

**ASSESSMENT OF HEAVY METAL CONTAMINATION IN IRISH POTATOES AND SOILS FROM AN ABANDONED MINING SITE IN JOS-SOUTH, USING AAS AND XRF TECHNIQUES.**

**BY**

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(M.Sc./SCIE/00432/2010-11)**

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**DEPARTMENT OF PHYSICS,  
FACULTY OF SCIENCE  
AHMADU BELLO UNIVERSITY ZARIA,  
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**JUNE, 2015.**

## **DECLARATION**

I hereby declare that this thesis entitled: **ASSESSMENT OF HEAVY METAL CONTAMINATION IN IRISH POTATOES AND SOILS FROM AN ABANDONED MINING SITE IN JOS-SOUTH, USING AAS AND XRF TECHNIQUES**, has been written by me and that it is an account of my own research, except that for references to other people's work which have been duly cited . No part of this thesis was previously presented for another degree or diploma at any university.

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**Yusuf Sadau SANDA**  
**(Student)**

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**Date**

## CERTIFICATION

This thesis titled: **Assessment of Heavy Metal Contamination in Irish Potatoes and Soils from an Abandoned Mining Site in Jos-South, Using AAS and XRF Techniques** by Yusuf Sadau Sanda meets the regulations governing the award of Master of Science (M.Sc.) of Ahmadu Bello University, Zaria and is approved for its contribution to scientific knowledge and literary presentation.

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## **DEDICATION**

I dedicate this work to my family for all they have done to me in the course of my studies here in ABU, zaria.

## ACKNOWLEDGEMENTS

All my profound gratitude, to my wife for all round encouragement in the course of this thesis work to be a success.

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## ABSTRACT

This study was undertaken to assay the elemental concentration in some Irish potatoes and soils from farmlands in an ex-mining area at Dahwol-vwana village, Jos-south L.G.A, Plateau state, Nigeria. The total heavy metal concentrations (for Irish potato and soil samples) were obtained using Atomic Absorption Spectrometer. It was observed from the soil sample concentration values gotten at the end of the AAS analysis (Pb, ranges from 0.0445-3.9343ppm; Cd, from 0.0086-0.1200ppm and Zn, from 0.0751-39.0302ppm) are higher than the concentration values obtained from control area (Pb- 0.0088ppm, Cd-0.0029ppm and Zn-0.0101ppm), but lesser than the international threshold values (EU:- Pb-300ppm, Cd-3.0ppm and Zn-300ppm. USA: - Pb-300ppm, Cd-3.0ppm and Zn-250ppm. UK:- Pb-70ppm, Cd-1.4ppm and Zn-200ppm). While that of Irish potatoes: - Pb, ranges from 0.0741-1.5042ppm; Cd, from 0.0081-0.0931ppm and Zn, from 0.1038-88.0503ppm). A modified sequential extraction procedure of Tessier *et. al.*, (1979) was used in separating the total metal concentrations into four operationally defined fractions (exchangeable and carbonate, Fe and Mn oxides, organic matter, and residual fractions). Where it was discovered that the bulk of metals were partitioned to the residual fraction (Zn- 138.85ppm, Pb-55.59ppm and Cd-2.5ppm) which implies that the soils of the farmland are not polluted by any of the metals studied. Pollution indices also as compared with Banat *et. al.*, (2005) standards, indicated minimal contamination of the soils matrix with Cd, which had enrichment factor value of 15.4 and I-geo factor of 4. The bulk partitioning of the metals onto the residual fraction indicates a lithogenic origin of the heavy metals, i.e. the heavy metals were directly inherited from the parent material, and also a low risk of contaminant transfer under normal cultural practices. However, heavy perturbation of the soil, such as mining, would lead to significant pollution of soil, and water bodies as well enhanced Irish potatoes and other plants uptake of the metals, thereby resulting in a threat of biomagnifications.

## TABLE OF CONTENTS

Title page - - - - -	i
Declaration - - - - -	ii
Certification - - - - -	iii
Dedication - - - - -	iv
Acknowledgement- - - - -	v
Abstract - - - - -	vi
Table of content - - - - -	vii
List of Tables - - - - -	xii
List of Figures- - - - -	xiii

## CHAPTER ONE

<b>1.0 INTRODUCTION</b> - - - - -	<b>-1</b>
<b>1.1 Background of the Study-</b> - - - - -	<b>-2</b>
1.1.1 Toxicity history- - - - -	-2
1.1.2 Heavy metal toxicity- - - - -	-4
<b>1.2 Statement of the Problem-</b> - - - - -	<b>-5</b>
<b>1.3 Aim and Objectives-</b> - - - - -	<b>-6</b>
<b>1.4 Justification of Research-</b> - - - - -	<b>-7</b>
<b>1.5 Scope and Limitation of Study--</b> - - - - -	<b>-7</b>

## CHAPTER TWO

### 2.0 LITERATURE REVIEW

<b>2.1 Introduction-</b>	-	-	-	-	-	-	-	-	-	<b>-10</b>
<b>2.2 Irish Potatoes, History and Benefits-</b>	-	-	-	-	-	-	-	-	-	<b>-10</b>
<b>2.3 Review of Previous Work-</b>	-	-	-	-	-	-	-	-	-	<b>-13</b>
<b>2.4 X-Ray Fluorescence Spectroscopy-</b>	-	-	-	-	-	-	-	-	-	<b>-17</b>
<b>2.5 Types of XRF Spectrometer-</b>	-	-	-	-	-	-	-	-	-	<b>-18</b>
<b>2.6 Basic Principles of XRF-</b>	-	-	-	-	-	-	-	-	-	<b>-19</b>
2.6.1 Operational principle of x-rays tubes	-	-	-	-	-	-	-	-	-	-20
<b>2.7 Physics of X-Ray Emission Spectra-</b>	-	-	-	-	-	-	-	-	-	<b>-20</b>
<b>2.8 X-Ray Excitation Sources-</b>	-	-	-	-	-	-	-	-	-	<b>-22</b>
<b>2.9 Interaction of X-Rays with Matter-</b>	-	-	-	-	-	-	-	-	-	<b>-24</b>
2.9.1 Photoelectric effect-	-	-	-	-	-	-	-	-	-	-25
2.9.2 Compton effect-	-	-	-	-	-	-	-	-	-	-26
2.9.3 Pair production-	-	-	-	-	-	-	-	-	-	-28
<b>2.10 Atomic Absorption Spectroscopy (AAS)-</b>	-	-	-	-	-	-	-	-	-	<b>-28</b>
2.10.1 Basic principles of atomic absorption	-	-	-	-	-	-	-	-	-	-31
2.10.2 Operational principle of atomic absorption spectrometer-	-	-	-	-	-	-	-	-	-	-31
<b>2.11 Accumulation in Soils -</b>	-	-	-	-	-	-	-	-	-	<b>-32</b>
<b>2.12 Trace Metal Concentrations in Agricultural Soils -</b>	-	-	-	-	-	-	-	-	-	<b>-33</b>
<b>2.13 Essential and Non-essential Heavy Metals in Plants -</b>	-	-	-	-	-	-	-	-	-	<b>-33</b>
<b>2.14 Toxicity to Human Beings-</b>	-	-	-	-	-	-	-	-	-	<b>-34</b>
<b>2.15 Effect of Heavy Metals on Plants -</b>	-	-	-	-	-	-	-	-	-	<b>-35</b>
<b>CHAPTER THREE</b>										
<b>3.0 MATERIALS AND METHODS -</b>	-	-	-	-	-	-	-	-	-	<b>-36</b>



<b>3.1</b>	<b>Materials-</b>	-	-	-	-	-	-	-	-	<b>-36</b>
3.1.1	Some needed materials for AAS analysis-	-	-	-	-	-	-	-	-	-37
<b>3.2</b>	<b>Sample Collection-</b>	-	-	-	-	-	-	-	-	<b>-37</b>
3.2.1	Sample collection at control area-	-	-	-	-	-	-	-	-	-42
<b>3.3</b>	<b>Samples Preparation for XRF-</b>	-	-	-	-	-	-	-	-	<b>-42</b>
<b>3.4</b>	<b>Procedure for XRF Analysis of Samples-</b>	-	-	-	-	-	-	-	-	<b>-42</b>
3.4.1	Energy Dispersive X-Ray Fluorescence (EDXRF) of environmental samples with isotopic source-	-	-	-	-	-	-	-	-	-43
3.4.2	Spectrum acquisition using standard XRF	-	-	-	-	-	-	-	-	-44
3.4.3	Quantitative analysis using standard XRF	-	-	-	-	-	-	-	-	-45
<b>3.5</b>	<b>Digestion of Samples (both Irish Potatoes and Soil) for AAS Analysis-</b>	-	-	-	-	-	-	-	-	<b>-46</b>
3.5.1	Preparation of wet digestion acid-	-	-	-	-	-	-	-	-	-46
3.5.2	Procedure for digestion-	-	-	-	-	-	-	-	-	-46
<b>3.6</b>	<b>AAS Measurements--</b>	-	-	-	-	-	-	-	-	<b>-47</b>
3.6.1.	Sequential extraction--	-	-	-	-	-	-	-	-	-47
<b>3.7</b>	<b>Data Analysis--</b>	-	-	-	-	-	-	-	-	<b>-49</b>
<b>3.8</b>	<b>Metal Enrichment-</b>	-	-	-	-	-	-	-	-	<b>-49</b>

#### CHAPTER FOUR

<b>4.0</b>	<b>RESULTS -</b>	-	-	-	-	-	-	-	-	<b>-51</b>
<b>4.1</b>	<b>Introduction-</b>	-	-	-	-	-	-	-	-	<b>-51</b>

#### CHAPTER FIVE

<b>5.0</b>	<b>DISCUSSION-</b>	-	-	-	-	-	-	-	-	<b>-60</b>
------------	--------------------	---	---	---	---	---	---	---	---	------------

<b>5.1 Total Metal Content-</b>	-	-	-	-	-	-	-	-	<b>-60</b>
<b>5.2 Fractionation of Pb, Cd, and Zn-</b>	-	-	-	-	-	-	-	-	<b>-61</b>
5.2.1 Lead fractions-	-	-	-	-	-	-	-	-	-61
5.2.2 Cadmium fractions-	-	-	-	-	-	-	-	-	-62
5.2.3 Zinc fractions--	-	-	-	-	-	-	-	-	-63
<b>5.3 Correlation between Zinc Concentration for Soil and Irish Potato Samples Using XRF and AAS.-</b>	-	-	-	-	-	-	-	-	<b>-63</b>
<b>5.4 Extractable Concentration of Pb, Cd, and Zn-</b>	-	-	-	-	-	-	-	-	<b>-64</b>
<b>5.5 Enrichment and Accumulation of Pb, Cd and Zn-</b>	-	-	-	-	-	-	-	-	<b>-64</b>

## CHAPTER SIX

<b>6.0 CONCLUSION AND RECOMMENDATIONS-</b>	-	-	-	-	-	-	-	-	<b>-66</b>
<b>6.1 Conclusion-</b>	-	-	-	-	-	-	-	-	<b>-66</b>
<b>6.2 Recommendations-</b>	-	-	-	-	-	-	-	-	<b>-67</b>
<b>REFERENCES-</b>	-	-	-	-	-	-	-	-	<b>-68</b>

## LIST OF TABLES

<b>Table 3.1:</b> Sample of the First Ex-Mining Hole Area (N09 <sup>0</sup> 44.662'E008 <sup>0</sup> 50.590')	-39
<b>Table 3.2:</b> Sample of the Second Ex-Mining Hole Area (N09 <sup>0</sup> 44.656'E008 <sup>0</sup> 50.591')	-40
<b>Table 3.3:</b> Sample of the Third Ex-Mining Hole Area (N09 <sup>0</sup> 44.638'E008 <sup>0</sup> 50.577')	-41
<b>Table 3.4:</b> Time of mechanical agitation and temperature at which the sequential extraction was performed.	-48
<b>Table 3.5:</b> Measurements of metal pollution in soils and sediments-	-50
<b>Table 4.1:</b> Total elemental concentrations of Zn, Pb and Cd, in both soils and Irish potatoes of the study-	-52
<b>Table 4.2a:</b> International threshold values for heavy metals concentration in soils (ppm)	-53
<b>Table 4.2b:</b> World Health Organization (WHO) threshold values for heavy metals concentration in Irish potatoes (Mg)-	-53
<b>Table 4.3 :</b> Mean and standard deviation and range of extractable concentration of Pb, Cd, and Zn in an ex-mining site of Dahwol-vwana village, Jos south, northern Nigeria.	-54
<b>Table 4.4:</b> Determination of F-values and significant difference of zinc concentrations using AAS and XRF method	-55
<b>Table 4.5:</b> Average and background concentration, enrichment factor, calculated I-geo index, and grade of pollution intensity of Pb, Cd and Zn in analyzed samples from Dahwol-vwana village, Jos-south.	-56

## LIST OF FIGURES AND PLATE

<b>Figure 1.1:</b> Sketch of Study Area-	-9
<b>Plate 2.1:</b> Irish Potatoes, with Nature of Its Leaves	-12
<b>Figure 2.1:</b> Schematic of an atomic-absorption experiment	-30

**Figure 4.1:** The distribution of Cd among the different geochemical fractions of sample

Collections around each of the ex-mining holes in Dahwol-vwana village,  
Jos-south, Nigeria- - - - - - - -57

**Figure 4.2:** The distribution of Pb among the different geochemical fractions of sample

Collection saround each of the ex-mining holes in Dahwol-vwana village,  
Jos-south, Nigeria- - - - - - - -58

**Figure 4.3:** The distribution of Zn among the different geochemical fractions of sample

Collections around each of the ex-mining holes in Dahwol-vwana village,  
Jos-south, Nigeria- - - - - - - -59

## CHAPTER ONE

### 1.0 INTRODUCTION

Tin mining industry which is also the largest producer of columbite in Jos plateau state started in 1902 (Adegboye, 2012). The mining of tin has been largely responsible for profound changes in the landscape and in the social economic structure of study area (Adegboye, 2012). Limited arable land is experienced in Jos plateau area, according to (Patterson, 1986) this is due to the high rate of surface mining. (Scholar, 1979) revealed that mined soils are poorer in agricultural value compared to adjoining natural land. Crops grown on such mined land are of low agricultural value, quick maturing and low-nutrient demanding, such as acha, dauro, maize, millet and Irish potato. (Calvert, 1990) revealed that the indiscriminate mining on the Jos plateau, led to many parts of the area being exposed to erosion and reduces the available arable land for crop production. The volume of mineral tripped off during mining reduces the nutrient present in the soil (Adegboye, 2012). Jos South local government area is an extensively mined area, which was dominated by use of heavy earth – moving equipment and draglines. As a result, the zone is characterized by deep excavations and dumping of high over burden, mine ponds, mine tailings and slurry wash deposits (Olaniyan, 1998; Musa et. al., 2011). According to (Gyang et. al., 2010), the major problem of the area still remains the devastated and de-vegetated land and mine spoils; depriving the inhabitants of fertile farmland. The deep mining which is an excavation of underlying sand has created mining pits, man-made lakes, pools and ponds which have great effect on both the people and agricultural practices. Mining ponds have always been death traps for people and animals (Davis, 2001).

The ponds are always sources of erosion especially in rainy season when most of the ponds overflow their banks as was the case of a paddock behind the Amalgamated Tin Mines of Nigeria LTD (ATMN) stadium Bukuru. Fully mechanized mining activities as well as formal mining are still in

operation around 'rayfield' area of the local government. The early inhabitants of the present tin mining areas of the study area were aware of the existence of the mineral in their locality long time ago when the mining started on a small scale, which later extended to take over large area of arable land. As a result of the drastic loss of farmlands to mining activities, attention of most of the inhabitants has shifted to the mining rather than farming (Morrison, 1994).

## **1.1 Background of the Study**

### **1.1.1 Toxicity history**

The first considered toxicity-related description in the western literature is the biological weapon or poison from the "many-headed" sea serpent, Hydra, used in poisoning Hercules's arrows. The knowledge on toxicity and poisonous substances is attributed to the earliest humans, who devised "poisonous" weapons using plant extracts and animal venom for hunting animals. ([www.rsc.org/toxicology](http://www.rsc.org/toxicology)).

Further toxicological studies have led to the establishment of safety standards, maximum allowable dosages, and detailed toxicity levels of substances, which are the scientific bases of medical treatments, environmental and health care systems. ([www.rsc.org/toxicology](http://www.rsc.org/toxicology)).

In a general sense, the toxicity of a substance could be defined as the capacity to cause injury to a living organism (NAS/NRC, 1970; Sanockij, 1970). A highly toxic substance will damage an organism if administered in very small amounts; a substance of low toxicity will not produce an effect unless the amount is very large. Thus, toxicity cannot be defined without reference to the quantity of a substance administered or absorbed (dose), the way in which this quantity is

administered (e.g. inhalation, ingestion, injection) and distributed in time (e.g. single dose, repeated doses), the type and severity of injury, and the time needed to produce that injury.

There is no generally agreed definition of "hazard" associated with a chemical, but the term is used to indicate the likelihood that a chemical will cause an adverse health effect (injury) under the conditions in which it is produced or used (Goldwater, 1968; NAS/NRC, 1970, Pravdin, 1934).

Risk is a statistical concept and has been defined by the Preparatory Committee of the United Nations Conference on the Human Environment, as the expected frequency of undesirable effects arising from exposure to a pollutant. Estimates of risk may be expressed in absolute terms or in relative terms. The absolute risk is the excess risk due to exposure. The relative risk is the ratio between the risk in the exposed population and the risk in the unexposed population (BEIR, 1972; ICRP, 1966).

The principle behind toxicity is based on the prescient statement of Philippus Theophrastus Aureolus (Paracelsus), a Swiss physician and alchemist, that "all substances are poisons; there is none which is not a poison. The right dose differentiates a poison and a remedy."([www.rsc.org/toxicology](http://www.rsc.org/toxicology)).

There are important factors in determining the toxicity of a substance. These factors, according to Dr. Emily Monosson, a toxicologist and an editor of the Encyclopedia of Earth, include "dosage, exposure route, form and innate chemical activity, species, age, sex, ability to be absorbed, metabolism, distribution within the body, excretion and presence of other chemicals." These factors may have significant impact on toxicity; however, the most critical factor is dosage ([www.rsc.org/toxicology](http://www.rsc.org/toxicology)).

Toxicity, in general, is classified according to the site affected by the toxicant (toxic substance). The toxic effect may occur at only one site and this is called organ specific toxicity. Some of the common organ specific toxicity includes hepatotoxicity (liver), immunotoxicity (immune system), neurotoxicity (nervous system) and nephrotoxicity (kidney). On the other hand, if the toxic effect occurs on multiple organs or parts, it is called systemic toxicity. The systemic toxicity may be developmental (developing fetus), carcinogenic (abnormal cell growth), acute (occurs immediately) and chronic (occurs gradually or over time) ([www.rsc.org/toxicology](http://www.rsc.org/toxicology)).

### **1.1.2 Heavy metal toxicity**

Heavy metals are metallic elements which have a high atomic weight and a density much greater (at least 5 times) that of water. There are more than 20 heavy metals, but four are of particular concern to human health: lead (Pb), cadmium (Cd), mercury (Hg), and inorganic arsenic (As) (Victor, 2011). These four heavy metals are four of the top six hazards present in toxic waste sites. They are highly toxic and can cause damaging effects even at very low concentrations. They tend to accumulate in the food chain and in the body and can be stored in soft (e.g., kidney) and hard tissues (e.g., bone). Being metals, they often exist in a positively-charged form and can bind on to negatively-charged organic molecules to form complexes (Victor, 2011).

The body has need for approximately 70 friendly trace element heavy metals, but there are another 12 poisonous heavy metals, such as Lead, Mercury, Aluminum, Arsenic, Cadmium, Nickel, etc., that act as poisonous interference to the enzyme systems and metabolism of the body. No matter how many good health supplements or procedures one takes, heavy metal overload will be a detriment to the natural healing functions of the body. Some metals are naturally found in the body and are essential to human health. Iron, for example, prevents anemia, and zinc is a cofactor in



over 100 enzyme reactions. Magnesium and copper are other familiar metals that, in minute amounts, are necessary for proper metabolism to occur (Victor, 2011). They normally occur at low concentrations and are known as trace metals; for example, high levels of zinc can result in a deficiency of copper, another metal required by the body. Heavy or toxic metals are trace metals that are at least five times denser than water. As such, they are stable elements (meaning they cannot be metabolized by the body) and bio-accumulative (passed up the food chain to humans). These include: mercury, nickel, lead, arsenic, cadmium, aluminum, platinum, and copper (metallic form versus ionic form). Toxic heavy metals have no function in the body and can be highly toxic. Heavy metals are taken into the body via inhalation, ingestion, and skin absorption. If heavy metals enter and accumulate in body tissue faster than the body's detoxification pathways can dispose of them, a gradual buildup of these toxins will occur. High-concentration exposure is not necessary to produce a state of toxicity in the body tissues and, over time, can reach toxic concentration levels (Victor, 2011).

## **1.2 Statement of the Problem**

Heavy metal contamination is one of the serious environmental problems limiting plant productivity and threatening human health (Luptaka *et al* 2002; Verma and Dubey, 2003; Kadukova *et. al.*, 2006 ). Inputs of heavy metals to agricultural soils can occur from a variety of sources. These include the application of biosolids, fertilisers, livestock manure, agrochemicals, and irrigation water and from atmospheric deposition. Some of the concerns about accumulation of heavy metals in agricultural soils stem from their possible negative impacts on soil fertility and in some case their potential to accumulate in the human chain (McLaugh *et. al.*, 1999; Gray *et. al.*, 2003). Among the substances that contribute anthropogenically to pollution of the biosphere, trace elements are the most toxic. Lead, Zinc and Cadmium are toxic metals of increasing environmental

concern as they enter the food chain in significant amounts (Luptaka et. al., 2002; Verma and Dubey, 2003; Kadukova et. al., 2006).

Currently, majority of the soil dug from the mining holes in Dahwol-vwana village, Jos-south L.G.A. have been scattered on their farmlands. Farm inputs like fertilisers are also used in the farming of Irish potatoes and all these might contain Cd, Zn and Pb metals, for Irish potato crops intake on the farms. There is therefore the need for studies to establish the level of these metals in the Irish potato crop and soil on these farms.

### **1.3 Aim and Objectives**

The aim of this thesis is to determine the amount of heavy metals and concentration of toxic elements in some selected soils and Irish potatoes samples in ex-mining areas of Jos and to analyze through the following objectives:-

1. Assay the elemental concentration in both Irish potatoes and the soils in which they will be transplanted in ex-mining area at Dahwol-vwana village, Jos-south L.G.A Plateau state, Nigeria.
2. To compare the concentration of the toxic elements both in the Irish potatoes and the soil used for their farming with concentration values from control and International threshold values.
3. To determine and evaluate the geochemical species (fractions) of Pb, Cd, and Zn in some farmlands in an ex-mining area in dahwol-vwana village, Jos-south L.G.A Plateau state, Nigeria.
4. Total enrichment factor and geo-index analyzed to assess the level of contamination.

#### **1.4 Justification of Research**

A comprehensive understanding that toxic elements are found within mining areas, in which farming around such areas need to be investigated. In this work Irish potatoes farmed in ex-mining area in Dahwol-vwana village, Jos south L.G.A Plateau state, Nigeria is to be investigated.

It is important to provide a necessary data required as baseline that will enable further study on the toxic elements in products farmed in mining areas.

In this study, Energy dispersive X-ray Fluorescence spectroscopy (EDXRF) and Atomic Absorption spectroscopy (AAS) techniques shall be employed for the analyses.

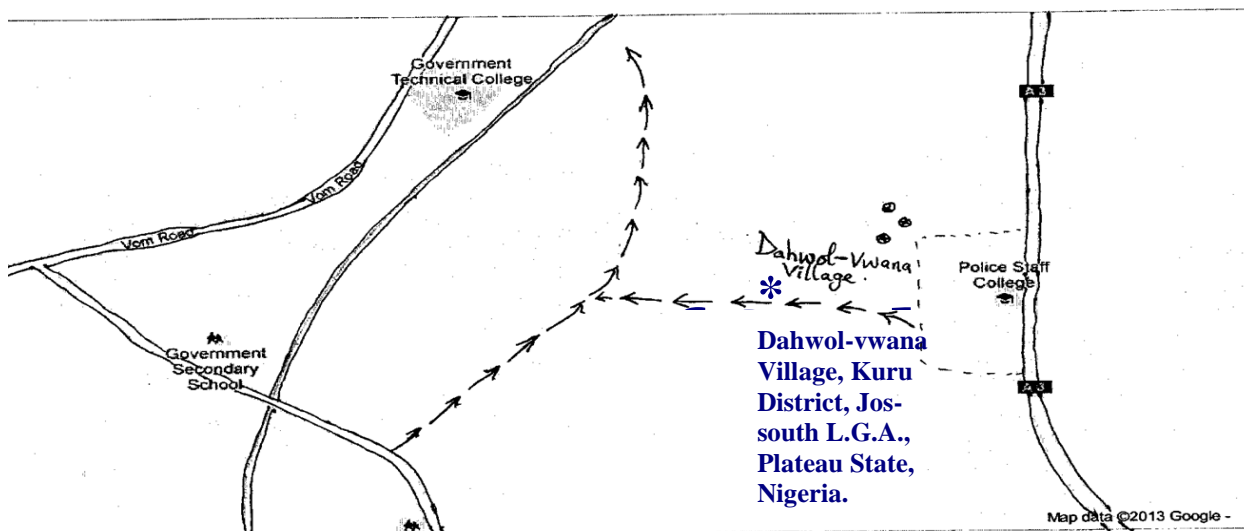
#### **1.5 Scope and Limitation of Study**

This work is to be carried out on some farms in an ex-mining site in Dahwol-vwana village, Kuru district, Jos-south L.G.A., Plateau state, to determine the amount of heavy metals and concentration of toxic elements in some selected soil and Irish potatoes samples. The samples' collections were done around three ex-mining hole areas (N09<sup>0</sup>44.662'E008<sup>0</sup>50.590'), (N09<sup>0</sup>44.656'E008<sup>0</sup>50.591') and (N09<sup>0</sup>44.638'E008<sup>0</sup>50.577'). While for the control samples gotten in a virgin area (N09<sup>0</sup>41.062'E008<sup>0</sup>45.003') in Trade-Centre village, along Vom road, in Kuru district, Jos-south L.G.A., Plateau state.

This site is an ex-mining site; mining activities took place last seven-eight years ago (Information; from some of the villagers).

The entire research will be conducted in raining season. Also, the short duration of the study period coupled with limited resources will force only one time sampling of the Irish potatoes and

the soil for measurements and analyzes. This could reduce the sample number to have error margin.



**Figure 1.1: Sketch of study area**  
**Figure 1.1: Sketch of Study Area**

## **CHAPTER TWO**

### **2.0 LITERATURE REVIEW**

#### **2.1 Introduction**

In this chapter, the various aspects of the topic under study are introduced. Irish potatoes, its history and benefits are briefly explained which are useful in this research. The reviews also covers other aspects like x-ray fluorescence spectroscopy, types of XRF spectrometer, physics of x-ray emission spectra, x-ray excitation sources, interaction of x-rays with matter, atomic absorption spectroscopy (AAS), accumulation in soils, trace metal concentrations in agricultural soils, essential and non-essential heavy metals in plants, chemistry, sources and toxicity of heavy metals in human beings and their effect on plants is also analyzed.

## **2.2 Irish Potatoes, History and Benefits**

The white or Irish potato (*Solanum tuberosum*), also called the "earth apple" (Fr. pomme de terre), needs no lengthy introduction. The tubers of this and other species were an important source of food to early South Americans, especially the Incas and their ancestors in the Andean highlands. In regions where climate is too cold for maize, natives have been able to grow potatoes; the archeological record of potato use dates back at least 13,000 years in Chile and 9000 years in Peru and Bolivia. In Peru the tuber is freeze-dried in the night air and then trampled to make a starch staple, and this is added to stews with other tubers (oca, *Oxalis tuberosa*; melloco, *Ullucustuberosus*). Potato is also used to make an alcoholic beverage called chicha ([www.irish potato tubers.com](http://www.irishpotato tubers.com)).

White potato became an essential staple in the diets of common people throughout Europe. In Ireland, where the crop did extremely well, potato was the only staple food; e.g., male farm workers consumed 12-14 pounds of potatoes daily. In 1845, after three weeks of wet weather, the Irish potato crop began to die. The leaves and, subsequently, the tubers were infected with a fungus known as the late blight of potato, *Phytophthora infestans*, but only one person, Reverend M.J.

Berkeley, knew and believed this. Tubers rotted, and from 1846 to 1851 nearly 1.5 million Irish (original population 8 million) died of starvation and other health complications. At the same time, over a million Irish people immigrated to the large eastern cities of the United States ([www.irishpotatotubers.com](http://www.irishpotatotubers.com)).

*Solanum tuberosum* is the fourth largest yielding crop plant in the world, behind wheat, rice, and maize, but compared with these three cereals, its production (nearly 225-285 million metric tons) occurs on 10% of the area. Potato trivia includes that this species is cultivated in 126 countries (1980 data), although Europe and the former Soviet Union contained 70% of the global potato area. One area in Switzerland produces 42 tons per acre, and other high yields come from the Netherlands and Israel. Five billion pounds of potatoes are made into fries every year!

Best potato production occurs where days are bright and sunny and nights are cool. Highest tuber production is related to very high leaf area. Tubers form on stolons when the plant flowers and they are no longer initiated after flowering. When the foliage dies with a frost, the tubers are harvested ([www.irishpotatotubers.com](http://www.irishpotatotubers.com)). About 7% of the crop is saved as "seed." A potato is cut into segments, which include at least one eye (a bud or node), from which emerge future shoots. (The starving Irish had to eat their seed potatoes during the famine, which left them with little for the next planting.) Potatoes to be eaten are stored at low temperatures to prevent buds from growing and to keep starch levels constant. Keeping them at higher storage temperatures is why they sprout in our pantries at home.



**Plate 2.1: Irish Potatoes, with Nature of Its Leaves**



The potato is nutritionally very good, high in starch (8-28%) but with 1-4% protein in the inner layers of the skin (periderm, i.e., cork cells). This species also has some vitamin C. In addition to the usual eating of the tuber, white potato is used in the fermentation of vodka and for adhesives and sizing in paper and textiles. You should never eat a green potato--THEY ARE DEADLY POISONOUS if much is consumed. The poisonous substance is the alkaloid solanine, which is made in all green tissues of the plant ([www.irishpotatotubers.com](http://www.irishpotatotubers.com)).

As for late blight of potato; the disease is still around and causes problems wherever Irish potatoes are grown. The disease can be controlled by the application of Bordeaux mixture, a substance that was only tried on potatoes in 1892. Potatoes are subject to attack by as many as 250 pests, and researchers at the International Potato Center in Lima, Peru are attempting to use the gene pool of eight cultivated species, 3000 varieties, and from the 160 tuber-producing species of *Solanum* to yield new cultivars for feeding the people living in the Andes ([www.irishpotatotubers.com](http://www.irishpotatotubers.com)).

### **2.3 Review of Previous Work**

1. An Evaluation of the Pollution by Toxic Elements around the Small-Scale Mining Area, Boroo, Mongolia (Bolormaa et. al., 2012) was carried out. Surface soil, ground water and human hair were collected as samples around the gold washing or milling places, grassland and village areas. After appropriate preparation, the samples analyses for major and toxic elements (TEs) by Particle-Induced X-ray Emission Spectrometry (PIXE) were carried even as soil texture, conductivity (EC), pH, total organic carbon (TC) and nitrogen (TN) contents were measured. The enrichment factor (EF) was estimated to assess the level of the contamination and the possible anthropogenic impact in soils from the mining activity. The EF of soil for Cu, As and Pb were in the highest values around gold washing place, indicating that around mining area surface soils were highly enriched toxic elements. It was

found that Mn, Fe and Ni concentrations of drinking waters exceed the WHO values and mean concentrations of Ca, Ti, As and Sr were higher in hair of Mongolian miners than in the hair of normal people in Japan, Mongolia and Philippines. The results from this work also indicated that the area around gold washing or milling could be the main contamination sources of As and other toxic elements (TEs) in the surface soil samples.

2. Marta et. al., (2012), worked on trace elements dispersion from a tailings dam and speciation study in surrounding agricultural soils: A Case study from Kombat Mine area, Otavi Mountain land, Namibia. It was found out that the farmland soils are contaminated with Pb and Cu, these metals are relatively strongly bound to the soils and there is probably a small risk for their release in soil, water and later to the groundwater, although lead possesses a risk of intermediate bioavailability to plants and humans if it is ingested via dust.
3. A research carried out on the impact of mining activities on the environment and surface drainage in the Copperbelt, Zambia (Sracek et. al., 2012). It was found that the environmental impact of mining is relatively limited due to neutral character of mine drainage, but metals in sediments can be mobilized in the case of acid spills or re-suspended during rainy period.
4. (Nkwocha et. al., 2011) studied on the Assessment of Heavy Metal Concentration in food crops grown around Etelebou Oil Flow Station in Bayelsa State, Nigeria. Three samples of each of the three tuber crops, namely cocoyam (*Xanthosomamataffa*), cassava (*Manihotessulenta*) and plantain (*Musa sapientum*) from the oil polluted farmland were collected, prepared, digested and analyzed in the laboratory with the aid of Atomic Absorption Spectrophotometer. Results obtained showed that the concentration levels of

the heavy metals analyzed (Fe, Zn, Cr, Cu, and Pb) in these food crops were relatively high and were gradually accumulated over time to become higher than the background values (controls). Of particular concern was the bioaccumulation of Pb in cassava (2.0mg/kg) and plantain (1.94mg/kg). These findings are indicative of potential health hazards faced by the indigenous population who feed on these crops. There is need to closely monitor the great danger posed by the bioaccumulation of these trace heavy metals on the health of the “population” animals and plants in the area.

5. Excavation involved in mining destroys useful soil for farming activities. Hence, this study was carried out by Michael, 2012, to investigate the effect of mining on farming in Jos-South Local Government Area of Plateau State. Random sampling technique was used to select 120 respondents from the area. The result reveals that 54.2% of the respondents identified low crop yield as the major consequence of mining on arable land in the area. Also, it was revealed that tin mining activities reduced farm land through soil erosion problems, swampy nature of neglected mined excavation, mine dump and pits on the arable land. Consequently, the farmers experienced low productivity in crop farming, land fragmentation, land disputes and conflicts in the area. It is therefore recommended that definite measures should be taken to bring mining affected land back to productive farm land. Also, a soil conservation strategy should be planned for future mining. (Adegboye et. al., 2012).
6. Girigisu et. al., (2012) Carried out an Investigation on the Determination of Heavy Metals and Other Elements in Artisanal Gold Mining Soils of Awwal and Bagega villages in Kebbi and Zamfara state. Where samples were collected and analyzed by X-Ray Fluorescence (XRF) technique. From the results, it was observed that four among other

elements (Pb, Si, Rb and Fe) showed relatively high concentrations. Two of these four elements presented, (Si and Pb) may pose latent and immediate hazards to health. Respiratory crystalline silica was found to be the major constituents of the ever-well pronounced mining dusts of the two sites. Its form of occurrence portends irreversible health problem called silicosis and is well linked to cancer forming properties; both of which develop through latency periods. Pb at whatever concentration portends both immediate and long term hazards with women and children at the greatest risks of exposures. Based on the results presented, there exists a possibility of an immediate and long term health risks associated with the artisanal gold mining exercises in the two sites studied.

7. Representative food samples from five different crops purchased from an open market in Zaria were analysed using the Energy Dispersive X-ray Fluorescence technique. Fe, Cu, Cd, Co, Cr, Zn, Mn, and Ba comprising of major, minor and trace elements in various proportions were determined. The results obtained indicated that some of the food items such as maize, beans, yam, cassava and guinea corn are characterized by high concentrations of specific elements such as Cd in beans, Zn in yam and cassava, manganese in maize, Cu in yam, Fe in cassava, Cr in guinea corn, and Co in cassava. Low concentration of 'Fe' which is about twice the order of magnitude observed in yam sample compared to maize sample makes it more suitable for consumption and poses less threat to the human system if other factors are to be kept at equilibrium or balanced. High Cd level observed in yam was also of utmost concern since frequent consumption or intake of such food can result to the accumulation of these elements in the body system and can cause threat and danger. On the other hand, high concentration of Cu observed in cassava sample

save as an indication of Cu pollution in that soil thus making it unsuitable for human consumption (Victor, 2011).

## **2.4 X-Ray Fluorescence Spectroscopy**

X-ray Fluorescence is a spectroscopic technique which is useful in identifying the presence and amount of many elements. Many XRF instruments can detect all elements heavier than sodium, and even detect elements as light as boron. This means that XRF is useful for inorganic materials, metals and inorganic or halogen-containing additives in polymers.

The proportionality between concentration and intensity upon which all x-ray emission analysis depend often is not directly linear. Furthermore, if a linear relationship were established for a given system, this by no means assures that the analysis of a specimen of that general type but of uncertain composition will be accurate by reference. The reasons for this are based fundamentally on the effects of x-ray matter interactions which take place between elements components themselves within the material or possibly with minute separate physical entities or particles existing therein. Interaction effects will of course be encountered in varying degrees on any practical scheme of analysis by x-rays (Kaelble, 1967). Ideally, one never totally escapes from these effects but successfully surmounts them only by compensation or by reducing them to an insignificant level.

Interaction effects therefore, probably produce the most perplexing problems with which the analyst must contend to obtain accurate results. Both theory and application recognize these effects.

## **2.5 Types of XRF Spectrometer**

The manner in which the X-rays of different energies are gathered distinguishes the XRF spectrometer as either wavelength dispersive (WDXRF) or energy dispersive (EDXRF). In WDXRF, a particular wavelength of the fluorescent X-rays is focused by a crystal onto the detector. The entire spectrum is collected as the crystal is rotated. WDXRF gives a very high resolution spectrum and allows for very low limits of detection, but these instruments are slower and more expensive than EDXRF instruments.

EDXRF instruments are able to distinguish the energies of incident X-rays. A given X-ray photon initiates a propagating event in the semiconductor (or gas-filled) detector. The degree of propagation depends on the incident energy, so the event is assigned to a certain channel based on that degree of propagation (Brouwer, 2003). Due to some variation in channel assignments, the peaks found in EDXRF are broader than those for WDXRF. The detection limits are also higher for EDXRF. The significantly lower price of EDXRF instruments, however, justifies their use in many applications.

The detection of certain elements can be optimized by controlling a combination of X-ray voltage, X-ray current, filters, measurement atmosphere, time, target (for tube systems) and X-ray source (for isotope source systems).

Since detectors are only able to handle a certain quantity of X-rays photons, detection is improved if the only energy reaching a detector is energy close to that of the element of interest. Filters can be used to block the lower energy X-rays from the sample. This allows one to isolate the higher energy (higher atomic weight) elements. The amount of energy cut off and the energy where this cut-off occurs varies depending on the type and thickness of the filter used.

One can also isolate lower energy elements by setting the voltage to something less than the maximum voltage. This allows excitation of only the lighter elements (and L and M lines of

heavier elements). With isotope source systems, the use of alternate sources has the same effect as decreasing the voltage for X-ray tube systems (Victor, 2011).

Another way to better observe the lighter elements is to make the measurement atmosphere inert and more transparent to X-rays. Argon, which is present in air at a concentration of 0.934% by weight, has  $K_{\alpha}$  and  $K_{\beta}$  peaks around 3keV. These peaks can partially overlap with the Cl peaks and also dominate the signal going to the detector. Also, the components in air ( $N_2$ ,  $O_2$  and Ar) absorb the characteristic energies of low atomic number elements. By replacing the air with Him or placing the sample under vacuum, one can improve the detection of lighter elements.

X-rays from the X-ray tube (or isotope source) are passed through an optional filter and onto the sample. The sample may be in air, or perhaps under helium or vacuum to improve detection of lighter elements. X-rays from the sample travel to the detector which is cooled either electrically or with liquid nitrogen, depending on the detector type. The signal from the detector is then processed by the electronics and sent to the computer, which also controls the X-ray tube. XRF spectra can then be analyzed qualitatively and/or quantitatively using software in the computer.

## **2.6 Basic Principles of XRF**

In XRF, X-rays produced by a source irradiate a sample. In most cases the source is an X-rays tube. The elements present in the sample will emit fluorescent X-ray radiation with discrete energies (equivalent to color for optical light) that are characteristic for these elements. A different energy is equivalent to a different color. By measuring the energies (determine the colors) of the radiation emitted by the sample it is possible to determine which elements are present. This step is called Qualitative Analysis. By measuring the intensities of the emitted energies (color) it is

possible to determine how much of each element is present in the sample. This step is called Quantitative Analysis (Brouwer, 2003).

### **2.6.1 Operational principle of x-rays tubes**

The basic design of an X-ray tube contains a filament (wire) and an anode (target) placed in a vacuum housing. An electrical current heat up the filament and electrons are emitted. A high voltage (20...100kV) is applied across the filament and the anode, this high voltage accelerates the electrons towards the anode, when the electron shits the anode they are decelerated, which causes the emission of X-rays. This radiation is called Brems-strahlung. The energy and intensity of the emitted X-rays is uniform, but a spectrum of energies each with its own intensity is emitted (Brouwer, 2003).

### **2.7 Physics of X-Ray Emission Spectra**

X-rays are generated from the distribution of the electron orbital of atom. This may be accomplished in several ways, the most common of which is to bombard a target element with high-energy electron, x-rays or accelerated charged particles. Electron bombardment results in both a continuum of x-ray energies and radiation that is characteristics of the target element. The continuum of the emission of X-rays with a smooth continuous function of intensity is with respect to energy. There are several ways they can be generated. However, the most important to us is the bombardment of a target in an x-ray tube. The continuum is generated as a result of the progressive declaration of high energy electrons of various energies.

The characteristics spectrum results from electron impacts with single atoms. The mechanism is not fully understood, but as a result an electron is removed from a low energy level and transported



either out of the atom or to an unoccupied level in the band of Fermi levels (conductors) or in the valence band (ionic crystals), (Compton, 1927) or complete removal from the atom.

The return of normal condition takes place in one or two steps with emission of characteristic x-ray wavelengths. Using the Bohr model of the atom a line can be regarded as arising from the transition of an electron from a high level to one of lower energy as well as from the transition of an electron in the opposite direction (Compton, 1927). An essential condition is that at the start of the emission process there must be a hole in one of the electronic shells of the atom. Since strongly bound electrons in normally completely filled shells are participating in the transition, a line spectrum is emitted although the emitter is in the solid state. As a consequence of the large interatomic distances in a solid the low energy levels of an atom can be compared to those of a free atom. The higher the energy of the electron the more the true conditions will deviate from those assumed. That is revealed by increasing line widths and by a measurable effect due to the inhomogeneous constitution of the emitter.

The continuous x-ray spectrum or "bremsstrahlung" is of interest in x-ray spectroscopy not only when studying absorption spectra but also as an inconvenient background to emission spectra. As the very often faint x-ray satellites mostly do not appear in fluorescence they have to be studied in primary spectra. Then the continuous background seriously decreases the possibilities of accurate measurements. Care has to be taken that the accelerating voltage is not selected so as to make the short wavelength limit of the continuous spectrum in a high order coincide with groups of emission lines to be investigated. This relation determines the position of the limit.

$$eV = h\nu \quad \dots (2.1)$$

giving that  $\nu$  is the frequency of absorption limit the accelerating voltage  $V$  necessary for the emission of the corresponding x-ray series can be calculated from the equation above.

## **2.8 X-Ray Excitation Sources**

Most x-ray spectrometry causes the elements in a sample to emit their characteristics x-rays. The excitation can be accomplished by several means. The target may be bombarded by high energy electrons or accelerated charged particles or irradiated by x-rays. The use of electron beams for excitation for x-ray detection coupled with the electron microprobe analysis (EMP) have been developed for elemental determinations in small samples. However, the electron beams method of excitation is not desirable for routine x-ray spectrometric determination. The use of an electron beam requires a high vacuum, which is not always needed or possible with routine samples. Direct x-ray excitation by electron beams require exceptionally reproducible condition, which cannot always be met in routine applications. Penetrating depths for electron excitation is low and this result is more of a surface than a bulk characterization of the sample. Similar arguments hold for particle induced x-ray emission (PIXE) techniques (Brouwer, 2003). In addition, non-conductive samples create serious problem for electrical charging. These techniques are useful in special application. They are not of practical value in the methodologies of analytical application of x-ray spectrometric determination.

Use of x-radiation for excitation of the elements in a sample is the more practical approach in x-ray spectrometry. One immediate advantage is that excitation by photons does not produce the continuous radiation generated by electron beam excitation. The background therefore will consist only of scattered x-rays. Even with photons excitation there are some choices. Radioactive isotopes which emit x-rays, gamma rays, or beta particles have been used for excitation of samples for energy dispersive spectrometry. These isotopes emit in one or two energy regions useful for the

photoelectric process leading to x-ray emission. These are two major deficiencies in these sources, which limit their usefulness in x-ray spectrometers. First, to be base for laboratory, the activity or flux from these sources must be very low. This means that the x-ray intensity from the sample will be low. Secondly, because energy of the source radiation must be greater than the absorption edge, any given source will be efficient for only a few elements. As a result, several sources may be required.

X-rays of properly selected energy sources for the excitation of x-ray emission by elements in a sample, the x-ray tube is a convenient source of generation of this radiation. An alternative to isotopic and tube excitation is the use of secondary target excitation. In this mode, an x-ray is used to irradiate a secondary target, the characteristic x-ray fluorescent of which in turn used to excite the x-ray emission of the sample. Because of substantial efficiency when using a secondary target, higher wattage x-ray tubes are required than would be needed for direct excitation.

Although the elements of many samples can be excited effectively using a combination of the characteristic x-ray lines from the tube anode element and the continuum, there are circumstances in which more monochromatic radiation is desired. One of these is to enhance the utilization of fundamental parameter computation, which permits the quantitative determination of elements without the need for concentration standards. In more frequent situation is to reduce the background in the spectrum energy range to be utilized in the analysis. Use of primary filters placed between the x-ray tube and the sample can be effective in their cases, and is usually incorporated under computer control in commercial spectrometers. The object is to filter the primary radiation from the x-ray tube, and selectively pass the characteristic lines of the anode element (Victor, 2011). This is accomplished using a filter made of the same element as the tube anode. Because of x-rays of given time (K $\alpha$ , etc.) of an element are lower in energy than the

absorption edge for that element, the photoelectric component of the mass absorption coefficient is small. The filter does not efficiently absorb the characteristic lines emitted by the x-ray tube. The higher energy x-rays from the continuum are efficient for the photo-electric process in the filter, and are highly attenuated by absorption. X-rays of lower energy than the filter material absorption edge are absorbed more efficiently as the energy decreases. The result is x-radiation striking the sample, the intensity of which is largely the characteristic lines of the tube anode, and which approximates monochromatic radiation.

## **2.9 Interaction of X-Rays with Matter**

The interaction between electromagnetic radiation and matter represents one of the most varied classes of phenomena in the whole of experimental physics. Even within the range of energies normally associated with x-rays (itself covering several magnitude of the electromagnetic spectrum) many different processes occur, all of which possess their own individual distinctive characteristics.

The nature of the matter with which the radiation interacts affects almost as work a range of phenomena as does the nature of the radiation. This is true even within the relatively restricted domain of x-ray physics. For example, the subject x-ray crystallography is essentially the study of the interactions between ordered matter and a radiation field, and any discussion of the absorption and scattering process in crystals must have as its basis the collective behaviours of a large number of atoms bound by chemical bonds or other inter-atomic forces into a recognizable structure.

However in the present work we are concerned mainly with situations in which the overall behaviours of an absorber or scatterer can be deduced by regarding it as a collection of individual atoms each absorbing or scattering independently of its surroundings. In such cases we can assert that interactions between x-ray photons and matter are single, identifiable processes, each

associated with an individual atom, and can therefore be characterized by a cross section. Such an interaction may be principally a scattering event in which little or no energy is imported to the atom in question or to any of the electron associated with it, or it may be essentially an absorption process, on which the great majority of the photon will be transferred to the atom or to one of its electrons. We shall see that the removal of photon from the incident beam and the absorption of energy by the irradiated atoms are two distinct consequences of x-ray interaction requiring careful distinction to be made in the theoretical treatment. We shall speak mainly of the removal cross sections, from which the main attenuation co-efficient of the interacting medium can be determined as follows.

### **2.9.1 Photoelectric effect**

This is one of the most interactions in the energy region of 1-100keV, and consists of the removal of a bound electron from an atom in the absorber. In general the inner electrons are the predominant contributions to the photoelectric interaction, so we speak of interaction in the K, L, M shell etc. This is subject to the overriding consideration that the incident photo energy must be greater than the binding energy of the electron in question, if photoelectric absorption is to take place.

Photoelectric absorption occurs most readily if the binding energy is comparable with the photon energy, and has certain of the qualities of a resonance process. For example, it decreases with increasing photon energy, corresponding to the physical notion that there is a decreasing probability of the electron being found in the field sufficiently strong for the resonance to take place.

The maximum kinetic energy  $k_{max}$  of an ejected electron is given by

$$k_{max} = hf - \varphi, \quad \dots (2.2)$$

where  $h$  is planck constant and  $f$  is the frequency of the incident photon. The term  $\varphi = hf_0$  is the work function (sometimes denoted  $\phi$ ), which gives the minimum energy required to remove a delocalized electron from the surface of the metal. The work function satisfies

$$\varphi = hf_0, \quad \dots (2.3)$$

where  $f_0$  is the threshold frequency for the metal. The maximum kinetic energy of an ejected electron is then

$$k_{max} = h(f - f_0). \quad \dots (2.4)$$

Kinetic energy is positive, so we must have  $f > f_0$  for the photoelectric effect to occur.

### 2.9.2 Compton effect

The second interaction, which we shall consider is that in which the electron may be considered free and not bound by an atom. This situation is not amenable to exact theoretical treatment than the photoelectric effect, because we apply the principle of the conservation of momentum to the electron and the incident and scattered photon in each to ascertain the division of energy between the photo and electron.

From conservation of energy we can write;

$$h\nu - h\nu' = T \quad \dots (2.5)$$

where  $T$  is the kinetic energy of the ejected electron and is given by the relativistic expression.

$$T(T + 2mc^2) = (pc)^2 \quad \dots (2.6)$$

where  $m$  is the rest mass as before the rest mass of the electron and  $p$  is the momentum.

In his paper, Compton derived the mathematical relationship between the shift in wavelength and the scattering angle of the x-rays by assuming that each scattered x-ray photon interacted with only one electron. His paper concludes by reporting on experiments which verified his derived relation:  
 $m_e$

$$\lambda' - \lambda = (h/m_e c) \{1 - \cos\theta\}, \quad \dots (2.7)$$

Where  $\lambda$  is the initial wavelength,  $\lambda'$  is the wavelength after scattering,  $h$  is the Planck's constant,  $c$  is the speed of light, and  $\theta$  is the scattering angle.

The quantity  $h/m_e c$  is known as the Compton wavelength of the electron; it is equal to  $2.43 \times 10^{-12}$  m. The wavelength shift  $\lambda' - \lambda$  is at least zero (for  $\theta = 0^\circ$ ) and at most twice the Compton wavelength of the electron (for  $\theta = 180^\circ$ ).

### 2.9.3 Pair production

Sometimes, a photon turns into a particle and its antiparticle, for example, an electron and a positron. It could not turn into just an electron, since this would leave the lepton number unbalanced. The photon must have enough energy to create the masses of the two particles. The energy required to create one of the particles is given by:

$$E = mc^2 \quad \dots (2.8)$$

where  $m$  is the mass of the particle, and  $c$  is the speed of light ( $3 \times 10^8 \text{ ms}^{-1}$ ). However, two particles must be created. Since the two particles are each other's antiparticle, they have identical masses. So, the total energy required is:

$$E = 2mc^2 \quad \dots (2.9)$$

Note that in annihilation, when a particle meets its antiparticle, the two annihilate each other to form 2 photons (due to conservation of momentum) with sum total energy equivalent to the total mass-energy of both particles.

Sometimes, a pair of particles annihilates, but then the photon produces another pair of particles. Also, a photon could produce a pair of particles which then annihilate each other. ([http://en.wikibooks.org/wiki/Alevel\\_Physics\\_\(Advancing\\_Physics\)/Pair\\_Production\\_and\\_Annihilation](http://en.wikibooks.org/wiki/Alevel_Physics_(Advancing_Physics)/Pair_Production_and_Annihilation)).

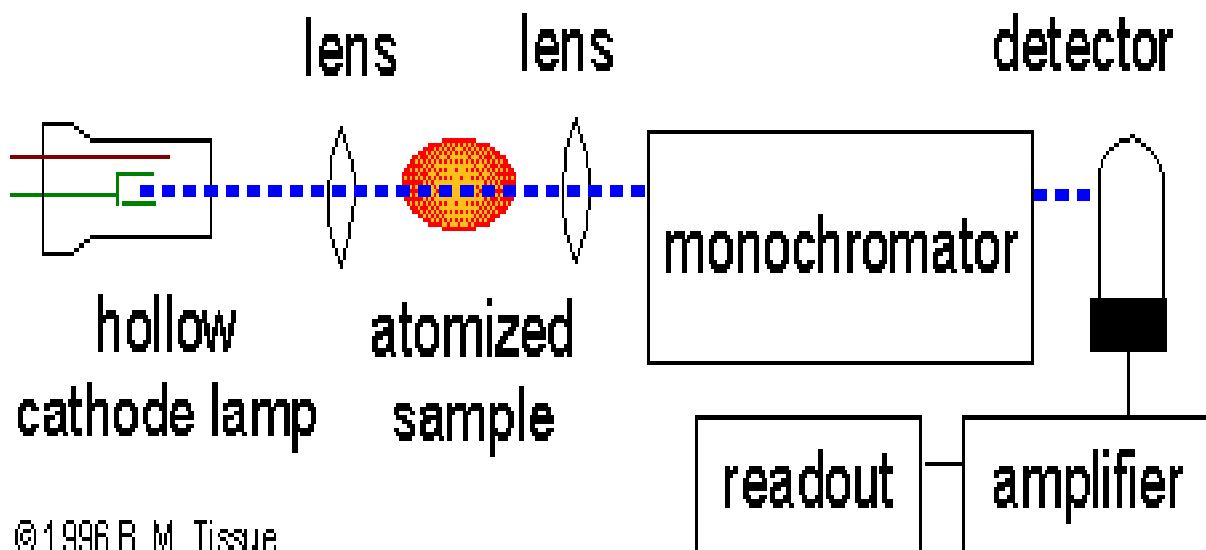
## **2.10 Atomic Absorption Spectroscopy (AAS)**

Atomic absorption spectrometry (AAS) is a spectro-analytical procedure for qualitative and quantitative assessment of chemical elements based on the absorption of light (optical radiation) by free atoms in the gaseous state. It is used to determine the concentration of a particular element in a sample. AAS can be used to determine over 70 different elements in a single sample. It was first used as an analytical technique in the second half of the 19th century. The modern form of AAS was largely developed during the 1950s by a team of chemists in Australia.

Atomic absorption spectroscopy is based on standards with known analyte content to establish the relation between the measured absorbance and the analyte concentration and on the Beer-Lambert



Law. The electrons in the atomizer can be placed in an excited state for a period of nanoseconds by absorbing the radiation of a given wavelength. This wavelength is specific to a particular electron transition in a particular element, so each wavelength corresponds to only one element, and the width of an absorption line is only a few picometers (pm), which gives the technique its elemental selectivity. The radiation flux with or without a sample in the atomizer is measured and the ratio between the two values is converted to analyte concentration or mass using the Beer-Lambert Law (source: <http://www.thebritishmuseum.ac.uk/science/techniques/sr-tech-aas.html>).



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*Figure 2.1: Schematic of an atomic-absorption experiment*

### **2.10.1 Basic principles of atomic absorption**

The basic principles of atomic absorption spectroscopy can be expressed by the following simple statements:

- All atoms can absorb light.
- The wavelength at which light is absorbed is specific for each element. If a sample containing nickel, for example, together with elements such as lead and copper is exposed to light at the characteristic wavelength for nickel, then only the nickel atoms will absorb this light.

- The amount of light absorbed at this wavelength will increase as the number of atoms of the selected element in the light path increases, and is proportional to the concentration of absorbing atoms.
- The relationship between the amount of light absorbed and the concentration of the analyte present in known standards can be used to determine unknown concentrations by measuring the amount of light they absorb. An atomic absorption spectrometer is simply an instrument in which these basic principles are applied to practical quantitative analysis.

### 2.10.2 Operational principle of atomic absorption spectrometer

The primary sources of radiation in atomic absorption are hollow cathode lamps. These lamps are composed of a cathode and an anode sealed in a tube with an inert gas (argon or neon). The cathode is made of the element to be determined. When a high voltage is applied the atoms of the inert gas are ionized and attracted by the cathode. These ions hit the cathode and excite the atoms of the elements used to make the cathode. Once the atoms are excited radiation is emitted at the characteristic wavelength of the element. The light from the hollow cathode lamp passes through the flame (Burner/nebulizer) where the sample is atomized. This fine mist of the sample is sprayed into the nebulizer. Atoms of the elements are formed from the sample mist and are able to absorb some of the light from the lamp at the wavelength set for that particular element. The light passed through the flame is received by the monochromator, which is set to accept and transmit radiation at the specified wavelength. The light emerges from the monochromator exit slit and falls on the photomultiplier detector. At this point an output current, proportional to the incident light, is intensified, amplified, processed electronically and finally presented to a readout device (i.e. printer, digital display).

## 2.11 Accumulation in Soils

As a result of the use of wastewater for irrigation, trace metals have accumulated in agricultural soils. The connection between soil and water contamination and metal uptake by plants is determined by many chemical and physical soil factors as well as the physiological properties of the crops. Soils contaminated with trace metals may pose both direct and indirect threats to plants: Direct, through negative effects of metals on crop growth and yield, and indirect, by entering the human food chain with a potentially negative impact on human health. Even a reduction of crop yield by a few percent could lead to a significant long-term loss in production and income. Some food importers are now specifying acceptable maximum contents of metals in food, which might limit the possibility for the farmers to export their contaminated crops.

Therefore the protection of soils from trace metal pollution is essential for maintaining a good soil and food quality. Once soil is contaminated, it is difficult and expensive to decontaminate it (Bjuhr, 2007).

## 2.12 Trace Metal Concentrations in Agricultural Soils

The total metal content ( $M_{tot}$ ) in the soil is the difference between all inputs and outputs. Input sources are weathering of parent material ( $M_p$ ), atmospheric deposition ( $M_{ad}$ ), fertilisers ( $M_f$ ), pesticides ( $M_{pe}$ ), organic wastes ( $M_{ow}$ ) and inorganic pollutants ( $M_{ip}$ ). Outputs are removal of crops ( $M_{cr}$ ), leaching ( $M_l$ ) and volatilisation ( $M_v$ ). The main input and output source of metals in this study is probably waste water (in) and crop up-take (out) respectively. The total metal content in the soil can thus be expressed by the following equation:

$$M_{tot} = (M_p + M_{ad} + M_f + M_{pe} + M_{ow} + M_{ip}) - (M_{cr} + M_l + M_v) \quad \dots (2.10)$$

The equation covers the total concentration of metals while metals speciation, i.e. identification of bio-available metal fractions is a more complex issue (Bjuhr, 2007).

### **2.13 Essential and Non-essential Heavy Metals in Plants**

Heavy metals are elements with a high relative atomic mass. They occur naturally in the earth's crust (Madyiwa, 2006). According to Glanze, (1996) and Sipitey, (2007), they are elements with a specific gravity that is at least five (5) times the specific gravity of water. Also Perk, (2006) and Amfo-Out, (2007) stated that heavy metals are elements having a density greater than  $3.6\text{-}6\text{g/cm}^3$ . Others define a heavy metal as a metal with atomic mass greater than that of sodium. Other definitions have it that a heavy metal is any of a number of higher atomic weight elements, which have properties of a metallic substance at room temperature. The "heavy metal" is used extensively in literature to refer to metals with atomic number greater than 20 and is also associated with toxicity or pollution. These include Cobalt, Chromium, Iron, Cadmium, Lead, Mercury, Zinc, Nickel, Manganese, Silver, etc (Madyiwa, 2006).

In general essential elements may be defined as metals that are necessary for a plant to complete its life cycle (Welch and Cary, 1987; Madyiwa, 2006). Heavy metals such as Iron, Copper and Zinc are essential for plant growth as they participate in oxidation, electron transfer and various enzyme reactions (Polette *et. al.*, 1997; Madyiwa, 2006).

Non-essential elements are metals with no known role in plant metabolism. Elements like Pb and Cd are not known to have any metabolic roles in plants and animals and are therefore non-essential (Johannesson, 2002; Elson and Haas, 2003; Madyiwa, 2006).

### **2.14 Toxicity to Human Beings**

Heavy metals are in the foods we eat, water we drink, and the air we breathe. We need very little of only a few heavy metals including zinc, copper, cobalt, manganese, molybdenum, vanadium and strontium. These good heavy metals become toxic to us when the quantity is too high and it takes really very little to be too much. On top of that, we take in more than twenty heavy metals which are non-essential for our healthy functioning (Victor, 2011). Once in the body they do damage on the cellular level by causing dangerous free radicals production. The damage that they do is on the cellular level, and can cause cancer and many other diseases.

Observed radiation effects and indeed the effects of other noxious agents can be broadly separated into two categories;

- Probabilistic or stochastic effects: Effects that occur randomly
- Deterministic or non-stochastic effects: Effects into which most biological effects will fall (Pwol, 2006).

### **2.15 Effect of Heavy Metals on Plants**

Heavy metals are toxic to higher plants by causing oxidative stress, displacing other essential metals in plant pigments or enzymes, leading to disruption of function of these molecules and of many metabolic processes, and finally reducing growth and yield (Rulkens *et. al.*, 1998; Seregin and Ivanov, 2001; Verma and Dubey, 2001; Zhang *et. al.*, 2002; Wang *et. al.*, 2003, Cheng *et. al.*, 2006). In general accumulation of heavy metals in the soil adversely affects the establishment of seedlings and forest regeneration. Heavy metals affect the catalytic function of enzymes, damaging cellular membrane, inhibition of root and shoot development, reduction of net carbon dioxide

assimilation and decreasing the stomatal conductance and transpiration, which in turn affect the soil water regime (Rosen, 2002; Amfo-Out, 2007).

## **CHAPTER THREE**

### **3.0 MATERIALS AND METHODS**

#### **3.1 Materials**

Analysis of selected samples (both the soil and Irish potatoes) from some farms in abandon mining site in Dahwol-vwana village, Kuru district, Jos-south L.G.A., Plateau state, will be carried out using X-Supreme EDXRF Oxford Instrument (MPL, Chem. Dept. ABU) and Atomic Absorption Spectrometer (AAS) in both NARICT and Soil Science Department, Faculty of Agriculture, ABU.

The X-Supreme EDXRF Oxford Instrument (MPL, Chem. Dept. ABU) consists of four major components such as:

- An x-ray source: this is an Ag-target x-ray tube having a minimum power of 9W.
- A sample changer that can accommodate up to 12 samples
- A Si (Li) detector cooled by liquid nitrogen that converts the x-ray generated photons emitted from the sample into measurable electronic signals. The Si (Li) is powered by a bias voltage power supply and the resulting signal is amplified by both amplifier and preamplifier included in the set up.
- A data processing unit, data display and storage system. The data processing unit contains a multi-channel analyser (MCA) that processes the signal into an x-ray energy spectrum from which elemental concentrations in the sample may be calculated.

In AAS experiments, they shall be performed with analytical grade chemicals. These include; perchloric acid ( $\text{HClO}_4$ ), nitric acid ( $\text{HNO}_3$ ), sulphuric acid ( $\text{H}_2\text{SO}_4$ ), distilled water.

### **3.1.1 Some needed materials for AAS analysis**

- Digestion tubes
- Digestion rock
- Weighing balance
- Volumetric flask (100ml)
- Micro Kjeldahl digestion apparatus

The NARICT Atomic Absorption Spectrometer (AAS) consists of some major components such as:

- A- Light Source
- B- Burner/Nebulizer
- C- Monochromator



- D- Photomultiplier Detector
- E- Output Device

### **3.2 Sample Collection**

The samples collections was done in farms that surrounded three abandon mining holes in Dahwol-Vwana village, in Kuru district, Jos-south L.G.A., Plateau state. This was done after the ridges formed and the Irish potatoes stems that have been transplanted grown, then the Irish potatoes and their surrounding soil on the farms closer to the ex-mining holes were dug with a clean machete and samples werecollected, even as the distance covered in each cases were measured. In each case, the soil samples collected were those around the Irish potatoes immediately when dug (i.e. ranging 10-20cm depth from the top of the ridge).

Furthermore, horizontal spacing range of distances were covered and measured, even as both the Irish potatoes and the soil around them were collected as shown below;

**Table 3.1: Sample of the First Ex-Mining Hole Area (N09<sup>0</sup>44.662'E008<sup>0</sup>50.590')**

<b>North-ward</b>	<b>Distance covered</b>	<b>East-ward</b>	<b>Distance covered</b>	<b>West-ward</b>	<b>Distance covered</b>	<b>South-ward</b>	<b>Distance covered</b>
A <sub>1</sub>	2.3m	A <sub>3</sub>	8.1m	A <sub>4</sub>	3.4m	A <sub>6</sub>	5.8m
B <sub>1</sub>	2.3m	B <sub>3</sub>	8.1m	B <sub>4</sub>	3.4m	B <sub>6</sub>	5.8m
A <sub>2</sub>	12.0m	HIP OF SAND		A <sub>5</sub>	10.0m	A <sub>7</sub>	14.2m
B <sub>2</sub>	12.0m			B <sub>5</sub>	10.0m	B <sub>7</sub>	14.2m

**Where sample A is the soil sample and sample B is the Irish potatoes sample.**

**Table 3.2: Sample of the Second Ex-Mining Hole Area (N09<sup>0</sup>44.656'E008<sup>0</sup>50.591')**

<b>North-ward</b>	<b>Distance covered</b>	<b>East-ward</b>	<b>Distance covered</b>	<b>West-ward</b>	<b>Distance covered</b>	<b>South-ward</b>	<b>Distance covered</b>
A <sub>8</sub>	1.8m	NO FARM		A <sub>10</sub>	3.1m	A <sub>12</sub>	9.2m
B <sub>8</sub>	1.8m			B <sub>10</sub>	3.1m	B <sub>12</sub>	9.2m
A <sub>9</sub>	8.5m			A <sub>11</sub>	11.2m	A <sub>13</sub>	15.1m
B <sub>9</sub>	8.5m			B <sub>11</sub>	11.2m	B <sub>13</sub>	15.1m

**Where sample A is the soil sample and sample B is the Irish potatoes sample.**

**Table 3.3: Sample of the Third Ex-Mining Hole Area (N09<sup>0</sup>44.638'E008<sup>0</sup>50.577')**

North-ward	Distance covered	East-ward	Distance covered	West-ward	Distance covered	South-ward	Distance covered
HIP OF SAND		STAGNATE WATER		NO FARM		A <sub>14</sub>	19.4m
						B <sub>14</sub>	19.4m
						A <sub>15</sub>	28.5m
						B <sub>15</sub>	28.5m

**Where sample A is the soil sample and sample B is the Irish potatoes sample.**

These samples were obtained, then carefully separated each in polythene bags to avoid mixing and further labeled with cellulose tape to avoid mistaken identity.

### **3.2.1 Sample collection at control area**

The samples collections (the control) was done in a virgin area (N09<sup>0</sup>41.062'E008<sup>0</sup>45.003') in Trade-Centre village, along Vom road, in Kuru district, Jos-south L.G.A., Plateau state. The expected processes were carried out even as Irish potatoes and soil samples were collected at the end.

### **3.3 Samples Preparation for XRF**

Each of both samples (soils and Irish potatoes) was taken to the laboratory. Each composite sample for both the Irish potatoes and the soils were spread on a tray and subjected to quartering process to obtain a laboratory sample which was reasonably representative of the composite sample. The representative of these samples was again individually dried to a constant weight. Other parts that

will not be able to be crushed into powdery form were manually removed from the sample and about 0.5g of each of the samples were subsequently homogenized in an agate mortar and then formed into stable pellets using hydraulic press equipped with diameter of 2.5cm at a compressive force of 10tons.

### **3.4 Procedure for XRF analysis of samples**

X-Supreme EDXRF Oxford Instrument is a compact energy dispersive x-ray spectrometer designed for the elemental analysis of a wide range of samples. The system is controlled by a PC running the dedicated analytical software.

The X-Supreme 8000 version EDXRF Oxford Instrument (MPL, Chem. Dept. ABU) is an energy dispersive microprocessor controlled analytical instrument designed for the detection and measurement of elements in a sample (solids, powders and liquids), from sodium(Na) to strontium (Sr).

The sample for analysis was weighed and grounded in an agate mortar and a binder (PVC dissolved in Toluene) was added to the sample, carefully mixed and pressed in a hydraulic press into a pellet.

The pellet was loaded in the sample chamber of the spectrometer and voltage (30kV maximum) and a current (1mA maximum) was applied to produce the X-rays to excite the sample for a preset time (8mins in this case). The spectrum from the sample was then be analyzed to determine the concentration of the elements in the sample.

#### **3.4.1 Energy Dispersive X-Ray Fluorescence (EDXRF) of environmental samples with isotopic source**

The samples were grounded manually to powder with an agate mortar and pestle to grain size of less than 125 $\mu$ m. Pellets of 19mm diameter were prepared from 0.3 -0.5g powder mixed with three drops of organic liquid binder and pressed afterwards at 10 tons with a hydraulic press.

Measurements were performed using an annular 25mCi  $^{109}\text{Cd}$  as the excitation source, that emits Ag-K X-rays (22.1keV) in which case all elements with lower characteristic excitation energies were accessible for detection in the samples. The system consists furthermore of a Si(Li) detector, with a resolution of 170eV for the 5.90keV line, coupled to a computer controlled ADC-card.

Quantitative analysis of the samples was carried out using the Emission-Transmission (E-T) method, for which a number of quantification methods has been developed and applied (LEROUX and MAHMOUD, 1966, GIAUQUE, et al., 1979, MARKOWICZ, 1979, MARKOWICZ and VAN GRIEKEN, 1993, KUMP, 1996, BERNASCONI et al., 1996, TANG et al., 1986). These quantification methods provide different approaches to correct the matrix absorption as well enhancement efforts. In this work quantification were carried out using a modified version of E-T method (KUMP, 1996, ANGEYO, et al., 1998, FUNTUA, 1999a, FUNTUA, 1999b) and it involves the use of pure target material (Mo) to measure the absorption factors in the sample.

The Mo target serves as a source of monochromatic X-rays, which are excited through the sample by primary radiation and then the sample on the way to the detector. In this way, the absorption factor was experimentally determined with the program uses in the quantification of concentration of the elements. In addition, the contribution to the Mo-K peak intensity by the Zr-K was then subtracted for each sample.

### **3.4.2 Spectrum acquisition using standard XRF**

ED-XRF analysis of the selected samples for both soil and Irish potatoes on some farms at a mining site in Dahwol-vwana village, Kuru district, Jos-south L.G.A., Plateau state, were carried out using EDXRF Oxford Instrument. These samples each was loaded in the sample chamber of the spectrometer and spectrum acquisition carried for 1000 seconds. All measurements were carried at the maximum power of 9W. The incident and the fluorescent x-rays were measured with a liquid nitrogen Si (Li) detector equipped with a thin Be window.

In order to maximize the ED-XRF for the ED-XRF  $k_{\alpha}$  line, intensities were measured for all elements except Br, Ba, Ce, Eu, Yb, Os, Au and Hg for which the  $L_{\alpha}$  line intensities were measured. Accurate elemental identification and x-ray intensity determination essential for the determination of the composition of the sample were carried out by the software installed in the PC-based X-Supreme 8000 EDXRF Oxford Instrument. This involves two steps. The first step involves elemental identification by continuous on-line, data processing including smoothing and peak search that are included in the software. The program distinguishes between real peaks and pseudo peaks, (i.e. intensity fluctuations in the background or on a peak). The background is then subtracted so that the accurate net peak intensity is obtained. The second step involves elemental identification, which is carried out using criteria such as the intensity ratio of  $k_{\alpha}$  to  $k_{\beta}$  and  $L_{\alpha}$  to  $L_{\beta}$ , for strong lines considering line overlap and also intensity ratios of strong lines to weak lines such as  $L_{\beta 2}, L_{\beta 3}, L_{\beta 1}$  as well as higher order lines included in the criteria. The identification algorithm is built with six stages including the identification of characteristic lines from the x-ray tube and very small peaks so that most possible lines are identified.

### **3.4.3 Quantitative analysis using standard XRF**



By using standards spiked with equal concentrations of selected elements. Correlations were established for the measured intensity, instrument sensitivity and element atomic number. These correlations were dependent on the condition set including x-ray tube voltage and current, filter used etc.

Once these relationships were established and stored in the sensitivity library for several elements, they were used to calculate relationships by interpolation, for elements for which standards were not available, thus establishing the basis for standard and matrices.

The following has been measured and stored in the instrument:

- Special intensity ratios for  $k_{\alpha}$  to  $k_{\beta}$  and  $L_{\alpha}$  to  $L_{\beta}$
- The intensity ratios for different sample areas, i.e. different diaphragm diameters, and
- Intensity ratios for the attenuator

On the basis of the above, several chemical elements will be determined in the Irish potatoes and soil samples.

### **3.5 Digestion of Samples (both Irish Potatoes and Soil) for AAS Analysis**

#### **3.5.1 Preparation of wet digestion acid**

$\text{HNO}_3$ ,  $\text{HClO}_4$  and  $\text{H}_2\text{SO}_4$  were mixed together in the ratio of 30:4:1 in order to form the wet digestion acid mixture.

#### **3.5.2 Procedure for digestion**

1.0g of each of the samples were accurately weighed and transferred into digestion tubes, 30ml of the wet digestion acid mixture were added to each sample in the digestion tubes, the digestion tube

containing acid mixture was placed on the digestion apparatus, which was allowed to digest for about 1½ hours until a clear solution is obtained. The end of the digestion was marked by the evolution of a white dense fume of perchloric acid (HClO<sub>4</sub>) and the reduction of volume to about 5ml, and then the digestion process was discontinued. The digest was allowed to cool and transferred quantitatively in a 100cm<sup>3</sup> volumetric flasks, then was made up to the mark with distilled water. The digest of each sample was transferred into different well stopper rubber container which was made ready for atomic absorption spectroscopic analysis.

### **3.6 AAS Measurements**

Total concentrations of Pb, Cd and Zn in the soils and Irish potatoes were determined using shimadzu Model 650 AAS equipped at a time when each of the lamps below:

- Hollow cathode lead lamp
- Hollow cathode cadmium lamp
- Hollow cathode zinc lamp,

are fixed on the AAS machine and each of these processes was done with a flame type consisting of air/acetylene and stoichiometric flue flow at 0.9-1.2L/min.

#### **2.6.1. Sequential extraction**

The sequential extraction method modified from Tessier *et. al.*, (1979) was used to separate Pb, Cd and Zn into four (4) operationally defined fractions: exchangeable and carbonate (EXCH + CARB; 1 M NaOAc+ HOAc at pH 5.0), Fe and Mn oxides (OX; 0.04 M NH<sub>2</sub>OH.HCl in acetic acid),

organic matter (OM; 0.02M HNO<sub>3</sub>+ 20% H<sub>2</sub>O<sub>2</sub>), and residual (RES) fractions. The concentration of Pb, Cd, and Zn in solution of each fraction was determined in AAS.

**Table 3.4. Time of mechanical agitation and temperature at which the sequential extraction was performed.**

Geochemical phase	Extraction reagent	Extraction condition	Final volume	Extracted sediment components
Fraction 1 (F1: Exchangeable + Carbonate)	1 M NaOAc adjusted to pH 5 with HOAc	Shake at room temperature for 5 hrs.	25ml	Exchangeable ions and carbonates
Fraction 2 (F2: Reducible)	0.25 M NH <sub>2</sub> OH.HCl in 25% (v/v) HOAc	Shake at 96°C for 6hrs.	25ml	Mn-Fe oxides
Fraction 3 (F3: Oxidizable)	0.02 M HNO <sub>3</sub> + H <sub>2</sub> O <sub>2</sub> ( at pH2 with HNO <sub>3</sub> ). On cooling add 3.2 M NH <sub>2</sub> OAc in 20% (v/v) HNO <sub>3</sub> .	Shaken occasionally at 85°C for 5 hrs then shaken on addition of NH <sub>4</sub> OAc for a further 0.5 hrs	25ml	Organic matter and sulphides
Fraction 4 (F4: Residual)	HF –HClO <sub>4</sub> Expectantly	Dissolved in 12 N HCl	100ml	Lithogenic crystalline

				minerals
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**Tessier *et. al.*, (1979)**

### 3.7 Data Analysis

Analysis of variance (ANOVA) was used to determine significant differences for zinc and in total extractable metal concentrations; the relationships among the various metal fractions and soil properties were determined using correlation analysis, and the sample means were compared using Fisher's Least Significant Difference (LSD<sub>0.05</sub>). All statistical data analyses were performed using SAS V 9.0 (SAS, 2002).

Metal enrichment factor (EF) for Pb, Cd and Zn was calculated based on the following relation, as proposed by Sposito (1989):

$$EF = (M_{soil}) / (M_{earth-crust}) \quad \dots (3.1)$$

where  $M_{soil}$  is the metal concentration in the soil and  $M_{earth-crust}$  is the average metal concentration in the earth crust, which is approximately 14.0, 0.2 and 75.0ppm for Pb, Cd and Zn respectively.

The geoaccumulation index (I-geo), as proposed by Muller (1969), was calculated by computing the base 2 logarithm of the measured total concentration of the metal over its background concentration using the following mathematical relation (Muller 1969; Ntekim *et. al.*, 1993):

$$I\text{-geo} = \log_2 (C_n/1.5B_n) \quad \dots (3.2)$$

Where  $C_n$  is the concentration of metal  $n$  in the soil,  $B_n$  is the soil background concentration of heavy metal  $n$  and 1.5 is a factor compensating the background data (correction factor) due to lithogenic effects.

### 3.8 Metal Enrichment

Measurements of metal pollution in soils and sediments by Banat *et. al.*, (2005), was used as standard to ascertain the pollution intensity of metals.

**Table 3.5: Measurements of metal pollution in soils and sediments**

Index of geochemical accumulation	I-geo Class	Designation of soil quality
10-5	6	Extremely contaminated
4-5	5	Strongly/extremely contaminated
3-4	4	Strongly contaminated
2-3	3	Moderately contaminated
1-2	2	Uncontaminated/moderately contaminated
0-1	1	Contaminated
0-0	0	Uncontaminated

Source: Banat *et. al.*, (2005).

## **CHAPTER FOUR**

### **4.0 RESULTS**

#### **4.1 Introduction**

In this chapter, total elemental concentrations of Zn, Pb and Cd, in both soils and Irish potatoes of the study were analyzed based on the international threshold values for heavy metals concentration in soils (ppm) by (CCME, 2001). Determination of f-values and significant difference of Zn concentrations gotten using AAS and XRF method were taken into concentration, even as the mean, standard deviation and range of extractable concentration of Pb, Cd, and Zn were calculated. Conclusively, the mean concentration from the fractionation analyses and background concentration were used for the calculation of enrichment factor and I-geo index of study area according to (Lindsay, 1979).

**Table 4.1: Total elemental concentrations of Zn, Pb and Cd, in both soils and Irish Potatoes of the study using AAS.**

Sample Type	Zn(ppm)		Pb(ppm)		Cd(ppm)	
	Sample A	Sample B	Sample A	Sample B	Sample A	Sample B
<b>Control (Average)</b>	0.0101	0.0213	0.0088	0.0041	0.0029	0.0017
1.	2.1204	1.0011	1.0080	0.7400	0.0113	0.0102
2.	1.0964	0.1038	0.5807	0.3932	0.0138	0.0094
3.	0.0751	-	1.1201	-	0.0086	-
4.	7.1509	4.0755	0.1483	0.7415	0.0102	0.0090
5.	4.4004	3.0621	0.8801	0.5721	0.0120	0.0093
6.	1.0466	0.3640	0.6783	0.3815	0.0194	0.0154
7.	5.0583	0.5210	1.0113	0.7223	0.0087	0.0081
8.	0.1528	-	0.0445	-	0.0138	-
9.	8.0601	-	0.5542	-	0.0157	-
10.	2.0587	0.2063	0.7661	0.5114	0.0242	0.0182
11.	1.1862	0.5906	1.0084	0.7414	0.0165	0.0138

12.	13.3446	59.0830	2.5932	0.3411	0.1200	0.0931
13.	31.1962	55.0503	3.9343	1.5042	0.0124	0.0110
14.	28.1887	84.0125	1.8008	0.4152	0.0344	0.0117
15.	39.0302	88.0503	0.4597	0.0741	0.0317	0.0145

Where sample A is the soil sample and sample B is the Irish potatoes sample.

**Table 4.2a: International threshold values for heavy metals concentration in soils (ppm)**

Heavy Metal	Regulatory System			
	EU	USA	Canada	UK
Cd	3.0	3.0	19.5	1.4
Zn	300	200-300	1400	200
Pb	300	300	150	70

Source: CCME (2001).

**Table 4.2b: World Health Organization (WHO) threshold values for heavy metals concentration in Irish potatoes (mg)**

Heavy Metals	Standard concentration
Cd	3.0



**Zn** **15**

**Pb** **0.1**

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Source: Friberg, 2007.

**Table 4.3: Mean and standard deviation and range of extractable concentration (ppm) of Pb, Cd, and Zn in an ex-mining site of Dahwol-vwana village, Jos-south, northern Nigeria.**

Heavy Metal	Sequential Extraction			
	Fraction 1: Exchangeable+ Carbonate bound	Fraction 2: Reducible	Fraction 3: Oxidizable	Fraction 4: Residual
Zn Mean, SD	<b>5.92± 3.65b</b>	<b>5.42±2.62b</b>	<b>4.49± 0.99a</b>	<b>138.85±34.33a</b>
Range	(3.95-7.30)	(2.40-6.99)	(3.39-5.32)	(116.93-178.41)
Pb Mean, SD	<b>6.04± 3.73a</b>	<b>6.31 ± 4.56c</b>	<b>9.86 ± 6.97b</b>	<b>55.59 ± 6.78b</b>
Range	(3.85-9.59)	(2.21-11.23)	(4.67-17.79)	(48.81-62.37)
Cd Mean, SD	<b>0.23± 0.12c</b>	<b>0.20± 0.18b</b>	<b>0.13 ± 0.07c</b>	<b>2.51 ± 0.09a</b>
Range	(0.09-0.44)	(0.09-0.44)	(0.09-0.20)	(2.40-2.56)

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Means followed by the same letters are not statistically different at 5% probability level according to Duncan Random Multiple Ratio (DMRT)

**Table 4.4: Determination of F-values and significant difference of zinc concentrations using AAS and XRF method.**

		Sum of Squares	df	Mean Square	F	Sig.
AAS	Irish Pot. Samples	21359.084	15 <sub>p.s</sub>	1423.939	7.465	.001
	Soil Samples	2861.382	15 <sub>s.s</sub>	190.759		
	Total	24220.466	30			
XRF	Irish Pot. Samples	38209.615	15 <sub>p.s</sub>	2547.308	4.038	.004
	Soil Samples	9462.510	15 <sub>s.s</sub>	630.834		
	Total	47672.125	30			

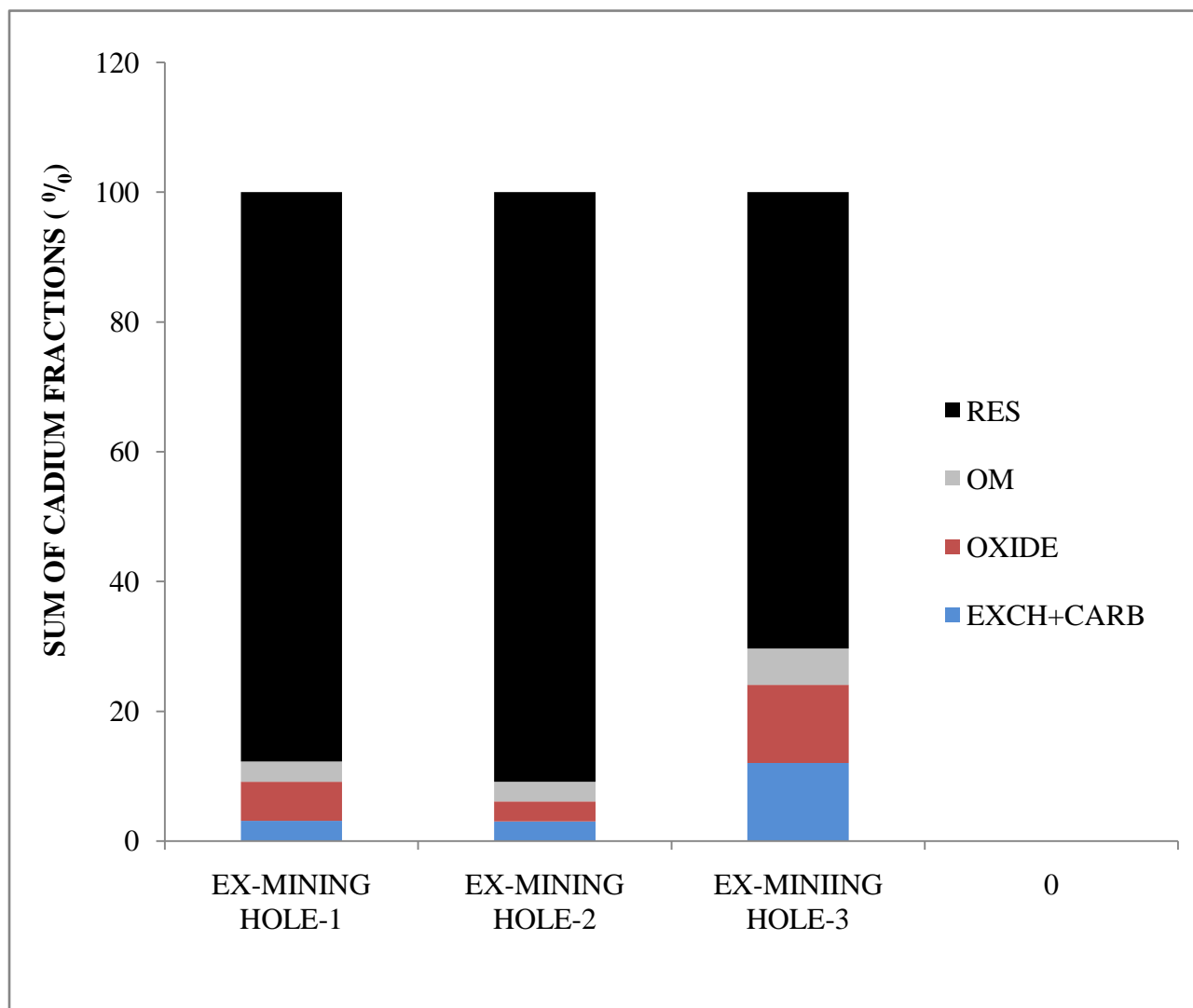
Where p.s

are Irish potato samples and s.s are the soil samples.

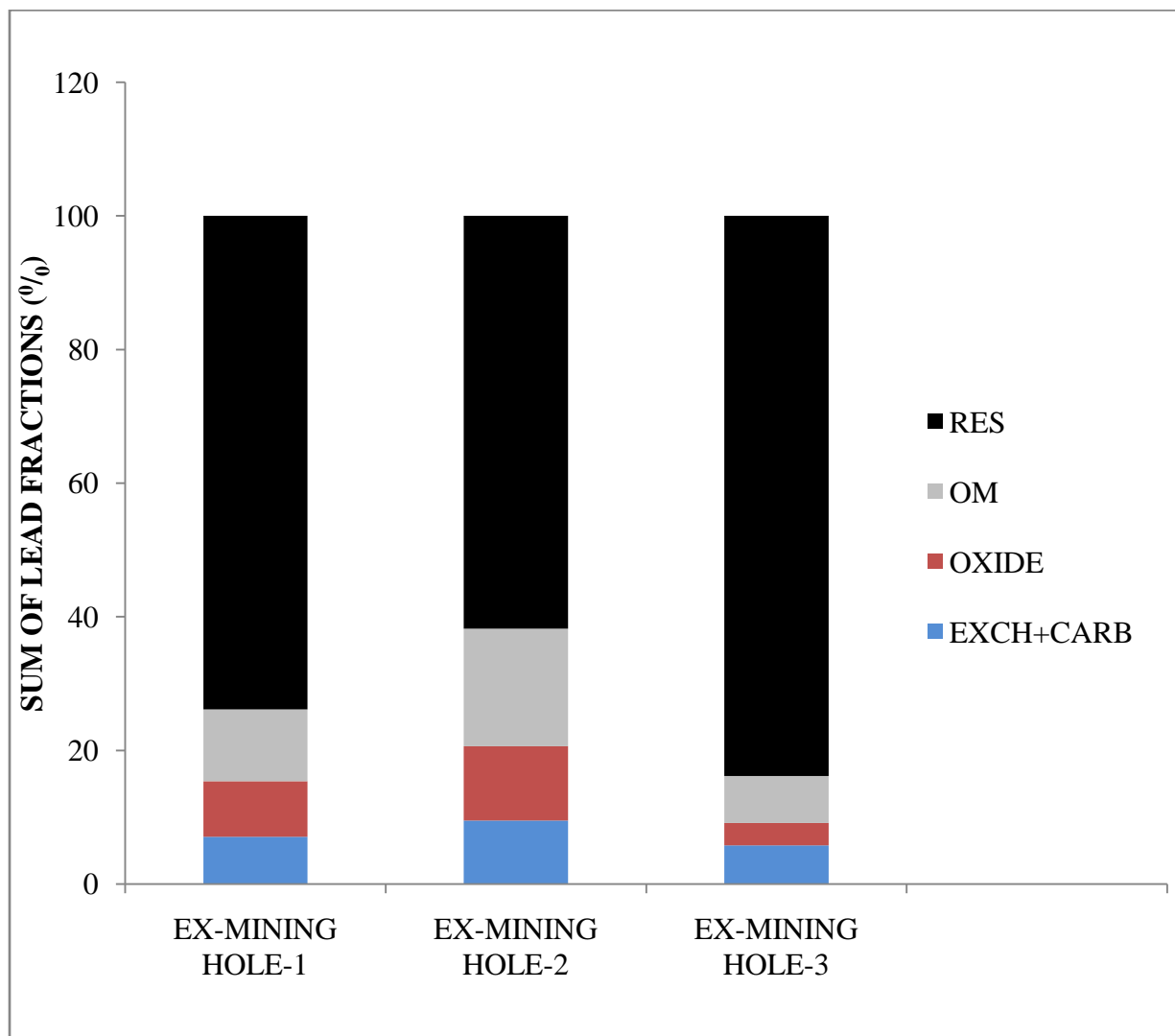
**Table 4.5: Average and background concentration, enrichment factor, calculated I-geo index, and grade of pollution intensity of Pb, Cd and Zn in analyzed samples from Dahwolvwana village, Jos-south.**

<b>Heavy metal</b>	<b>Average value (ppm)</b>	<b>*Background Concentration (ppm)</b>	<b>EF</b>	<b>I-geo</b>	<b>I-geo grade</b>	<b>Pollution intensity</b>
<b>Pb</b>	<b>77.8</b>	<b>14.0</b>	<b>5.6</b>	<b>1.9</b>	<b>2</b>	<b>Moderately contaminated</b>
<b>Cd</b>	<b>3.07</b>	<b>0.2</b>	<b>15.4</b>	<b>3.4</b>	<b>4</b>	<b>Strongly contaminated</b>
<b>Zn</b>	<b>154.7</b>	<b>75.0</b>	<b>2.1</b>	<b>0.5</b>	<b>1</b>	<b>Contaminated</b>

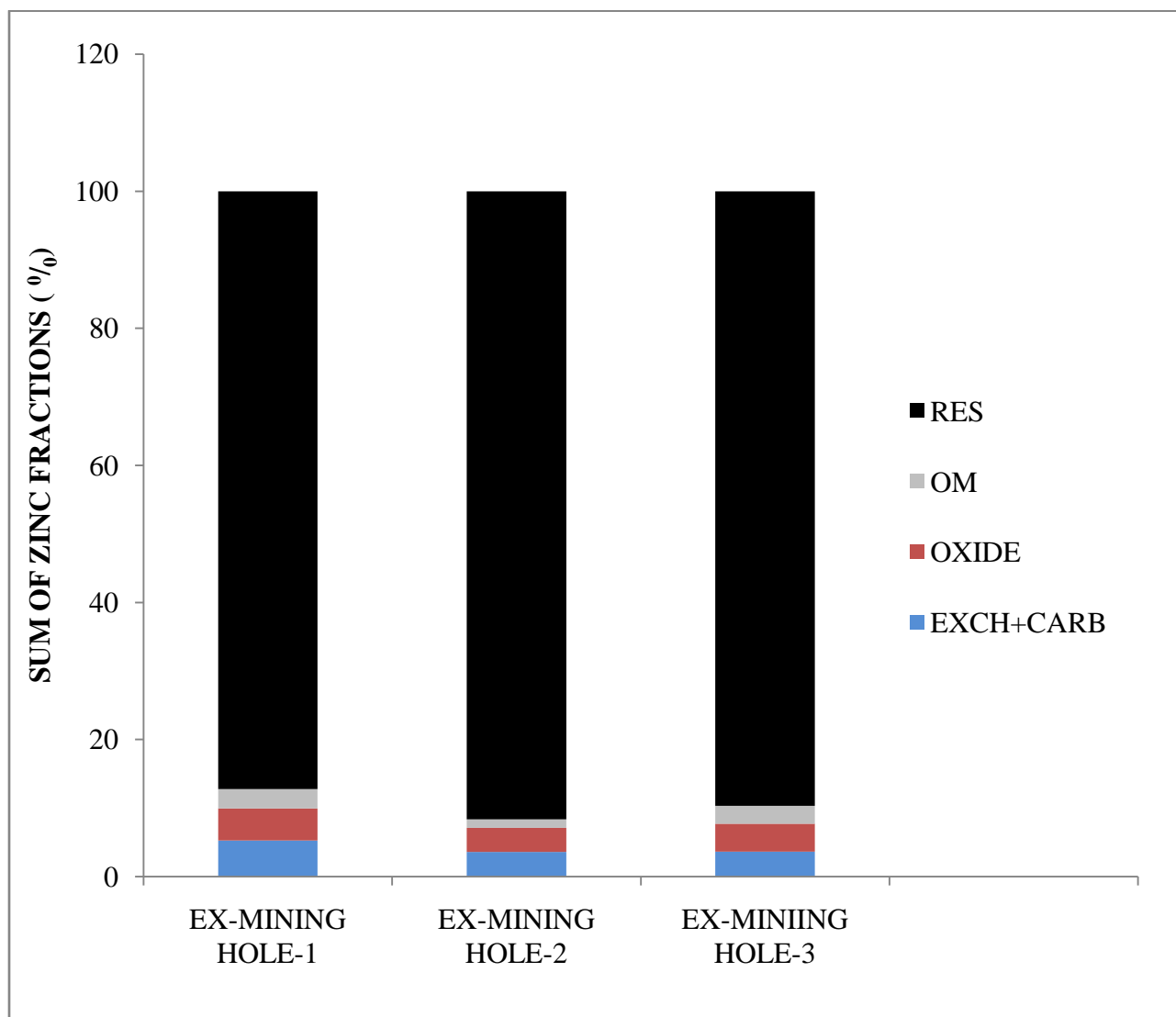
\*Lindsay (1979)



**Figure 4.1: The distribution of Cd among the different geochemical fractions of sample collections around each of the ex-mining holes in Dahwol-vwana village, Jos-south, Nigeria.**



**Figure 4.2: The distribution of Pb among the different geochemical fractions of sample collections around each of the ex-mining holes in Dahwol-vwana village, Jos-south, Nigeria.**



**Figure 4.3: The distribution of Zn among the different geochemical fractions of sample collections around each of the ex-mining holes in Dahwol-vwana village, Jos-south, Nigeria.**

## CHAPTER FIVE

### 5.0 DISCUSSION

#### 5.1 Total Metal Content

The total concentrations of Pb, Cd and Zn are presented in the soils of Dahwol-vwana village, are shown in Table 4.1. It can be seen from the data that the concentrations of the three metals of soils varied as follows: Cd, 0.0086-0.1200ppm; Pb, 0.0445-3.9343ppm; Zn, 0.0751-39.0302ppm. The values show a significant range. These observations indicate that all sample values of soils are lower than the recommended international threshold of 300ppm for Pb, 300ppm for Zn and 3ppm for Cd in arable soils set by EU, also are quite lower than the standard set by the regulatory bodies in Canada (Table4.2a).

But for Irish potatoes sample values (table 4.1), Pb, and Zn in some samples were higher than that of metal values from control. World Health Organization (WHO) recommended threshold values (table 4.2b) can also be compared based on the same unit.

However, the elemental concentrations recorded can be worrisome if accumulated with time. The values indicate relatively low level of contamination when compared with the standard thresholds for arable soils (Lindsay 1979; Sparks 2003).

The absence of local threshold figures necessitated comparisons only with thresholds set by international regulators. Despite the minimal values recorded for the heavy metals studied which are all higher than elemental values from the control, it is tenuous to conclude metal relative pollution of the farmlands, except a fractionation procedure partitions a larger proportion of the total metal onto the readily available fraction (Table 4.3).

## 5.2 Fractionation of Pb, Cd, and Zn

### 5.2.1 Lead fractions

Fractionation results partitioned the bulk of the total concentration of Pb to the residual fractions (figure 4.2). The residual fraction represents metals associated with silicate clay minerals (Hlavay *et. al.*, 2004). The relatively high percentage of the residual fractions in this soil indicates a lithogenic origin of the metal contaminants (McLean & Bledsoe, 1992). In Dahwol-vwana village, as high as 71.5% of the total Pb concentration were bound to the residual fractions. The exchangeable+carbonate fraction of the soil held the least percentage (7.8%) of the total Pb concentration recorded. The exchangeable+carbonate metal ions measure those trace metals that are released most readily into the environment; this fraction corresponds to the form of metals most available for plant uptake and could be released by merely changing the ionic strength of the soil medium (Filguerias *et.al.*, 2002).

Elements held unto the exchange fraction are easily exchangeable by other cations due to the weak electrostatic force of attraction in operation. The low proportion of metals held on this fraction is an indication of a low risk of Pb release into the environment and also a low potential of food chain contamination. Fractionation results reported by Rauret, (1998) and Krishnamurti *et. al.*, (1995) also observed that the exchangeable+carbonate fraction usually represented a small fraction of the total metal content in unpolluted soils (figure 4.2).

The oxide bound fractions were the next most important fractions controlling Pb availability. The percentage of Pb partitioned to this fraction is 12.7%. The oxide bound fractions include Pb bound to FeO and MnO. Heavy metal desorption from this fraction is majorly controlled by soil redox condition (McBride 2004; Abdu *et al.* 2011; Filguerias *et. al.*, 2002), because the oxide fractions are thermodynamically unstable under anoxic conditions (Filguerias *et. al.*, 2002). The onset of



reducing conditions would activate metal desorption from the Fe and Mn oxides fraction. Therefore, this result suggests a positive relationship between the metal released into the environment and changes in soil redox state.

The concentration of Pb fraction was held unto the OM fraction as 8.1 %. Organic matter has an affinity for heavy metals, forming stable complexes with them; especially the divalent ions, for which organic matter exhibits a high degree of selectivity compared to monovalent ions (Filguerias *et. al.*, 2002). Kennedy *et. al.*, (1997) observed that metallic pollutants associated with this phase remains in the soil for longer periods but may be mobilized by decomposition processes (because they are oxidizable). Hence, the degradation of OM under oxidizing conditions would facilitate the release of Pb bound to this fraction (Filguerias *et. al.*, 2002).

### **5.2.2 Cadmium fractions**

The bulk of the total Cd was partitioned to the residual fraction (81.8% of the total Cd), followed by the exchangeable+carbonate fraction which held 7.5% of total Cd (figure 4.1).

Thus, Cd has a high potential to be released from the soil by electrostatic adsorption (into any plants especially in tuber plants) and simple ion exchange reactions (Rogan *et. al.*, 2010), thereby representing potential phytotoxic and human hazards (Udom *et. al.*, 2004; USEPA, 2005) especially when it undergoes solubilization. However, the distributions of Cd among the oxide, OM and carbonate fractions were similar to those of Pb.

The exchangeable+carbonate bound Cd was lower than that of Pb for the whole study area, however the oxide bound fraction was next to the residual. The percentage of Cd partitioned to the oxide fraction is 6.5 % for the study area.

### **5.2.3 Zinc fractions**

Organically bound fraction of Zn accounted for 89.8% of total Zn (figure 4.3). The strong ability of Zn to form complexes with OM reduces Zn phytotoxicity in the environment (Kashem *et. al.*, 2007), thereby making the risk of pollution from Zn in this region minimal. The oxide fraction accounted for 2.9% of the total Zn concentration. Under reducing conditions, metals bound to this fraction become very important (Chao, 1972). The association of Zn with Fe-Mn oxide has also been reported in several other studies (Ma & Rao, 1997; Wilcke *et. al.*, 1998; Kashem *et. al.*, 2007) some of which suggested that the association of Zn with the oxide fraction reflects the high stability constant characteristic of Zn oxide. The major process controlling metal release from this fraction is redox. The onset of reducing conditions enhances desorption of metals held onto this fraction due to the reductive dissolution of Fe and Mn oxides (Dong & Ma, 2004). Also, as the soil reaction becomes more acidic, the Zn metal cation is easily displaced by more electronegative and higher valence cations such as  $H^+$  and  $Al^{3+}$ , respectively (McLean & Bledsoe, 1992). However, the relatively higher proportion of residual fractions of Zn is similar to the observations for Pb and Cd, and it further suggest a lithogenic origin of Zn in these soils.

### **5.3 Correlation between Zinc Concentration for Soil and Irish Potato Samples Using XRF and AAS.**

Significant positive correlation was observed between the Zn concentrations results obtained from XRF and AAS method (table 4.4). It was also observed from the Zinc data gotten from XRF were consistently higher than data from AAS. This discrepancy can be due to the limitation of the sample digestion procedure based on Method 3050B for organic-bound zinc. This indicate that AAS may be preferable for sample metal concentration analysis (with low detection limit) than that of XRF.

#### **5.4 Extractable Concentration of Pb, Cd, and Zn**

The amounts of metals extractable by 0.01M CaCl<sub>2</sub> represent quantities exchangeable and carbonate bound with Ca and the portion that form complexes with chloride ions (Egwu, 2010). These forms of metals are labile and readily available for soil biota and uptake. The concentrations of extractable Zn, Pb, and Cd ranged from (3.95-7.30)ppm, (3.85-9.59)ppm and (0.09-0.44)ppm. The difference in these extractable among the various soil samples grouped based on the three abandon mining hole extracted was not statistically significant (Table 4.3). The percentage of the total extractable of Zn, Pb, and Cd by CaCl<sub>2</sub> ranged from (0.03-0.05), (0.05-0.12) and (0.03-0.14). These low levels of extractable in the soils indicate high insolubility of the metal. Therefore, the leaching of Zn, Pb, Cd and potential uptake of the metals by plants are highly limited. Likewise, the potential for each of these metals accumulation in the food chain is relatively low. The low level of extractables implies bulk partitioning of the metals to the non-exchangeable fractions of the soil and it also indicates a lithogenic origin of the contaminant (Table 4.3).

#### **5.5 Enrichment and Accumulation of Pb, Cd and Zn**

The EF is the ratio of soil to crustal rock concentration of an element. It gives a quantitative measure of the relative enrichment (or depletion) of an element in soil as compared with rock. Sposito (1989) gave metal enrichment factor values of between 2 and 10 as indication of some enrichment of the element under consideration while EF values of < 0.5 and >10 would indicate significant depletion and strong enrichment respectively.

The calculated metal EF (according to Table 4.5) for Pb for the soils of Dahwol-vwana village is 5.6 across the study area. This means that there is some superficial enrichment of the element. Similarly observation was made for Cd, in which the metal gave EF of 15.4 that indicated strong

superficial enrichment of the element as a result of anthropogenic activities. While Zn just as Pb indicated some level of enrichment compared to the average rock concentration. The calculated value for Zn is 2.1.

The calculated I-geo index (Table 4.5) for the soils of this study is 2 for Pb; 4 for Cd; and 1 for Zn. These indices were interpreted according to Table 3.5. The highest grade, 4, means that the soil matrix is strongly contaminated, and it also reflects a relative metal concentration relative to background values (Banat *et. al.*, 2005). Although EF and I-geo allow for quick inferences on the status of a metal relative to mean soil and lithosphere concentration, it is important to point out that these indices are based solely on total concentration of a metal in the environment which is a poor indicator of pollution; therefore EF and I-geo are not strong indicators for making inferences on pollution or risk assessment. A summary of the mean Pb, Cd, and Zn concentration including their EF and I-geo index is presented in table 4.5.

## **CHAPTER SIX**

### **6.0 CONCLUSION AND RECOMMENDATIONS**

#### **6.1 Conclusion**

Results of this research showed that the soils of the farmlands are not contaminated with Pb, Cd, and Zn. However, the bulk of the metals were partitioned to the residual fraction. This implies that the soils of the farmlands are not polluted by any of the metals studied.

Therefore, there is a low risk of metal transfer from the soil to the growing crops. The enrichment level of the metals as calculated from the enrichment factor and I-geo factor only indicate the buffering of soil solution metal concentration through the slow process of weathering. Observations from this study reflects that, except for geological time, the total metal concentrations recorded for these soils would not play a significant role with respect to the Irish potatoes and other plants' growth or in terms of most environmental processes. However, in order to establish more definitive inference on the risk of metal transfer to the food chain, further research is needed on the effect of the protons released by the organic acids produced in the rhizosphere on the solubilization of metals bound to the residual fractions of the soil. This is of concern in soils such as those of this study with metals concentrations derived from parent materials and which also have relatively high metal enrichment factors.

## **6.2 Recommendations**

It is recommended that soil sample collections should be done in such a way that mobility index can be calculated, because it is a more reliable indicator which considers the weakly adsorbed fractions alone, after a sequential extraction has been done.

In the case of further similar work, the concentration state of the stem should be known before transplanting.

Further studies should therefore be carried out on the metals' concentrations in Irish potatoes of study area (using other methods such as NAA) in order to monitor the discrepancies in the concentration level with time.

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