physicochemical Parameters of Soil

Pearson correlation coefficients indicated that all metals were highly correlated with each other ($P \leq 0.01$; Appendix 3). Such strong inter-element correlation is an indication that the elements originated from similar sources possibly subjected to the same pedogenic processes. The strong positive correlations observed between these metals

are in agreement with the reports of Abdu *et al*. (2011b) and Bhuiyan *et al*. (2010). The significant correlation between soil pH and heavy metals in this study is contrary to the results obtained by Manta *et al*. (2002) and Tume *et al*. (2006). High soil pH showed negative effect on all microbial indices including MBC, MBN, Fungi and Bacteria counts (Appendix 3). The result indicates that soils with the highest pH level showed the lowest soil microbial biomass and activities. Positive correlation was found between microbial biomass and organic carbon with total nitrogen. The fungal counts values were also significantly correlated with organic carbon and total nitrogen. Similar results were found by Yuan *et al.* (2007) and Li *et al*. (2007). The dynamics of N in mineral soil is closely linked to C, because most N exists in organic compounds and heterotrophic microbial biomass, which utilize organic C for energy. As a result, the microbial biomass N showed a significant positive correlation with microbial biomass C. This result is in consonant with previous studies (Sharma *et al*., 2004; Wright *et al*., 2005).

V1-V21 means microbial biomass carbon, microbial biomass nitrogen, pH, available phosphorus, organic carbon, acidity, calcium, magnesium, potassium, sodium, available cupper, total cupper, available chromium, total chromium, available lead, total lead, available cadmium, total cadmium, total bacteria count and total fungi count respectively (Appendix 3).

5.11: Correlation Coefficient Matrix between Cu and Cr Fractions

According to Jones and Jarvis (1981), processes of metal mobilization-immobilization are affected by a variety of soil properties. To examine this influence, correlations between the six chemical phases of the sequential extraction have been established for all soils. For Cu, water soluble fraction correlate positively with the exchangeable

fraction, carbonate fraction and organic matter fraction but correlates negatively with the residual fractions (P<0.01; Appendix 4) indicating that the latter residual fraction may suppress the availability of these fractions thereby reducing the risk of plant uptake. No reliable correlation was observed between the fractions of oxides (P<0.01; Appendix 4).

In contrast, water soluble fraction (WS) in Cr does not show any significant correlation with all the fractions. However, the exchangeable fraction correlates positively with carbonate fraction similar levels of correlation were also observed between the exchangeable, oxide and organic matter fractions ($p < 0.01$; Appendix 4). This suggests a strong buffering of the exchangeable Cr concentration by the oxide, carbonate and organic matter fractions, thereby increasing the risk of Cr release into the environment. The residual fraction correlates negatively with all the fractions.

5.12 Correlation Coefficient Matrix between Cd and Pb Fractions

Significant positive correlation was observed between the water soluble Cd fractions, exchangeable Cd fractions; carbonate Cd fractions and organic matter fractions. But the residual fraction correlates negatively with all the fractions (Appendix 5; $p \leq 0.05$). This is an indication that the residual fraction may suppress the availability of these fractions thereby reducing the risk of plant uptake. However, for the Pb fractions only the residual fraction correlates negatively with the carbonate fraction (Appendix 5; $p<0.05$).

CHAPTER SIX

6.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary and Conclusions

Results from this study indicated differences in the physico-chemical properties and heavy metals characteristics of the soil across the six study locations. This was as a result of chemical contaminants present in the textile effluent. The outcome of this study also shows diversity of bacteria and fungi isolated from soils as a result of dye effluent contamination. The distinct types of bacteria and fungi isolated were generally similar, though occurring at different locations during the period of the study. The abundance of bacteria and fungi in this study were typical of environment with high species richness and functional diversity. Despite the fact that it is possible that a number of bacteria and fungi might have been missed in this study. The dominant genera are (*Bacillus* and *Aspergillus*). This studies gave an insight into the population dynamics and distribution of culturable aerobic bacteria and fungi diversity around dye and non dye areas of Zaria city.

High soil pH showed negative effect on all microbial indices such as MBC, MBN, bacteria and fungi counts. The results indicated that soils with the highest salinity level had the lowest soil microbial biomass.

Metal pollution has harmful effect on biological systems and does not undergo biodegradation. Toxic heavy metals such as Pb and Cd can be differentiated from other pollutants, since they cannot be biodegraded but can be accumulated in living organisms, thus causing various diseases and disorders even in relatively lower concentrations. Although the contaminated soil samples showed the presence of high level of metal contamination due receiving of textile effluent. Soil heavy metal

concentrations trend in the locations followed the sequence Mabuga>Kofar Jatau>Angwan Iya > Kofar Kuyanbana> Kusfa >Kofar Gayan. High Cd concentration in the control suggests that the major sources in Zaria city may be anthropogenic activities. High values of Pb, Cd and Cr were found in soils locations at the dye areas when compared to control samples. However, it was found that Pb generally had the highest concentrations in the soil layers while Cd generally has the least. The order of the elements observed for this study is Pb > Cr > Cu > Cd.

The values of Cd obtained from this study were far above the permissible level for soils in most countries. This raises significant environmental concern and calls for urgent attention and appropriate response. This level of Cd content in the effluent is toxic in nature, harmful to man and other living organisms and can deteriorate soil quality as well as fertility. This requires proper treatment before disposal on land as it is not safe for final release. The total concentration of the metals was separated into operationally defined fractions by sequential extraction. The largest proportions for Pb, Cu, Cd and Cr were extracted in the residual phase, in which metals are strongly retained in the soil minerals. The results obtained from speciation studies showed that most of the metals considered had the highest abundance in the residual fraction. This indicates that the metals were immobile. This shows that soil in the environment was not likely polluted by these metals through anthropogenic activities.

The relatively high Cr found organic fraction was the exchangeable fraction, indicating that it could be easily released to the environment from soil. This may be toxic in the environment. The potential mobility of Cr, Cu, Pb, and Cd in the soil samples studied were quite high implying that under favorable conditions they can be released to pollute the environment. The results of the speciation have given the present status of metal pollution and the potential pollutants in all the locations. However fractionation of the

heavy metals could give their effect on mobility, solubility and bioavailability for better understanding the ecotoxicity of Zaria city environment.

Based on the calculated metal enrichment factor, geoaccumulation index, there seems to be no apparent contamination of the four heavy metals in soils studied except for Cd and Pb which are very high. Such indices of pollution can be used to identify likely sources of total metal contamination in soils of the Zaria city. Of all elements studied only Cd and Pb had I-geo and EF values above unity suggesting anthropogenic input of this element.

Though the volume of effluents from individual small-scale dyers might be small, the concentration of pollutants is generally high. The impact is significant where several producers are located at one place and discharge effluents into the soil. It is therefore concluded that the contaminated soil samples in Zaria city showed the presence of high level of metal contamination far from the prescribed limits, toxic in nature and require proper treatment before disposal on land as it is not safe for final release which is also harmful to man and other living organisms which consequently decrease soil fertility and damage food quality.

6.2 Recommendations

1. Although the partitioning of the total heavy metal concentration to the soil residual fraction does not pose immediate threat to soil quality, however it is recommended that there should be caution in the discharge of the dye effluents in the environment so as to avoid long-term contamination of the soil through anthropogenic accumulation of heavy metals in environment, which may consequently decrease soil quality and damage food chain.

2. Strict compliance should be ensured so as to limit the volume of dye effluents discharged by the dyers into the environment in Zaria city.
3. It is recommended that legislation be made to restrict heavy metal loadings on land in order to limit heavy metal discharges from industries.
4. The use of modern biological techniques such as PCR should also be used to ascertain the behaviour and diversity of soil microbial community in Zaria city.
5. For the greater benefits of our country, all people involved in textile dyeing including the local dyers should be enlightened on the danger and the damage of what the effluent does to the environment.

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APPENDICES

Appendix 1: Average and background concentration, enrichment factor, calculated I-geo index, and grade of pollution intensity of Cd, Pb, Cu and Cr in analyzed soil samples from Zaria city

Heavy metal	Average value (mg/kg)	*Background Concentration (mg/kg)	EF	I-geo	I-geo grade	Pollution intensity
Cd	27.33	0.2	27.33	6.41	6	Strongly/extremely contaminated
Pb	154.25	15	10.28	2.75	3	Moderately contaminated
Cu	33.74	33	1.02	-0.60	0	Uncontaminated
Cr	126.54	72	1.76	-0.16	0	Uncontaminated

***(**Abdu *et al*., 2011c)

Appendix 2 :International threshold values for heavy metals concentration in soils ($mgkg^{-1}$)

Heavy Metal	Regulatory system			
	UK	**EU**	**USA**	**Canada**
Cd	1.4	3.0	3.0	19.5
Zn	200	300	200-300	1400
Cr	6.4	180	400	1500
Cu	63	140	80-200	170
Pb	70	300	300	150
Ni	50	75	50-110	210

Source: CCME (2001)

Appendix 3: The correlation matrix of bacterial counts, fungal Counts, microbial biomass and physicochemical parameters of soil samples of the dye effluents locations.

	V1	V2	V3	V4	V5	V6	V7	V8	V9	V10	V11	V12	V13	V14	V15	V16	V17	V18	V19	V20	V21
V1	1																				
V2	.51	1																			
V3	-.42*	-.54*	1																		
V4	-.23*	-.23*	.53*	1																	
V5	-.22*	-.22*	.50*	.78*	1																
V6	-.45	-.49	-.17	69	.52	1															
V7	.64**	.56**	.72**	.24*	.25*	.23*	1														
V8	.35	.52	.38	-.23*	-.58	-.83	-.27*	1													
V9	-.34	-.32	.48	.56*	.56*	.77	.46*	-.38*	1												
V10	-.05	.47	.24*	.48	.20	.53	-.50	.42	-.22	1											
V11	.64**	..41*	.69**	-.21*	-.21*	.42	.27*	.36	-.23*	.20	1										
V12	.52*	.87**	.51**	.48*	.52*	.32	.93**	.62**	.55*	-.45	.89**	1									
V13	.49*	.67**	.50*	.73**	.71**	.94**	.81**	.71**	.27*	.31*	.78**	.24*	1								
V14	.72**	.82**	.09	.26*	.37	.67**	.77**	.54*	.25*	.58	.60**	.34*	.51*	1							
V15	.50*	.71**	.07	.43	.51*	.56*	.54*	.80**	.25*	.77*	.74**	.93**	.62**	.39*	1						
V16	.78**	.60**	.45*	.44*	.47*	.51*	.95**	.52*	.38*	.84	.92**	.96**	.52*	.73**	.53*8	1					
V17	.67**	.34*	.44*	.44*	.47*	.74**	.55*	.88**	.38*	.78	.94**	.56*	.60**	.82**	.43*	1	1				
V18	.53*	.58*	.48**	.55	.48*	.29*	.61**	.67**	.63**	.76	.62**	.66**	.73**	.38*	.96**	.62**	.72**	1			
V19	.44*	.81**	.52*	.35*	.36*	.88**	.83**	.65**	.56*	.37*	.53*	.74**	.39*	.66**	.42*	.45*	.52*	.45*	1		
V20	-.52	.42	.40	.64	.71	-.56	-.55	-.51	-.58	-.52	.32	-.57	-.53	.54	-.45	-.58	-.58	.54*	.31	1	
V21	.39	.22	-.50	-.59*	.63**	-.38	-.23*	-.44	-.32*	-.44*	.44	-.62*	-.57*	-.43*	.51	-.43	-.23	-.26*	.58*	.37	1

NOTE: * and ** implies significant and highly significant correlation at P≥0.05 and P≥0.01 respectively

Appendix 4: Correlation coefficient matrix between the different Cu and Cr fractions

		Cr					
		WS	**EXCH**	**CARB**	**OXIDE**	**OM**	**RESI**
	WS	1	-0.298	-0.342	-0.142	-0.229	0.163
	EXCH	0.938**	1	0.993**	0.799	0.987**	-0.980**
Cu	**CARB**	0.988**	0.959**	1	0.792	0.990**	-0.976**
	OXIDE	0.790	0.638	0.745	1	0.848*	-0.868*
	OM	0.963**	0.983**	0.985**	0.0673	1	-0.997**
	RESI	-0.981**	-0.983**	-0.992**	-0.738	-0.994**	1

The lower left-hand section is correlation coefficient for Cu while the upper, right-hand part is correlation coefficient for Cr; *, ** Significant at p≥0.05 and 0.01 respectively.

Appendix 5: Correlation coefficient matrix between the different Cd and Pb fractions

		Pb					
		WS	**EXCH**	**CARB**	**OXIDE**	**OM**	**RESI**
Cd	**WS**	1	0.158	0.410	0.680	-0.359	-0.530
	EXCH	0.938**	1	-0.238	0.804	-0.233	0.203
	CARB	0.988**	0.959**	1	0.005	-0.406	-0.898*
	OXIDE	0.790	0.638	0.745	1	-0.455	0.059
	OM	0.963**	0.983**	0.985**	0.673	1	0.026
	RESI	-0.981*	-0.992**	-0.992**	-0.738	-0.994	1

The lower left-hand section is correlation coefficient for Cd while the upper, right-hand part is correlation coefficient for Pb; *, ** Significant at p≥0.05 and 0.01 respectively.



Appendix 6: ***Alternaria***



Appendix 7: *Fusarium*



Appendix 8: ***Monilla***



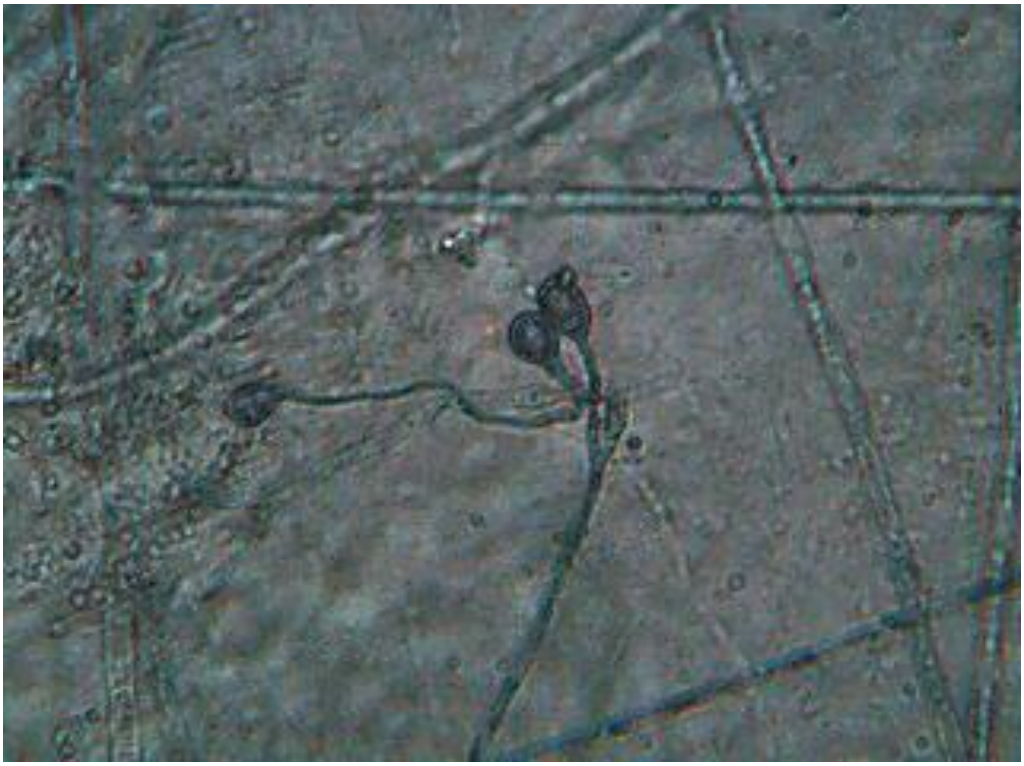
Appendix 9: Rhizoctonia



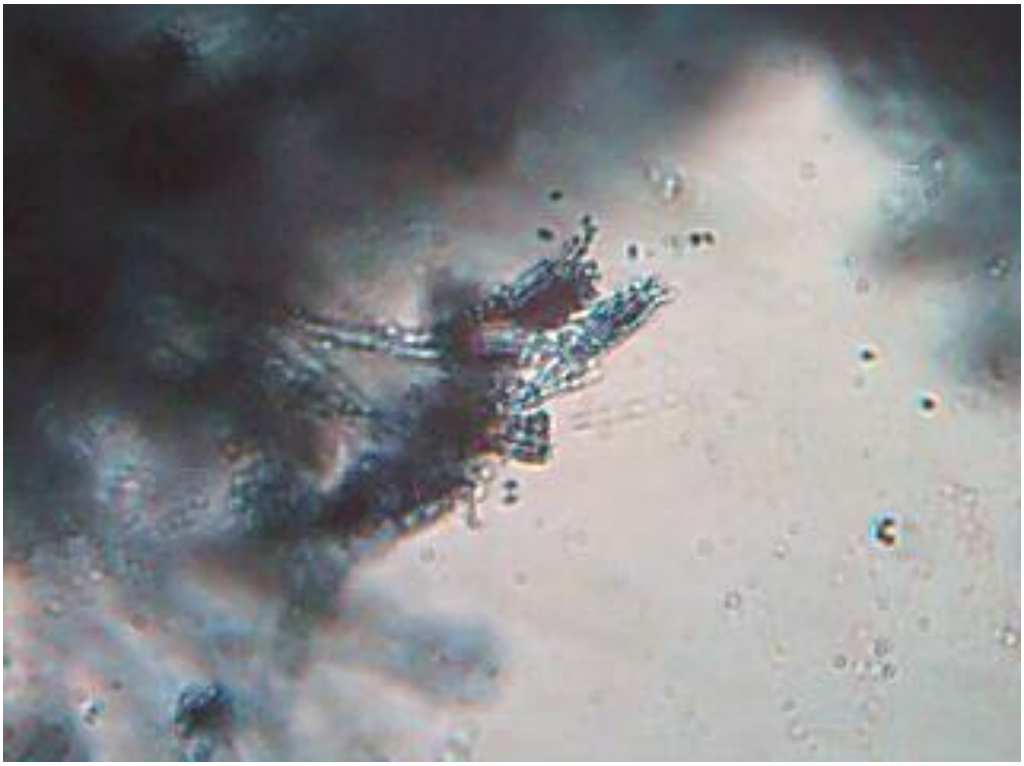
Appendix 10: ***Trichoderma***



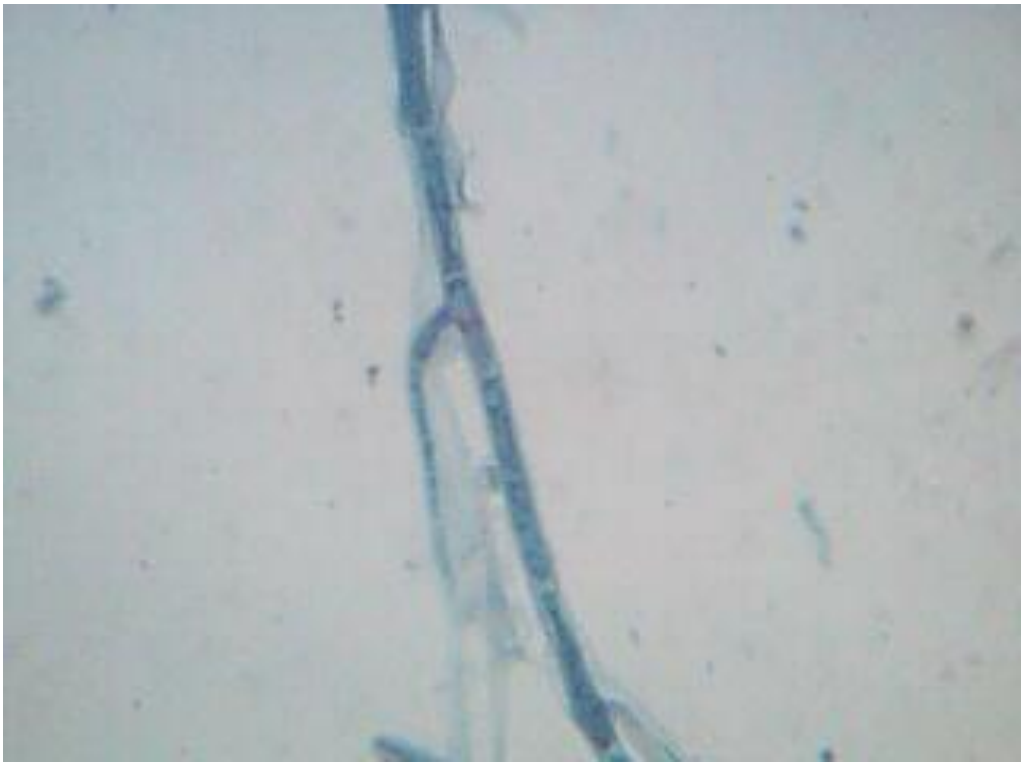
Appendix 11: *Candida*



Appendix 12: *Genicularia*



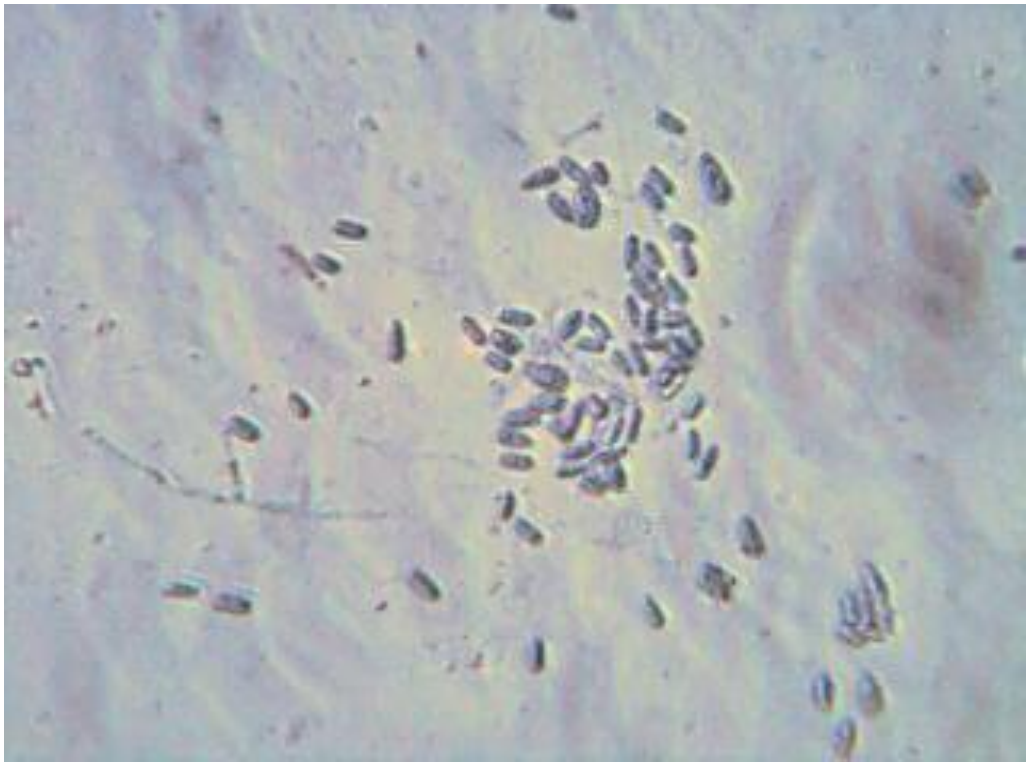
Appendix 13: ***Penicillium***



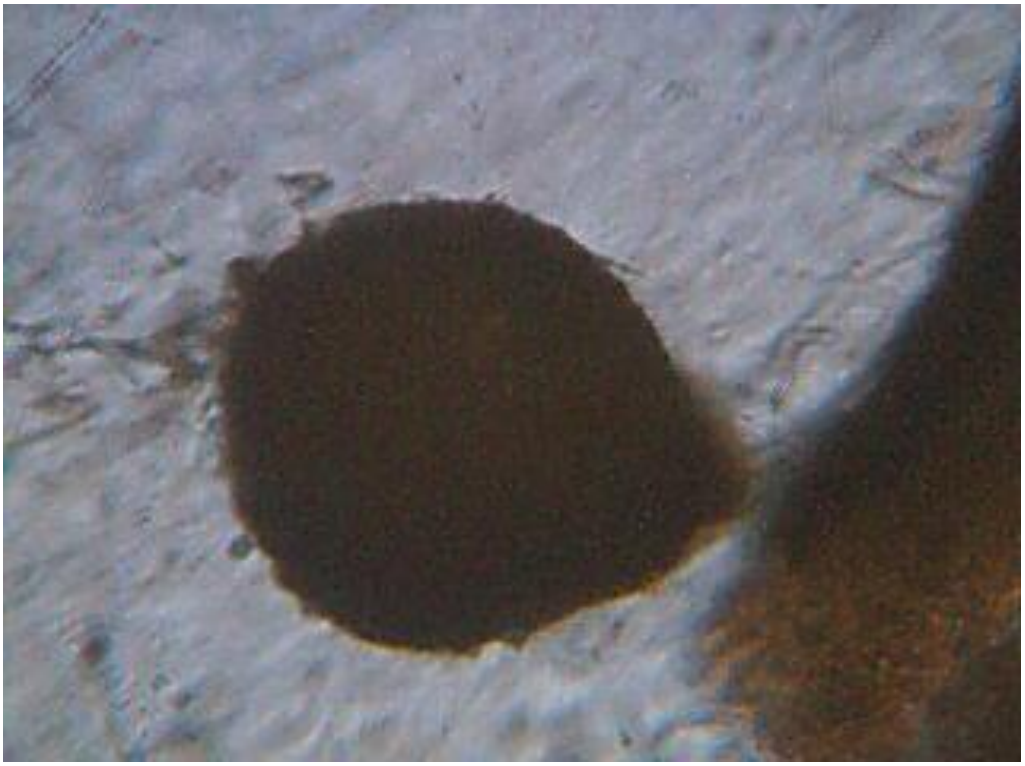
Appendix 14: *Sclerotium*



Appendix 15: *Cladosporium*



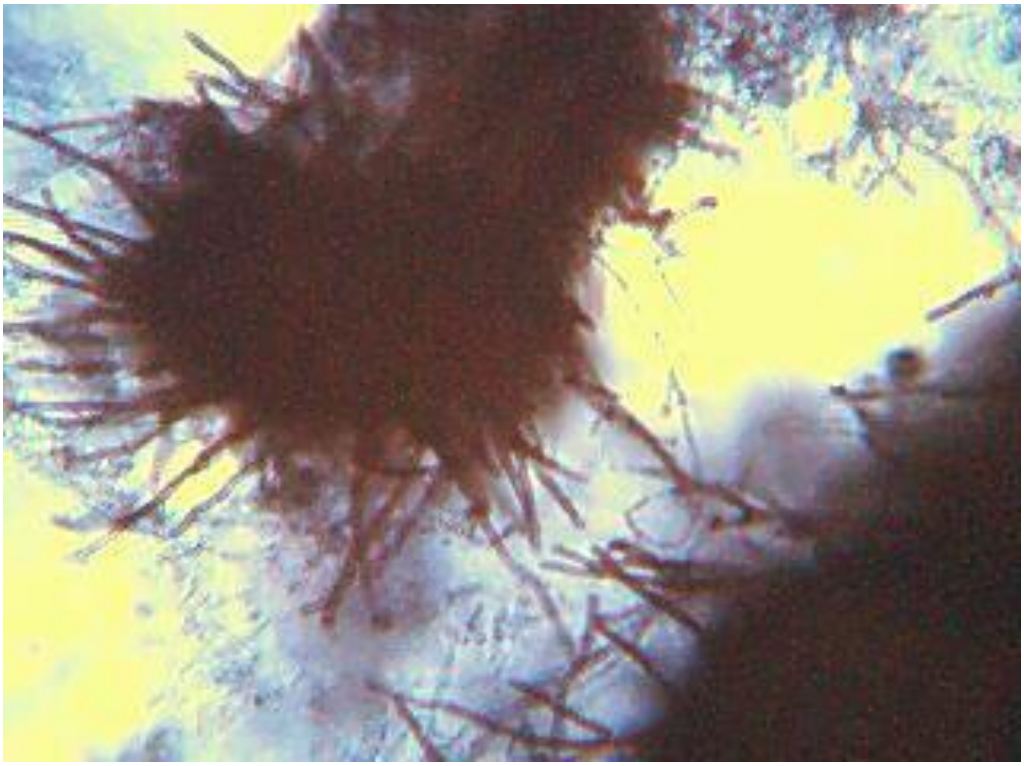
Appendix 16: ***Gleosporium***



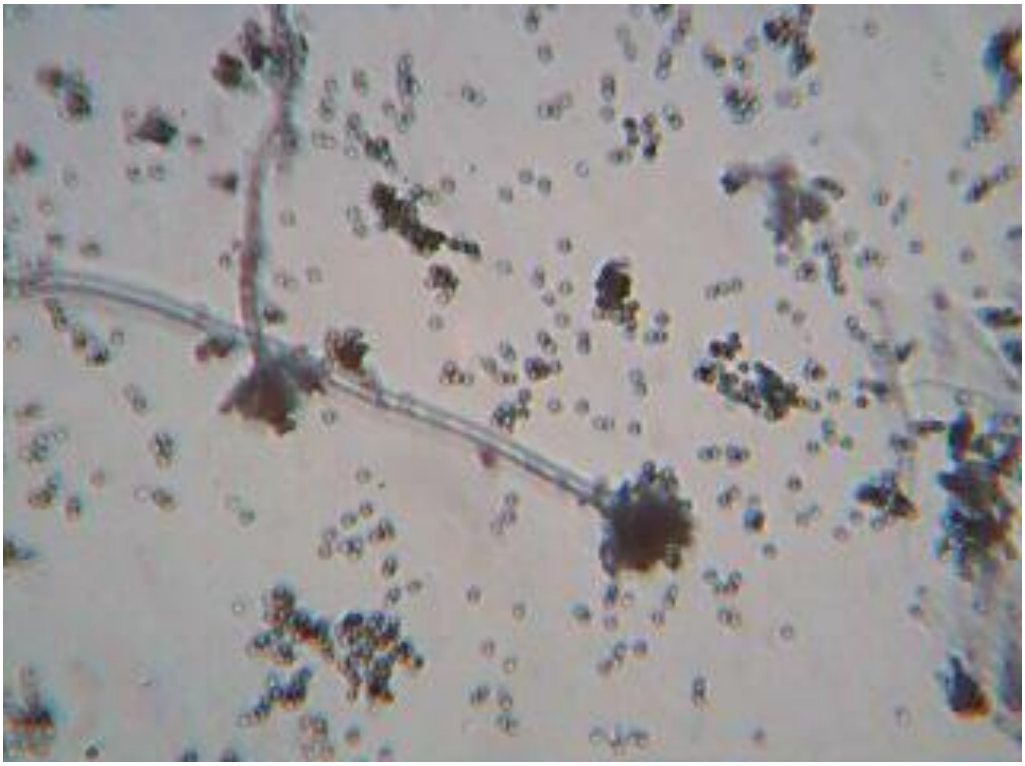
Appendix 17: *Phoma*



Appendix 18: ***Vulvularia***



Appendix 19: *Cheatomilla*



Appendix 20: *Aspergillus*



Appendix 21: *Canoplea*



Appendix 22: *Cephallospora*



Appendix 23: ***Neurospora***