CHEMICAL FRACTIONATION AND BIOAVAILABILITY OF SELECTED HEAVY METALS IN SEDIMENTS OF RIVER CHALLAWA, KANO, NIGERIA

BY

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DECLARATION

I hereby declare that the work in the thesis entitled "Chemical Fractionation and Bioavailability of Some Selected Heavy Metals in Sediment of River Challawa, Kano, Nigeria" has been performed by me in the Department of Chemistry under the supervision of Dr. A. Uzairu, Dr. J. A. Kagbu and Prof. G. F. S. Harrison

The information derived from literature has been duly acknowledged in the text and list of references provided. No part of this thesis was previously presented for another Degree or Diploma at any University.

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CERTIFICATION

This dissertation entitled "Chemical Fractionation and Bioavailability of Some Selected Heavy Metals in Sediment of River Challawa, Kano, Nigeria" by Babale, Abdullahi meets the regulations governing the award of the degree of Master of Science of Ahmadu Bello University, Zaria, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This work is dedicated to my late parents, Adamu and Bara'atu for all their parental guidance, care, prayers and protection which has gone a long way in making me different. I am eternally grateful to them.

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ABSTRACT

River Challawa, Kano was divided into two parts, study and control areas. 10 sampling points were chosen as study area while 5 sampling points as control area. The point of effluent discharge from Challawa industrial area into the river demarcated the two areas. The physico-chemical parameters of the sediment were studied. The total metal (Zn, Cu, Pb, Cd and Cr) concentrations in the sediment were also determined. Sequential extraction was used to fractionate the five heavy metals into five operationally defined groups: exchangeable, carbonate, Fe-Mn oxide, organic and residual. Organic matter content of sediment ranged from 7.1 - 10.25% with the study area having the higher organic matter content. The pH of the sediment ranged from 5.0 - 5.75 in the study area while that of control area ranged from 5.25 - 6.0. pH value obtained revealed the slight acidic environment of the sediment. Other physicochemical parameters determined showed higher values in the study area than in the control area. The distribution pattern of Zn in the operationally defined phase followed: Fe-Mn oxide bound > carbonate bound > residual > organic bound > exchangeable in both the study and control areas. Chromium in different fractions were in the order: residual > carbonate bound > Fe-Mn oxide bound > organic bound > exchangeable in the study area. Chromium was associated mainly (65 – 93.3%) with the residual fractions. Pb in the river sediment showed the order of association: residual > Fe-Mn oxide bound > organic bound > carbonate bound > exchangeable. The association of Cu was dominated by the organic phase (44.88%) with Fe-Mn oxide bound (16.82%) carbonate bound 5.55% and exchangeable 2.79%. The Cd association with different sediment fraction followed the order: residual >> exchangeable > carbonate bound > Fe-Mn oxide bound > organic bound The result indicated that Cd is

potential bioavailable since metals present in the exchangeable are usually readily available for plant or organism uptake. The potential bioavailablility of the metals in the sediment in this study are Cd>>Zn>>Cu>>Pb>.Cr

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the study

Rivers have been used by man since the dawn of civilization as a source of water, food, transport, defensive barrier, power, to drive machinery and as means of disposal of waste. Advancement in the level of industrialization has led to even more waste discharge in the form of effluents containing heavy metals into our aquatic environment (Warren, 1981). In fact Industrial discharges have been identified as a major component of water pollution (DWAF and WRF, 1995; Morrison *et al*., 2001 and Nasruallah *et al*., 2006).

Although water is commonly employed as a pollution indicator by heavy metals, sediment can also provide a deeper insight into the long term pollution state of the water body. Hence, the use of sediments as indicator of heavy metals pollution has been a major environmental focus especially in the last decade (Ikem *et al*., 2003).

Heavy metals are one of the main pollution factors in aquatic systems because some metals are persistent and potentially dangerous to biota. The metals are transported by particulate matter to the sediment and this is not necessarily the final fate of metallic species because a fraction of these can be released to the water column when the physicochemical conditions have changed (Jaime *et al*., 2003). Hence, the behaviour and concentration of heavy metals in sediment can play a relevant role in detecting sources, degree of pollution and distribution mechanism in aquatic environment.

Kano holds about 70% of Nigeria's tanning industries and most of them are located in Challawa Industrial Estate (World Bank, 1995 and Faboya, 1997). The

effluents from the tanneries in this Industrial Estate are channeled into drains which end up into the Challawa River untreated.

The treatment and processing of animal hides and skins can be a source of considerable environmental impact. Discharged waste water contains pollutants from the hide's products, from their decomposition and from the tanning process. According to Birle and Lock (1998), the immediate environmental threat posed by the presence of large number of tanneries which discharge substantial quantities of chromium salts and numerous other toxins into the rivers are of major concern.

Therefore, the need to assess the state and quality of Challawa river sediment in terms of its metallic load becomes imperative since the direct transfer of chemicals from sediments to organisms is now considered to be a major route of exposure for many species (Zoumis *et al*., 2001).

1.2 Research Problem

The Kano environment covers an area extending between latitudes 12^0 $40^{'}$ E and 10^0 30'E and longitude 7^0 40'N and 9^0 30'N. Kano is a booming industrial establishment comprising of chemical and cosmetics industries, tanneries, textile and food processing factories which release waste water untreated into rivers. This led to the deterioration of aquatic system (Bichi, 2000). Industrial survey showed sixty (60) industries in Kano discharge untreated effluents into rivers (Dada, 1997).

The Challawa River flows eastwards stranding the region south-west of Kano municipality and draining into Lake Chad via Hadejia River. Its main tributary is Kano River; others include River Jatau, Goronyo, Shinar, Takawani, Dawaza and Toba. On

either side of the river lies an extensive dulating to flat plain. The discharges from Challawa Industrial Estate are mostly from tannery and textile industries. The Challawa Dam supplying water to Kano municipality is located some 75km upstream from the point where tanneries discharge their effluents into the Challawa River.

River Challawa is an important river in Kano state. The river is used for various human activities including washing, fishing, farming and drinking. The domestic water supply for the area comes from this River. Some peasant farmers along the course of the river also use the water from the river to irrigate their food crops, especially vegetables during the dry season. This river receives untreated municipal waste and waste water from the Challawa Industrial areas as shown in Fig 1.1 -1.8.

River sediments are important sinks for various pollutants like pesticides and heavy metals and also play a significant role in the remobilization of contaminants in aquatic systems under favorable conditions and in interactions between water and sediment. (Ikem *et al*., 2003)The release of heavy metals from sediment into the water body and consequently to fish will depend on the chemical fractionation and other factors such as sediment pH and other physical and chemical characteristics of the aquatic system (Morgan and Stumm 1991).However, in sediments, heavy metals can be present in various chemical forms and generally exhibit different physical and chemical behaviour in terms of chemical interaction, mobility, bioavailability and potential toxicity. These species include: exchangeable, carbonate bound, iron-manganese oxide bound, organic matter bound and silicate or residual bound species.

It is therefore necessary to identify and quantify the forms in which a metal is present in the sediments of Challawa River to gain a more precise understanding of the potential and actual impacts of the operations in the river.

1.3 Justification

The many human activities in the last decade have increased the metal mobility in the environment. Heavy metals are one of the main pollution factors in aquatic systems because some metals are persistent and potentially dangerous to biota.

The total metal concentration in sediment is relevant; nevertheless, the bioaccumulation, availability, reactivity, mobility and toxicity are determined by the metal chemical form thus making a chemical fractionation study necessary.

Most of the past investigations on River Challawa concentrate on total metal concentration in river water (Bichi, 2000), sediment (Akan *et al*., 2007) and farmland food crops along the bank (Abdullahi *et al*., 2008; Awode *et al*., 2008). There is no literature information yet on the chemical fractionation of heavy metals in bottom sediment of River Challawa. There is, therefore, the need to determine the speciation or fractionation of heavy metals in the bottom sediment of River Challawa in order to answer the following questions arising from the unregulated discharge of untreated tannery effluents into River Challawa :

(i) What are the levels of heavy metals- zinc, copper, cadmium, chromium and lead in the sediments of River Challawa?



Figure 1.1 A Picture Showing Effluent Discharge Pathway into River Challawa from Textile and Chemical Industries



Figure 1.2 A Picture Showing Human Activities in River Challawa



Figure 1.3 A Picture Showing Effluent Discharge Pathway into River Challawa from Tannery Industries



Figure 1.4 Picture Showing Effluent Discharge Pathway into River Challawa from Tannery Industries



Figure 1.5 Picture Showing Effluent Discharge into River Challawa from Tannery Industries



Figure 1.6 Picture Showing Effluent Discharge into River Challawa from Tannery Industries



Figure 1.7 Picture Showing Farming Activities along Challawa River Bank



Figure 1.8 Picture Showing Men on Voyage

(ii) What are the levels of the physicochemical parameters in the sediments of River Challawa

(iii) What are the levels of metal species partitioned into the various phases of the sediments of River Challawa?

(iv) Are the physicochemical parameters related to the mobility of the metal species in the different phases of River Challawa?

1.4 Aims and Objectives

The main aim of this study is to investigate the bioavailability of selected heavy metals in sediments of River Challawa. This would be achieved by pursuing the following objectives:

a) Determination of the physicochemical parameters of River Challawa sediments before and after the point of effluent discharge into the River.

b) Determination of concentration of copper, lead, cadmium, chromium and zinc in bottom sediments of River Challawa.

c) To ascertain the mobility and hence bioavailability by solid phase chemical fractionation of these metals using sequential extractions.

1.5 Scope and Limitation of the Study

The study concentrated on River Challawa before and after the point of effluent discharge from the Challawa Industrial areas and it is aimed at determining the concentration levels of heavy metals and partitioning of the metals in the River Challawa sediments. The physicochemical parameters of the sediment would also be studied.

However, limitations include collecting samples only in dry season. Cost was also a major limitation in this study. The AAS analysis was done at a cost of two hundred and fifty naira (student price) per element per sample. This limited the number of samples collected. Another major limitation is the technical difficulties associated with achieving selective dissolution and complete recovery of trace metals from geochemical phases of sediments.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Pollution of Aquatic Sediments

Sediment is a matrix of material which comprised of detritus inorganic or organic particles and is relatively heterogenous in terms of physical, chemical and biological characteristics (Hankinson, 1992).

Aquatic sediments are ready sinks or reservoirs of pollutants such as heavy metals where they concentrate according to the levels of pollution (Becker *et al.*, 2001 and Onyari *et al.,* 2003). These in many cases serve as major source of contamination of food chains (Forstner 1990)

Sediments are widely recognized as suitable media for assessing environmental quality as they reflect and integrate contaminant inputs to the aquatic environment. Sedimentation is the most obvious source of contamination of aquatic system (Vonotry et al., 1993). The overlying water column could be polluted by contaminated aquatic sediments. Hydrophobic compounds and metals accumulated in the bottom sediments over time are transported via variety of mechanisms to the water column and air (Valsaraj *et al.*, 1993). These transport mechanisms which affect the geochemistry in aquatic sediments include molecular diffusion within the interstitial water, adsorption/desorption between aquatic sediment particles and the pure water, chemical reaction, biodegradation sediment deposition, re-suspension, relocation.

The extent of contamination in aquatic sediments is not often vigorously evaluated. Decision regarding dredging and remediation of polluted sediments in rivers or

lakes requires reliable estimate of volume of sediments and the extent of contamination (Cahill and Unger, 1993).

Aquatic sediments are important sources for assessment of man-made heavy metal pollution in rivers and lakes (Forstner and Wittman 1983). The adsorption of heavy metals by silica organic fraction is used as pollution indicators. However, due to diagenetic processes, the sediment bound metals and other pollutants may be remobilized and released to the overlying waters and in turn impose adverse effects on aquatic organisms.

Sediments are composed of different geochemical phases and metal ions partition between these fractions, namely, exchangeable, carbonate, reducible, oxidization and residual fractions (Lee *et al.*, 2003).

2.2 Heavy Metals in Aquatic Sediments

Heavy metals are an inexact term used to describe more than a dozen elements that are metals and metalloids. Generally, heavy metals have densities above 5g/cm^3 (Hawkes, 1997). Heavy metals are persistent in all parts of the environment because they cannot be degraded or destroyed.

Heavy metals enter an aquatic environment through industrial or consumer waste or even from acid rain breaking down soils and releasing heavy metals into streams, lakes, rivers and ground water (Stumm and Morgan, 1996). Heavy metals occurring in most rivers are carried by suspended particles and only a fraction is transported in soluble form (Horowith 1991; and Moore and Ramamworthy, 1984).

Human activities affect the natural geological and biological redistribution of heavy metals by altering the chemical form of the metals released to the aquatic system. Such alterations often affect a heavy metal's toxicity by allowing it to accumulate in plants and animals, bioconcentrate or attack specific organs of the body (Goyer, 1996).

Heavy metals tend to accumulate more in sediments than in water and aquatic organisms. Lee *et al.* (2003) studied the incidence of heavy metals in water and suspended sediments of Anyang River, Korea and found that more than 99% of the metals were associated with bed sediment. Metal concentrations in the bed sediments and the biota have been determined for a variety of aquatic environments. According to Bower (1970), water sediments are the major deposits of metals. In some cases, these sediments hold over 99% of the total level of metal present in the system while the fractions in biota are small (less than 1.0%). In sediments, heavy metals can be present in various chemical forms and generally exhibit different physical and chemical behaviour in terms of chemical interaction, mobility, biological availability and potential toxicity (Xiangdong *et al.,* 2000).

2.3 Effect of Physiochemical Parameters on Heavy Metals Mobility

Heavy metals mobility in sediments is affected by some factors which include; grain size distribution, pH, temperature and organic matter content. Grain size distribution and resulting total surface area available for adsorption are important factors in adsorption processes and can affect metal mobility (Luoma, 1989). Grain size also affects heavy metal content in sediments. Small particles with large surface area to mass ratios allow more adsorption than an equivalent mass of large particles with small surface

area to mass ratios. Trace metals have relative potential for sorption on clay mineral, hydrous oxides and organic matter surfaces all due to their small grain sizes. The amount of extractable metal increases with decreasing grain sizes (Ackay *et al.,* 2003 and Ikem *et al.*, 2003).

pH influences the trace metal forms, concentration levels, mobility, transformation and accumulation processes in the ecosystem. pH affects both solubility of metal hydroxides minerals and adsorption processes. Most metal hydroxides have very low solubility under high pH conditions in natural water. pH of aquatic systems is generally lower. This is as result of a combination of processes which include production of carbon (IV) oxide, organic acids and nitrification. Because hydroxide ion activity is directly related to pH, the solubility of metal hydroxide minerals increases with decreasing pH and more dissolved metals become potentially available.

Adsorption, which occurs when dissolved metals are attached to surfaces of particulate matter (notably iron, manganese and aluminum oxide minerals, clay and organic matter), is also strongly dependent on pH (Bourg, 1988 and Elder, 1989). Sorption capacities of oxide surfaces generally vary from near 0 to near 100% over a range of 2pH units. The adsorption edge, the pH range over which the rapid charge in sorption capacity occurs, varies among metals. Cadmium and Zinc tend to have adsorption edges at higher pH than Iron and Copper and consequently they are likely to be more mobile and more widely dispersed.

Temperature exerts an important effect on metal speciation because most chemical reactions are highly sensitive to temperature changes (Elder, 1989). Temperature may also affect quantities of metal uptake by an organism because

biological processes typically double with every 10^0C increment (Luoma, 1983; Prosi, 1989).

Heavy metals binding forms greatly depend on the different stages of redox processes and flooding (Hong and Wang, 1984). When anoxic aquatic sediments are exposed to the atmospheric redox conditions, a new distribution and transformation of trace metal binding forms in the sediments take place (Calmano *et al.,* 1993).

Organic matter content is important in determining the chemistry of sediments. The reducing condition in sediment makes most of ion-exchange site to be occupied by hydrogen. Therefore the cation exchange capacity of the sediment is high (Forstner and Wittmann, 1979).

2.4 Bioavailability of Heavy Metals in Aquatic Sediments

The bioavailability of heavy metals is the proportion of total metals that are available for incorporation into biota. Total metal concentrations do not necessarily correspond with metal bioavailability. Metals of major interest in bioavailability studies as listed by the US Environmental Agency (EPA) include Cd, Cr, Cu and Pb (McKinney and Rogers, 1992).

Bioavailability is a function of factors such as total metal concentration, speciation, pH, redox potential, temperature, total organic content, water volume and water velocity (McKinney and Rogers, 1992).

Particulate size and resulting total surface area affect metal bioavailability (Luoma, 1989). Reduced adsorption can increase metal bioavailability by increasing concentrations of dissolved metals in associated water.

Elevated chloride contents tend to enhance chloride complex formation which decreases the adsorption of cadmium on sediment, and subsequent decrease in the concentration of dissolved Cd^{2+} and bioavailability (Luoma 1983).

Iron rich sediment inhibits Lead bioavailability. In polluted river environment, Lead is most efficiently scavenged by non detrital carbonate and iron-manganese oxide minerals and is less mobile than cadmium (Prusty *et al.*, 1994).

The bioavailability of heavy metals in aquatic sediments also depends on the prevailing conditions. Complexation of heavy metals by ligands controls its dissolved ion concentration. In addition, organic complexion increases or decreases adsorption of heavy metal fate and transport (Han *et al.,* 2000)

The presence of polar groups and the high molecular weight of humic and fulvic acids lead to their solubility in water (Connel, 1997). These polar groups have the capacity of forming chelating complexes with attachment of metal ions to more sites in the organic molecule. These chelates complexes exhibit stability resistance to biodegradation in the environment. Chelation reduces bioavailability of heavy metals to benthic organism in the aquatic ecosystem, thus reducing their potential toxicity (Ikem *et al.*, 2003).

2.5 Effect of Heavy Metal on Aquatic Environment

The effect of heavy metal on man and animal can be additive, antagonistic or synergistic (Underwood, 1970 and Ellis *et al.*, 1989). Zinc and copper are cadmium antagonists and thus the high cadmium intake has its effects reduced by normal amounts of zinc and copper in the body.

Heavy metals lead to all sorts of diseases in man and animal and virtually all, including the essential heavy metals are toxic if safe limits are exceeded.

Toxicity of heavy metals is dependent on dosage (Oladimeji, 1983 and Eicher *et al*., 2006). Acute toxicity is as a result of large doses of metal toxicant and symptoms appear rapidly while chronic toxicity is as a result of prolong exposure to small doses and symptoms appear gradually and both cases may lead to eventual death (Luckey and Venugophal, 1978).

Ionic forms of heavy metals induce acute poisoning in aquatic animals leading to immediate death while complexed forms lead to chronic poisoning and bioaccumulation (Ellis *et al*., 1989). Concentration, speciation dissolved oxygen content, hardness, temperature, physicochemical form, pH and the presence of other metals determine the toxicity of heavy metals in aquatic environment.

Lead is very toxic and after adsorption by the body is transported to delicate areas such as the brain, lungs, spleen and heart by the blood and accumulates in the bone where 90% of the total body lead is found. Lead damages those delicate tissues causing kinds of disease in man and aquatic animal (Lovei *et al.*, 2000).

Chromium enhances insulin activity in the body and thus essential to the body. Chromium (VI) is one of the pronounced toxins. It easily permeates biological membrane due to its oxidizing potential and chromium (VI) causes renal damage, cancer in man and disease of central nervous system (Bae *et al*, 2001).

Cadmium has no known beneficial effect and is toxic to man and animals. It stimulates the production of reactive oxygen species. Toxic effects of cadmium in man include renal damage and dysfunction, protenuria, bone lesion and prostate cancer. It is

also teratogenic (Friedberg and Elinder 1988). Bioaccumulation of cadmium leads to mortality of fish and growth retardation.

Zinc is relatively non-toxic especially if taken orally, however, high amount can cause system dysfunction that results in impairment of growth and reproduction (Nolan 2003). Acute toxicity in man causes depression of nervous system while chronic toxicity causes faulty reproduction, anemia (Luckey and Venugophal, 1977).

Copper toxicity leads to organs damage in fish which would lead to mortalities. In man, acute copper toxicity causes cardiovascular collapse while chronic toxicity leads to fever, jaundice and diarrhea (Bae *et al,* 2001).

2.6 Fractionation of Heavy Metals in River Sediment

A knowledge of the chemical forms of soluble heavy metals (Stumm and Morgan, 1981) or of heavy metals associated with particulates or colloids (Jenne, 1968; and McLaren and Crawford, 1973) is essentially for estimating bioavailability, mobility and chemical reactivity in sediments.

Sequential extraction procedures have been used to partition heavy metals among various sediment chemical fractions. Such procedures utilize a series of selective extractants to remove metals from various component fractions. These methods are operationally defined by the sequence of extractants used. Several attempts were made to fractionate the heavy metals in contaminated systems such as harbour sediments (Gupta and Chen, 1975).

Each of the chemical fractions has been operationally defined by the method of extraction. In relatively complex systems such as sediments, a given extract ant cannot be

expected to be entirely specific for a given phase. Hickey (1982) has suggested that the use of 1.00moldm^{-3} $MgCl_2$ as an extract ant may result in overestimation of exchangeable Cd as defined on mechanistic basis. The carbonate fraction as defined by 1M NaOAc extraction at pH 5 is predominantly made up of metals bound to carbonate minerals (Tessier *et al*., 1979) but may contain contributions from other fractions as well. Acetate may also extract some metals bound to Fe oxides through adsorption or occlusion (McLaren and Crawford, 1973 and Gupta and Chen, 1975).

Harrison *et al.* (1981) suggested that mobility and bioavailability of the metal decreases approximately in the order of the extraction sequence. The operationally defined extraction sequence follows the order of decreasing solubility of the geochemical forms of the metals; hence the exchangeable fraction may indicate which metals are most available for plant uptake (Stover *et al.,* 1976).

Fujiyoshi and Katayama (1996) found that Zn sorbs on marine sediment was not extractable with 1 moldm^{-3} CH_3COONH_4 implying that sorption did not occur via a non-specific, outer-specific, electrostatic mechanism. This contrasts with results for metal fractionation in fresh water sediments where previous investigations found that exchangeable metals are often not negligible (Jain, 2004). This reflects the importance of the ionic strength of the aqueous matrix which in some fresh water systems allows aqueous trace metals to occupy cation exchange sites. Calmano *et al*. (1992) showed that increased salinity enhanced desorption of heavy metals from sediments.

Gleyzes and Astrue (2002) cautioned that metals extracted from soils or sediments with 1M NaOAc adjusted to pH 5 may have also been specifically absorbed to

low energy sites on the surface of clay minerals, organic matter and oxide minerals as well as co-precipitated with carbonate minerals.

Turner and Olsen (2000) determined extractability of trace metals in contaminated estuarine sediments by chemical extractions and of the chemical reagents that they examined, acetic acid best represented the fraction that was likely to be bioavailable to sediment ingesting biota. Lopez-Sanchez *et al.* (1996) who studied metal partitioning in benthic sediments off the Spanish coast found very little Cu in association with the carbonate fraction.

Zn is commonly found to exist in contaminated soils and sediments mainly in association with Zn and Mn oxides (Lopez-Sanchez *et al.*, 1996). This may be at least partly attributable to the ability of Zn to substitute for Fe in the structure of oxide minerals (Stumm and Morgan, 1996). Reductive dissolution of the oxide mineral occurs at Eh less than approximately +250mV for Mn oxides and +100mV Fe oxides (Patrick and Jugsujinda, 1992).

The tendency of Cu to be associated with the oxidisable fraction which implies association with organic matter in the sediments has been reported in several previous studies (Pardo *et al.,* 1990; Lopez-Sanchez *et al.,* 1996 and Galan *et al.,* 2003). This is attributed to the greater stability of organo-Cu complexes when compared with Pb and Zn (Stumm and Morgan 1996).

The residual fraction is not available to biological or diagenetic processes except over very long time scales (Tessier *et al.,* 1979). The association between heavy metals and the residual fraction of uncontaminated sediments or soils is so strong that metal

association with non-residual fraction has been used as an indicator of anthropogenic enrichment (Arakel and Hongjum, 1992 and Sutherland and Verloo, 2000).

2.7 Effect of Industrial Effluent on Aquatic Environment

Industrial effluents are highly complex and as a result difficult to determine which factor is operating in an aquatic biota. Most of the documented effects of tannery effluent on the aquatic biota have been on fish and little is known of the effects on phytoplankton and useful zooplankton that are very important as fish food. It is assumed that the deterioration of water bodies as a result of tannery effluents discharge would affect these valuable resources (Lawal and Kolo, 2000).

Tannery effluents in particular affect the physicochemical properties of water bodies in which it is discharged. When the level of tannery effluent is high, the biological activities of receiving water bodies are affected. The chlorides which are in large amounts in tannery waste water affect the purity of the aquatic environment. Biodegradation of organic matter is greatly hindered due to the presence of caustic alkalinity which kills useful bacteria (Lawal and Kolo, 2000). The total number of organic matter and heavy metals (such as chromium, Lead and zinc) in the bottom sediments increased (Dura and Jakel, 1980). Generally the high alkalinity, suspended matter, sulphides and heavy metals in the effluents are injurious to fish.

The river communities are forced to adapt to all the problems presented by those pollutants simultaneously. The extent and speed of adaptability of the communities to pollution are remarkably great but cannot keep pace with gross pollutants discharges. The result tends to increase greater drop in diversity, which might be expected as many

species which would grow well under normal conditions are excluded by the intermittently varying condition, whilst those specially adapted to particular intermittent pollutants never have time to establish themselves before conditions change and they lose their advantage. (Lawal and Kolo, 2000).

2.8 Principle of Atomic Absorption Spectrophotometry

Flame atomic absorption spectrometry (FAAS) was first proposed and developed by Walsh (1955). Atomic absorption spectra are formed by the absorption of radiation of certain wavelength by atoms whose electrons are in the ground state. On absorbing this energy the atoms become excited. The extent of absorption is dependent on the number of atoms in the ground state in the path of radiation beam at any one time and can thus be used as quantitative method of determining this number (Allen *et al*., 1974).

In practice, air is blown through a venturi, and the sample solution is drawn into the throat of the venturi and into the air stream as a spray of fine droplets. A large fraction (~ 90%) of the drops falls out of the air stream in the cloud chamber but the very small ones remain suspended (Goulden, 1978). In the flame the sample vaporizes and forms a cloud of atoms in the gaseous state. Radiation of a characteristic wavelength corresponding to the radiation (energy) required to raise the atoms of the particular element being analysed from their ground state to an excited state from a hollow cathode discharge lamp is passed through the flame. The decrease in intensity is measured, using a monochromator and detector system. This decrease is related to the concentration of the element in the sample solution.

2.8.1 Wavelength and slit width of measurement

Air-acetylene flame was used for the AAS analysis. The characteristic wavelengths of absorption of each metal used in the analysis together with the slit width are given in Table 2.1

Table 2.1 Characteristic wavelengths and slit width used in FAAS analysis

Element	Wavelength (nm)	Slit width (nm)
Cadmium	228.8	0.4
Chromium	357.9	0.3
Copper	324.8	0.3
Lead	283.3	0.7
Zinc	213.9	0.5

CHAPTER THREE

3.0 Materials and Methods

3.2 Materials

3.2.1 Apparatus/Equipment

1. Volumetric flasks, 50ml, 100ml, 250ml and 100ml
2. Measuring cylinder, 100ml, 10ml,
3. Plastic bottle for samples and digest.
4. Conical flasks, 125ml, 250ml
5. Polythene bags
6. Funnels
7. Wash bottles
8. Filter paper Whatman No. 42
9. Mortar and pestle
10. Eye goggles
11. Nose guard
12. Drying oven Gallenkamp Model No 237887c
13. Dessicator
14. Hot plates Bibby Sterlin Ltd. Model No HC500
15. Analytical balance Mettler Model No 38544
16. Fume cupboard
17. Thermometer
18. pH meter Hanna (Model H1991000)
19. Steam bath Gallenkamp Model No 587542B

20. Secchi disk
21. Flask shaker Tamson PMT Model No 5657HAAN
22. Glass rod
23. Centrifuge Baird and Tatlock Model No B93129
24. Pipette
25. Kjeldahl flask
26. Teflon cup
27. Deionizer Zerorif England Model No 5202
28. Carbolite furnace (Model GLM 3)
29. Crucible
30. Butchner funnel
31. Sieve Endecotts Model No H5369

3.1.2 Reagents

1. Magnesium Nitrate Mg $(NO_3)_2$ Analar Grade, BDH
2. Hydrofloric acid, HF Analar Grade, BDH
3. Double distilled water
4. Hydrogen peroxide H_2O_2 Analar Grade, BDH
5. Conc. HNO_3 Analar Grade, BDH
6. Sodium – EDTA Analar Grade, BDH
7. Ammonium acetate CH_3COONH_4 Analar Grade, BDH
8. $NH_2OH.HCl$
9. Deionized water

10. Conc. HCl Analar Analar Grade, BDH
11. Cadmium Nitrate Analar Grade, BDH
12. Copper Nitrate Analar Grade BDH
13. Zinc Chloride Analar Grade, BDH
14. Perchloric acid Analar Grade BDH
15. Distilled water
17. Ammonium chloride Analar Grade, BDH
18. Sodium Chloride Analar Grade, BDH
19. Stannous Chloride Analar Grade, BDH
20. NH_4F Analar Grade,BDH
21. Devardo's Alloy
22. KCl Analar Grade BDH
23. Conc. H_2SO_4 Analar Grade BDH
24. Boric Acid H_3BO_3 Analar Grade BDH
25. K_2SO_4 Analar BDH
26. $K_2Cr_2O_4$ Analar grade, BDH
27. Sodium metaphosphate $(NaPO_3)_6$ Analar Grade, BDH

3.1.3 Preparation of Solutions

3.1.3.1 Stock Solutions

1. Lead stock solution was prepared by dissolving 1.58g $Pb(NO_3)_2$ in distilled water and making up to 1 litre giving 1000mgL^{-1} lead solution.

2. Zinc stock solution was prepared by dissolving 1.244g of ZnO in 5ml of water, adding 25ml of Conc. HNO_3 and making up to 1 litre with distilled water giving 1000mgL^{-1} Zinc solution.

3. Cadmium solution was prepared by dissolving 2.743g $Cd(NO_3)_2.4H_2O$ in 5ml concentrated HNO_3. The solution was made up to 1 litre with distilled water in a volumetric flask giving 1000mgL^{-1} cadmium solution.

4. Copper solution was prepared by dissolving 3.8031g of $Cu(NO_3)_2.3H_2O$ in 5ml concentrated HNO_3 and making up to 1 litre with distilled water giving 1000ppm copper solution.

5. Chromium stock solution was prepared by dissolving 3.7353g $K_2Cr_2O_4$ in 10ml concentrated HNO_3 and making up to 1 litre giving 1000mgL^{-1} chromium solution.

3.1.3.2 Standard working solution

Using the dilution formula:

$$C_{\text{stock solution}} \times V_{\text{stock solution required}} = C_{\text{standard working solution}} \times V_{\text{standard working solution}}$$

$$V_{\text{stock solution required}} = \frac{C_{\text{standard working solution}} \times V_{\text{standard working solution}}}{C_{\text{stock solution}}}$$

and after a range finding test, working standard concentrations: 0.1, 0.5, 1.0, 2.0, and 5.0mgL^{-1} of Zn; 0.1, 0.5, 1.0, 2.0, and 5.0mgL^{-1} of Cu; 0.1, 1.0, 1.5, 2.0, and 3.0mgL^{-1} of Cd ; 0.1, 0.5, 3.0, 10.0, and 20.0mgL^{-1} of Cr ; 1.0, 2.0, 5.0, 20.0, and 50.0mgL^{-1} of Pb standard working solutions were prepared from 1000mgL^{-1} of each metal stock solutions by serial dilution. All solutions were prepared in distilled water.

3.1.3.3 Other Solutions

1. 1 Molar Solution of Mg $(NO_3)_2$: 1 molar solution of Magnesium Nitrate was prepared by dissolving 148g of Mg $(NO_3)_2$ in 1000cm^3 of water and then stored in polythene bottle.
2. 3.5M Ammonium Acetate solution: 266g of Ammonium acetate was dissolved in 200cm^3 of water diluted to form a 1000cm^3 solution in a volumetric flask and then stored in polythene bottle.
3. 30% (v/v) Hydrogen peroxide solution: 500cm^3 of hydrogen peroxide of 60% concentration was diluted to 1000cm^3 with water in a volumetric flask and was stored in a polythene bottle.
4. 2.5% (m/v) Ammonium Chloride solution: 2.5g Ammonium Chloride was dissolved and diluted to 100cm^3 with water and stored in polythene bottle.
5. 0.5M Potassium dichromate solution: 49.04g potassium dichromate reagent was dried at 103^{0}C for two hours and dissolved in 100ml of water and then diluted to 1000cm^3 in a volumetric flask and stored in polythene bottle.
6. 0.05M sodium – EDTA: 8.4g of sodium – EDTA was dissolved in 100cm^3 of water and then diluted to 500cm^3 in a volumetric flask and stored in a polythene bottle.
7. 0.02M HNO_3 solution: 1.0cm^3 of stock solution of HNO_3 was dissolved in 100cm^3 in order to obtain a 0.02 M solution of the acid
8. 3.0M HCl standard solution: 250cm^3 of 12M solution of HCl was diluted in 1000cm^3 to obtain a 3.0 M solution.

9. 0.1M solution of $NH_2OH.HCl$: 6.59g of solid $NH_2OH.HCl$ was dissolved in distilled water to make a $1000cm^3$ solution in order to obtain 0.1M solution of $NH_2OH.HCl$

3.1.4 Study Area

The study area is part of Challawa River that passes near Challawa Industrial Estate in Kumbotso local Government area of Kano State where effluent discharges enter the river as shown in Fig. 3.1. Kano State is located in the Northern part of Nigeria covering an area extending between latitudes $12^0 40'$ and $10^0 30'$ and longitude $7^0 40'$ and $9^0 30'$. Fig 3.2 shows the location of Kano State on map of Nigeria. Challawa the centre of Nigeria's tanning industry is located in Kano metropolis and is home to about 70% of Nigeria's tanning industries (Faboya, 1997) (Fig 3.3).

The climate of the Challawa area is dominated by the migration of the inter tropical convergence zone. The marked season of climate, the dry season, is longer than the wet, with highest rainfall in July and August (Kabiru, 2007).

3.1.5 Description of Sampling Sites

The sampling sites are located along the Challawa River as shown in fig. 3.1. Ten sampling points were chosen as the study area (points A to J) while five sampling points (points 1 to 5) as control areas. In choosing the sampling points, preference was given to factors such as point of effluent discharge into the river. The sampling points are shown on fig. 3.1 which also shows the layout of part of Challawa River studied.

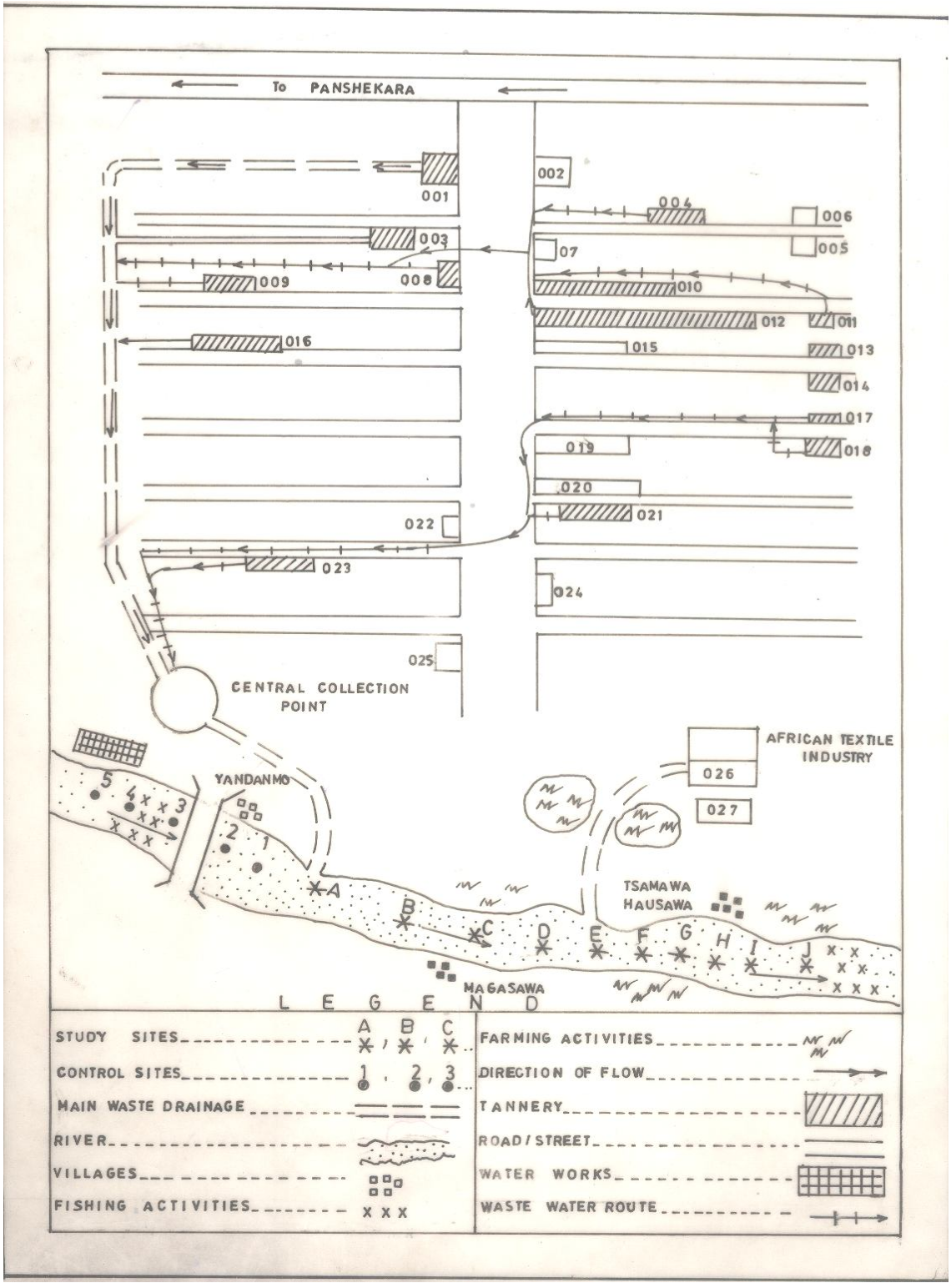

FIG. 3.1 SKETCH MAP OF CHALLAWA INDUSTRIAL ESTATE SHOWING THE SAMPLING SITES

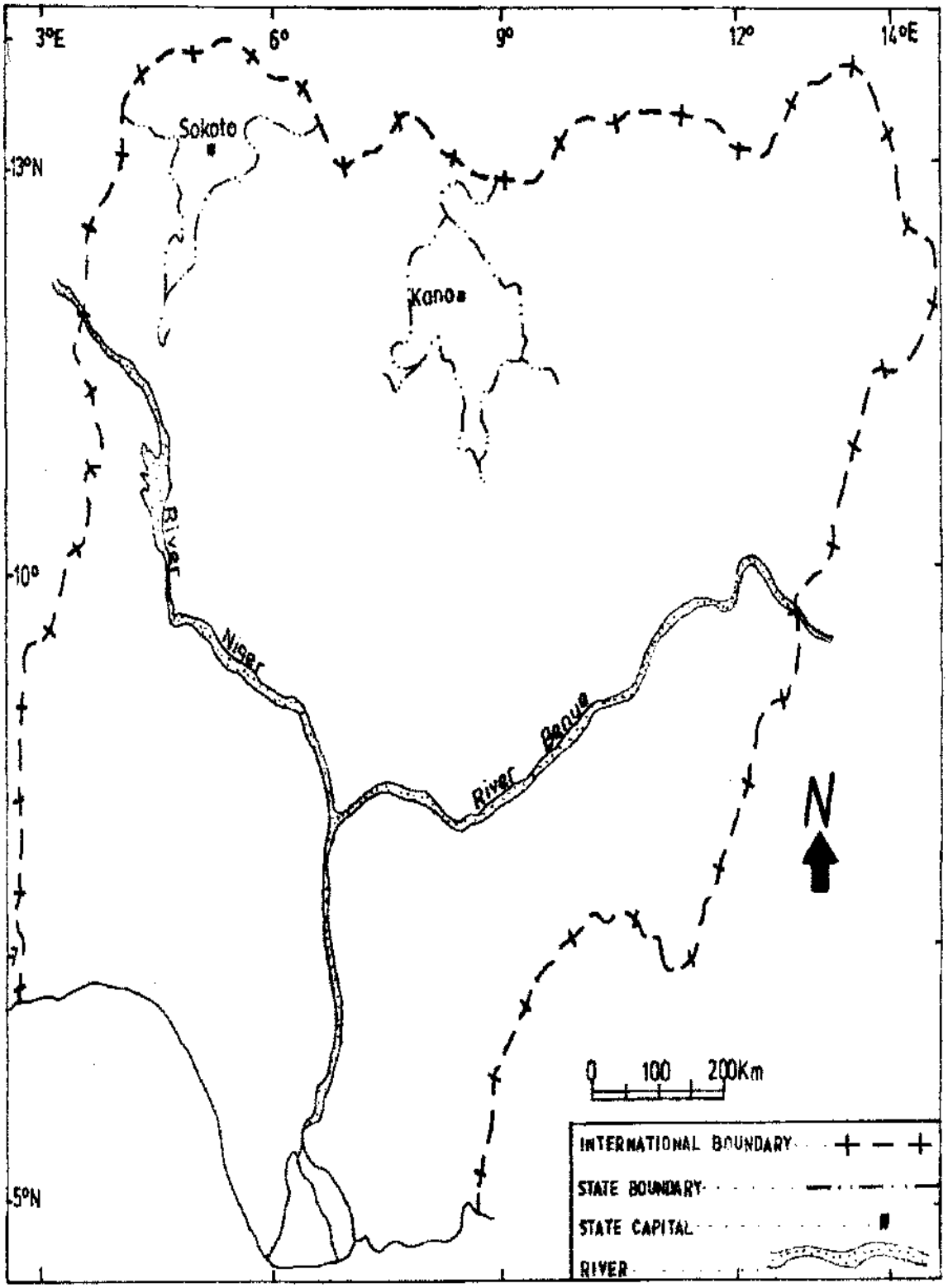

FIG. 3.2: NIGERIA SHOWING KANO STATE

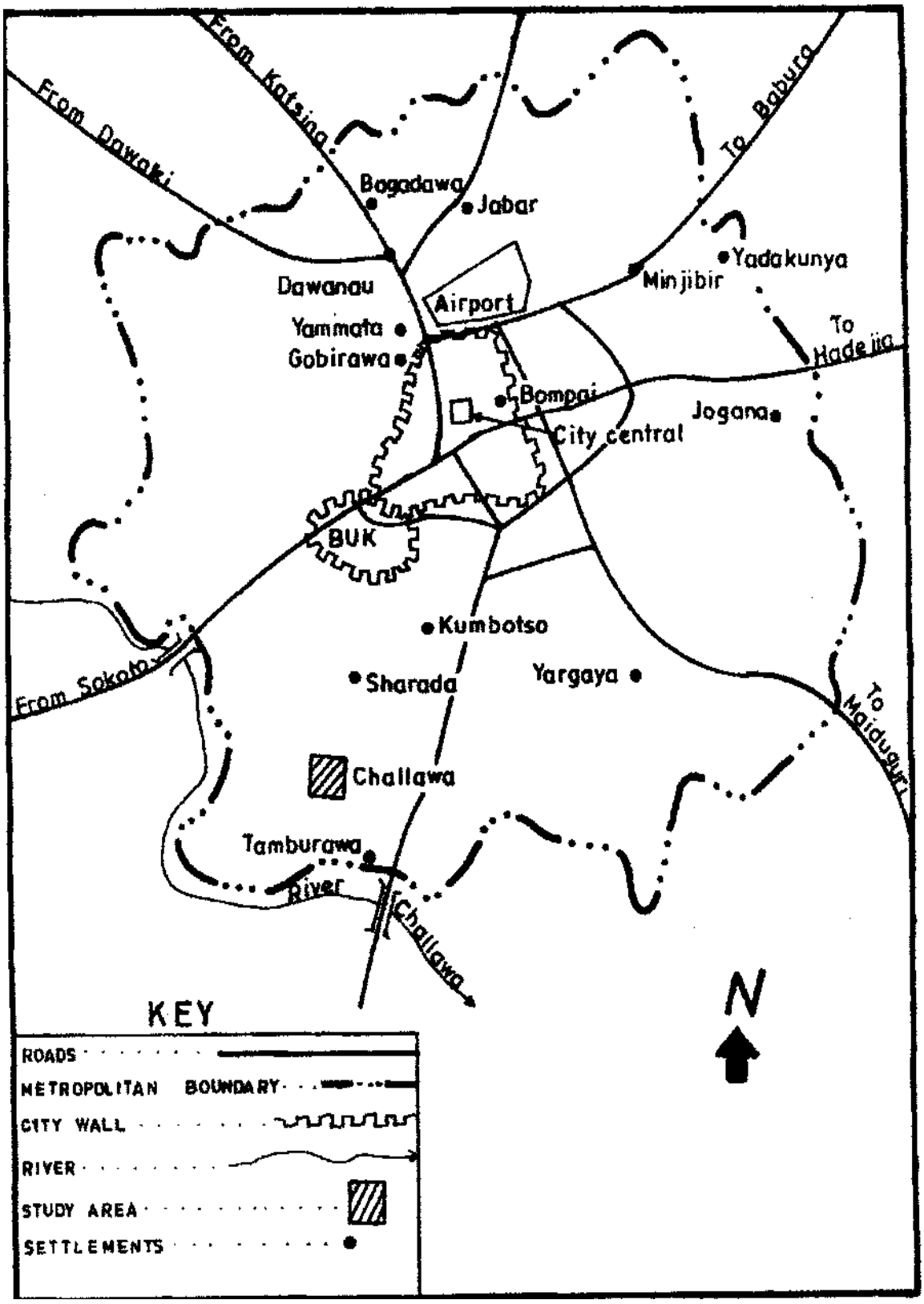

FIG. 3.3 SKETCH MAP OF KANO METROPOLIS SHOWING CHALLAWA INDUSTRIAL ESTATE – STUDY AREA

3.1.6 Samples collection

A canoe was used as sampling craft and at each point the canoe was stopped for samples to be collected. Samples of the bottom sediment were collected during the dry season (between May and June 2006) using a core sampler at each point. Sediment samples collected were wrapped with polythene bags and all the samples kept on ice and subsequently transported to the laboratory where they were frozen in a deep freezer.

3.1.7 Sample Pre-Treatment

(a) **Drying**: sediment samples for metal analysis were allowed to defrost and then allowed to air-dry. The textures of the dry sediments were determined for each site.

(b) **Grinding**: dry sediments were ground into fine powder and homogenized using an acid-washed clean mortar and pestle. They were then stored in desiccators to attain constant weight before being stored in air-tight plastic bottles.

(c) **Sieving**: dry sediment samples were sieved with 200µm sieve before being used for sediment analysis. All metallic determination from sediment samples was based on the fine particles obtained.

3.2 Methods

3.2.1 Determination of Physicochemical Parameters of Sediment

3.2.1.1 Determination of pH (Herdershot *et al*., 1993)

The pH of sediment samples were measured with sediment to water ratio 1:2 using Crison MicropH 2000, pH meter as follows: 10g of 200µm sieved air-dried sediment samples were weighed into plastic containers and 20cm^3 of distilled – deionized water was added. The mixture was stirred several times for 30 minutes. Then the sediment suspensions were allowed to stand for 30 minutes more undisturbed. The electrode of the pH meter was then inserted into the settled suspension and the pH of the soil measured (Bamgbose *et al*., 2000). Before use, the pH meter was calibrated with standard buffer solutions of pH 4, 7 and 9.

3.2.1.2 Organic Matter Determination (Walkley and Black, 1934)

The organic matter of the sediment samples was determined by the method of Walkley and Black (1934): 1g of the sediment sample was weighed in triplicates for each site into 250cm^3 conical flask. 10cm^3 of 0.20 M potassium dichromate was pipette into each flask and was swirled gently to disperse the sediment followed by addition of 20cm^3 concentrated H_2SO_4. The flask was swirled gently until the sediment and reagent were thoroughly mixed. The mixture was then allowed to stand for 30minutes on a glass plate. 100cm^3 of distilled water was added followed by the addition of 4 drops of ferroin indicator, after which it was titrated with 0.25M ammonium ferrous sulphate. Blank titration was similarly carried out.

$$\% \text{ Organic carbon is given by the equation} = \frac{(\text{Blank Titre} - \text{Actual Titre}) \times 0.3 \times m \times f}{\text{Weight of air – dried sediment taken}}$$

Where f = correction factor = 1.33

m = concentration of ammonium ferrous sulphate

Then % Organic matter in sediment = % Organic carbon x 1.729

3.2.1.3 Particle Size Distribution (Bouyocos, 1951)

Particle size distribution was determined by the hydrometer method as described by Bouyocos (1951): 50g of 200µm sieved sediment was weighed into a 250cm^3 plastic beaker. 100cm^3 of 50% calgon was added and then stirred with a glass rod. Then 100cm^3 of distilled water was added and stirred. The beaker was left to stand for about 30minutes with occasional stirring. The mixture was then transferred into 250cm^3 plastic container and shaken on an end-to-end shaker for 10 minutes. The shaken sample was next transferred into a 1000cm^3 measuring cylinder and made to the 1000cm^3 mark with distilled water. Before the hydrometer reading was taken, the suspension in the cylinder was mixed vigorously using a long handle plunger making sure that the sediment at the bottom was thoroughly disturbed. Hydrometer reading at 40 seconds and 2 hrs were taken. A blank cylinder was prepared by making 100cm^3 of the 50% calgon solution up to 1000cm^3 mark with distlled water. The blank hydrometer reading was taken at the respective time interval. The temperature of the suspension and blank was also taken. The corrected hydrometer readings C (g/l) were obtained by subtracting the blank reading R_L (g/l) from the hydrometer readings in the sediment suspensions R (g/l) and adding 0.36g/l for every degree above 20^0C.

$C = R - R_L + (0.36T)$

Where T = Room temperature at 20^0C.

$$\text{Clay} = \frac{\text{Corrected 2 hrs reading} - \text{Blank} \times 100}{\text{Weight of sediment taken}}$$

$$\text{Silt} = \frac{\text{Corrected 40 secs reading} - \text{Blank} \times 100}{\text{Weight of sediment taken}}$$

Sand = 100 – (% Clay + % Silt)

3.2.1.4 Chloride (Allen, 1974)

Sediment sample of 10g was added to 40 ml of distilled water stirred with glass and allowed to stand overnight. 20 ml of the extract was pipetted into 25 ml conical flask and 4 drops of 5% K_2CrO_4 indicator was added. It was titrated with 0.0l $moldm^{-3}$ $AgNO_3$ in micro – burette to the end point.

$$\text{Mg kg}^{-1}\text{of Cl}^- = \frac{\text{Titre (ml)} \times \text{Molarity } (AgNO_3) \times \text{Extraction volume} \times 103}{\text{Weight of sample} \times \text{aliquot volume (ml)}}$$

3.2.1.5 Sulphate – Sulphur (SO_4^{2-} –S) (Allen, 1974)

2.14g KH_2PO_4 were dissolved in 1 litre of distilled water (500ppm phosphorous solution) giving the extracting solution. 5g of air-dried sediment sample was weighted into a 250ml conical flask and 25ml of extracting agent added. It was shaken on mechanical shaker for 30 minutes, centrifuged and supernatant decanted.

0.5434g of anhydrous K_2SO_4 was dissolved in 1 litre of distilled water in volumetric flask giving 1.00 M SO_4^{2-} - S stock solution (1 ml =100µgS). 25ml of the stock solution was diluted to 1 litre giving intermediate solution (1 ml =25µgS). This was used to prepare working standards of 5, 10, 15, 20 and 25µgS. Absorbance was measured with Chroma calorimeter (model 257) and calibration curve of absorbance against

concentrations was plotted (appendix I). 5g of air-dried sieved sediment sample was weighed into Erlenmeyer flask and 25ml distilled water added. The mixture was shaken for 30 minutes and filtered (Whatman no. 42 filter paper). 10 ml of the filtrate was pipetted into a 25ml volumetric flask and distilled water added to bring the volume to about 20ml. 1ml of gelatin $BaCl_2$ reagent was added and volume made up to 25ml with distilled water. The contents were mixed thoroughly and allowed to stand for 30 minutes. Absorbance of this solution was measured with colorimeter along with that of the blank or extracting solution. Each determination was repeated three times.

mg kg^{-1} SO_4^{2-}-S = mgSO_4^{2-} from curve x Extractant volume

3.2.1.6 Nitrate – Nitrogen (Allen, 1974; Agbenin, 1995)

250g of KCl was dissolved in distilled water in a beaker and transferred into 1 litre volumetric flask. The solution was made up to 1 litre giving 2M KCl solution 2g NH_2SO_3H (Sulphamic acid) was dissolved in 100ml of 2M KCl solution. The bottle was shaken for 1 hour on a mechanical shaker. The suspension was filtered through Whatman no. 42 filter paper to give the sediment extract. 10ml of the filtrate was pipetted into a Kjeldahl flask and 0.2g MgO was added. It was digested to drive away NH_3 as NH_3-N and 1ml of Sulphamic acid solution was added to destroy NO_2-N. 0.2g of provided Devarda's alloy was added to convert NO_3-N to NH_4-N. 5ml of Boric acid (H_3BO_3) indicator was transferred into a 50ml Erlenmeyer flask and 30ml level was marked which was then placed under the condenser of a steam distillation apparatus. Steam distillation of the filtrate commenced immediately and was stopped when the distillate reached the 30ml level on the Erlenmeyer's flask. The distillate was titrated with standard 0.01M

H_2SO_4 from a micro burette until colour change from green to permanent pink. The determination was done three times.

1 ml 0.01M H_2SO_4 = $70gL^{-1}$. NH_4-N = $70gL^{-1}NO_3$ – N = 0.07mg NO_3 – N. mg $kg\text{-}^1NO_3^-$-N = mgNO_3^--N (from Titre) x Extractant volume

3.2.1.7 Nitrite – Nitrogen, NO_2^--N (Agbenin, 1995)

Sediment extract of 10ml from section 3.2.1.6 above was subjected to the same treatment but without the addition of Sulphamic acid. 0.0lM H_2SO_4 was used for the titration and amount of (NO_3 + NO_2) was obtained. The amount of NO_3^--N obtained in section (3.2.1.6) above subtracted from this value gave the amount of NO_2^--N per sample.

3.2.1.8 Phosphate – Phosphorus, PO_4^{3-} - P (Agbenin, 1995)

15ml of 1.000moldm^3, NH_4F and 25ml of 0.5M KCl was mixed with 460ml of distilled water and the mixture stored in a glass bottle giving the extraction solution. 0.2197g of KH_2PO_4 was oven dried at 105^0C for 1hour, dissolved in distilled water and diluted to 1000ml in a volumetric flask giving phosphate stock solution (1ml = 0.05mg). Working standards of 5, 10, 15, 20 and 25µgPO_4^{3-}P, were prepared. Absorbance was read with colorimeter at 690nm and a calibrations curve of absorbance versus concentration was plotted (appendix 2).5g of sediment was weigh into an extraction bottle and 35ml of extraction solution was added. The bottle was shaken for 1 minute and filtered into dry beaker. Filtration was repeated until filtrate was clear. 10ml of the filtrate was shaken and 0.4ml of ammonium molybdate reagent (Denige's reagent) and 2 drops

of stannous chloride were added. Absorbance was measured after 11 minutes for all samples at 690nm and concentration read from the Curve.

$$MgPO^3_4\text{-}Pkg^{-1} = \frac{\text{Conc. (from Curve) x Extracting volume}}{\text{Aliquot of sample x sample weight}}$$

3.2.2 Digestion of Sample

Dry sediment samples were digested according to Awofolu (2005). 5g of sieved sample was placed into a beaker (100ml). 3ml of 30% H_20_2 was added. This was left to stand for 60min and then extracted with 75ml of 0.5M solution of HCl,then the content heated at low heat (90^0C) on hot plate for about 2 hours. The digest was then filtered into 50ml standard flask. The beaker was then rinsed with small portions of double distilled water and then filtered into the flask. The mixture was made to mark with the same acid solution and used for metal determinations.

3.2.3 Quality Assurance

Quality control test was conducted on digested sediment samples in order to evaluate the experimental procedures**.** This was done by spiking the pre-digested sediment samples with multi element metal standard solution (0.5mgL^{-1} of Cd, Pb and Cr and 5mgL^{-1} of Zn and Cu) (Awofolu, 2005).

3.2.3.1 Treatment of Glass wares, Sample Containers and Crucibles

Glass wares, crucibles and plastic containers were washed with liquid soaps, rinsed with distilled water and soaked in 10% HNO_3 for 24hrs; cleaned with distilled – deionized water and in such a manner that no contamination occurred (Adnan, 2003).

3.2.3.2 Preparation of Multi element Standard Solution (MESS)

0.0055g of $Cd(NO_3)_2.4H_2O$ was weighed out, dissolved in 2ml distilled water in a beaker and transferred into a 1000cm^3 Erlenmeyer flask. The beaker was rinsed thoroughly with distilled water into the flask. 0.190g of $Cu(NO_3)_2.3H_2O$ was also weighed dissolved in 2ml concentrated HNO_3 in a beaker and transferred into the same 1 litre volumetric flask. The beaker was rinsed with distilled water into the volumetric flask. 0.0075g of K_2CrO_4 was dissolved in 2ml HNO_3 in a beaker and transferred into the volumetric flash. This was followed by separately weighing out of 0.0048g of $Pb(NO_3)_2$ and 0.0062g of ZnO dissolving them in distilled water and HNO_3 respectively and transferring them into the same volumetric flask. The flask was made up to mark with distilled water to give the multi-element standard solution (MESS). Aliquot of this solution was used in the spiking experiment.

3.2.3.3 Spiking Experiment

20ml of the multi-element standard solution was drawn with graduated pipette from the MESS and used to spike one sample of the sediment. This was then digested in triplicate as in section 3.2.2. The digestion was done in triplicate with blank digestion. The digests were run on AAS. Concentrations of metals in spiked and unspiked sample were used to calculate percentage recovery in order to validate the method as follows:

Amount of metal used to spike a sample

$$= \frac{\text{Volume of MESS used x conc. of metal in MESS}}{1000}$$

= X mg of metal used to spike a sample (calculated)

Amount of metal in unspiked sample

$$= \frac{\text{Vol. of digest of unspiked sample x conc. of metal in digest of unspiked sample}}{1000}$$

= Y_0mg of metal in Zg of unspiked sample

Amount of metal in spiked sample

$$= \frac{\text{Volume of digest of spiked sample x conc. of metal in digest of spiked sample}}{1000}$$

= Y_1mg of metal in Zg of sample spiked.

Estimate of amount of metal used to spike a sample

= Amount of metal in spiked sample (Y_1) – Amount of metal in unspiked sample (Y_0)

= X' mg of metal used to spike a sample (determined)

= Recovery of metal

$$\% \text{ Recovery of metal} = \frac{\text{Amount of metal used to spike a sample determined}}{\text{Amount of metal used to spike a sample calculated}} \times 100$$

$$= \frac{X'}{X} \times 100$$

3.2.7 Sequential extraction

Sequential extraction was carried out on the principle of selective extraction proposed by Tessier *et al* (1979) with some modifications. These include the use of Mg $(NO_3)_2$ instead of $MgCl_2$ to extract exchangeable fractions because the chloride ion complex metals (Shuman, 1985)

The extraction of the oxidizable phase was undertaken after the extraction of the exchangeable phase. This method allows the destruction of the organic matters which entraps the mineral materials and thus provides a better extraction of the phases that

follow (Meguellati, 1982). For the residual fraction a combination of Aqua regia/hydrofluoric acid (HCl–HNO_3/HF) was used instead of the HF – $HClO_4$ (Sanchez, et al 1994; Maiz et al 1997).

Three sub-sample of 1g each of samples from the study and control area were subjected to sequential extraction separately. The extraction was aimed at differentiating fractions in five stages as follows; -

1. Exchangeable phase

Each sample was shaken at room temp. with 16ml of 1M $Mg(NO_3)_2$ at pH 7.0 for 1 hour, centrifuged and supernatant decanted and made up to 40ml with double distilled water prior to analysis.

2. Oxidizable phase (Bound to organic matter)

Residue from (1) + 10ml of 8.8M H_2O_2 + 6ml of 0.02moldm^{-3} HNO_3 was shaken for 5 + 1 hour at 98^{0}C. 10ml of 3.5M CH_3COONH_4 was added as an extracting agent, centrifuged and supernatant made up to 40ml with distilled water prior to analysis.

3. Acid soluble phase (Bound to carbonates)

25ml of 0.05M Na_2EDTA was added to the residue from (2) shaken for 6hrs and centrifuged. The supernatant was decanted and made up to 40ml with distilled water prior to analysis.

4. Reducible phase (Bound to Fe/Mn oxide and hydroxides)

Residue from (3) + 17.5ml of 3.5 M $NH_2OH.HCl$ + 17.5ml of 3.5moldm^{-3} CH_3COONH_4 shaken for 4+1 hr at 98 ^{o}C Extracted with 10ml of 3.5M CH_3COONH_4 shaken for 1 hr , centrifuge, the supernatant decanted and made up to 40ml with distilled water prior to analysis.

5. Residual Fraction

Residue from (4) was digested by using HCl–HNO_3/HF (0.35:12 with sediment/solution ratio) in acid digestion Teflon cup. It was dry ashed for 2 hours and evaporated to dryness. The residue was made up to 40ml with distilled water prior to analysis.

After each successive extraction, the sample was centrifuged at 45000rpm for 15 minutes (Legret *et al.*, 1988). The supernatants were removed with pipette and filtered with Whatman No 42 filter paper. The residue was washed with deionized water followed by vigorous handshaking and then followed by 15 minutes of centrifugation before next extraction. The volume of rinse water used was kept to a minimum to avoid excessive solubilization of solid materials.

3.2.8 Calibration Curve

A calibration curve of absorbance against concentration for each metal ion was prepared as shown in Appendices I – X for Zn, Cu, Cd, Cr, Pb, respectively which yielded a good linearity. This implies that the instrument responded very well to the standard analyte of interest and therefore would respond to analyte in the samples. The calibration curves were used for the determination of metal concentrations in samples. The actual concentration of the metal in the sample was determined as follows:

$$\text{Amount of metal in volume of digested solution} = \text{Vol. of digest solution} \times \frac{\text{Conc. of Metal in sample solution from calibration curve}}{1000}$$

$$= X \text{ mg}$$

$$\text{Amount of metal in mgkg}^{-1} \text{ In sediment sample} = \frac{\text{Amount of metal in volume of digested solution}}{\text{Weight of sample digested (kg)}}$$

$$= \frac{X}{\text{Weight of sample digested (kg)}}$$

3.2.9 Statistical Analysis

The results of this study were analyzed using Pearson Correlation analysis and ANOVA single factor analysis of variance. Pearson correlation coefficient, r is an index without dimension that has a range -1.0 to +1.0 inclusive. The index indicates the extent of linear relationship between two variables X and Y. The coefficient is always 1 when there is a perfect linear relationship which gives a positive slope between the two variables. A coefficient of -1 is obtained when there is a perfect linear relationship which gives a negative slope between data of the two variables. A +1 coefficient is obtained when one variable has a high value and so does the other while a -1 coefficient is obtained when one variable has a high value while the other has low value.

A correlation coefficient is 0 when there is no linier relationship between two variables. An ANOVA is an analysis of the variation present in a given experiment. It is a test of the hypothesis of that the variation in an experiment is no greater than that due to normal variation of individual's characteristics and error in their measurement. The tests in an ANOVA are based on the F – ratio: the variation due to an experimental treatment or effect directed by the variation due to experimental error. ANOVA puts all the data into one number (F) and gives us one P for the null hypothesis.

The t –test tells us if the variation between two groups is "significant" P reports the significance level.

CHAPTER FOUR

4.0 Results and Discussions

4.1 Methods Validation

The efficiency of the digestion method, the precision and accuracy of the atomic absorption spectrophotometer were validated by spiking experiment. The results as shown in Table 4.1 revealed that the percentage recovery for the aqua-regia digestion ranged from 88.65 – 105.55% for all the metals, with Pb having the least and Cd having the highest. The Table also revealed the percentage recovery for the sequential extraction. It ranged from 95.40 – 105.20% for the sequential extraction, Cr has the least percentage recovery,(95.40%) while cadmium had the highest, (105.20%) The pattern of recovery efficiency in sediment for both sequential extraction and aqua-regia digestion were found to follow the same but decreasing order: Cd > Cu > Zn > Cr > Pb. However, the high percentage recoveries above 85% obtained imply that the procedures used for the 200 µm sieved air dried sediment samples treatment and analysis were efficient and reliable.

4.2 Sediment Physicochemical Parameters

The results of all the physicochemical parameters of the 200 µm sieved air-dried sediment samples from the study and control areas of the Challawa River determined are presented in Tables 4.2 and 4.3, respectively. In the study area, organic matter content varied from 7 – 10.5% while that of control area ranged from 7 – 8.35%. The difference in the sediment organic matter between the study and control areas may be attributed to the tannery effluent discharge into the river. Tannery effluents are discharged raw into the Challawa River and contains high organic matter due to animal hide product in it. It may

also be seen from Table 4.2 that organic matter content return to values similar to those of control area as from sampling points F to J. This shows that deposition of animal hide occurs mainly from the point of tannery effluent discharge to sampling point E. The decrease in organic matter content with the distance from the point of entry of tannery effluent may also be due to possible biodegradation of organic matter by microorganism in the sediment, an indication of self-cleaning effect of the river.

In the study area, the pH of the sediment samples varied from 5.75 – 7.2. The low pH at sampling points A to D observed might be due to discharges of acidic waste in the tannery effluents from pickling process which prepares the hides by providing an acidic environment. There is no much considerable variation in the pH values for sampling points 1 to 5 as shown in Table 4.3. The sampling point 1 has the lowest value, which might be due to the proximity of that point to the point of entry of the tannery waste into the river. The pH values obtained in the study area revealed that the sediment samples were slightly acidic. This is similar to the pH range of 4.0 – 7.0 reported by Lee et al (2003) in their study of the implications to water quality, heavy metals in bed and suspended sediments of Anyang River, Korea. The pH range found in this investigation falls within the limits of 4.0 – 7.00 (WHO, 2005) for the survival of fish in the aquatic environment. The slightly acidic medium of the sediment of River could indicate possible mobility of the metals to other environments since metals are known to be more soluble in acidic medium than in alkaline medium (Chimuka *et al*., 2005).

The chloride content of the sediment samples as shown in Table 4.2 and 4.3 respectively ranged from 0.30 – 0.725 mg/kg^{-1} for the study area and 0.150 – 0.350 mg/kg^{-1} for the control area.

Table 4.1 Percentage recovery of heavy metals in sequential extraction and aqua-Regia digestion

Metals	Sequential extraction	Aqua-regia digestion
Pb	96.50±0.90	88.65±0.74
Cu	103.13±0.15	105.20±0.30
Cd	105.20±0.75	105.55±0.20
Zn	98.30±0.25	90.05±0.20
Cr	95.40±0.10	92.30±0.10

Table 4.2 Mean (±SD) of physicochemical parameters of study area sediment samples

Sites	Parameter								
	pH	**OM (%)**	**$CaCO_3$ ($mgkg^{-1}$)**	**NO_3^--N ($mgkg^{-1}$)**	**NO_2^-- N ($mgkg^{-1}$)**	**PO_4^{3-}-P ($mgkg^{-1}$)**	**SO_4^{2-}-S ($mgkg^{-1}$)**	**Cl^- ($mgkg^{-1}$)**	**NH_3-N ($mgkg^{-1}$)**
A	5.25±0.25	10.25±0.25	14.25±0.25	0.650±0.100	0.500±0.001	5.02±0.28	12.00±0.20	0.725±0.125	0.170±0.020
B	5.50±0.00	10.15±0.39	14.15±0.35	0.400±0.001	0.600±0.000	6.60±0.30	10.80±0.20	0.450±0.050	0.400±0250
C	5.55±0.00	10.55±0.00	13.75±0.25	0.900±0.000	0.400±0.010	4.50±0.20	11.65±0.25	0.400±0.100	0.850±0.012
D	5.00±0.00	8.90±0.00	10.10±0.10	0.700±0.000	0.400±0.000	6.15±0.25	12.60±0.20	0.525±0.015	0.260±0.040
E	5.00±0.25	9.40±0.00	10.25±0.25	0.700±0.000	0.500±0.001	7.35±0.15	8.95±0.150	0.450±0.050	0.510±0.030
F	5.75±0.00	8.05±0.05	10.85±0.15	0.500±0.001	0.400±0.001	3.50±0.20	14.30±0.30	2.415±0.085	0.250±0.040
G	5.75±0.00	8.10±0.10	10.25±0.25	0.200±0.000	0.600±0.000	4.40±0.10	17.20±0.30	1.500±0.001	0.350±0.040
H	5.00±0.00	7.70±0.20	10.90±0.10	0.600±0.001	0.400±0.000	5.92±0.12	19.70±0.30	1.900±0.100	0.310±0.015
I	5.50±0.00	7.00±0.00	10.30±0.30	0.100±0.001	0.600±0.000	4.21±0.29	10.70±0.20	0.500±0.100	0.220±0.021
J	6.60±0.00	7.25±0.25	10.20±0.20	0.200±0.001	0.300±0.010	2.41±0.29	15.55±0.25	0.690±0.110	0.021±0.007

Table 4.3 Mean (±SD) of physico-chemical parameters of control area sediment samples

Sites	Parameter								
	pH (H_2O)	OM (%)	Alkalinity ($mgkg^{-1}$)	NO_3^--N ($mgkg^{-1}$)	NO_2^-- N ($mgkg^{-1}$)	PO_4^{3-}-P ($mgkg^{-1}$)	SO_4^{2-}-S ($mgkg^{-1}$)	Cl^- ($mgkg^{-1}$)	NH_3-N ($mgkg^{-1}$)
1	5.75±0.75	7.90±0.10	10.40±0.60	0.500±0.000	0.600±0.001	10.30±0.30	4.35±0.15	0.325±0.002	0.820±0.090
2	6.00±0.00	8.35±0.15	10.35±0.35	0.400±0.001	0.000±0.000	14.35±0.15	6.55±0.15	0.275±0.007	0.150±0.003
3	5.25±0.25	7.65±0.15	10.50±0.50	0.600±0.002	0.200±0.001	11.05±0.15	5.35±0.25	0.150±0.005	0.087±0.002
4	5.75±0.25	7.40±0.29	10.50±0.50	0.100±0.000	0.030±0.002	9.55±0.45	5.00±0.20	0.350±0.005	0.140±0.004
5	6.00±0.00	7.1±0.10	10.30±0.30	0.400±0.10	0.505±0.00	8.00±0.30	4.50±0.20	0.275±0.075	0.016±0.004

The variations in the chloride content of the sediment in the study and control areas may be attributed to the tannery effluent discharged into the river. Sampling points A to F showed a higher chloride content because of their proximity to the point of discharge into the river since the tannery waste is known to contain high chloride content (Yisa, 2004). The decrease in the chloride content from points G to J might be due to formation of complexes with heavy metals downstream. The range of chloride content in this study are lower than the ranges of 3.5 – 15.5 $mgkg^{-1}$ reported by Odokuma and Abah (2003) in a study of sediment of New Calabar River.

Alkalinity measured in $mgkg^{-1}$ $CaCO_3$ was in the range of 10 – 17 mg/kg^{-1} for the study area while that of the control area ranged from 10.30 – 10.40 mg/kg^{-1}. There is a difference in the alkalinity between sediments samples of study and control areas. This could be attributed to the discharge by tannery effluents that are generally known to be alkaline as reported by (Yisa et al., 2004) in the study of impact of tannery operations on Challawa River. There is no significant variation in alkalinity between sampling points 1 – 5 in the control area while in the study area, alkalinity decreases downstream from points A to F. This could imply the possible reaction of the acidic sediment with the $CaCO_3$.

The content of NO^-_3 – N, NO^-_2 – N and NH_3 – N in the sediment of River Challawa are shown in tables 4.2 and 4.3. The content ranged from 0.10 to 0.90 $mgkg^{-1}$, 0.3 – 0.6 mg/kg^{-1} and 0.21 – 0.70 mg/kg for the NO^-_3 – N, NO^-_2 – N and NH_3 – N, respectively in the study area. The control area has NO_3^- – N in the sediment in the range of 0.4 – 0.6 $mgkg^{-1}$ NO_2^--N, 0.2 – 0.6 $mgkg^{-1}$ and NH_3 – N, 0.45 – 0.82 $mgkg^{-1}$. There is no significant difference between the values in the study and control areas. This implies

that there is no significant contribution the tannery effluent is making to the level of those parameters. Such parameters might have passed into the sediments from fertilizer applied on farms from the banks of the river Challawa. Generally, the values of nitrate and nitrite obtained in this study are lower than 1 mg kg^{-1}, since high levels (> 1 mg kg^{-1}) of nitrate and nitrite are not good for aquatic life (Adeyemo *et al*., 2008).

In the study area, the sulphate - sulphur content ranged from 10.55 to 12.00 mg kg^{-1} while the sulphate - sulphur sediment samples from the control area ranged from 4.15 – 6.55 $mgkg^{-1}$. There is a significant variation between the sulphate -sulphur level in the study and control areas. This could be due to the discharge of tannery effluents untreated into the river. There is no significant variation in the sulphate -sulphur content between sampling points 1 to 5 because the sources of the sulphate -sulphur include agricultural run-off which contains sulphate from applied fertilizers and pesticides.

The level of PO_4^{3-} - P in the sediment samples ranged from 2.45 – 7.35 mg kg^{-1} in the study area while in the control area, the PO_4^{3-} - P ranged from 8.10 – 14.30 mg kg^{-1}. The phosphate level in the control area is very much greater than the level of the phosphate in the study area. This could be as a result of the amount of the phosphate contained in the agricultural run-offs is higher in the control area because the number of farmlands on the banks of the river is higher in the control area that the study area.

The particles size distribution as shown in Table 4.4 and 4.5 revealed that all samples form study and control areas were dominated by high percentage sand fraction followed by silt and finally clay. The percentage of sand ranged from 84.0 – 94.00% silt 3.5 – 9.00% and clay 2.5 – 7.00% in the study area while in the control area, the percentage of sand ranged from 88.5 – 92.00%, silt 3.5 – 7.0 and clay 4.0 – 7.5%

respectively. Generally, there is no significant variation in the particle size distribution between the study and control areas. The high percentage sand content in the studied sediment samples suggested the poor retention capacity of the sediment for heavy metals because the smaller the size of the particles, the higher the retention capacity for metals.

Lee *et al*. (2003) observed high clay and silt contents in the sediment at points on Anyang River, Korea where the flow rate of the river showed down.

Statistical analysis across the sites showed significant differences ($P < 0.05$) in the value of organic matter content, alkalinity, SO_4^{2-} - S and chloride of sediment samples collected in the study and control areas. This could lead to the deduction that the difference might have been influenced by the discharge of untreated tannery effluent into the river. There was no significant difference in the values of NH_3 – N, PO_4^{3-} – P, NO^-_3 – N in the study and control areas. This implies that the discharge of tannery effluents does have influence on the concentration of such parameters in the sediment.

Correlation matrix among physicochemical parameters of the sediment as shown in Table 4.6 showed significant positive correlation at $P \leq 0.05$ between PO_4^{3-}- and Cl^- this indicates the influence of one parameter on the other. Negative correlation at $P \leq 0.05$ was observed between pH and SO_4^{2-} - S, clay and sand clay and NO^{3-} - N and PO_4^{3-} - P and NO^{3-} - N. This implies that the levels of those parameters have no influence on each other.

Table 4.4 Mean (±SD) of particle size distribution of study area sediment samples

Sites	Clay	Silt	Sand	Textural class
A	7.0±0.5	9.0±0.1	84.0±2.0	Sandy loam
B	2.5±0.5	6.5±0.5	92.0±2.0	Sandy loam
C	4.0±0.1	6.0±0.1	90.0±1.5	Sandy loam
D	2.5±0.5	3.5±0.5	94.0±1.5	Sandy loam
E	4.0±1.0	7.0±0.1	89.0±1.0	Sandy loam
F	3.5±0.5	5.5±0.5	91.0±0.5	Sandy loam
G	3.0±0.5	9.0±0.1	88.0±0.5	Sandy loam
H	3.0±0.1	7.0±0.1	90.0±0.1	Sandy loam
I	3.0±0.1	6.5±0.5	90.5±0.5	Sandy loam
J	3.0±0.1	7.0±0.5	90.0±0.1	Sandy loam

Table 4.5 Mean (±SD) of particle size distribution of control area sediment samples

Sites	Clay	Silt	Sand	Textural class
1	6.0±0.1	5.5±0.5	88.5±0.15	Sandy loam
2	4.0±0.1	3.5±0.5	92.5±0.5	Sandy loam
3	6.0±0.1	5.5±0.5	88.5±0.5	Sandy loam
4	7.5±0.1	5.0±0.1	87.5±0.5	Sandy loam
5	4.0±0.5	7.0±0.1	89.0±0.5	Sandy loam

Table 4.6 Correlation matrix among physico-chemical parameters of the sediment

Parameters	OM	Cl^-	$CaCO_3$	NH_3-N	NO_3^--N	NO_2^-- N	SO_4^{2-}- S	PO_4^{3-}- P	pH	Sand	Silt	Clay
OM	1.000											
Cl^-	-0.081	1.000										
$CaCO_3$	0.333	0.142	1.000									
NH_3-N	0.370	0.115	0.170	1.000								
NO_3^-N	0.171	-0.250	-0.077	0.245	1.000							
NO_2^-N	0.251	0.116	-0.397	0.183	-0.079	1.000						
SO_4^{2-}S	0.469	-0.267	0.224	0.009	0.039	-0.395	1.000					
PO_4^{3-}P	-0.101	0.703**	0.246	0.091	-0.577*	-0.085	-0.169	1.000				
pH	-0.398	-0.107	-0.115	-0.190	0.090	-0.061	-0.515*	-0.107	1.000			
Sand	-0.120	0.052	-0.290	-0.082	-0.179	0.145	0.070	-0.081	-0.361	1.000		
Silt	0.238	0.094	-0.082	-0.088	-0.128	0.319	-0.015	-0.003	-0.031	-0.504	1.000	
Clay	-0.190	-0.243	-0.454	-0.231	0.141	-0.622*	0.111	-0.100	0.508	-0.630*	0.073	1.000

***Significant at $p \leq 0.05$**
****Significant at $p \leq 0.01$**

4.3 Total Heavy Metal Content in Sediment

The results of total heavy metal concentration collected from the study and control areas are presented in Tables 4.7 and 4.8. The results ranged from 1.70 – 2.61 mg kg^{-1}, 8.77 – 12. 32 mg kg^{-1} and 5.41 – 8.18 mg kg^{-1} for Cr, Cu, Cd, Zn and Pb respectively for the study area while the control area results ranged from 1.667 – 2.20 mg kg^{-1}, 2.71 – 2.93 mg kg^{-1}, 2.63 – 2.83 mg kg^{-1}, 10.89 – 11.41 mg kg^{-1} and 6.73 – 8.15 for Cr, Cu, Cd, Zn and Pb. There was significant variation in concentration of Cr, Cu, and Cd between the sediments samples of study and control areas. This could be the direct influence of tannery effluent which is untreated and discharged into the river. The levels of Cu, Cr and Cd decreases from points A to G while H to J have the concentration almost similar to those of sampling points 1 to 5. The profile of average metal content in both areas were found to be Zn > Pb > Cu > Cd > Cr, in order of decreasing magnitude. Analysis of variance (ANOVA) showed significant variation ($P < 0.05$) between sites for all heavy metals determined.

Tariq *et al*. (1996) analyzed sediment sample collected from eleven sampling points on Indus River, Pakistan and obtained mean metal contents (0.593; Cr, 8.3; Cu, 17.3; Pb, 1.205 and Zn 2.55 mg kg^{-1}) which with the exception of lead were all higher than the values obtained for metal contents in both areas of this study. Oyewale and Musa (2006) analyzed sediment samples from Kanji Lake and found that the mean values of metals (Zn, 59; Cu, 25; Cr, 27 and Pb, 19mgkg^{-1}). These values are all higher than the metal sediment contents found in this investigation.

All metals with the exception of cadmium in this study were below the maximum threshold effect (USEPA, 1997).

Table 4.7 Mean (±SD) total heavy metal concentration ($mgkg^{-1}$) in sediment of Study area

Site	Metals				
	Cr	**Cu**	**Cd**	**Zn**	**Pb**
A	2.60±0.08	3.44±0.11	2.94±0.06	8.77±0.01	7.86±0.00
B	2.61±0.22	3.62±0.14	2.81±0.06	11.35±0.06	7.75±0.02
C	2.48±0.01	3.32±0.05	2.86±0.07	11.71±0.02	7.81±0.22
D	2.56±0.02	3.00±0.04	2.50±0.06	9.54±0.05	7.22±0.25
E	2.27±0.00	2.90±0.00	3.21±0.05	12.72±0.03	7.27±0.05
F	2.26±0.13	1.60±0.01	2.77±0.06	10.13±0.05	8.18±0.00
G	2.35±0.07	2.80±0.05	2.72±0.01	10.58±0.01	7.03±0.05
H	1.78±0.08	2.93±0.02	2.68±0.11	11.06±0.05	6.94±0.08
I	1.81±0.05	2.66±0.11	1.99±0.09	11.35±0.10	7.79±0.05
J	1.70±0.04	3.69±0.03	1.92±0.05	11.47±0.10	6.82±0.06
USEPA (1997)		18.7	0.676	124	30.2

Table 4.8 Mean (±SD) total heavy metal concentration ($mgkg^{-1}$) in sediment of Control area

Site	Metals				
	Cr	**Cu**	**Cd**	**Zn**	**Pb**
1	1.79±0.20	2.93±0.01	2.83±0.03	11.41±0.03	8.15±0.01
2	1.67±0.04	2.71±0.08	2.63±0.04	11.26±0.01	7.00±0.03
3	1.78±0.00	2.88±0.01	2.70±0.05	10.89±0.03	7.13±0.00
4	1.94±0.07	2.84±0.07	2.81±0.03	11.34±0.04	7.56±0.01
5	2.20±0.06	2.84±0.01	2.64±0.025	11.14±0.05	6.73±0.02
USEPA (1997)		18.7	0.676	124	30.2

This indicated that the concentration of cadmium has reached dangerous levels in the sediments of River Challawa.

A correlation matrix for total heavy metals in the sediment of different sites was calculated to see if some metals were interrelated with each other and the results are presented in Table 4.9. A positive correlation at $P \leq 0.1$ between Pb and Cr, Cd and Cr was obtained. This indicates a significant influence of one metal on another. It also suggests the possibility of the metals coming from the same source.

Correlation matrix between heavy metals in the sediment and the physicochemical parameters revealed negative correlation between Zn and Cl^-, NO_3^- - N, pH, silt and clay which indicated that changes in values of those physicochemical parameters would not affect the content of zinc in the sediment of River Challawa. A positive correlation though not significant is revealed between Zn and O.M, SO_4^{2-} - S, PO_4^{3-} - P, sand and alkalinity. This could imply that changes in the concentration of the parameters would influence the level of zinc in the sediment. A positive correlation is also revealed in Table 4.9 between Cd and sand which may imply that change in the level of sand could influence the concentration of cadmium in the sediment. A positive correlation could also indicate the parameter could have an affect on the amount of heavy metal in the sediment since the mobility and bioavailability of metals present in sediments depend on the physicochemical properties of both the metal and the sediment (McEldowney *et al*., 1993).

Table 4.9 Correlation among total heavy metals in sediments

Metals	Zn	Pb	Cr	Cd	Cu
Zn	1.000				
Pb	0.365**	1.000			
Cr	-0.154**	0.735**	1.000		
Cd	-0.356**	0.297**	0.662**	1.000	
Cu	-0.052	0.347**	0.304**	-0.119	1.000

4.4 Sequential Extraction

The sequential extraction scheme adopted in this study analyzed distribution pattern of the metals in five geochemical phases of the sediments of River Challawa. The extraction scheme is useful in assessing the mobility and bioavailability of heavy metals in river sediment.

The distribution pattern of zinc in the five geochemical phases of the sediments showed similarity in both the study and control areas. Tables 4.10 and 4.11 showed that Fe – Mn oxides adsorbed the highest percentage of zinc while the exchangeable fraction had the least percentage. The pattern of zinc distribution followed Fe – Mn oxide bound > carbonate bound > residential > organic bound > exchangeable.

Majority of zinc metal was associated with Fe – Mn oxide fraction, which may be due to the high stability constants of zinc oxides. Earlier studies on soils, sediments and street dusts arrived at similar results (Fergusson and Ryan, 1984; Pardo et al., 1990; Levy et al., 1992). The studies of Shuman on sediments (1976, 1977) showed that Fe – Mn oxides absorbed considerable quantities of Zn and these oxides may also occlude Zn in the lattice structure. The carbonate was the second most important non-residual fraction for this element, containing approximately 21% of Zn. The presence of Zn in this fraction might indicate a pH suitable for metal precipitation. $CaCO_3$ may act as strong adsorbents for heavy metals and could complex double salts like $CaCO_3$. $ZnCO_3$. Very little enrichment of Zn in the residual fraction was noted. The percentages of total zinc in exchangeable fraction observed in the present study are very low, 1.94 – 9.13%. This indicated the low tendency of zinc in this investigation to be bioavailable.

Table 4.10 Chemical fractionation of Zn ($mgkg^{-1}$) in the sediment of study area (Mean ±SD, n=3)

	SITES									
FRACTIONS	A	B	C	D	E	F	G	H	I	J
Exchangeable	0.22±0.21	0.17±0.00	0.23±0.00	0.40±0.00	0.38±0.03	0.52±0.25	0.53±0.03	0.32±0.03	0.19±0.06	0.35±0.05
% Exch.	2.51	1.94	1.96	3.42	29.87	5.13	5.01	2.89	1.67	3.05
CB	2.23±0.21	2.51±0.02	2.80±0.02	2.60±0.03	3.00±0.06	2.03±0.15	2.71±0.04	2.63±0.46	2.28±0.03	2.58±0.68
%CB	25.43	28.62	23.91	22.20	23.58	2.00	25.61	23.78	20.09	22.49
Fe-MnO	3.72±0.03	6.20±0.15	6.34±0.36	4.34±0.45	5.60±0.11	5.05±0.05	5.19±0.08	5.12±0.10	5.14±0.04	5.59±0.08
% Fe-MnO	42.42	70.69	54.14	37.06	44.03	49.85	49.05	46.29	45.29	48.74
Org. B	1.75±0.05	1.41±0.10	1.42±0.02	1.05±0.05	1.52±0.02	1.03±0.21	0.62±0.03	1.24±0.05	1.15±0.05	1.40±0.02
% Org. B	19.95	16.08	12.13	8.97	11.95	10.17	5.86	11.21	10.13	12.21
Residual	0.85±0.04	1.06±0.05	0.92±0.02	1.15±0.13	2.22±0.03	1.50±0.03	1.53±0.03	1.75±0.05	2.59±0.02	1.55±0.05
$\sum_T$	8.77	11.35	11.71	9.54	12.72	10.13	10.58	11.06	11.35	11.47
% Non-Residual	90.31	90.66	92.14	87.95	82.55	85.19	85.54	84.18	77.18	86.49
% Residual	9.69	9.34	7.86	12.05	17.45	14.81	14.46	15.82	22.82	13.51

Table 4.11 Chemical fractionation of Zn ($mgkg^{-1}$) in the sediment of control area (Mean ±SD, n=3)

	SITES				
FRACTIONS	1	2	3	4	5
Exchangeable	0.32±0.03	0.30±0.05	0.35±0.05	0.35±0.05	0.33±0.11
% Exch.	2.80	2.66	3.21	3.09	2.96
CB	3.00±0.10	2.59±0.09	2.47±0.07	2.66±0.15	2.58±0.29
%CB	26.29	23.00	22.68	23.46	23.16
Fe-MnO	5.29±0.04	5.28±0.07	5.09±0.09	5.27±0.15	5.48±0.55
% Fe-MnO	46.36	46.89	46.74	46.47	49.19
Org. B	1.31±0.07	1.09±0.05	1.30±0.09	0.79±0.61	1.22±0.32
% Org. B	11.48	9.68	11.94	6.97	10.95
Resid.	1.49±0.40	2.00±0.10	1.68±0.07	2.27±0.04	1.53±0.03
$\sum_T$	11.41	11.26	10.89	11.34	11.14
% Non-Resid.	86.94	82.24	84.57	79.98	84.22
% Resid.	13.06	17.76	15.43	20.02	15.78

The distribution pattern of chromium as shown in Tables 4.1and 4.13 revealed some similarity in the distribution of the metal in both the study and control areas. Chromium was associated mainly (65 – 93.3%) with the residual fraction in all the samples of the study and control areas. A relatively small amount of chromium occurs in the non-residual factions. Studies of Stone and Marsalek (1996) on soils have shown similar results.

The distribution pattern of copper in the five phases showed similarity in both study and control areas as shown in Tables 4.14 and 4.15. The order of distribution in the fractions followed residual > carbonate – Fe – Mn oxide bound > organic bound > exchangeable for both the study and control areas. The association of copper with the non-residual fraction was dominated by the organic phase, (44.88%) with Fe –Mn oxide, (16.82%), carbonate, (5.55%) and exchangeable, (2.79%) phase being of secondary importance.

Exchangeable fraction accounted for a low percentage of copper and varied from 1.00 – 7.18% in both the study and control areas with an average of 2.79%. Exchangeable copper was quite low probably due to strong covalent interaction of copper with organic matter and other surfaces. The presence of copper in organic fraction is supported by the high formation constants of Cu – organic complexes (Stumm and Morgan, 1981).The level of Cu in organic fraction in both study and control areas is 44.86% This is in strong agreement with what was observed in many earlier studies in sediments (Pardo et al., 1992 and Ma and Rao, 1997) and street dusts (Sutherland and Verloo, 2000).

Fe – Mn oxide bound form of Cu (16.82%) is also another important non-residual fraction. Adsorption of Cu onto this phase may be an important control of copper levels

in the sediment Jenne (1968), McLaren ad Crawford (1973). The high surface area and adsorbing capacity of Fe –Mn oxides coupled with ability of Cu to replace Fe^{2+} in some Fe – oxides (Taylor, 1965) may be responsible for such adsorption.

The partitioning of Lead in the river sediment in both study and control areas are shown in Tables 4.16 and 4.17. The order of association is residual > Fe-Mn oxide > The association of Lead with the residual fraction is the most prominent, 34.22 – 42.25% of it in the study area and 33.71 – 46.70% in the control area. This implies that Lead may not be bioavailable. The high percentage of Lead in the residual fraction has also been observed in the speciation of heavy metals in sediments of Pisuerga River (Pardo*et al*., 1990). The mean of 28.26% of Lead association with the Fe –Mn oxide fraction of the study area and about 28.10% in the control area made it the second predominant fraction.

This could be attributed to the adsorption of Pb cations on the hydrous (armophic) oxides of Iron and Mn which is considered a reasonable universal fixation mechanism. This is in broad agreement with the fractionalization of Pb in sediments (Pardo *et al*., 1990; Belzunce – Segarra *et al*., 1992; Ramos *et al*., 1993).

Approximately 16% of the Pb in the sediment was captured by the organic fraction. This was observed in both the study and control areas. The association was probably due to the ability of lead to form organic complexes (Zimhdahl and Skogerbee, 1977). The average concentration of Pb in the carbonate fraction was (12%). This was the pattern of association.

The association of Cd with different geochemical fractions followed the order: residual > exchangeable > carbonate > Fe –Mn oxide > organic as shown in Tables 4.18 and 4.19 respectively for study and control areas

Table 4.12 Chemical fractionation of Cr ($mgkg^{-1}$) in the sediment of study area (Mean ±SD, n=3)

	SITES									
FRACTIONS	A	B	C	D	E	F	G	H	I	J
Exchangeable	0.02±0.02	0.02±0.00	0.05±0.00	0.01±0.00	0.02±0.00	0.02±0.01	0.15±0.05	0.05±0.00	0.08±0.01	0.08±0.04
% Exch.	0.77	0.77	2.02	0.39	0.88	0.88	6.38	2.89	4.42	4.71
CB	0.24±0.00	0.24±0.00	0.22±0.00	0.40±0.00	0.24±0.00	0.18±0.01	0.07±0.09	0.19±0.00	0.06±0.01	0.03±0.00
%CB	9.20	9.20	8.87	15.63	10.57	7.96	2.98	10.98	3.31	1.76
Fe-MnO	0.07±0.02	0.10±0.01	0.05±0.01	0.12±0.01	0.17±0.01	0.14±0.10	0.09±0.03	0.00±0.00	0.01±0.00	0.00±0.00
% Fe-MnO	2.68	3.83	2.02	4.69	4.49	6.19	3.83	0.00	0.55	0.00
Org. B	0.05±0.00	0.02±0.00	0.07±0.00	0.12±0.00	0.04±0.32	0.13±0.30	0.10±0.30	0.04±0.00	0.04±0.01	0.07±0.00
% Org. B	1.92	0.77	2.82	4.69	1.76	5.75	4.26	2.31	2.21	4.12
Residual	2.23±0.03	2.23±0.03	2.09±0.01	2.03±0.06	1.80±0.04	1.69±0.09	1.62±0.02	1.45±0.04	1.62±0.02	1.52±0.07
$\sum_T$	2.61	2.61	2.48	2.56	2.27	2.16	2.35	1.73	1.81	1.70
% Non-Residual	14.56	14.56	15.73	20.70	20.70	25.22	31.06	16.82	10.49	10.59
% Residual	85.44	85.44	84.27	79.30	79.30	78.24	68.94	83.82	89.51	89.41

Table 4.13 Chemical fractionation of Cr ($mgkg^{-1}$) in the sediment of control area (Mean±SD, n=3)

	SITES				
FRACTIONS	1	2	3	4	5
Exchangeable	0.04±0.01	0.04±0.00	0.08±0.00	0.33±0.01	0.04±0.00
% Exch.	2.23	2.40	4.49	17.01	1.82
CB	0.02±0.00	0.04±0.00	0.03±0.00	0.04±0.00	0.26±0.02
%CB	1.11	2.40	1.69	2.06	11.82
Fe-MnO	0.03±0.00	0.05±0.00	0.06±0.00	0.07±0.00	0.44±0.01
% Fe-MnO	1.68	3.00	3.37	3.61	20.00
Org. B	0.03±0.00	0.05±0.00	0.06±0.00	0.06±0.00	0.03±0.00
% Org. B	1.68	3.00	3.37	3.09	1.36
Residual	1.67±0.01	1.49±0.03	1.55±0.04	1.44±0.03	1.433±0.31
$\sum_T$	1.79	1.67	1.78	1.94	2.20
% Non-Residual	6.70	10.78	12.92	25.77	35.00
% Residual	93.30	89.22	87.08	74.23	65.00

Table 4.14 Chemical fractionation of Cu ($mgkg^{-1}$) in the sediment of study area (Mean ±SD, n=3)

	SITES									
FRACTIONS	A	B	C	D	E	F	G	H	I	J
Exchangeable	0.14±0.03	0.26±0.03	0.04±0.00	0.03±0.01	0.08±0.02	0.06±0.00	0.07±0.00	0.07±0.00	0.04±0.00	0.06±0.00
% Exch.	4.07	7.18	1.20	1.00	2.76	3.75	2.50	2.39	1.49	1.63
CB	0.25±0.05	0.21±0.01	0.21±0.01	0.18±0.00	0.12±0.01	0.21±0.01	0.05±0.00	0.06±0.00	0.05±0.00	0.26±0.13
%CB	7.27	5.80	6.33	6.00	4.14	13.13	1.79	2.05	1.87	7.08
Fe-MnO	0.41±0.01	0.44±0.04	0.56±0.02	0.62±0.03	0.71±0.01	0.35±0.04	0.38±0.03	0.47±0.01	0.42±0.03	0.55±0.04
% Fe-MnO	11.92	12.15	16.87	20.67	24.48	21.88	13.57	16.04	15.67	14.99
Org. B	2.10±0.10	2.11±0.16	1.85±0.05	1.22±0.02	0.87±0.03	0.86±0.03	0.63±0.03	0.74±0.01	0.52±0.02	1.83±0.15
% Org. B	61.05	58.28	55.72	40.67	30.00	53.75	22.50	25.26	61.57	49.86
Residual	0.54±0.02	0.60±0.01	0.66±0.05	0.95±0.05	1.12±0.11	0.12±0.09	1.67±0.03	1.59±0.04	1.65±0.04	0.97±0.03
$\sum_T$	3.44	3.62	3.32	3.00	2.90	1.60	2.80	2.93	2.68	3.67
% Non-Residual	84.30	83.43	80.12	68.33	61.38	92.50	40.36	45.73	38.43	73.57
% Residual	15.70	16.57	19.88	31.67	38.62	7.50	59.64	54.27	61.57	26.43

Table 4.15 Chemical fractionation of Cu ($mgkg^{-1}$) in the sediment of control area (Mean ±SD, n=3)

	SITES				
FRACTIONS	1	2	3	4	5
Exchangeable	0.06±0.00	0.06±0.00	0.08±0.01	0.06±0.00	0.08±0.00
% Exch.	2.05	2.21	2.78	2.11	3.14
CB	0.14±0.00	0.10±0.00	0.13±0.03	0.16±0.00	0.12±0.02
%CB	4.78	3.69	4.51	5.63	4.70
Fe-MnO	0.55±0.01	0.43±0.15	0.47±0.03	0.46±0.03	0.42±0.07
% Fe-MnO	18.77	15.87	16.32	16.20	16.47
Org. B	1.21±0.09	1.24±0.05	1.50±0.10	1.21±0.18	1.12±0.45
% Org. B	41.30	45.76	52.08	42.61	43.92
Residual	0.97±0.01	0.88±0.03	0.70±0.02	0.95±0.05	0.81±0.04
$\sum_T$	2.93	2.71	2.88	2.84	2.55
% Non-Residual	66.89	67.52	75.69	66.55	68.24
% Residual	33.11	32.48	24.31	33.45	31.76

Table 4.16 Chemical fractionation of Pb ($mgkg^{-1}$) in the sediment of study area (Mean ±SD, n=3)

	SITES									
FRACTIONS	A	B	C	D	E	F	G	H	I	J
Exchangeable	0.30±0.02	0.38±0.03	0.34±0.03	0.54±0.61	0.23±0.03	0.46±0.04	0.50±0.10	0.49±0.09	1.09±1.39	0.52±0.07
% Exch.	3.82	4.90	4.35	7.48	4.25	5.62	7.11	7.06	13.99	7.62
CB	1.07±0.06	1.07±0.11	0.93±0.03	1.08±0.10	0.75±0.05	1.13±0.15	0.86±0.40	0.86±0.15	0.83±0.08	0.70±0.02
%CB	13.61	13.79	11.91	14.96	13.86	13.80	12.23	12.39	10.65	10.26
Fe-MnO	2.40±0.20	2.46±0.06	2.45±0.03	1.92±0.03	1.95±0.02	1.97±0.03	2.03±0.15	2.21±0.81	2.31±0.81	1.91±0.15
% Fe-MnO	30.53	31.70	31.37	26.59	26.82	24.05	28.88	31.84	29.65	28.01
Org. B	1.40±0.05	1.23±0.03	1.20±0.20	0.95±0.13	0.94±0.04	1.17±0.16	1.21±0.19	0.96±0.04	1.11±0.08	0.86±0.12
% Org. B	17.81	15.85	15.36	13.15	17.37	14.29	17.21	13.83	14.25	12.61
Residual	2.69±0.04	2.62±0.04	2.89±0.04	2.73±0.06	3.40±0.20	3.46±0.06	2.43±0.064	2.42±0.08	2.45±0.05	2.83±0.09
$\sum_T$	7.86	7.76	7.81	7.22	7.27	8.19	7.03	6.94	7.29	6.82
% Non-Residual	65.78	66.24	63.00	62.19	53.24	57.75	65.43	65.13	68.55	58.50
% Residual	34.22	33.76	37.00	37.81	46.76	42.25	34.57	34.87	31.45	41.50

Table 4.17 Chemical fractionation of Pb ($mgkg^{-1}$) in the sediment of control area (Mean ±SD, n=3)

	SITES				
FRACTIONS	1	2	3	4	5
Exchangeable	0.35±0.00	0.29±0.00	0.22±0.01	0.26±0.00	0.20±0.00
% Exch.	4.29	4.14	3.09	3.44	2.97
CB	0.89±0.17	0.96±0.15	1.02±0.16	0.82±0.08	0.70±0.10
%CB	10.92	13.71	14.31	10,85	10.40
Fe-MnO	2.16±0.15	2.10±0.10	1.80±0.10	2.19±0.20	1.85±0.05
% Fe-MnO	26.50	30.00	25.25	28.97	27.49
Org. B	1.23±0.16	1.29±0.10	0.76±0.23	1.04±0.15	1.13±0.11
% Org. B	15.09	18.43	10.66	13.76	16.79
Residual	3.52±0.14	2.36±0.05	3.33±0.15	3.25±0.15	2.85±0.05
$\sum_T$	8.15	7.00	7.13	7.56	6.73
% Non-Residual	56.81	66.29	53.30	57.01	57.65
% Residual	43.19	33.71	46.70	42.99	42.35

About 60% of the total Cd in sediment samples in the study and control areas was associated with the exchangeable, carbonate and Fe – Mn oxide fractions with the exchangeable fraction averaging the highest amount of cadmium (27%). This contrasts with Cu, Pb and to some extent Cr where the exchangeable fraction was lower with respect to other fractions. This high percentage of Cd indicates the availability of the metals to the biota, because the operationally defined extraction sequence follows the order of decreasing solubility of the geochemical forms of the metals (Stover *et al*., 1976). The carbonate bound Cd has a higher concentration in the control area than in the study area because of the ease of substitution of Cd^{2+} by Ca^{2+} in calcite.

The results agree with the observations of Elsokkary and Lag (1978) in their study of polluted soils and Harrison *et al*. (1981) in the speciation of street dusts. The residual fraction has an average of about 43% for the residual bound Cd in the study area and about 21% in the control area. This may be indicative of background metal levels. A relative high percentage of cadmium in the residual might suggest Cd being associated with silicate materials.

The sequential extraction in this study is useful in assessing the potential mobility and bioavailability of the heavy metals in the River Challawa sediments. The mobility of these metals are related to their solubility and geochemical forms, and decreases in the order of extraction sequence, i.e. exchangeable > carbonate > Fe –Mn oxide bound > organic bound > residual bound.

Table 4.18 Chemical fractionation of Cd ($mgkg^{-1}$) in the sediment of study area (Mean ±SD, n=3)

	SITES									
FRACTIONS	A	B	C	D	E	F	G	H	I	J
Exchangeable	0.68±0.00	0.58±0.03	0.68±0.03	0.57±0.03	0.87±0.01	0.69±0.03	0.58±0.05	0.72±0.01	0.49±0.01	0.57±0.02
% Exch.	24.28	23.11	28.21	28.96	27.10	24.91	21.32	26.87	24.62	29.69
CB	0.78±0.03	0.53±0.01	0.78±0.02	0.70±0.01	0.71±0.01	0.67±0.05	0.62±0.03	0.57±0.03	0.47±0.01	0.00±0.00
%CB	27.85	21.11	32.36	27.32	22.12	24.19	22.79	21.27	23.62	0.00
Fe-MnO	0.20±0.01	0.15±0.02	0.21±0.01	0.18±0.01	0.26±0.01	0.20±0.02	0.24±0.01	0.17±0.02	0.02±0.01	0.04±0.00
% Fe-MnO	7.10	5.98	11.48	7.65	8.10	7.22	8.82	6.34	1.01	2.08
Org. B	0.21±0.26	0.05±0.01	0.07±0.00	0.05±0.01	0.09±0.00	0.05±0.10	0.06±0.01	0.08±0.01	0.04±0.01	0.03±0.000
% Org. B	1.42	1.99	2.90	2.73	2.80	1.88	2.21	2.99	2.01	1.56
Residual	1.10±0.10	1.20±0.05	1.12±0.50	1.00±0.37	1.28±0.11	1.16±0.13	1.22±0.18	1.14±0.14	0.97±0.02	1.28±0.08
$\sum_T$	2.8	2.51	2.86	2.5	3.21	2.77	2.72	2.68	1.99	1.92
% Non-Residual	62.96	52.20	60.84	60.00	60.12	58.12	58.15	57.46	51.26	33.33
% Residual	39.28	47.80	39.16	40.00	39.88	44.88.	44.85	42.54	48.74	66.67

Table 4.19 Chemical fractionation of Cd ($mgkg^{-1}$) in the sediment of control area (Mean ±SD, n=3)

	SITES				
FRACTIONS	1	2	3	4	5
Exchangeable	1.30±0.05	1.23±0.04	1.28±0.11	1.28±0.14	1.25±0.04
% Exch.	45.94	46.77	47.41	45.55	47.35
CB	0.50±0.23	0.51±0.03	0.55±0.01	0.50±0.03	0.57±0.03
%CB	17.67	19.39	20.37	17.79	21.59
Fe-MnO	0.20±0.02	0.20±0.03	0.19±0.11	0.20±0.02	0.20±0.03
% Fe-MnO	7.07	7.60	7.04	7.12	7.58
Org. B	0.25±0.35	0.05±0.00	0.07±0.00	0.25±0.03	0.05±0.00
% Org. B	8.83	1.90	2.59	8.90	1.89
Residual	0.58±0.02	0.64±0.07	0.61±0.12	0.58±0.05	0.57±0.02
$\sum_T$	2.83	2.63	2.70	2.81	2.64
% Non-Residual	79.51	75.67	77.41	79.36	78.41
% Residual	20.49	24.33	22.59	20.64	21.59

This order is just a generalization and offers only quantitative information on metals mobility. The first two phases can release their metal loads by lowering the pH and are more mobile than the other phases. Accordingly, these two phases influence the mobility and hence the bioavailability. Speciation data in this study indicated that Cd has the greatest overall affinity in the exchangeable fractions while other metals showed much less affinity.

Metals extracted in these fractions are sorbed on solid matrices by relatively weak electrostatic interaction and can be released by ion-exchange. This indicates the highest mobility of Cd. 21.25% of Cd was associated with carbonate fraction which can be released under acidic conditions. The comparative heavy metal affinities in the different phases as shown on Tables 4.9, showed the highest percentage of Cd in exchangeable and carbonate fractions

Inspite of the high levels of Cr in the tannery waste, the very low percentages of the metal found in the non-residual fraction indicates its limited environmental mobility.

The result indicated that Cd is associated more with exchangeable and carbonate fractions, which is an indication of potential bioavailability of the metals, since metals present in the exchangeable are usually readily available for plant or organism uptake (Xian, 1989).

It was also found that copper is less mobile than cadmium, lead and zinc. The mobility of copper tends to increase when the chloride content is elevated since elevated chloride contents decrease adsorption of copper on sediment due to chloride complexation which results in greater solubility (Bourg, 1988).

Bioavailability studies indicate that aquatic organisms uptake free metal more efficiently than via direct particulate metal ingestion.

The large particle or sediment sizes of the sediment found in this study indicate that sand enhances dissolved metal abundance by reducing adsorption. The low pH of the sediment in the study area also enhances the bioavailability of the metals. Where aquatic organisms ingest particulate matter, metal assimilation is also important because metals are highly concentrated in this form (Luoma, 1989).

CHAPTER FIVE

5.0 Conclusion and Recommendation

5.2 Conclusion

The study revealed the discharge of tannery effluents from the tannery industries into River Challawa untreated, lead to introduction of heavy metals into water and subsequently to the sediment. The heavy metal content was generally more in the study area than in the control area. Metal content observed has not accumulated to unsafe levels since they were all below USEPA threshold effects.

The raw effluents were implicated to also cause changes in the levels of some physicochemical parameters of the river sediment. It is evident that changes in some physicochemical parameters such as pH and organic matter favour the release of metals bounded to the sediment back to the water body

The sequential extraction procedure used in this study assumes mobility and biological availability to decrease in the order of the metal extraction sequence. On this basis the apparent mobility and potential bioavailability of the metals for the sediment in the study area are Cd>Zn>Cu>Pb>Cr.

It is apparent that the pollution of Challawa River by tannery industrial effluents is significant. Though workshops and symposia on toxic waste minimization and prevention are being organized by Federal Ministry of Environment, little has been done to prevent the loading of the Challawa River with metals and persistent organics.

5.2 Recommendation

At the end of this research, it was observed that further investigation on the effect of tannery effluents on river system is necessary. The following recommendations are given to assist in controlling the menace;

1. Discharging of untreated waste water into the nearby Challawa River which is a common practice in Kano should be stopped and an extensive waste management should be instituted.

2. Industrial waste should be sorted and separated to facilitate safe and appropriate treatment and disposal

3. Communities around the rivers should be made to be aware of the dangers so that they form a pressure group that can pressurize companies into improving their environmental performance.

4. The high concentration of cadmium in River Challawa should be further investigated in order to find its source.

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